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REPUBLICA DE COLOMBIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES

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APORTACION DE NUEVA DOCUMENTACION A
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MODELO DE UTILIDAD O DISEÑO INDUSTRIAL

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Dependencia: 2003 DIVISION DE NUEVAS CREACIONES

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Expediente No.00 028.953

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Observaciones ☐
Otros ☐
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☒ PATENTE ☐ MODELO DE UTILIDAD ☐ DISEÑO INDUSTRIAL

TITULO: **COMPUESTOS QUIMICOS**

SOLICITANTE: **ZENECA LIMITED**

INDICE DE DOCUMENTOS QUE SE ACOMPAÑAN

1 Copias certificadas por la Oficina de Patentes del Reino Unido de las dos primeras solicitudes presentadas para la misma invención, de las cuales REIVINDICAMOS PRIORIDAD, junto con sus correspondientes traducciones al español. ☐ a favor del solicitante, junto con su correspondiente traducción oficial al español.

2 Documento de cesión de derechos sobre la invención ☐

APODERADO: RAMIRO CASTRO DUQUE Código 340

DOMICILIO: Cra. 7 No. 16-56 Piso 9 TEL: 2-812424

FIRMA:

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Junio 12, 2000
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Signed Andrew Crerar

Dated 16 March 2000

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ANA GEORGINA CHARRY
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1/77

Request for grant of a patent

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20 APR 1999

The Patent Office
Cardiff Road
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Gwent NP9 1RH

1. Your reference

PPD 50402/GB/P

2. Patent application number
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9909062.3 ✓

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

ZENECA Limited
15 Stanhope Gate
London W1Y 6LN
UNITED KINGDOM

Patents ADP number *(if you know it)*

6254007002 ✓

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention

CHEMICAL COMPOUNDS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Francis John TIERNEY
Intellectual Property Department
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P O Box 3538
Bracknell Berkshire RG42 6YA
UNITED KINGDOM

Patents ADP number *(if you know it)*

06796941001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

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11. I/We request the grant of a patent on the basis of this application.

ZENECA LIMITED
Signature VKMallipeddi Date 20/4/99
Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

VIJAYA KUMARI MALLIPEDDI 01344 414365
DAWN LISA ROYAL 01344 414079

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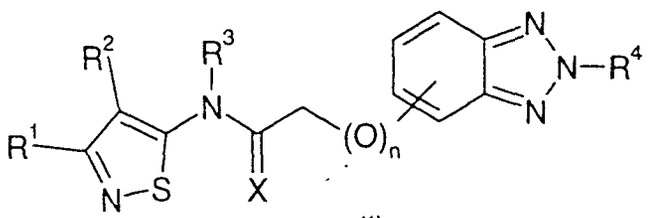
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CHEMICAL COMPOUNDS

The present invention relates to isothiazole derivatives, to processes for preparing them, to fungicidal, insecticidal, acaricidal, molluscicidal and nematicidal compositions comprising them, to methods of using them to combat fungal diseases (especially fungal diseases of plants) and to methods of using them to combat and control insect, acarine, mollusc and nematode pests.

Isothiazole derivatives are disclosed in WO 95/31448, WO 97/18198, WO 98/02424 and WO 98/05670.

The present invention provides a compound of formula (I):



(I)

wherein R^1 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{3-6} cycloalkyl or C_{1-6} alkoxy(C_{1-6})alkyl; R^2 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, cyano, nitro, CHO, CH=NOR^5, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or C_{1-6} alkylS(O)$_q$; or together R^1 and R^2 form a five or six membered saturated or unsaturated carbocyclic ring, optionally substituted by one or two C_{1-6} alkyl groups; R^3 is hydrogen, C_{1-6} alkyl, CH_2(C_{1-4} haloalkyl), C_{3-6} alkenyl, C_{3-6} alkynyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, formyl, optionally substituted phenoxycarbonyl, optionally substituted phenyl(C_{1-4})alkyl or S(O)$_p$R^6; R^4 is hydrogen, C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{3-6} alkenyl, C_{3-6} alkynyl, C_{3-7} cycloalkyl, C_{3-6} cycloalkyl(C_{1-6})alkyl, C_{3-6} haloalkenyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted phenyl(C_{1-4})alkyl or optionally substituted heteroaryl; R^5 is hydrogen, C_{1-6} alkyl, optionally substituted phenyl or optionally substituted phenyl(C_{1-4})alkyl; R^6 is C_{1-6} alkyl, C_{1-6} haloalkyl or optionally substituted phenyl; X is O or S; n is 0 or 1; and p and q are, independently, 0, 1 or 2.

Alkyl is straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl or *neo*-pentyl.

Halogen is fluorine, chlorine, bromine or iodine.

Haloalkyl groups are optionally substituted with one or more of the same or different halogen atoms and are, for example, CF_3, CH_2CF_3 or CH_2CHF_2.

Phenyl(C_{1-4})alkyl is, for example, 1-phenyleth-1-yl, 2-phenyleth-1-yl, 2-phenylprop-2-yl, 3-phenylprop-1-yl, but is preferably benzyl.

The term heteroaryl refers to an aromatic ring containing one or more heteroatoms (preferably one or two heteroatoms) selected from O, S and N. Examples of such rings include pyridine, pyrimidine, furan, thiophene, thiazole, oxazole and isoxazole.

It is preferred that phenyl moieties and heteroaryl groups are optionally substituted by one or more substituents independently selected from halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{2-6} alkenyl, C_{2-6} haloalkenyl, C_{2-6} alkynyl, C_{3-6} cycloalkyl, nitro, cyano, CO_2H, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, R^8R^9N or $R^{10}R^{11}NC(O)$; wherein R^8, R^9, R^{10} and R^{11} are, independently, hydrogen or C_{1-6} alkyl.

It is preferred that R^1 is ethyl or, especially, methyl.

It is preferred that R^2 is hydrogen, halogen (especially chloro) or cyano.

It is preferred that n is 0.

It is preferred that the compounds of the invention are of formula (Ia).

In one particular aspect the present invention provides a compound of formula (Ia) wherein R^1 is C_{1-4} alkyl (especially methyl or ethyl); R^2 is hydrogen, halogen (especially chloro or bromo) or cyano; or R^1 and R^2 together form a cyclopentyl, cyclohexyl or phenyl ring; R^3 is hydrogen, C_{1-4} alkyl (especially methyl or ethyl), phenyl(C_{1-4})alkyl (especially benzyl), C_{1-4} alkylcarbonyl (especially acetyl) or C_{1-4} alkylsulfonyl (especially methanesulfonyl); n is 0; X is oxygen; and R^4 is C1-6 alkyl [optionally substituted with halogen, C_{1-4} alkoxy, phenyl (itself optionally substituted with halogen), CO_2H, $CONH_2$ (itself optionally substituted with C_{1-4} alkyl), cyano, C_{3-6} cycloalkyl or $CO(C_{1-4}$ alkoxy)], C_{3-6} alkenyl, C_{3-6} alkynyl, C_{3-6} cycloalkyl, phenyl [optionally substituted with halogen, C_{1-4} haloalkyl (especially CF_3), nitro, CO_2H, or cyano] or heteroaryl (especially pyridyl or pyrimidinyl) [optionally substituted with C_{1-4} alkyl or C_{1-4} haloalkyl].

The compounds in the following Tables illustrate compounds of the invention.

TABLE 1

The compounds of Table 1 are compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 is as given in the table below.

Compound No.	R^4	^{1}H NMR δ ppm ($CDCl_3$ unless stated)
1	*n*-propyl	1.0(t,3H); 2.15(m,2H); 2.35(s,3H); 4.0(s,2H); 4.7(t,2H); 7.35(dd,1H); 7.85(d,1H); 7.95(d,1H); 8.15(b,1H)
2	4-CF_3-C_6H_4	2.4(s,3H); 4.1(s,2H); 7.5(m,1H), 7.8-7.9(m,4H); 8.5(bd,2H); 10.35(s,1H)
3	methyl	2.35(s,3H); 4.0(s,2H); 4.5(s,3H); 7.35(dd,1H), 7.8(d,1H); 7.9(d,1H); 8.05(b,1H)
4	4-F-$C_6H_4CH_2$	(DMSO-d_6): 2.35(s,3H); 4.05(s,2H); 5.8(s,2H); 7.0(m,2H); 7.4(m,3H); 7.8(m,2H); 10.9(b,1H)
5	CF_3CH_2	2.4(s,3H); 4.0(s,2H); 5.3(q,2H); 7.4(dd,1H); 7.85(d,1H); 7.95(d,1H); 8.15(b,1H)
6	*n*-pentyl	0.9(t,3H); 1.35(m,4H); 2.15(m,2H); 2.4(s,3H); 4.05(s,2H); 4.7(t,2H); 7.35(dd,1H); 7.85(d,1H); 7.9(d,1H); 8.15(b,1H)
7	2-Cl-3-CF_3-C_6H_3	2.4(s,3H); 4.05(s,2H); 7.45(dd,1H); 7.75(dd,1H); 7.95(m,3H); 8.05(m,1H); 8.2(b,1H)
8	1-methylpropyl	0.85(t,3H); 1.7(d,3H); 2.0-2.2(m,2H); 2.35(s,3H); 4.0(s,2H); 4.9(m,1H); 7.3(dd,1H); 7.85(d,1H); 7.9(d,1H); 8.15(b,1H)
9	ethyl	1.75(t,3H); 2.35(s,3H); 4.0(s,2H); 4.8(q,2H); 7.35(dd,1H); 7.8(b,1H); 7.9(d,1H); 8.1(b,1H)
10	2,2-dimethylpropyl	1.05(s,9H); 2.4(s,3H); 4.05(s,2H); 4.55(s,2H); 7.35(dd,1H); 7.85(b,1H); 7.95(d,1H); 8.15(b,1H)
11	*n*-butyl	
12	2-methylpropyl	
13	2-methoxyethyl	

14	methoxymethyl
15	$CH_2CH=C(CH_3)_2$
16	2-chloroethyl
17	allyl
18	propargyl
19	CH_2CO_2H
20	$CH_2CO_2CH_3$
21	$CH_2CO_2C_2H_5$
22	$CH(CH_3)CO_2H$
23	$CH(CH_3)CO_2CH_3$
24	$CH(CH_3)CO_2C_2H_5$
25	$C(CH_3)_2CO_2H$
26	$C(CH_3)_2CO_2CH_3$
27	$C(CH_3)_2CO_2C_2H_5$
28	CH_2CONH_2
29	$CH(CH_3)CONH_2$
30	$C(CH_3)_2CONH_2$
31	$CH_2CONHCH_3$
32	$CH_2CON(CH_3)_2$
33	$CH(CH_3)CONHCH_3$
34	$CH(CH_3)CON(CH_3)_2$
34	$CH_2CO_2C(CH_3)_3$
35	cyanomethyl
36	pentafluoroethyl
37	cyclopentyl
38	2-fluoroethyl
39	difluoromethyl
40	2-thioethoxyethyl
41	CH_2-cyclopropyl
42	CH_2-cyclopentyl
43	CH_2-cyclohexyl
44	$2\text{-}NO_2\text{-}C_6H_4$

45	2-pyridyl
46	5-CF_3-2-pyridyl
47	C_6F_5
48	4-CO_2H-C_6H_4
49	2-Cl-4-CN-C_6H_3
50	3,5-dimethyl-pyrimidin-2-yl

TABLE 2

Table 2 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 3

Table 3 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 4

Table 4 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 5

Table 5 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 6

Table 6 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 7

Table 7 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is hydrogen, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 8

Table 8 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is fluoro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 9

Table 9 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is bromo, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 10

Table 10 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is cyano, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 11

Table 11 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 1 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 12

Table 12 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 13

Table 13 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 14

Table 14 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 15

Table 15 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 16

Table 16 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 17

Table 17 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 18

Table 18 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is hydrogen, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 19

Table 19 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is fluoro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 20

Table 20 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is bromo, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 21

Table 21 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is cyano, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 22

Table 22 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 1 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 23

Table 23 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 24

Table 24 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 25

Table 25 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 26

Table 26 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 27

Table 27 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 28

Table 28 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 29

Table 29 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 30

Table 30 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 31

Table 31 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 32

Table 32 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 33

Table 33 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 34

Table 34 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 35

Table 35 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 36

Table 36 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 37

Table 37 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 38

Table 38 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 39

Table 39 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 40

Table 40 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

Compounds of formula (I) can be prepared by acylation of an appropriate 5-aminoisothiazole (II) with an appropriate carboxylic acid (III), preferably in the presence of a known coupling agent such as 1,3-dicyclohexylcarbodiimide or 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide. Alternatively the carboxylic acid (III) may first be converted to an acid chloride, anhydride or chloroformate suitable for reaction with an amine to form an amide; such procedures are described, for example in J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985, pps 370-376 and references therein.

5-Aminoisothiazoles (II) are either available commercially, or can be prepared from commercially available starting materials by methods described in the literature. (See, for example, C. Oliver Kappe, Robert Flammang, and Curt Wentrup, Heterocycles, Vol. 37, No. 3, 1615, (1994); A. Adams and R. Slack, J. Chem. Soc., 3061, (1959); and Ronald E Hackler, Kenneth W. Burow, Jr., Sylvester V. Kaster and David I. Wickiser, J. Heterocyclic Chem, 26, 1575, (1989)).

Carboxylic acids (III) can be prepared by hydroylsis of their corresponding esters (IV) by methods described in the art. The esters can be chosen to be hydrolysed under neutral, basic or acidic conditions, and the conditions are chosen such that the substituent R^4 is not affected by the hydrolysis reaction. Esters capable of ready hydrolysis under different conditions are known in the literature, and suitable esters may be selected, for example, by reference to Theodora W. Greene, Protective Groups in Organic Synthesis, Chapter 5, John Wiley and Sons, New York, 1981.

Esters (IV) can be prepared by reacting a benzotriazoles (V) with a compound R^4L. wherein L is a suitable leaving group such as halogen. (For suitable coupling reactions see, for example, Comprehensive Heterocyclic Chemistry, ed. Alan R Katritzky and Charles W Rees, Volume 5, pps 669-732 Pergamon Press, 1984 and references therein.) Reactions such as these can give rise to isomeric products. The desired isomer (IV) can usually be separated from any others present by standard techniques such as flash column chromatography or crystallisation from a solution containing one or more suitable solvents.

Benzotriazoles (V) may be prepared by the sequential diazotisation and hydrolysis of an acylated diamine (VI), or by hydrolysis of an acylated diamine (VI) to give a diamine (VII) which is then diazotised. Procedures for forming benzotriazoles (V) from such precursors are well known in the literature. (See, for example, Comprehensive Heterocyclic Chemistry, ed. Alan R Katritzky and Charles W Rees, Volume 5, pps 722-723 Pergamon Press, 1984 and references therein.)

Acylated diamines (VI) can be prepared by the reduction of a corresponding nitroanilide (VIII), which in turn is prepared by the nitration of an anilide (IX). Procedures for effecting these transformations are well known in the literature. (See, for example, references given in J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985). Anilides (IX) are known in the art and can be prepared from known compounds using procedures described in the art.

Compounds of formula (I) wherein R^3 is other than hydrogen can be prepared by reacting a compound of formula (I) wherein R^3 is hydrogen with a compound R^3L^*, wherein L* is a leaving group (such as halogen), optionally in the presence of a base and a phase transfer catalyst. Examples of suitable alkylating agents include, alkyl halides such as methyl iodide and alkyl sulfates such as dimethylsulfate. Suitable acylating agents include anhydrides such as acetic anhydride, acid chlorides such as acetyl chloride or benzoyl chloride and chloroformates such as ethyl chloroformate. Suitable bases include organic bases such as triethylamine, pyridine, alkali metal alkoxides such as potassium *tert*-butoxide and inorganic bases such as sodium hydride and sodium hydroxide. Suitable phase transfer catalysts may be selected by reference to the literature (see, for example, J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985, pps 320-322 and references therein).

A compound of formula (I) wherein X is sulfur can be prepared from a compound of formula (I) wherein X is oxygen by reacting that compound with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent) or phophorus pentasulfide in a solvent (such as toluene).

The compounds of formula (I) can be used to combat and control infestations of insect pests such as Lepidoptera, Diptera, Homoptera and Coleoptera and also other invertebrate pests, for example, acarine, nematode and mollusc pests. Insects, acarines, nematodes and molluscs are hereinafter collectively referred to as pests. The pests which

may be combated and controlled by the use of the invention compounds include those pests associated with agriculture (which term includes the growing of crops for food and fibre products), horticulture and animal husbandry, companion animals, forestry and the storage of products of vegetable origin (such as fruit, grain and timber) and also those pests associated with the transmission of diseases of man and animals.

Examples of pest species which may be controlled by the compounds of formula (I) include: *Myzus persicae* (aphid), *Aphis gossypii* (aphid), *Aphis fabae* (aphid), *Lygus* spp. (capsids), *Dysdercus* spp. (capsids), *Nilaparvata lugens* (planthopper), *Nephotettix cincticeps* (leafhopper), *Nezara* spp. (stinkbug), *Euschistus* spp. (stinkbugs), *Leptocorisa* spp. (stinkbugs), *Frankliniella occidentalis* (thrip), *Thrips* spp. (thrips), *Leptinotarsa decemlineata* (Colorado potato beetle), *Anthonomus grandis* (boll weevil), *Aonidiella* spp. (scale insects), *Trialeurodes* spp. (white flies), *Bemisia tabaci* (white fly), *Spodoptera littoralis* (cotton leafworm), *Heliothis virescens* (tobacco budworm), *Helicoverpa armigera* (cotton bollworm), *Pieris brassicae* (white butterfly), *Plutella xylostella* (diamond back moth), *Agrotis* spp. (cutworms), *Chilo suppressalis* (rice stem borer), *Chortiocetes terminifera* (locust), *Diabrotica* spp. (rootworms), *Panonychus ulmi* (European red mite), *Panonychus citri* (citrus red mite), *Tetranychus urticae* (two-spotted spider mite), *Tetranychus cinnabarinus* (carmine spider mite), *Phyllocoptruta oleivora* (citrus rust mite), *Polyphagotarsonemus latus* (broad mite), *Brevipalpus* spp. (flat mites), *Liriomyza* spp. (leafminers), *Musca domestica* (housefly), *Aedes aegypti* (mosquito), *Anopheles* spp. (mosquitoes), *Culex* spp. (mosquitoes), *Blattella germanica* (cockroach), *Periplaneta americana* (cockroach), *Blatta orientalis* (cockroach), *Ostrinia nubilalis* (European corn borer), *Meloidogyne* spp. (root knot nematodes), *Globodera* spp. and *Heterodera* spp. (cyst nematodes), *Pratylenchus* spp. (lesion nematodes) and *Deroceras reticulatum* (slug). Further examples include insects which adversely affect the health of the public or of animals.

The compounds of formula (I) are also active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia recondita*, *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet, vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Erysiphe graminis* (powdery mildew) on barley, wheat, rye and turf and other

powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fuliginea* on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum*), *Pseudocercosporella herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frogeye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; *Plasmopara viticola* on vines; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas,

peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon. pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes; *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium* spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarus*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seditiosum*) or lumber, notably *Cephaloascus fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

A compound of formula (I) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (I) may be volatile enough to be active in the vapour phase against one or more fungi on the plant.

The invention therefore provides a method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a pest, a locus of pest, or to a plant susceptible to attack by a pest, and a method of combating and controlling fungi which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a plant, to a seed of a plant, to the locus of the plant or seed or to soil. The compounds of formula (I) are preferably used against insects, acarines, nematodes or fungi.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicant and antisporulant treatments.

As fungicides, the compounds of formula (I) are preferably used for agricultural, horticultural and turfgrass purposes in the form of a composition.

In order to apply a compound of formula (I) as an insecticide, acaricide, nematicide or molluscicide to a pest, a locus of pest, or to a plant susceptible to attack by a pest, or, as a fungicide to a plant, to a seed of a plant, to the locus of the plant or seed or to soil, a compound of formula (I) is usually formulated into a composition which includes, in addition to the compound of formula (I), a suitable inert diluent or carrier and, optionally, a surface active agent. Surface active agents are chemicals which are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersibility and wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (I). The composition is generally used for the control of pests or fungi such that a compound of formula (I) is applied at a rate of from 0.1g to10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (I) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides an insecticidal, acaricidal, nematicidal, molluscicidal or fungicidal composition comprising an insecticidally, acaricidally, nematicidally, molluscicidally or fungicidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor. The composition is preferably an insecticidal, acaricidal, nematicidal or fungicidal composition.

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), emulsions (both oil in water (EW) and water in oil (EO)), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed

dressings. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (I).

Dustable powders (DP) may be prepared by mixing a compound of formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) can be prepared by mixing a compound of formula (I) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) can be prepared by mixing a compound of formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include aliphatic and aromatic petroleum solvents, alcohols, polyvinyl acetates, polyvinyl alcohols, ethers, ketones, esters, dextrins, sugars and vegetable oils. One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Soluble concentrates (SL) can be prepared by dissolving a compound of formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may

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contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil in water emulsions (EW) may be prepared by dissolving a compound of formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents) and, for an emulsion, subsequently adding, under high shear agitation, the mixture to water (which may contain one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol). Suitable organic solvents for use in ECs or EWs include vegetable oils, *N*-substituted pyrrolidones, glycol ethers, chlorinated hydrocarbons (such as chlorobenzenes) and aromatic solvents (such as alkylbenzenes or alkylnaphthalenes).

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (I). SCs may be prepared by ball or bead milling the solid compound of formula (I) in a suitable medium with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle.

Aerosol formulations comprise a compound of formula (I) and a suitable propellant (for example *n*-butane). A compound of formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula (I) can be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

Capsule suspensions (CS) can be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (I) and, optionally, a carrier or diluent therefor. The compositions may provide for controlled release of the compound of formula (I) and they can be used for seed treatment. A compound of formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A composition may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (I)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soya bean and rape seed oil), and blends of these with other bio-enhancing adjuvants.

A compound of formula (I) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and SL compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil).

Wetting agents, dispersing agents and emulsifying agents may be of the cationic, anionic, amphoteric or non-ionic type.

Suitable agents of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic agents include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-*iso*propyl- and tri-*iso*propyl-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid, additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable agents of the amphoteric type include betaines, propionates and glycinates.

Suitable agents of the non-ionic type include condensation products of ethylene oxide with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or

hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters) or their ethoxylated derivatives; amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (I) can be applied by any of the known means of applying pesticidal or fungicidal compounds. For example, it can be applied, formulated or unformulated, to the pests or to a locus of the pests (such as a habitat of the pests, or a growing plant liable to infestation by the pests) or to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it can be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (I) may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include SLs, SCs, ECs, EWs, SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula (I) (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of formula (I) can be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types

include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula (I).

The invention therefore also provides a fertiliser composition comprising a fertiliser and a compound of formula (I).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematicidal or acaricidal activity.

By including another fungicide, the resulting composition can have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (I) alone. Further the other fungicide can have a synergistic effect on the fungicidal activity of the compound of formula (I).

The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of formula (I); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition.

Examples of suitable pesticides include the following:

a) Pyrethroids, such as permethrin, cypermethrin, fenvalerate, esfenvalerate, deltamethrin, cyhalothrin (in particular lambda-cyhalothrin), bifenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids (for example ethofenprox), natural pyrethrin, tetramethrin, s-bioallethrin, fenfluthrin, prallethrin or 5-benzyl-3-furylmethyl-(*E*)-(1*R*,3*S*)-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl)cyclopropane carboxylate;

b) Organophosphates, such as profenofos, sulprofos, acephate, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, profenofos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chlorpyrifos, phosalone, terbufos, fensulfothion, fonofos, phorate, phoxim, pirimiphos-methyl, pirimiphos-ethyl, fenitrothion, fosthiazate or diazinon;

c) Carbamates (including aryl carbamates), such as pirimicarb, triazamate, cloethocarb, carbofuran, furathiocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur, methomyl or oxamyl;

d) Benzoyl ureas, such as diflubenzuron, triflumuron, hexaflumuron, flufenoxuron or chlorfluazuron;

e) Organic tin compounds, such as cyhexatin, fenbutatin oxide or azocyclotin;

f) Pyrazoles, such as fipronil, tebufenpyrad and fenpyroximate;

g) Macrolides, such as avermectins or milbemycins, for example abamectin, emamectin benzoate, ivermectin, milbemycin, spinosad or azadirachtin;

h) Hormones or pheromones;

i) Organochlorine compounds such as endosulfan, benzene hexachloride, DDT, chlordane or dieldrin;

j) Amidines, such as chlordimeform or amitraz;

k) Fumigant agents, such as chloropicrin, dichloropropane, methyl bromide or metam;

l) Chloronicotinyl compounds such as imidacloprid, acetamiprid, nitenpyram or thiomethoxam;

m) Diacylhydrazines, such as tebufenozide;

n) Diphenyl ethers, such as diofenolan or pyriproxifen;

o) Indoxacarb;

p) Chlorfenapyr; or

q) Pymetrozine.

In addition to the major chemical classes of pesticide listed above, other pesticides having particular targets may be employed in the composition, if appropriate for the intended utility of the composition. For instance, selective insecticides for particular crops, for example stemborer specific insecticides for use in rice (such as cartap or buprofezin) can be employed. Alternatively insecticides or acaricides specific for particular insect species/stages may also be included in the compositions (for example acaricidal ovo-larvicides, such as clofentezine, flubenzimine, hexythiazox or tetradifon; acaricidal motilicides, such as dicofol or propargite; acaricides, such as bromopropylate or chlorobenzilate; or growth regulators, such as hydramethylnon, cyromazine, methoprene, chlorfluazuron or diflubenzuron).

Examples of fungicidal compounds which may be included in the composition of the invention are (*E*)-*N*-methyl-2-(2-phenoxyphenyl)-2-methoxyiminoacetamide, (*E*)-*N*-methyl-

2-[2-(2,5-dimethylphenoxymethyl)phenyl]-2-methoxy-iminoacetamide, (*RS*)-1-aminopropyl-phosphonic acid, (*RS*)-4-(4-chlorophenyl)-2-phenyl-2-(1*H*-1,2,4-triazol-1-ylmethyl)butyronitrile, (Z)-*N*-but-2-enyloxymethyl-2-chloro-2',6'-diethylacetanilide, 1-(2-cyano-2--methoxyiminoacetyl)-3-ethyl urea, 4-(2,2-difluoro-1,3-benzodioxol-4-yl)-pyrrole-3-carbonitrile, 4-bromo-2-cyano-*N*,*N*-dimethyl-6-trifluoromethyl-benzimidazole-1-sulphonamide, 5-ethyl-5,8-dihydro-8-oxo(1,3)-dioxol-(4,5-g)quinoline-7-carboxylic acid, α-[*N*-(3-chloro-2,6-xylyl)-2-methoxy-acetamido]-γ-butyrolactone, *N*-(2-methoxy-5-pyridyl)-cyclopropane carboxamide, acibenzolar (CGA245704), alanycarb, aldimorph, ampropylfos, anilazine, azaconazole, azoxystrobin, benalaxyl, benomyl, biloxazol, binapacryl, bitertanol, blasticidin S, bromuconazole, bupirimate, butenachlor, buthiobate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA41396, CGA41397, chinomethionate, chloroneb, chlorothalonil, chlorozolinate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate, and Bordeaux mixture, cycloheximide, cymoxanil, cyproconazole, cyprodinyl, cyprofuram, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, dichlone, diclobutrazol, diclomezine, dicloran, didecyl dimethyl ammonium chloride, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O*,*O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethomorph, dimethirimol, diniconazole, dinocap, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, etaconazole, ethirimol, ethoxyquin, ethyl (*Z*)-*N*-benzyl-*N*-([methyl(methyl-thioethylideneamino-oxycarbonyl)amino]thio)-β-alaninate, etridiazole, famoxadone, fenaminosulph, fenapanil, fenarimol, fenbuconazole, fenfuram, fenhexamid (KBR 2738), fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, fluoroimide, fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fuberidazole, furalaxyl, furametpyr, furconazole-cis, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, ipconazole, iprobenfos, iprodione, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metconazole, methfuroxam, metiram, metiram-zinc, metominostrobin, metsulfovax, myclobutanil, neoasozin, nickel dimethyldithiocarbamate, nitrothal-*iso*propyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole,

oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosetyl-Al, phosphorus acids, phthalide, picoxystrobin (ZA1963), polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propiconazole, propineb, propionic acid, prothiocarb, pyracarbolid, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinconazole, quinomethionate, quinoxyfen, quintozene, rabenazole, sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thicyofen, thifluzamide, 2-(thiocyanomethylthio)benzothiazole, thiophanatemethyl, thiram, timibenconazole, tolclofos-methyl, tolylfluanid, triacetate salt of 1,1'-iminodi(octamethylene)diguanidine, triadimefon, triadimenol, triazbutyl, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triforine, triflumizole, triticonazole, validamycin A, vapam, vinclozolin, XRD-563, zineb and ziram. The compounds of formula (I) can be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Examples of suitable synergists for use in the compositions include piperonyl butoxide, sesamex, safroxan and dodecyl imidazole.

Suitable herbicides and plant-growth regulators for inclusion in the compositions will depend upon the intended target and the effect required.

An example of a rice selective herbicide which can be included is propanil. An example of a plant growth regulator for use in cotton is PIX™.

Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The invention is illustrated by the following Examples, in which the ingredients below are referred to by their Registered Trade Marks and have the following compositions.

Registered Trade Mark	Composition
SYNPERONIC NP8 } SYNPERONIC NP13 }	Nonylphenol-ethylene oxide condensate
SYNPERONIC A7	Synthetic primary alcohol-ethylene oxide condensate
AROMASOL H	Alkylbenzene solvent
SOLVESSO 200	Inert organic diluent
KELTROL	Polysaccharide
PROXEL	Bactericide

The following abbreviations are used throughout:

s = singlet	b = broad	q = quartet
d = doublet	m = multiplet	dd = double doublet
t = triplet	bd = broad doublet	

EXAMPLE 1

This Example illustrates the preparation of N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)acetamide (Compound No. 1 of Table I).

Step 1

4-Aminophenylacetic acid (100g) was suspended in methanol (1000ml) and gaseous hydrogen chloride was passed through until the mixture was saturated. The mixture was heated at 50°C for 2 hours and was then allowed to cool to room temperature. The solvent was evaporated *in vacuo*, the residue taken up aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl 4-aminophenylacetate as a pale brown liquid.

^{1}H NMR ($CDCl_3$) δ ppm: 3.5(s,2H); 3.7(s,3H); 6.65(m,2H); 7.05(m,2H).

Step 2

Methyl 4-aminophenylacetate (110g, 0.667mol) was added dropwise to acetic anhydride (600ml), maintaining the temperature of the reaction mixture below 30°C by external cooling. Once the addition was complete the mixture was cooled to below 10°C and concentrated nitric acid (85 ml) was added dropwise. Once the addition of the acid was

complete, the mixture was allowed to warm to room temperature and poured onto a mixture of ice and water. The precipitated solid was collected by filtration and dried to give methyl 4-acetamido-3-nitrophenylacetate (120g) as a pale yellow solid.

^{1}H NMR ($CDCl_3$) δ ppm: 2.3(s,3H); 3.65(s,2H); 3.7(s,3H); 7.55(dd,1H); 8.1(d,1H); 8.7(d,1H); 10.3(b,1H).

Step 3

Methyl 4-acetamido-3-nitrophenylacetate (40g, 0.159mol)) was dissolved in methanol (400ml) and hydrogenated at 5bar over a 5% palladium on carbon catalyst. The catalyst was removed by filtration and the filtrate evaporated *in vacuo* to give methyl 4-acetamido-3-aminophenylacetate.

Step 4

Methyl 4-acetamido-3-aminophenylacetate (77g, 0.373mol) was taken up in a mixture of acetic acid (210ml) and water (210ml) and cooled to below 5°C. A solution of sodium nitrite (38.63g, 0.559mol) in water (200ml) was added dropwise, and once the addition was complete the mixture was stirred for 4hours, warming slowly to room temperature. The mixture was diluted with ethyl acetate and the insoluble material removed by filtration. The filtrate was washed with brine, dried over anhydrous magnesium sulfate, filtered and the solvent evaporated *in vacuo*, to give a viscous residue (51g) used directly in the next step.

Step 5

The product obtained in Step 4 above was dissolved in a solution of methanol (400ml) previously saturated with hydrogen chloride and the mixture stirred for 2hours. The solvent was removed *in vacuo*, the residue taken up in water, neutralised with saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl 5-benzotriazoleacetate (35g) as a reddish liquid which crystallised on standing.

^{1}H NMR ($CDCl_3$) δ ppm: 3.7(s,3H); 3.8(s, 2H); 7.35(d,1H); 7.8(b,2H); 13.6(b,1H).

Step 6

A solution of methyl 5-benzotriazoleacetate (10g, 0.0523mol) in N,N-dimethylformamide was added dropwise to a chilled (ice-bath) suspension of sodium hydride (60% dispersion in oil, 2.3g, 0.0575mol) in N,N-dimethylformamide. When the addition was

complete, the ice-bath was removed and the mixture stirred for 1hour. N-Propyl iodide (9.78g, 0.0575mol) was added dropwise, and once the addition was complete the mixture was stirred at room temperature for 3hours. The reaction mixture was poured onto ice/water, and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by column chromatography to afford methyl (2-propylbenzotriazol-5-yl)acetate (4.8g).

^{1}H NMR ($CDCl_3$) δ ppm: 0.9(t,3H); 2.1(m,2H); 3.7(s,3H); 3.8(s,2H); 4.65(t,2H); 7.3(dd,1H); 7.7(d,1H); 7.8(d,1H).

Step 7

The acetate prepared in Step 6 above (4.8g, 0.0206mol) was dissolved in methanol (60ml) and potassium hydroxide flakes (1.27g, 0.0226mol) added. The mixture was refluxed for 2hours, then cooled and the solvent evaporated *in vacuo*. The residual solid was dissolved in water and extracted with diethyl ether. The aqueous solution was acidified to pH 1 by addition of dilute aqueous hydrochloric acid and extracted with ethyl acetate. The ethyl acetate extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford (2-propylbenzotriazol-5-yl)acetic acid (3.6g) as a colourless solid.

Step 8

The acid prepared in Step 7 (0.438g, 0.002mol) was dissolved in dichloromethane (5ml) and one drop of N,N-dimethyl formamide was added. Oxalyl chloride (0.307g, 0.0022mol) was added dropwise, and the mixture stirred at room temperature for 2hours. The solvent was removed *in vacuo*, the residue taken up in xylene and added to a mixture of 5-amino-4-chloro-3-methylisothiazole (0.446g, 0.003mol) in xylene and heated at reflux for 2hours. The mixture was cooled to room temperature and the solvent evaporated *in vacuo*. The residue was taken up in ethyl acetate, washed sequentially with saturated aqueous sodium bicarbonate solution and brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by flash column chromatography, eluting with 2:1 hexane : ethyl acetate, to give the title compound (0.34g) as a sandy-coloured solid.

^{1}H NMR ($CDCl_3$) δ ppm: 1.0(t,3H); 2.15(m,2H); 2.35(s,3H); 4.0(s,2H); 4.7(t,2H); 7.35(dd,1H); 7.85(d,1H); 7.95(d,1H); 8.15(b,1H).

EXAMPLE 2

This Example illustrates an emulsifiable concentrate composition which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The emulsifiable concentrate has the following composition:

	% by weight
Compound No. 1	25.0
SYNPERONIC NP13	2.5
Calcium dodecylbenzenesulphonate	2.5
AROMASOL H	70.0

EXAMPLE 3

This Example illustrates a wettable powder composition which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The wettable powder has the following composition:

	% by weight
Compound No. 1	25.0
Silica	25.0
Sodium lignosulphonate	5.0
Sodium lauryl sulphate	2.0
Kaolin	43.0

EXAMPLE 4

This Example illustrates a dustable powder which may be applied directly to plants or other surfaces. The dustable powder has the following composition:

	% by weight
Compound No. 1	1.0
Talc	99.0

EXAMPLE 5

This Example illustrates an oil miscible liquid formulation suitable for application by ultra low volume techniques after mixing with an organic diluent. The formulation has the following composition:

	% by weight
Compound No. 1	10.0
SOLVESSO 200	90.0

EXAMPLE 6

This Example illustrates a capsule suspension concentrate which is readily convertible, by addition to water, into a preparation suitable for application as an aqueous spray. The capsule suspension concentrate has the following composition:

	% by weight
Compound No. 1	10.0
AROMASOL H	10.0
Toluene di-isocyanate	3.0
SYNPERONIC A7	1.0
Polyvinyl alcohol	2.0
Bentonite	1.5
KELTROL	0.1
Water	72.4

EXAMPLE 7

This Example illustrates a ready for use granular formulation that is prepared from a preformed granular carrier. The granular formulation has the following composition:

	% by weight
Compound No. 1	0.5
SOLVESSO 200	0.2
SYNPERONIC A7	0.1
Calcium carbonate granules (diameter 0.3-0.7mm)	99.2

EXAMPLE 8

This Example illustrates a ready for use granular formulation that is prepared by granulation of the powdered components. The granular formulation has the following composition:

	% by weight
Compound No. 1	0.5
Sodium lignosulphonate	5.0
Kaolin	94.5

EXAMPLE 9

This Example illustrates an aqueous suspension concentrate composition which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The suspension concentrate has the following composition:

	% by weight
Compound No. 1	25.0
Sodium lignosulphonate	3.0
Propylene glycol	10.0
Bentonite	2.0
KELTROL	0.1
PROXEL	0.1
Water	59.8

EXAMPLE 10

This Example illustrates a water dispersible granule formulation which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The water dispersible granule has the following composition:

	% by weight
Compound No. 1	25.0
Silica	5.0
Sodium lignosulphonate	10.0
Sodium lauryl sulphate	5.0
Sodium acetate	10.0
Montmorillonite powder	45.0

EXAMPLE 11

This Example illustrates the pesticidal/insecticidal properties of compounds of formula (I). The activities of individual compounds of formula (I) were determined using a variety of pests. With the exception of nematodes, the pests were treated with a liquid composition containing 500 parts per million (ppm) by weight of a compound unless otherwise stated. Each composition was made by dissolving the compound in an acetone and ethanol (50:50 by volume) mixture and diluting the solution with water containing 0.05% by volume of a wetting agent, SYNPERONIC NP8, until the liquid composition contained the required concentration of the compound.

The test procedure adopted with regard to each pest, except nematodes, was essentially the same and comprised supporting a number of the pests on a medium which was usually a substrate, a host plant or a foodstuff on which the pests feed, and treating either or both the medium and the pests with a composition. Pest mortality was assessed usually between [redacted] and five days after treatment. Knockdown of housefly (*Musca domestica*) was assessed 15 minutes after treatment.

The test procedure for nematodes involved dissolving the compound in an acetone and ethanol (50:50 by volume) mixture and diluting the solution with water to obtain a final concentration of the compound of 12.5ppm. J2 infective juveniles of *Meloidogyne incognita* were suspended in the solution in a glass vial and mortality assessed after a period of three days.

The results of the tests are presented below. The results indicate a grading of mortality (score) designated as 99, 55 or 0 wherein 99 indicates 80-100% mortality, 55 indicates 40-79% mortality and 0 indicates less than 40% mortality.

Compound No. (Table)	TETRUR	MYZUPE	MUSCDO AK	MUSCDO AC	HELIVI	LAPHEG	MELGIN
1 (1)	99	0	-	-	99	99	55
3 (1)	0	99	0	55	55	55	0
4 (1)	0	0	0	0	55	0	0
5 (1)	99	0	99	99	0	55	99
6 (1)	55	55	0	55	0	99	99
7 (1)	99	55	0	99	99	99	0
8 (1)	99	99	99	99	55	99	55
9 (1)	0	99	99	99	55	0	0
10 (1)	99	55	99	99	99	99	0

TETRUR = *Tetranychus urticae* MYZUPE = *Myzus persicae*

MUSCDO AK = *Musca domestica* (kill) MUSCDO AC = *Musca domestica* (knockdown)

HELIVI = *Heliothis virescens* LAPHEG = [redacted]

MELGIN = *Meloidogyne incognita*

EXAMPLE 12

This Example illustrates the fungicidal properties of compounds of formula (I). The compounds were tested against a variety of foliar fungal diseases of plants. The technique employed was as follows.

Plants were grown in John Innes Potting Compost (No. 1 or 2) in 4cm diameter, 3.5cm depth minipots. The test compounds were individually formulated as a solution either in acetone or acetone/ethanol (1:1 by volume) which was diluted in deionised water to a concentration of 100ppm (that is, 1mg of compound in a final volume of 10ml) immediately before use.

Individual compounds of formula (I) were applied as a foliar (Folr) application (where the chemical solution was applied to the foliage of the test plants by spraying the plant to maximum droplet retention). When foliar sprays were applied to monocotyledonous crops, TWEEN™ 20 (0.1% by volume) was added.

These tests were carried out against *Plasmopara viticola* (PLASVI), on vines; *Phytophthora infestans lycopersici* (PHYTIN), on tomatoes; *Erysiphe graminis f.sp. tritici* (ERYGST) and *Puccinia recondita* (PUCCRT), on wheat. Each treatment was applied to two replicate plants for *Plasmopara viticola* and *Phytophthora infestans lycopersici.* In tests on *Erysiphe graminis f.sp. tritici* and *Puccinia recondita* two replicate pots each containing 6 to10 plants were used for each treatment. The *Plasmopara viticola*, *Phytophthora infestans lycopersici* and *Puccinia recondita* plants were inoculated with a calibrated fungal spore suspension one day after (Prev) chemical application. The *Erysiphe graminis f.sp. tritici* were inoculated using a 'shake' inoculation technique, six hours after (Prev) chemical application.

After chemical application and inoculation, the *Plasmopara viticola*, *Phytophthora infestans lycopersici* and *Puccinia recondita* plants were incubated under high humidity conditions and then put into an appropriate environment to allow infection to proceed, until

the disease was ready for assessment. After chemical application and inoculation, the *Erysiphe graminis f.sp. tritici* plants were put directly into an appropriate environment to allow infection to proceed. For *Plasmopara viticola*, the plants were reincubated under high humidity conditions for 24hours prior to assessment. The time period between inoculation and assessment varied from four to fourteen days according to the disease and environment. However, each individual disease was assessed after the same time period for all compounds.

Assessments were performed on a single leaf of each of the two replicate plants for *Plasmopara viticola*. For *Phytophthora infestans lycopersici,* assessments were carried out on two leaves on each of the replicate plants and a mean disease level across the two leaves was recorded per replicate. For *Erysiphe graminis f.sp. tritici* and *Puccinia recondita* assessments were carried out collectively on the plants in each replicate pot.

The disease level present (that is, the percentage leaf area covered by actively sporulating disease) was assessed visually using the banded assessment scale shown below). For each treatment, the assessed value for each replicate was then meaned before being expressed as a percentage of the mean level of disease present on the untreated control plants. This calculated value is referred to as a POCO (Percentage of Control) value.

An example of a typical calculation is as follows:

Mean disease level for treatment A = 25

Mean disease level on untreated controls = 90

$$\text{POCO} = \frac{\text{Mean disease level for treatment A}}{\text{Mean disease level on untreated controls}} \times 100 = \frac{25}{90} \times 100 = 27.8$$

This POCO value is then rounded to the nearest whole number on a 0-100% scale; in this particular example, the POCO result will be 28.

The POCO results are shown below.

Compound Number (Table)	ERYSGT (foliar)	PHYTIN (foliar)	PLASVI (foliar)	PUCCRT (foliar)
1 (1)	0	3	0	0
3 (1)	0	0	33	0
4 (1)	0	100	100	0
5 (1)	0	100	0	0
6 (1)	0	-	0	0
7 (1)	0	100	100	0
8 (1)	0	0	0	0
9 (1)	100	0	3	0

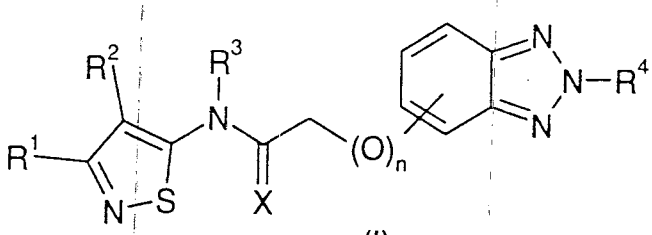
ERYSGT = *Erysiphe graminis tritici*

PHYTIN = *Phytophthora infestans lycopersici*

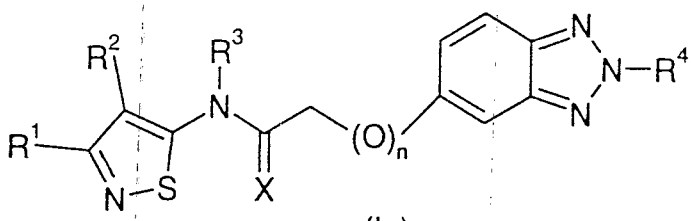
PLASVI = *Plasmopara viticola*

PUCCRT = *Puccinia recondita*

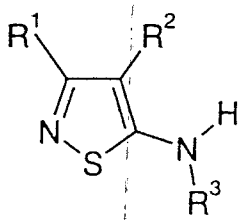
Chemical Formulae in the Description



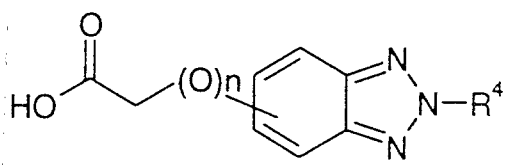
(I)



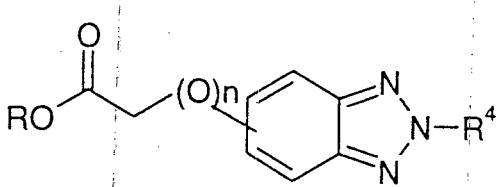
(Ia)



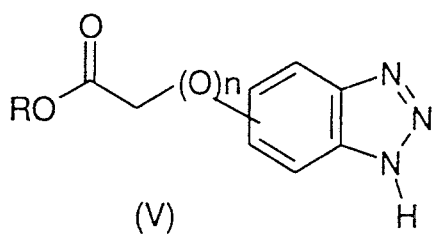
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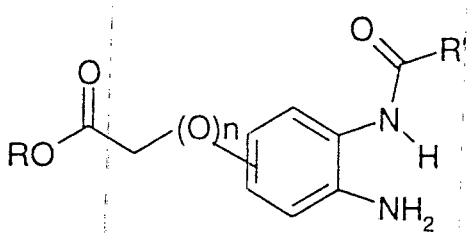
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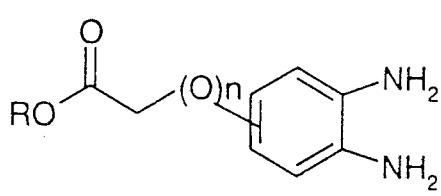
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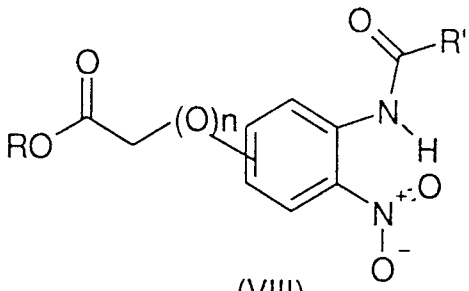
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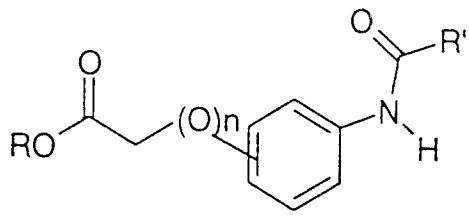
(VI)



(VII)



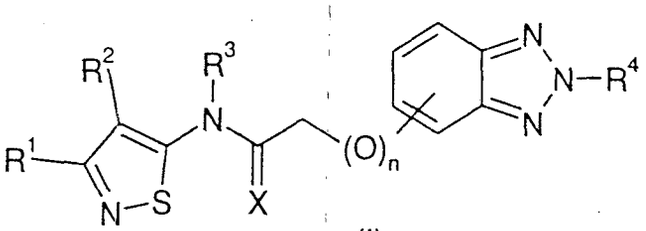
(VIII)



(IX)

CLAIMS

1. A compound of formula (I):



(I)

wherein R^1 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{3-6} cycloalkyl or C_{1-6} alkoxy(C_{1-6})alkyl; R^2 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, cyano, nitro, CHO, CH=NOR^5, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or C_{1-6} alkyl$S(O)_q$; or together R^1 and R^2 form a five or six membered saturated or unsaturated carbocyclic ring, optionally substituted by one or two C_{1-6} alkyl groups; R^3 is hydrogen, C_{1-6} alkyl, CH_2(C_{1-4} haloalkyl), C_{3-6} alkenyl, C_{3-6} alkynyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, formyl, optionally substituted phenoxycarbonyl, optionally substituted phenyl(C_{1-4})alkyl or $S(O)_pR^6$; R^4 is hydrogen, C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{3-6} alkenyl, C_{3-6} alkynyl, C_{3-7} cycloalkyl, C_{3-6} cycloalkyl(C_{1-6})alkyl, C_{3-6} haloalkenyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted phenyl(C_{1-4})alkyl or optionally substituted heteroaryl; R^5 is hydrogen, C_{1-6} alkyl, optionally substituted phenyl or optionally substituted phenyl(C_{1-4})alkyl; R^6 is C_{1-6} alkyl, C_{1-6} haloalkyl or optionally substituted phenyl; X is O or S; n is 0 or 1; and p and q are, independently, 0, 1 or 2.

2. Processes for making compounds of formula (I) as defined in claim 1.

3. A fungicidal, insecticidal, acaricidal, molluscicidal or nematicidal composition comprising a fungicidally, insecticidally, acaricidally, molluscicidally or nematicidally effective amount of a compound of formula (I) and a carrier or diluent therefor.

4. A method of combating and controlling fungi comprising applying to a plant, to a seed of a plant, to the locus of the plant or seed or to the soil a fungicidally effective amount of a compound of formula (I) as claimed in claim 1, or a composition containing a compound of formula (I) as claimed in claim 3.

5. A method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I) as claimed in claim 1, or a composition containing a compound of formula (I) as claimed in claim 3.

6. A method as claimed in claim 5 wherein the insect pests are insect pests of plants.

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TRADUCCION

Oficina de Patentes - Autoridad Ejecutiva del Departamento de Comercio e Industria.

Oficina de Patentes - Cardiff Road, Newport, South Wales NP10 8QQ

El que suscribe, funcionario debidamente autorizado para firmar y expedir certificados en representación del Controlador General, en virtud de Artículo 74(1) y (4) de la Ley de Desregulación y Contrataciones de 1994, certifica por la presente que los documentos adjuntos son copia fiel de la documentación presentada originariamente en relación con la solicitud de patente identificada en el presente certificado.

De acuerdo con el Reglamento de Patentes (Reinscripción de Sociedades) de 1982, si una compañía mencionada en este certificado y los documentos adjuntos ha sido reinscripta de acuerdo a la Ley de Sociedades de 1980 con el mismo nombre que aquél con el cual estaba inscripta inmediatamente antes de la reinscripción, excepto la sustitución o inclusión en la última parte del nombre de las palabras "public limited company" o su equivalente en galés, las referencias al nombre de la sociedad que figuren en este certificado y cualesquiera documentos adjuntos se considerarán como referidas al nombre con el cual ha sido reinscripta.

De acuerdo con la norma, las palabras "public limited company" pueden ser sustituidas por p.l.c., plc, P.L.C. o PLC.

Con la reinscripción de acuerdo a la Ley de Sociedades no se constituye una nueva entidad legal, sino que simplemente se somete a la sociedad a determinadas reglas legales societarias adicionales.

Firmado, ilegible. Fecha: 16 de marzo del 2000

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(Sello en relieve sobre oblea y cinta)

En la hoja siguiente dice:

Formulario de Patente 1/77

OFICINA DE PATENTES Oficina de Patentes - Cardiff Road, Newport, Gwent NP9 1RH

Solicitud de Patente

Recibido en mano el 20 de abril de 1999

1. Su referencia: PPD 50402/ GB/ P

2. Solicitud de patente número: **9909062.3**

3. Nombre completo, domicilio y código postal del o los solicitantes:

ZENECA Limited, 15 Stanhope Gate, LONDON WIY 6LN, REINO UNIDO

Número ADP de patentes: 6254007002

Si el solicitante es una corporación, indicar el país/estado : REINO UNIDO

4. Título de la Invención : **COMPUESTOS QUIMICOS**

5. Nombre del agente (si corresponde) :

FRANCIS JOHN TIERNEY

Domicilio de servicio en el Reino Unido al cual se debe enviar la correspondencia:

Intellectual Property Dept., ZENECA Pharmaceuticals, Jealott's Hill Research Station, PO Box 3538, Bracknell Berkshire RG42 6YA, Mereside, REINO UNIDO

Número de ADP de patentes: 06786941001

9. Indique la cantidad de hojas de todos los siguientes adjuntos que ingresa con este formulario. No cuente copias de un mismo documento.

Hojas de continuación de este formulario :

793
191

Memoria descriptiva: 35

Reivindicaciones: 2

11. Solicito/solicitamos el otorgamiento de una patente sobre la base de esta solicitud. Firmado. Fecha: 20/04/99

12. Nombre y número telefónico del representante en el Reino Unido:

VIJAYA KUMARI MALLIPEDDI - 01344 414365

DAWN LISA ROYAL - 01344 414079

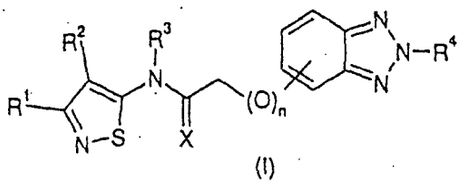
Otros items en blanco.

COMPUESTOS QUÍMICOS

La presente invención se relaciona con derivados isotiazol, con procesos para prepararlos, con composiciones fungicidas, insecticidas, acaricidas, molusquicidas y nematicidas que los comprenden, con métodos para usarlos para combatir enfermedades provocadas por hongos (especialmente enfermedades provocadas por hongos en las plantas) y con métodos para usarlos para combatir y controlar plagas de insectos, ácaros, moluscos y nematodos.

En WO95/31448, WO97/18198, WO98/02424 y WO98/05670 se describen derivados isotiazol.

La presente invención provee un compuesto de fórmula (I):



(I)

en donde R^1 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi, C_{1-6} haloalcoxi, C_{1-6} alquiltio, C_{3-7} cicloalquilo o C_{1-6} alcoxi (C_{1-6}) alquilo; R^2 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, ciano, nitro, CHO, $CH=NOR^5$, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo o C_{1-6} alquil$S(O)_q$; o juntos R^1 o R^2 forman un anillo carbocíclico saturado o insaturado de cinco o seis miembros, opcionalmente sustituido por uno o dos grupos C_{1-6} alquilo; R^3 es hidrógeno, C_{1-6} alquilo, CH_2(C_{1-4} haloalquilo), C_{3-6} alquenilo, C_{3-6} alquinilo, C_{1-6} alcoxi(C_{1-6})alquilo, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo, formilo, fenoxicarbonilo opcionalmente sustituido, fenil(C_{1-4})alquilo opcionalmente sustituido o $S(O)_pR^6$; R^4 es hidrógeno, C_{1-8} alquilo, C_{1-6} haloalquilo, C_{1-6} cianoalquilo, C_{3-6} alquenilo, C_{3-6} alquinilo, C_{3-7} cicloalquilo, C_{3-7} cicloalquil (C_{1-6})

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alquilo, C_{3-6} haloalquenilo, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{1-6} carboxialquilo, C_{1-6} alquilcarbonil (C_{1-6}) alquilo, C_{1-6} alcoxicarbonil (C_{1-6}) alquilo, C_{1-6} alquiltio (C_{1-6}) alquilo, C_{1-6} alquilsulfinil (C_{1-6}) alquilo, C_{1-6} alquilsulfonil (C_{1-6}) alquilo, aminocarbonil (C_{1-6}) alquilo, C_{1-6} alquilaminocarbonil (C_{1-6}) alquilo, di(C_{1-6}) alquilaminocarbonil (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^5 es hidrógeno, (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^6 es C_{1-6} alquilo, C_{1-6} haloalquilo, o fenilo opcionalmente sustituido; X es O o S; n es 0 o 1; y p y q son, independientemente, 0, 1 o 2.

Cada porción alquilo es una cadena lineal o ramificada y es, por ejemplo, metilo, etilo, n-propilo, n-butilo, n-pentilo, n-hexilo, iso-propilo, n-butilo, sec-butilo, iso-butilo, tert-butilo o neo-pentilo.

Halógeno es flúor, cloro, bromo o yodo.

Los grupos haloalquilo son grupos alquilo que son opcionalmente sustituidos con uno o más entre los mismos u otros átomos de halógeno y son, por ejemplo, CF_3, CH_2CF_3 o CH_2CHF_2.

Fenil (C1-4) alquilo es, por ejemplo, 1-fenilet-1-il, 2-fenilet-1-il, 2-fenilprop-2-il, 3-fenilprop-1-il, pero es preferentemente bencilo.

El término heteroarilo se refiere a un anillo aromático que contiene uno o más heteroátomos (preferentemente uno o dos heteroátomos) seleccionados entre O, S y N. Entre los ejemplos de tales anillos se incluyen piridina, pirimidina, furano, tiofeno, tiazol, oxazol e isoxazol.

Para porciones de fenilo o grupos heteroarilo se prefiere que estén opcionalmente sustituidos por uno o más sustituyentes seleccionados

independientemente entre halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{1-6} alcoxi, C_{1-6} haloalcoxi, C_{1-6} alquiltio, C_{1-6} haloalquiltio, C_{1-6} alquilsulfinilo, C_{1-6} haloalquilsulfinilo, C_{1-6} alquilsulfonilo, C_{1-6} haloalquilsulfonilo, C_{2-6} alquenilo, C_{2-6} haloalquenilo, C_{2-6} alquinilo, C_{3-7} cicloalquilo, nitro, ciano, CO_2H, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo, R^8R^9N o $R^{10}R^{11}NC(O)$; en donde R^8, R^9, R^{10} y R^{11} son, independientemente, hidrógeno o C_{1-6} alquilo.

Se prefiere que R1 sea etilo o, especialmente, metilo.

Se prefiere que R2 sea hidrógeno, halógeno (especialmente cloro) o ciano.

Se prefiere que n sea 0.

Se prefiere que los compuestos de la invención sean de la fórmula (Ia).

En un aspecto adicional, la presente invención provee un compuesto de fórmula (Ia), en donde R^1 es C_{1-4} alquilo (especialmente metilo o etilo); R^2 es hidrógeno, halógeno (especialmente cloro o bromo) o ciano; o juntos R^1 y R^2 forman un anillo ciclopentilo, ciclohexilo o fenilo; R^3 es hidrógeno, C_{1-4} alquilo (especialmente metilo o etilo), fenil (C_{1-4}) alquilo (especialmente bencilo), C_{1-4} alquilcarbonilo (especialmente acetilo) o C_{1-4} alquilsulfonilo (especialmente metansulfonilo); R^4 es C_{1-6} alquilo [opcionalmente sustituido con halógeno, C_{1-4} alcoxi, fenilo (el mismo opcionalmente sustituido con halógeno), CO_2H, $CONH_2$ (el mismo opcionalmente sustituido con C_{1-4} alquilo), ciano, C_{3-6} cicloalquilo o $CO(C_{1-4}$ alcoxi)], C_{3-6} alquenilo, C_{3-6} alquinilo, C_{3-6} cicloalquilo, fenilo [opcionalmente sustituido con halógeno, C_{1-4} haloalquilo (especialmente CF_3), nitro, CO_2H, o ciano] o heteroarilo (especialmente piridilo o pirimidinilo) [opcionalmente sustituido con C_{1-4} alquilo o C_{1-4} haloalquilo].

Los compuestos en la siguientes Tablas ilustran los compuestos de la

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invención.

TABLA 1

Los compuestos de la Tabla 1 son compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es hidrógeno. X es oxígeno, n es 0 y R^4 es como se describe en la Tabla de más abajo.

Compuesto Nro. R^4 ^{1}H NMR □ ppm ($CDCl_3$ salvo que se establezca lo contrario)

1 n-propilo 1.0 (t, 3H); 2,15 (m, 2H); 2,35 (s, 3H); 4,0 (s, 2H); 4,7 (t, 2H); 7,35 (dd, 1H); 7,85 (d, 1H); 7,95 (d, 1H); 8,15 (b, 1H)

2 4-CF_3-C_6H_4 2,4 (s, 3H); 4,1 (s, 2H); 7,5 (m, 1H), 7,8-7,9 (m, 4H); 8,5 (bd, 2H); 10,35 (s, 1H)

3 metilo 2,35 (s, 3H); 4,0 (s, 2H); 4,5 (s, 3H); 7,35 dd, 1H), 7,8 (d, 1H); 7,9 (d, 1H); 8,05 (b, 1H)

4 4-F-$C_6H_4CH_2$ (DMSO-d6): 2,35 (s, 3H); 4,05 (s, 2H); 5,8 (s, 2H); 7,0 (m, 2H); 7,4 (m, 3H); 7,8 (m, 2H); 10,9 (b, 1H)

5 CF_3CH_2 2,4 (s, 3H); 4,0 (s, 2H); 5,3 (q, 2H); 7,4 (dd, 1H), 7,85 (d, 1H); 7,95 (d, 1H); 8,15 (b, 1H)

6 n-pentilo 0,9 (t, 3H); 1,35 (m, 4H); 2,15 (m, 2H); 2,4 (s, 3H); 4,05 (s, 2H); 4,7 (t, 2H); 7,35 (dd, 1H); 7,85 (d, 1H); 7,9 (d, 1H); 8,15 (b, 1H)

7 2-Cl-3-CF_3-C_6H_3 2,4 (s, 3H); 4,05 (s, 2H); 7,45 (dd, 1H); 7,75 (dd, 1H); 7,95 (m, 3H); 8,05 (m, 1H); 8,2 (b, 1H)

8 1-metilpropil 0,85 (t, 3H); 1,7 (d, 3H); 2,0-2,2 (m, 2H); 2,35 (s, 3H); 4,0 (s, 2H); 4,9 (m, 1H); 7,3 (dd, 1H); 7,85 (d, 1H); 7,9 (d, 1H); 8,15 (b, 1H)

9 etil 1,75 (t,3H); 2,35 (s, 3H); 4,0 (s, 2H); 4,8 (q, 2H); 7,35 (dd, 1H); 7,8 (b, 1H); 7,9 (d, 1H); 8,1 (b, 1H)

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10 2,2-dimetilpropilo 1,05 (s, 9H); 2,4 (s, 3H); 4,05 (s, 2H); 4,55 (s, 2H); 7,35 (dd, 1H); 7,85 (b, 1H); 7,95 (d, 1H); 8,15 (b, 1H)

11 n-butilo

12 2-metilpropilo

13 2-metoxietilo

14 metoximetilo

15 $CH_2CH=C(CH_3)_2$

16 2-cloroetilo

17 alilo

18 propargilo

19 CH_2CO_2H

20 $CH_2CO_2CH_3$

21 $CH_2CO_2C_2H_5$

22 $CH(CH_3)CO_2H$

23 $CH(CH_3)CO_2CH_3$

24 $CH(CH_3)CO_2C_2H_5$

25 $C(CH_3)_2CO_2H$

26 $C(CH_3)_2CO_2CH_3$

27 $C(CH_3)_2CO_2C_2H_5$

28 CH_2CONH_2

29 $CH(CH_3)CONH_2$

30 $C(CH_3)_2CONH_2$

31 $CH_2CONHCH_3$

32 $CH_2CON(CH_3)_2$

33 $CH(CH_3)CONHCH_3$

34	$CH(CH_3)CON(CH_3)_2$
34	$CH_2CO_2C(CH_3)_3$
35	cianometilo
36	pentafluoroetilo
37	ciclopentilo
38	2-fluoroetilo
39	difluorometilo
40	2-tioetoxietilo
41	CH_2-ciclopropilo
42	CH_2-ciclopentilo
43	CH_2-ciclohexilo
44	2-NO_2-C_6H_4
45	piridilo
46	5-CF_3-2-piridilo
47	C_6F_5
48	4-CO_2H-C_6H_4
49	2-Cl-4-CN-C_6H_3
50	3,5-dimetil-pirimidin-2-ilo

TABLA 2

La Tabla 2 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 3

La Tabla 3 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el

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compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 4

La Tabla 4 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 5

La Tabla 5 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 6

La Tabla 6 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 7

La Tabla 7 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es hidrógeno, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 8

La Tabla 8 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es flúor, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 9

La Tabla 9 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es bromo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

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TABLA 10

La Tabla 10 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es ciano, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 11

La Tabla 11 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es hidrógeno, X es oxígeno, n es 1 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 12

La Tabla 12 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 13

La Tabla 13 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 14

La Tabla 14 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 15

La Tabla 15 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 16

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La Tabla 16 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 17

La Tabla 17 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 18

La Tabla 18 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es hidrógeno, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 19

La Tabla 19 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es flúor, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 20

La Tabla 20 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es bromo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 21

La Tabla 21 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es ciano, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 22

La Tabla 22 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es

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etilo, R^2 es cloro, R^3 es hidrógeno, X es oxígeno, n es 1 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 23

La Tabla 23 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 24

La Tabla 24 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 25

La Tabla 25 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 26

La Tabla 26 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 27

La Tabla 27 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 28

La Tabla 28 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1

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y R^2 forman un anillo ciclopentilo, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 29

La Tabla 29 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 30

La Tabla 30 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 31

La Tabla 31 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 32

La Tabla 32 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 33

La Tabla 33 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 34

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La Tabla 34 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 35

La Tabla 35 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 36

La Tabla 36 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 37

La Tabla 37 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 38

La Tabla 38 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 39

La Tabla 39 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 40

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La Tabla 40 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

Los compuestos de la fórmula (I) pueden hacerse por acilación de un 5-aminoisotiazol (II) con un ácido carboxílico apropiado (III), preferentemente en presencia de un agente conocido de unión tal como la 1,3-diciclohexilcarbodiimida o la 1-(3-dimetilaminopropil)-3-etilcarbodiimida. Como alternativa, el ácido carboxílico (III) puede convertirse primero en un cloruro ácido, un anhídrido o un cloroformiato adecuado para su reacción con una amina con el fin de dar una amida; tales procedimientos se describen, por ejemplo, en J March, Advanced Organic Chemistry, Tercera Edición, John Wiley and Sons, Nueva York, 1985, páginas 370-376, y en las referencias presentes en el mismo.

Los 5-aminoisotiazoles (II) son compuestos que se pueden conseguir comercialmente o pueden ser preparados a partir de materiales iniciales disponibles comercialmente por métodos descriptos en la literatura (véanse, por ejemplo, C Oliver Kappe, Robert Flammang y Curt Wentrup, Heterocycles, Vol 37 Nº 3, 1616 (1994), A Adams y R Slack, J Chem Soc, 3061 (1959), y Ronald E Hackler, Kennet W Burow Jr, Sylvester V Kaster y David I Wickisier, J Heterocyclic Chem, 26, 1575, (1989).

Los ácidos carboxílicos (III) pueden ser preparados pos hidrólisis de sus correspondientes ésteres (IV) por los métodos descriptos en el arte. Los ésteres pueden ser elegidos para ser hidrolizados bajo condiciones neutras, básicas o acídicas, y las condiciones se eligen de tal forma que el sustituyente

R^4 no sea afectado por la reacción de hidrólisis. Los ésteres capaces de ser hidrolizados en forma rápida en cualquier condición se conocen en la literatura, y ésteres adecuados se pueden seleccionar, por ejemplo, de la siguiente referencia: Theodor W. Greene, Protective Groups in Organic Synthesis, Capítulo 5, John Wiley & Sons, New York, 1981.

Los ésteres (IV) pueden prepararse por reacción de benzotriazoles (V) con un compuesto R^4L, en donde L es un grupo saliente adecuado tal como un halógeno. (Para reacciones de acoplamiento adecuadas véase, por ejemplo, Alan R Katritzky y Charles W Rees, Comprehensive Heterocyclic Chemistry, Pergamon Press, 1984 y las referencias allí presentes). Las reacciones tales como éstas pueden dar lugar a productos isoméricos. El isómero (IV) deseado usualmente se separa de los otros presentes por medio de técnicas estándar tales como cromatografía en columna rápida o por cristalización de una solución conteniendo uno o más solventes adecuados.

Los benzotriazoles (V) se pueden preparar por la diazotación secuencial y la hidrólisis de la diamina acilada (VI), o por hidrólisis de una diamina acilada (VI) para dar una diamina (VII) que puede ser entonces diazotada. Los procedimientos para la formación de benzotriazoles (V) de tales precursores son bien conocidos en la literatura. (véase, por ejemplo, Alan R Katritzky y Charles W Rees, Comprehensive Heterocyclic Chemistry, Pergamon Press, 1984 y las referencias allí incluidas)

Las diaminas aciladas (VI) se pueden preparar por la reducción de la correspondiente nitroanilida (VIII), que a su vez se prepara por nitración de una anilida (IX). Los procedimientos para realizar estas transformaciones son bien conocidos en la literatura. (Ver, por ejemplo, las referencias dadas en J March,

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Advanced Organic Chemistry, Tercera Edición, John Wiley and Sons, Nueva York, 1985). Las anilidas (IX) son conocidas en el arte y se pueden preparar a partir de compuestos conocidos usando procedimientos descriptos en el arte.

Los compuestos de fórmula (I) en donde R^3 es diferente a hidrógeno, se pueden preparar por medio de la reacción de un compuesto de fórmula (I) en donde R^3 es hidrógeno con un compuesto R^3L^*, en donde L^* es un grupo saliente (tal como halógeno), en forma opcional en la presencia de una base y un catalizador de transferencia de fase. Ejemplos de agentes alquilantes adecuados incluyen, haluros de alquilo tales como ioduro de metilo y sulfatos de alquilo tales como dimetilsulfato. Agentes acilantes adecuados incluyen anhídridos tales como anhídrido acético, cloruros de ácido tales como cloruro de acetilo o cloruro de benzoílo y cloroformiatos tales como etil cloroformiato. Bases adecuadas incluyen bases orgánicas tales como trietilamina, piridina, alcóxidos de metales alcalinos tales como ter-butóxido de potasio y bases inorgánicas tales como hidruro de sodio y hidróxido de sodio. Catalizadores de transferencia de fase adecuados pueden seleccionarse usando las referencias de la literatura (ver, por ejemplo, en J March, Advanced Organic Chemistry, Tercera Edición, John Wiley and Sons, Nueva York, 1985, págs. 320-322 y las referencias allí incluidas).

Un compuesto de fórmula (I) cuando X es azufre puede prepararse a partir de un compuesto de fórmula (I), cuando X es oxígeno, mediante la reacción de dicho compuesto con 2,4-bis(4-metoxifenil)–1,3-ditia–2,4-difosfetan–2,4-disulfuro (reactivo de Lawesson) o pentasulfuro de fósforo en un solvente (tal como tolueno).

Los compuestos de fórmula (I) pueden usarse para combatir y controlar

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infestaciones de plagas de insectos tales como Lepidoptera, Diptera, Homoptera y Coleoptera, y también otros invertebrados plagas, por ejemplo, plagas de ácaros, de nematodos y de moluscos. Los insectos, los ácaros, los nematodos y los moluscos se indican colectivamente de aquí en más como plagas. Las plagas que pueden ser combatidas y controladas mediante el uso de los compuestos de la invención incluyen aquellas plagas asociadas con la agricultura (término que incluye el crecimiento de cultivos para productos de comida y de fibra), con la horticultura y con la cría de animales, con los animales de compañía, con la forestación y con el almacenamiento de productos de origen vegetal (tales como la fruta, el grano y la madera), aquellas plagas asociadas con el daño a estructuras hechas por el hombre y con la transmisión de enfermedades al hombre y a los animales.

Los ejemplos de especies que pueden ser controladas por los compuestos de fórmula (I) incluyen: *Myzus persicae* (pulgón), *Aphis gossypii* (pulgón), *Aphis fabae* (pulgón), *Lygus* spp (chinche), *Dysdercus* spp (chinche del algodón), *Nilaparvata lugens* (saltamontes), *Nephotettixc incticeps* (saltamontes), *Nezara* spp (chinche de olor), *Euschistus* spp (chinche de olor), *Leptocorisa* spp (chinche de olor), *Frankliniella occidentalis* (trip), Thrips spp (trip), *Leptinotarsa decemlineata* (escarabajo de la papa de Colorado), *Anthonomus grandis* (gorgojo), *Aonidiella* spp (cochinilla), *Trialeurodes* spp (mosca blanca), *Bemisia tabaci* (mosca blanca), *Spodoptera littoralis* (oruga marchadora del algodón), *Heliothis virescens* (oruga del tabaco), *Helicoverpa armigera* (oruga del algodón), *Pieris brassicae* (mariposa blanca), *Plutella xylostella* (polilla espalda de diamante), *Agrotis* spp (oruga cortadora), *Chilo suppressalis* (taladro del arroz), *Chortiocetes terminifera* (langosta), *Diabrotica*

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spp (taladros de las raíces), *Panonychus ulmi* (ácaro rojo europeo), *Panonychus citri* (ácaro rojo de los cítricos), *Tetranychus urticae* (ácaro de dos manchas), *Tetranychus cinnabarinus* (ácaro carmín), *Phyllocoptruta oleivora* (ácaro pardo de los cítricos), *Polyphagotarsonemus latus* (ácaro ancho), *Brevipalpus* spp (ácaro chato), *Liriomyza* spp (oruga minadora de las hojas), *Musca domestica* (mosca doméstica), *Aedes aegypti* (mosquito), *Anopheles* spp (mosquito), *Culex* spp (mosquito), *Blattella germanica* (cucaracha), *Periplaneta americana* (cucaracha), *Blatta orientalis* (cucaracha), *Ostrinia nubilalis* (taladro europeo del maíz), *Meloidogyne* spp (nematode de los nudos de las raíces), *Globodera* spp y *Heterodera* spp (nematode de cistos), *Pratylenchus* spp (nematode de las lesiones) y *Deroceras reticulatum* (babosa). Ejemplos adicionales incluyen insectos que afectan en forma adversa la salud del público y de los animales.

Los compuestos de fórmula (I) son también fungicidas activos y pueden usarse para controlar uno o más de los siguientes patógenos: *Pyricularia oryzae* (*Magnaporthe grisea*) en arroz y trigo y otras *Pyricularia* spp en otros hospedadores; *Puccinia recondita*, *Puccinia striiformis* y otros hongos en trigo, *Puccinia hordei*, *Puccinia striiformis* y otros hongos en cebada, y hongos en otros hospedadores (por ejemplo, pasto, avena, café, peras, manzanas, maníes, remolacha, verduras y plantas ornamentales); *Erysiphe cichoracearum* en cucúrbitas (por ejemplo, melón); *Erysiphe graminis* (musgo polvoriento) en cebada, trigo, avena y pasto, y otros musgos polvorientos en varios hospedadores, tales como *Sphaerotheca macularis* en lúpulo, *Sphaerotheca fuliginea* en cucúrbitas (por ejemplo, pepino), *Leveillula taurica* en tomates, radicheta y pimienta verde, *Podosphaera leucotricha* en manzanas y *Uncinula*

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necator en enredaderas; *Cochliobolus* spp, *Helminthosporium* spp, *Drechslera* spp (*Pyrenophora* spp), *Rhynchosporium* spp, *Mycosphaerella graminicola* (*Septoria tritici*) y *Phaeosphaeria nodorum* (*Stagonospora nodorum*), *Pseudocercosporella herpotrichoides* y *Gaeumannomyces graminis* en cereales (por ejemplo, trigo, centeno, avena), pasto y otros hospedadores; *Cercospora arachidicola* y *Cercosporidium personatum* en maníes y otras *Cercospora* spp en otros hospedadores, por ejemplo, remolacha, bananas, soja y arroz; *Botrytis cinerea* (moho gris) en tomates, frutillas, verduras, enredaderas y otros hospedadores, y otras *Botrytis* spp en otros hospedadores; *Alternaria* spp en verduras (por ejemplo, zanahorias), aceite de colza, manzanas, tomates, papas, cereales (por ejemplo, trigo) y otros hospedadores; *Venturia* spp (incluyendo *Venturia inaequalis* (costra)) en manzanas, peras, fruta de hueso, nueces de los árboles y otros hospedadores; *Cladosporium* spp en una variedad de hospedadores, incluyendo cereales (por ejemplo, trigo) y tomates; *Monilinia* spp en fruta de hueso, nueces de los árboles y otros hospedadores; *Didymella* spp en tomates, pasto, trigo, cucúrbitas y otros hospedadores; *Phoma* spp en aceite de colza, pasto, arroz, papas, trigo y otros hospedadores; *Aspergillus* spp y *Aureobasidium* spp en trigo, plantas leñosas y otros hospedadores; *Ascochyta* spp en arvejas, trigo, centeno y otros hospedadores; *Stemphylium* spp (*Pleospora* spp) en manzanas, peras, cebollas y otros hospedadores; enfermedades de verano (por ejemplo, hongo amargo (*Glomerella cingulata*), hongo negro o hongo manchador de hojas (*Botryosphaeria obtusa*), hongo manchador de la fruta de Brooks (*Mycosphaerella pomi*), moho Cedar de la manzana (*Gymnosporangium juniperi-virginianae*), moho manchado (*Gloeodes pomigena*), mancha de mosca

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(*Schizothyrium pomi*) y hongo blanco (*Botryosphaeria dothidea*)) en manzanas y peras; *Plasmopara viticola* en enredaderas; otros mohos infecciosos, tales como *Bremia lactucae* en lechuga, *Peronospora* spp en soja, tabaco, cebollas y otros hospedadores, *Pseudoperonospora humuli* en lúpulo y *Pseudoperonospora cubensis* en cucúrbitas; *Pythium* spp (incluyendo *Pythium ultimum*) en pasto y otros hospedadores; *Phytophthora infestans* en papas y tomates, y otras *Phytophthora* spp en verduras, frutillas, palta, pimienta, ornamentales, tabaco, cacao y otros hospedadores; *Thanatephorus cucumeris* en arroz y pasto, y oras *Rhizoctonia* spp en varios hospedadores tales como trigo y centeno, maníes, verduras, algodón y pasto; *Sclerotinia* spp en pasto, maníes, papas, aceite de colza y otros hospedadores; *Sclerotium* spp en pasto, maníes y otros hospedadores; *Gibberella fujikuroi* en arroz; *Colletotrichum* spp en una variedad de hospedadores, incluyendo pasto, café y verduras; *Laetisaria fuciformis* en pasto; *Mycosphaerella* spp en bananas, maníes, cítricos, pecanas, papaya y otros hospedadores; *Diaporthe* spp en cítricos, soja, melón, peras, lupino y otros hospedadores; *Elsinoe* spp en cítricos, enredaderas, aceitunas, pecanas, rosas y otros hospedadores; *Verticillium* spp en una variedad de hospedadores, incluyendo lúpulo, papas y tomates; *Pyrenopeziza* spp en aceite de colza y otros hospedadores; *Oncobasidium theobromae* en cacao causando muerte vascular; *Fusarium* spp, *Typhula* spp, *Microdochium nivale*, *Ustilago* spp, *Urocystis* spp, *Tilletia* spp y *Claviceps purpurea* en una variedad de hospedadores, pero en particular en trigo, centeno, pasto y maíz; *Ramularia* spp en remolacha, centeno y otros hospedadores; enfermedades pos cosecha, particularmente sobre fruta (por ejemplo, *Penicillium digitatum*, *Penicillium italicum* y *Trichoderma viride* en

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naranjas, *Colletotrichum musae* y *Gloeosporium musarum* en bananas y *Botrytis cinerea* en uvas); otros patógenos en enredaderas, notablemente *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarus*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* y *Stereum hirsutum;* otros patógenos en árboles (por ejemplo, *Lophodermium seditiosum*) o de leña, notablemente *Cephaloascus fragrans*, *Ceratocystis* spp, *Ophiostoma piceae*, *Penicillium* spp, *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* y *Aureobasidium pullulans;* y vectores fúngicos de enfermedades virales (por ejemplo, *Polymyxa graminis* en cereales como el vector del virus mosaico amarillo del centeno (BYMV) y *Polymyxa betae* en remolacha como el vector de rhizomania).

Un compuesto de fórmula (I) puede estar localizado acropética, basipética o localmente en un tejido vegetal para que sea activo contra uno o más hongos. Aún más, un compuesto de fórmula (I) puede ser lo suficientemente volátil como para ser activo en la fase vapor contra uno o más hongos en la planta.

La invención provee entonces un método para combatir y controlar insectos, ácaros, nematodos o moluscos que comprende aplicar una cantidad efectiva para la eliminación de insectos, de ácaros, de nematodos o de moluscos de un compuesto de fórmula (I), o de una composición que contiene un compuesto de fórmula (I), a una plaga, al sitio de una plaga o a una planta susceptible de ser atacada por una plaga, un método para combatir y controlar hongos que comprende aplicar una cantidad efectiva para la eliminación de hongos de compuesto de fórmula (I), o de una composición que contiene un compuesto de fórmula (I), a una planta, a la semilla de una planta, al sitio de la

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planta o de la semilla, al suelo o a cualquier medio de crecimiento (por ejemplo, una solución nutritiva). Los compuestos de fórmula (I) se usan preferiblemente contra insectos, ácaros, nematodos u hongos.

El término "planta", como se lo usa en la presente documentación, incluye retoños, arbustos y árboles. Además, el método fungicida de la invención incluye tratamientos protectores, curativos, sistémicos, erradicadores y antiesporulantes.

Como fungicidas, los compuestos de fórmula (I) se usan preferiblemente para propósitos agrícolas, hortícolas o decorativos bajo la forma de una composición.

Para aplicar un compuesto de fórmula (I) como un insecticida, un acaricida, un nematicida o un molusquicida a una plaga, al sitio de una plaga o a una planta susceptible de ser atacada por una plaga, o como un fungicida a una planta, a la semilla de una planta, al sitio de la planta o de la semilla, al suelo o a cualquier otro medio de crecimiento, se formula comúnmente un compuesto de fórmula (I), un diluyente o un vehículo adecuado inerte, y, opcionalmente, un agente activo en superficie. Los agentes activos en superficie son sustancias químicas que son capaces de modificar las propiedades de una interfase (por ejemplo, de una interfase sólido/líquido, líquido/aire o líquido/líquido) disminuyendo la tensión interfacial y conduciendo así a cambios en otras propiedades (por ejemplo, la dispersión, la emulsificación y el humedecimiento). Se prefiere que todas las composiciones (tanto las formulaciones sólidas como las líquidas) comprendan, en peso, de 0,0001 a 95 %, más preferiblemente de 1 a 85 %, por ejemplo, de 5 a 60 %, de un compuesto de fórmula (I). La composición de usa generalmente para el

control de plagas o de hongos, de manera que el compuesto de fórmula (I) se aplica a una tasa de 0,1 g a 10 kg por hectárea, preferiblemente de 1 g a 6 kg por hectárea, más preferiblemente de 1 g a 1 kg por hectárea.

Cuando se lo emplea en una cobertura para semillas, se usa el compuesto de fórmula (I) a una tasa de 0,0001 g a 10 g (por ejemplo, de 0,001 g a 0,05 g), preferiblemente de 0,005 g a 10 g, más preferiblemente de 0,005 g a 4 g, por kilogramo de semilla.

En otro aspecto, la presente invención provee una composición insecticida, acaricida, nematicida, moluscicida o fungicida que comprende una cantidad efectiva para la eliminación de insectos, de ácaros, de nematodos, de moluscos o de hongos de un compuesto de fórmula (I), y un vehículo o un diluyente para el mismo. La composición es preferiblemente una composición insecticida, acaricida, nematicida o fungicida.

Las composiciones pueden elegirse entre una cantidad de tipos de formulación, incluyendo polvos esparcibles (DP), polvos solubles (SP), gránulos solubles en agua (SG), gránulos dispersables en agua (WG), polvos humedecibles (WP), gránulos (GR) (de liberación rápida o lenta), concentrados solubles (SL), líquidos miscibles con aceites (OL), líquidos de volumen ultra bajo (UL), concentrados emulsificables (EC), emulsiones (tanto de aceite en agua (EW) como de agua en aceite (EO)), concentrados en suspensión (SC), aerosoles, composiciones de niebla/humo, suspensiones en cápsulas (CS) y formulaciones para el tratamiento de semillas. El tipo de formulación elegido en cada caso dependerá del propósito particular planeado y de las propiedades biológicas del compuesto de fórmula (I).

Los polvos esparcibles (DP) pueden prepararse mezclando un

compuesto de fórmula (I) con uno o más diluyentes sólidos (por ejemplo, arcillas naturales, caolina, pirofilita, bentonita, alúmina, montmorillonita, kieselguhr, tiza, tierras de diatomeas, fosfatos de calcio, carbonatos de calcio y de magnesio, azufre, cal, harinas, talco y otros vehículos sólidos orgánicos e inorgánicos), y moliendo mecánicamente la mezcla hasta dar un polvo fino.

Los polvos solubles (SP) pueden prepararse mezclando un compuesto de fórmula (I) con una o más sales inorgánicas solubles en agua (tales como bicarbonato de sodio, carbonato de sodio y sulfato de magnesio), o con uno o más sólidos orgánicos solubles en agua (tales como los polisacáridos), y, opcionalmente, con uno o más agentes humectantes, con uno o más agentes dispersantes o con una mezcla de dichos agentes para mejorar la dispersibilidad/solubilidad en agua. La mezcla se muele luego para dar un polvo fino. Pueden granularse también composiciones similares para dar gránulos solubles en agua (SG).

Los polvos humedecibles (WP) pueden prepararse mezclando un compuesto de fórmula (I) con uno o más diluyentes o vehículos sólidos, con uno o más agentes humectantes y, preferiblemente, con uno o más agentes dispersantes, y, opcionalmente, con uno o más agentes suspensores para facilitar la dispersión en líquidos. La mezcla se muele luego para dar un polvo fino. Pueden granularse también composiciones similares para dar gránulos dispersables en agua (WG).

Los gránulos (GR) pueden formarse granulando una mezcla de un compuesto de fórmula (I) y uno o más diluyentes o vehículos sólidos en polvo, o a partir de gránulos vacíos previamente formados, absorbiendo un compuesto de fórmula (I) (o una solución del mismo en un agente adecuado)

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en un material granular poroso (tal como pumita, arcillas de atapulgita, tierra de Fuller, kieselguhr, tierras de diatomeas o granos de maíz molidos) o adsorbiendo un compuesto de fórmula (I) (o una solución del mismo en un agente adecuado) en un tercer material de núcleo duro (tal como arena, silicato, carbonatos, sulfatos o fosfatos minerales), y secando si resulta necesario. Los agentes que se usan comúnmente para ayudar en la absorción o en la adsorción incluyen solventes (tales como solventes aromáticos y alifáticos de petróleo, alcoholes, éteres, cetonas y ésteres) y agentes adhesivos (tales como polivinil acetatos, polivinil alcoholes, dextrinas, azúcares y aceites vegetales). Pueden incluirse también uno o más aditivos diferentes en los gránulos (por ejemplo, un agente emulsificador, un agente humectante o un agente dispersante).

Los concentrados dispersables (DC) pueden prepararse disolviendo un compuesto de fórmula (I) en agua o en un solvente orgánico, tal como una cetona, un alcohol o un éter de glicol. Estas soluciones pueden contener un agente activo en superficie (por ejemplo, para mejorar la dilución en agua o para evitar la cristalización en un tanque de rociado).

Los concentrados emulsificables (EC) o las emulsiones de aceite en agua (EW) pueden prepararse disolviendo un compuesto de fórmula (I) en un solvente orgánico (que contiene opcionalmente uno o más agentes humectantes, uno o más agentes emulsificadores o una mezcla de dichos agentes) y, para una emulsión, adicionando sucesivamente, con agitación de corte fuerte, la mezcla a agua (que puede contener uno o más agentes humectantes, uno o más agentes emulsificadores o una mezcla de dichos agentes). Los solventes orgánicos adecuados para su uso en los ECs incluyen

cetonas (tales como ciclohexanona o metilciclohexanona) y alcoholes (tales como alcohol bencílico, alcohol furfurílico o butanol). Los solventes adecuados para su uso en los ECs o EWs incluyen aceites vegetales, pirrolidonas N-sustituidas, éteres glicólicos, hidrocarburos clorados (tales como clorobencenos) y solventes aromáticos (tales como alquilbencenos o alquilnaftalenos).

Los concentrados en suspensión (SC) pueden comprender suspensiones acuosas o no acuosas de partículas sólidas insolubles finamente divididas de un compuesto de fórmula (I). Los SCs pueden prepararse moliendo con balón o con esferas el compuesto sólido de fórmula (I) en un medio adecuado, opcionalmente con uno o más agentes dispersantes, para producir una suspensión fina de partículas del compuesto. Pueden incluirse en la composición uno o más agentes humectantes y puede incluirse un agente suspensor para reducir la tasa a la cual se establecen las partículas.

Las formulaciones de aerosol comprenden un compuesto de fórmula (I) y un propelente adecuado (por ejemplo, n-butano). Puede disolverse o dispersarse también un compuesto de fórmula (I) en un medio adecuado (por ejemplo, agua o un líquido miscible con agua, tal como n-propanol) para proveer composiciones que pueden ser usadas en bombas de rocío no presurizadas de acción manual.

Puede mezclarse un compuesto de fórmula (I) en estado seco con una mezcla pirotécnica con el fin de formar una composición adecuada para generar, en un espacio cerrado, un humo que contenga el compuesto.

Las suspensiones de cápsulas (CS) pueden prepararse de una forma similar a la preparación de formulaciones EW con un estado adicional de

polimerización, de manera que se obtiene una suspensión acuosa de gotas de aceite, en la cual cada gota de aceite está encapsulada por una cubierta polimérica y contiene un compuesto de fórmula (I) y, opcionalmente, un vehículo o un diluyente del mismo. Las composiciones pueden proveer la liberación controlada del compuesto de fórmula (I) y pueden usarse para el tratamiento de semillas. Puede formularse también un compuesto de fórmula (I) en una matriz polimérica biodegradable para proveer una liberación lenta y controlada del compuesto.

Una composición puede incluir uno o más aditivos para mejorar el desempeño biológico de la composición (por ejemplo, mejorando el humedecimiento, la retención o la distribución en superficies, la resistencia a la lluvia en superficies tratadas, o la asimilación y la movilidad de un compuesto de fórmula (I)). Tales aditivos incluyen agentes activos en superficie, agregados de rocío basados en aceites, por ejemplo, algunos aceites minerales o aceites vegetales naturales (tales como aceite de soja y aceite de semilla de colza), y mezclas de éstos con otros coadyuvantes bio-mejoradores.

Puede formularse también un compuesto de fórmula (I) para su uso en el tratamiento de semillas, por ejemplo, como una composición en polvo, incluyendo un polvo para el tratamiento seco de semillas (DS), un polvo soluble en agua (SS) o un polvo dispersable en agua para un tratamiento con jarabe (WS), o como una composición líquida, incluyendo un concentrado fluido (FS), una solución (LS) o una suspensión en cápsula (CS). Las preparaciones de DS, SS, WS, FS y las composiciones de LS son muy similares, respectivamente, a las preparaciones de DP, SP, WP, SC y a las composiciones de DC descriptas con anterioridad. Las composiciones para el

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tratamiento de semillas pueden incluir un agente para asistir en la adhesión de la composición a la semilla (por ejemplo, un aceite mineral).

Los agentes humectantes, dispersantes y emulsificadores pueden ser de tipo catiónico, anfotérico o no iónico.

Los agentes adecuados de tipo catiónico incluyen compuestos de amonio cuaternario (por ejemplo, bromuro de cetiltrimetil amonio), imidazolinas y sales de amina.

Los agentes aniónicos adecuados incluyen sales de metales alcalinos de ácidos grasos, sales de monoésteres alifáticos de ácido sulfúrico (por ejemplo, lauril sulfato de sodio), sales de compuestos aromáticos sulfonados (por ejemplo, dodecilbencensulfonato de sodio, sulfonato de butilnaftaleno y mezclas de sulfonatos de sodio de diisopropil y trimetil naftaleno), sulfatos de éter, sulfatos de alcoholes de éteres (por ejemplo, sulfato de lauret-3 sodio), carboxilatos de éter (por ejemplo, carboxilato de lauret-3 sodio), ésteres de fosfato (productos de la reacción entre uno o más alcoholes grasos y ácido fosfórico (predominantemente monoésteres) o pentóxido de fósforo (predominantemente diésteres), por ejemplo, la reacción entre alcohol laurílico y ácido tetrafosfórico, adicionalmente puede etoxilarse estos productos), sulfosuccinamatos, sulfonatos de parafina o de olefina, tauratos y lignosulfonatos.

Los agentes adecuados de tipo anfotérico incluyen las betaínas, los propionatos y los glicinatos.

Los agentes adecuados de tipo no iónico incluyen los productos de la condensación de óxido de etileno con alcoholes grasos (tales como alcohol oleílico o alcohol cetílico) o con alquilfenoles (tales como octilfenol, nonilfenol u

octilcresol), ésteres parciales derivados de ácidos grasos de cadena larga o de anhídridos de hexitol, productos de la condensación de dichos ésteres parciales con óxido de etileno, polímeros en bloque (que comprenden óxido de etileno y óxido de propileno), alcanolamidas, ésteres simples (por ejemplo, ésteres de polietilen glicol de ácidos grasos) o sus derivados etoxilados; óxidos de amina (por ejemplo, óxido de lauril dimetil amina); y lecitinas.

Los agentes suspensores adecuados incluyen coloides hidrofílicos (tales como polisacáridos, polivinilpirrolidona o carboximetilcelulosa de sodio) y arcillas de condensación (tales como bentonita o atapulgita).

Puede aplicarse un compuesto de fórmula (I) por medio de cualquiera de los métodos de aplicación conocidos para aplicar compuestos pesticidas o fungicidas. Por ejemplo, puede aplicárselo formulado o sin formular, a las plagas o a los sitios de las plagas (tales como un hábitat de las plagas, o a una planta en crecimiento que puede se afectada por las plagas) o a cualquier parte de la planta, incluyendo el follaje, los tallos, las ramas o las raíces, a la semilla ante de plantarla, o a otro medio en el cual estén creciendo las plantas o donde se las vaya a plantar (tal como el suelo que rodea las raíces, el suelo en general, el agua de riego o los sistemas hidropónicos de cultivo), en forma directa o por medio de rocío, de polvo, por volcado, como crema o como una formulación de pasta, como vapor o a través de su distribución y de su incorporación a una composición (tal como una composición granular o como una composición empaquetada en una bolsa soluble en agua) en el ambiente del suelo o en el agua.

Puede inyectarse también un compuesto de fórmula (I) en las plantas o puede rociárselo sobre la vegetación usando técnicas electrodinámicas de

rocío u otros métodos de bajo volumen, o aplicárselo por medio de sistemas de irrigación terrestre o aérea.

Las composiciones para su uso como preparaciones acuosas (soluciones o dispersiones acuosas) se suplen generalmente bajo la forma de un concentrado que contiene una alta proporción del ingrediente activo, agregándose el concentrado al agua antes de usarlo. Se requiere comúnmente que estos concentrados, que pueden incluir SLs, SCs, ECs, EWs, SGs, SPs, WPs, WGs y CSs, resistan el almacenamiento por períodos prolongados y, después de tal almacenamiento, que sean capaces de mezclarse con agua para formar preparaciones acuosas que permanezcan homogéneas por un tiempo suficiente como para permitirles ser aplicadas por medio de un equipo convencional de rocío. Tales preparaciones acuosas pueden contener cantidades variables de un compuesto de fórmula (I) (por ejemplo, de 0,0001 a 10 % en peso), dependiendo del propósito para el cual quiera usárselas.

Puede usarse un compuesto de fórmula (I) en mezclas con fertilizadores (por ejemplo, fertilizadores con nitrógeno, con potasio o con fósforo). Los tipos adecuados de formulación incluyen gránulos de fertilizador. Las mezclas contienen adecuadamente hasta un 25 % en peso del compuesto de fórmula (I).

La invención provee entonces una composición fertilizadora que comprende un fertilizador y un compuesto de fórmula (I).

Las composiciones de esta invención pueden contener otros compuestos que tengan actividad biológica, por ejemplo, micronutrientes o compuestos que tengan una actividad fungicida complementaria o que posean actividad de regulación del crecimiento vegetal, herbicida, insecticida,

nematicida o acaricida.

Mediante la inclusión de otro fungicida, la composición resultante puede tener un mayor espectro de actividad o un mayor nivel de actividad intrínseca que el compuesto de fórmula (I) por sí solo. Además, el otro fungicida puede tener un efecto sinergístico sobre la actividad fungicida del compuesto de fórmula (I).

El compuesto de fórmula (I) puede ser el único ingrediente activo de la composición o puede estar mezclado con uno o más ingredientes activos adicionales tales como un pesticida, un fungicida, un sinergista, un herbicida o un regulador del crecimiento vegetal, cuando resulte apropiado. Un ingrediente activo adicional puede proveer una composición que tenga un mayor espectro de actividad o una mayor persistencia e un lugar, que sinergice la actividad o complemente la actividad (por ejemplo, aumentando la velocidad del efecto o sobrepasando la repelencia) del compuesto de fórmula (I), o puede ayudar a evitar o prevenir el desarrollo de resistencia a componentes individuales. El ingrediente activo particular dependerá de la utilidad pretendida de la composición.

Los ejemplos de pesticidas adecuados incluyen los siguientes:

a) Piretroides, tales como permetrina, cipermetrina, fenvalerato, esfenvalerato, deltametrina, cihalotrina (en particular, lambda-cihalotrina), bifentrina, fenpropatrina, ciflutrina, teflutrina, piretroides seguros para peces (por ejemplo, etofenprox), piretrinas naturales, tetrametrina, s-bioaletrina, fenflutrina, praletrina o carboxilato de 5-bencil-3-furilmetil-(E)-(1R, 3S)-2,2-dimetil-3-(2-oxotiolan-3-ilidenmetil) ciclopropano;

b) Organofosfatos tales como, profenofos, sulprofos, acefato, metil paratión,

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metil-azinfos, s-metil demeton, heptenofos, tiometon, fenamifos, monocrotofos, profenofos, triazofos, metamidofos, dimetoato, fosfamidón, malatión, clorpirifos, fosalona, terbufos, fensulfotión, fonofos, forate, foxim, metil-pirimifos, etil-pirimifos, fenitrotión, fostiazato o diazinón;

c) Carbamatos (incluyendo carbamatos de arilo) tales como pirimicarb, triazamato, cloetocarb, carbofurano, furatiocarb, etiofencarb, aldicarb, tiofurox, carbosulfano, bendiocarb, fenobucarb, propoxur, metomil u oxamil;

d) Benzoil ureas tales como diflubenzurona, triflumurona, hexaflumurona, fllifenoxurona o clorfluazurona;

e) Compuestos orgánicos de estaño tales como cihexatina, óxido de fenbutatina o azociclotina;

f) Pirazoles tales como fipronil, tebufenpirad y fenpiroximato;

g) Macrólidos tales como avermectinas o milbernicinas, por ejemplo, abamectina, benzoato de emamectina, ivermectina, milbernicina, spinosad o azadiractina;

h) Hormonas o feromonas;

i) Compuestos organoclorados tales como endosulfano, hexacloruro de benceno, DDT, clordano o dieldrina;

j) Amidinas tales como clordimeform o amitraz;

k) Agentes fumigadores tales como cloropicrina, dicloropropano, bromuro de metilo o metam;

l) Compuestos de cloronicotinilo tales como imidacloprid, acetamiprid, nitenpiram o tiiametoxam;

m) Diacilhidrazines, tales como tebufenozida;

n) Ésteres de difenilo tales como diofenolan o piriproxifeno;

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o) Indoxacarb;

p) Clorfenapir; o

q) Pimetrozina.

Además de las clases mayores de pesticidas que se indicaron anteriormente, pueden emplearse en al composición otros pesticidas que tengan blancos particulares, si resultan apropiados para la utilidad pretendida de la composición. Por ejemplo, pueden emplearse insecticidas selectivos para cultivos particulares, por ejemplo, insecticidas específicos para taladros (tales como cartap) o insecticidas específicos para saltamontes para su uso sobre arroz. Como alternativa, pueden incluirse insecticidas o acaricidas específicos para especies/estadíos específicos de insectos en las composiciones (por ejemplo, ovo-larvicidas acaricidas tales como clofentezina, flubencimina, hexitaiazox o tetradifon; motilicidas acaricidas tales como dicofol o propargita; acaricidas tales como bromopropilato o clorobencilato; o reguladores del crecimiento tales como hidrametilnon, ciromazina, metopreno, clorfluazuro o difllibenzuro).

Los ejemplos de compuestos fungicidas que pueden incluirse en la composición de la invención son (E)-N–metil-2-(2-fenoxifenil)-2-metoxiiminoacetamida, (E)-N-metil-2-[2-(2,5- dimetiilfenoximetil) fenil]-2-metoxi-iminoacetamida, ácido (RS)-1-aminopropil-fosfónico, (RS)-4-(4-clorofenil)-2-fenil-2-(1H-1,2,4-triazol-1-ilmetil)butironitrilo, (Z)-N-but-2-eniloximetil-2-cloro-2',6'-dietilacetanilida, 1-(2-ciano-2-metoxiiminoacetil)-3-etil urea, 4-(2,2-difluoro-1,3-benzodioxol-4-il)-pirrol-3-carbonitrilo, 4-bromo-2-ciano-N,N-dimetil-6-trifluorometil-bencimidazol-1-sulfonamida, ácido 5-etil-5,8-dihidro-8-oxo(1,3)-dioxol-(4,5-g)quinolina-7-carboxílico, α-[N-(3-cloro-2,6-xilil)-2-metoxi-

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acetamido]-γ-butirolactona, N-(2-metoxi-5-piridil)-ciclopropan carboxamida, acibenzolar (CGA245704), alanicarb, aldimorph, anilazina, azaconazol, azoxistrobina, benalaxil, benomil, biloxazol, bitertanol, blasticidina S, bromuconazol, bupirimato, butenacor, butiobate, captafol, captan, carbendazim, clorhidrato de carbendazim, carboxina, carpropamid, carvona, CGA41396, CGA41397, chinometionato, cloroneb, clorotalonilo, clorozolinato, clozilacon, compuestos que contienen cobre tales como oxicloruro de cobre, oxiquinolato de cobre, sulfato de cobre, talato de cobre y mezcla de Bordeaux, cicloheximida, cymoxanilo, ciproconazol, ciprodinilo, ciprofuram, debacarb, 1,1'-dióxido de di-2-piridil disulfuro, diclofluanid, diclone, diclobutrazol, diclomezina, dicloran, cloruro de didecil dimetil amonio, dietofencarb, difenoconazol, difenzoquat, diflumetorim, tiofosfato de O, O–di–iso–propil–S-bencilo, dimefluazol, dimetconazol, dimetomorf, dimetirimol, diniconazol, dinocap, dipiritiona, ditalimfos, ditianon, dodemorf, dodina, doguadina, edifenfos, epoxiconazol, etaconazol, etirimol, etoxiquin, etil (Z)–N–bencil–N-([metil(metil-tioetilidenamino-oxicarbonil)amino]tio)-β-alaninato, etridiazol, famoxadona, fenaminosulf, fenapanil, fenarimol, fenbuconazol, fenfuram, fenhexamid (KBR2738), fenpiclonil, fenpropidin, fenpropimorf, fentin acetato, fentin hidróxido, ferbam, ferirnzone, fluazinam, fludioxonil, flumetover, fluoroimida, fluquinconazol, flusilazol, flutolanil, flutriafol, folpet, fuberidazol, furalaxil, furametpir, furconazole-cis, guazatine, hexaconazol, hidroxiisoxazol, himexazol, imazalil, imibenconazol, ipconazol, iprobenfos, iprodiona, isopropanil butil carbamato, isoprotiolano, kasugamicina, metil-kresoxim, LY186054, LY211795, LY248908, mancozeb, maneb, mefenoxam, mepanipirim, mepronil, metalaxil, metconazol, metiram, metiram-cinc, metominostrobin, metsulfovax,

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miclobutanil, neoasozina, dimetilditiocarbamato de níquel, nitrotal-isopropilo, nuarimol, ofurace, compuestos de organomercurio, oxadixil, oxasulfuron, ácido oxolínico, oxpoconazol, oxicarboxina, pefurazoato, penconazol, pencicuron, óxido de fenazin, fosetil–Al, ácidos fosforosos, ftalida, picoxistrobin (ZA1963), polioxina D, poliram, probenazol, procloraz, procimidona, propamocarb, propiconazol, propineb, ácido propiónico, pyrazofos, pirifenox, pirimetanil, piroquilon, piroxifur, pirrolnitrina, compuestos de amonio cuaternario, quinconazole, quinometionato, quinoxifen, rabenazole, pentaclorofenato de sodio, espiroxamina, estreptomicina, azufre, tebuconazol, tecloftalam, tecnazeno, tetraconazol, tiabendazol, tifluzamida, 2-(tiocianometiltio)benzotiazol, metil-tiofanato, tiram, timibenconazol, metil-tolclofos, tolilfluanid, sal triacética de 1,1'-iminodi(octametilene)diguanidina, triadimefon, triadimenol, triazbutilo, triazóxido, triciclazol, tridemorf, trifloxistrobin, triforina, triflumizol, triticonazol, validamicina A, vapam, vinclozolin, XRD-563, zineb y ziram. Los compuestos de fórmula (I) pueden mezclarse con el suelo, con la turba o con el medio de generación de raíces para la protección de las plantas contra enfermedades fúngicas propias de las raíces, propias del suelo o foliares.

Los ejemplos de sinergistas adecuados para su uso en las composiciones incluyen butóxido de piperonilo, sesamex, safroxan y dodecil imidazol.

Los herbicidas y los reguladores del crecimiento vegetal que pueden incluirse en las composiciones dependerán del blanco pretendido y del efecto requerido.

Un ejemplo de herbicida selectivo para arroz que puede incluirse es el

propanilo. Un ejemplo de regulador del crecimiento vegetal que puede usarse sobre algodón es PIX™.

Algunas mezclas pueden comprender ingredientes activos que tengan diferentes propiedades físicas, químicas o biológicas, de manera que no se presten al mismo tipo de formulaciones. En estas circunstancias, pueden prepararse otros tipos de formulaciones. Por ejemplo, cuando un ingrediente activo es un sólido insoluble en agua y el otro es un líquido insoluble en agua, puede ser aún posible dispersar cada ingrediente activo en la misma fase acuosa dispersando el ingrediente activo sólido como una suspensión (usando una preparación análoga a la de un SC) pero dispersando el ingrediente activo líquido como una emulsión (usando una preparación análoga a la de un EW). La composición resultante es una formulación de suspoemulsión (SE).

La invención está ilustrada por los siguientes Ejemplos, en los que los ingredientes de más abajo son nombrados por medio de su marca comercial registrada y tienen las siguientes composiciones.

Marca Comercial Registrada	**Composición**
SYNPERONIC NP8 } SYNPERONIC NP13 }	Condensado de nonilfenol y óxido de etileno
SYNPERONIC A7	Condensado sintético de alcohol primario y óxido de etileno
AROMASOL H	Solvente de alquilbenceno
SOLVESSO 200	Diluyente orgánico inerte
KELTROL	Polisacárido
PROXEL	Bactericada

Las siguientes abreviaturas se usan a lo largo de la descripción:

s = singulete b = ancho q = cuarteto

d = doblete m = multiplete dd = doble doblete

t = triplete bd = doblete ancho

EJEMPLO 1

Este ejemplo ilustra la preparación de N-(4-cloro-3-metilisotiazol-5-il)-(2-propilbenzotriazol-5-il)acetamida (Compuesto N° 1 de la Tabla I).

Paso 1

Se suspendió ácido 4-aminofenilacético (100 g) en metanol (1000 ml) y se hizo pasar cloruro de hidrógeno gaseoso hasta que se saturó la mezcla. La mezcla se calentó a 50 °C durante 2 horas y luego se la dejó enfriar hasta temperatura ambiente. El solvente se evaporó al vacío, el residuo se capturó en una solución acuosa de bicarbonato de sodio y se lo extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío para dar 4-aminofenilacetato de metilo bajo la forma de un líquido marrón claro.

^{1}H NMR ($CDCl_3$) δ ppm: 3.5 (s,2H); 3.7 (s,3H); 6.65 (m,2H); 7.05 (m,2H).

Paso 2

Se agregó por goteo 4-aminofenilacetato de metilo (110 g, 0,667 mol) a anhídrido acético (600 ml), manteniendo la temperatura de la mezcla de reacción por debajo de 30 °C por enfriamiento externo. Una vez finalizada la adición la mezcla se enfrió a menos de 10 °C y se agregó por goteo ácido nítrico concentrado (85 ml). Una vez finalizada la adición de ácido nítrico, la mezcla se dejó calentar hasta temperatura ambiente y se la vertió sobre una mezcla de hielo y agua. El sólido precipitado se recolectó por filtrado y se los secó para dar 4- acetamido -3 - Nitrofenilacetato de metilo (120 g) bajo la forma

de un sólido amarillo pálido.

^{1}H NMR ($CDCl_3$) δ ppm: 2,3 (s,3H); 3,65 (s,2H); 3,7 (s,3H); 7,55 (dd,1H); 8,1 (d,1H); 8,7 (d,1H); 10,3 (b,1H).

Paso 3

Se disolvió 4-acetamido-3-nitrofenilacetato de metilo (40 g, 0,159 mol) en metanol (400 ml) y se hidrogenó a 5 bar sobre un catalizador de paladio sobre carbón al 5 %. El catalizador se eliminó por filtración y el filtrado se evaporó al vacío para dar 4-acetamido-3-aminofenilacetato de metilo.

Paso 4

Se capturó 4-acetamido-3-aminofenilacetato de metilo (77 g, 0,373 mol) en una mezcla de ácido acético (210 ml) y agua (210 ml), y se lo enfrió a menos de 5 °C. Se agregó una solución de nitrito de sodio (38,63 g, 0,559 mol) en agua (200 ml) por goteo, y, una vez finalizada la adición, la mezcla se agitó durante 4 horas, calentando lentamente hasta temperatura ambiente. La mezcla se diluyó con acetato de etilo y el material insoluble se eliminó por filtrado. El filtrado se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el solvente se evaporó al vacío para dar un residuo viscoso (51 g) que se empleó en el siguiente paso.

Paso 5

El producto obtenido en el Paso 4 anterior se disolvió en una solución de metanol (400 ml) previamente saturada con cloruro de hidrógeno, y la mezcla se agitó durante 2 horas. El solvente se eliminó al vacío, el residuo se capturó en agua, se lo neutralizó con solución saturada acuosa de bicarbonato de sodio y se lo extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se

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evaporó al vacío para dar 5-benzotriazoleacetato de metilo (35 g) bajo la forma de un líquido rojizo que se cristalizó con el reposo.

^{1}H NMR ($CDCl_3$) □ ppm: 3,7 (s,3H); 3,8 (s, 2H); 7,35 (d,1H); 7,8 (b,2H); 13.6 (b,1H).

Paso 6

Se agregó una solución de 5-benzotriazolacetato de metilo (10 g, 0,0523 mol) en N, N-dimetilformamida por goteo a una suspensión enfriada (baño de hielo) de hidruro de sodio (dispersión al 60% en aceite, 2,3 g, 0,0575 mol) en N, N - dimetilformamida. Cuando se completó la adición, el baño de hielo se eliminó y la mezcla se agitó durante 1 hora. Se agregó ioduro de N - propilo (9,78 g, 0,0575 mol) por goteo, y, una vez finalizada la adición, la mezcla se agitó a temperatura ambiente durante 3 horas. La mezcla de reacción se vertió en hielo/agua, y se la extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío, El residuo se purificó adicionalmente por cromatografía de columna para dar (2- propilbenzotriazol -5- il) acetato de metilo (4,8 g).

^{1}H NMR ($CDCl_3$) □ ppm: 0,9 (t,3H); 2,1 (m,2H); 3,7 (s,3H); 3,8 (s,2H); 4.65 (t,2H); 7.3 (dd,1H); 7,7 (d,1H); 7.8 (d,1H).

Paso 7

El acetato preparado en el paso 6 anterior (4.8 g, 0.0206 mol) se disolvió en metanol (60 ml) y se agregaron escamas de hidróxido de potasio (1,27 g, 0,0226 mol). La mezcla se calentó a reflujo durante 2 horas, luego se enfrió y el solvente se evaporó al vacío. El sólido residual se disolvió en agua y se extrajo con éter dietílico. La solución acuosa se acidificó a pH 1 mediante el agregado

de ácido clorhídrico diluido acuoso y se la extrajo con acetato de etilo. El extracto de acetato de etilo se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío para dar ácido (2- propilbenzotriazol -5- il) acético (3,6 g) bajo la forma de un sólido incoloro.

Paso 8

El ácido preparado en el paso 7 (0,438 g, 0,002 mol) se disolvió en diclorometano (5 ml) y se agregó una gota de N,N-dimetilformamida (0,307 g, 0,0022 mol), se agregó cloruro de oxalilo por goteo, y la mezcla se agitó a temperatura ambiente durante 2 horas. El solvente se eliminó al vacío, el residuo se capturó en xileno, se lo agregó a una mezcla de 5- amino -4- cloro - 3- metilisotiazol (0,446 g, 0,003 mol) en xileno y se calentó a reflujo durante 2 horas. La mezcla se enfrió a temperatura ambiente y el solvente se evaporó al vacío. El residuo se capturó en acetato de etilo, se lo lavó secuencialmente con solución saturada acuosa de bicarbonato de sodio y con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío. El residuo se purificó adicionalmente por cromatografía instantánea en columna, eluyendo con 2:1 hexano:acetato de etilo, para dar el compuesto del título (0,34 g) bajo la forma de un sólido color arena.

^{1}H NMR ($CDCl_3$) □ ppm: 1,0 (t,3H); 2,15 (m,2H); 2,35 (s,3H); 4,0 (s,2H); 4.7 (t,2H); 7.35 (dd,1H); 7,85 (d,1H); 7.95 (d,1H); 8,15 (b,1H).

EJEMPLO 2

Este Ejemplo ilustra una composición concentrada emulsificable que es convertida con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. El concentrado emulsificable tiene la siguiente composición.

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	% en peso
Compuesto Nro. 1	25,0
SYNPERONIC NP13	2,5
Dodecilbencensulfonato de calcio	2,5
AROMASOL H	70,0

EJEMPLO 3

Este Ejemplo ilustra una composición en polvo mojable que es convertida con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. El polvo mojable tiene la siguiente composición.

	% en peso
Compuesto Nro. 1	25,0
Sílica	25,0
Lignosulfonato de sodio	5,0
Laurilsulfato de sodio	2,0
Caolín	43,0

EJEMPLO 4

Este ejemplo ilustra un polvo capaz de ser espolvoreado que puede ser aplicado directamente a las plantas u otras superficies. El polvo espolvoreable tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	1,0
Talco	99,0

EJEMPLO 5

Este Ejemplo ilustra una formulación líquida miscible en aceite adecuada para la aplicación por técnicas de volúmenes ultra bajos después de mezclar

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con un diluyente orgánico. La formulación tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	10,0
SOLVESSO 200	90,0

EJEMPLO 6

Este Ejemplo ilustra un concentrado en suspensión en cápsulas que es convertido con facilidad, por adición en agua, en una preparación adecuada para su aplicación como un asperjado acuoso. El concentrado en suspensión en cápsulas tiene la siguiente composición.

	% en peso
Compuesto Nro. 1	10,0
AROMASOL H	70,0
Di-isocianato de tolueno	2,5
SYNPERONIC A7	1,0
Alcohol polivinílico	2,0
Bentonita	1,5
KELTROL	0,1
Agua	72,4

EJEMPLO 7

Este Ejemplo ilustra una formulación granular lista para usar que se prepara a partir de un portador granular preformado. La formulación granular tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	0,5
SOLVESSO 200	0,2

SYNPERONIC A7	0,1

Gránulos de carbonato de calcio (diámetro 0,3 - 0,7 mm) 99,2

EJEMPLO 8

Este Ejemplo ilustra una formulación granular lista para usar que se prepara por granulación de los componentes convertidos en polvo. La formulación granular tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	0,5
Lignosulfonato de sodio	5,0
Caolín	94,5

EJEMPLO 9

Este Ejemplo ilustra un concentrado en suspensión acuoso que es convertido con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. El concentrado en suspensión tiene la siguiente composición.

	% en peso
Compuesto Nro. 1	25,0
Lignosulfonato de sodio	3,0
Propilénglicol	10,0
Bentonita	2,0
KELTROL	0,1
PROXEL	0,1
Agua	59,8

EJEMPLO 10

Este Ejemplo ilustra una formulación en gránulos dispersable en agua que

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es convertida con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. Los gránulos dispersables en agua tienen la siguiente composición.

	% en peso
Compuesto Nro. 1	25,0
Sílica	5,0
Lignosulfonato de sodio	10,0
Laurilsulfato de sodio	5,0
Montmorillonita en polvo	45,0

EJEMPLO 11

Este ejemplo ilustra las propiedades pesticidas/insecticidas de los compuestos de fórmula (I). Se determinaron las actividades de compuestos de fórmula (I) individuales usando una variedad de plagas. Con excepción de los nematodos, las plagas se trataron con una composición líquida que contenía 500 partes por millón (ppm) en peso de un compuesto, salvo indicación en contrario. Cada composición se hizo disolviendo el compuesto en una mezcla de acetona y etanol (50:50 en volumen) y diluyendo la solución con agua que contenía 0,05 % en volumen de un agente humectante, SYNPERONIC NP8, hasta que la composición líquida contuvo la concentración deseada de compuesto.

El procedimiento de prueba adoptado respecto de cada plaga, excepto para nematodos, fue esencialmente el mismo y comprendió apoyar una cantidad de la peste en un medio que era comúnmente un sustrato, una planta hospedadora o un alimento sobre el cual se alimentaban las plagas, y tratar el medio y/o las plagas con una composición. Se evaluó la mortalidad de las

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plagas usualmente entre tres y cinco días después del tratamiento. La capacidad de volteo de la mosca doméstica (*Musca domestica*) se evaluó 15 minutos después del tratamiento.

El procedimiento de prueba para nematodos involucró la disolución del compuesto en una mezcla de acetona y etanol (50:50 en volumen) y diluyendo la solución con agua para obtener una concentración final del compuesto de 12,5 ppm. 12 ejemplares juveniles infecciosos de *Meloidogyne incognita* se suspendieron en la solución en un recipiente de vidrio y se calculó la mortalidad después de un período de tres días.

Los resultados de las pruebas se presentan a continuación. Los resultados indican un grado de mortalidad (puntuación) designado como 99, 55 ó 0, en donde 99 indica un 80 a 100 % de mortalidad, 55 indica un 40 a 79 % de mortalidad y 0 indica menos de 40 % de mortalidad.

Compuesto Nro. (Tabla)	TETRUR	MYZUPE	MUSCDOA	MUSCDOAC	HELIVI	LAPHEG	MELGIN
1 (1)	99	0	-	-	99	99	55
3 (1)	0	99	0	55	55	55	0
4 (1)	0	0	0	0	55	0	0
5 (1)	99	0	99	99	0	55	99
6 (1)	55	55	0	55	0	99	99
7 (1)	99	55	0	99	99	99	0
8 (1)	99	99	99	99	55	99	55
9 (1)	0	99	99	99	55	0	0
10 (1)	99	55	99	99	99	99	0

TETRUR = Tetranycus urticae MYZUPE = Myzus persicae

MUSCO AK=Musca domestica (muerte) MUSCDO AC=Musca domestica (volteo)

HELIVI=Heliotis viriscens LAPHEG=

MELGIN=Meloidogyne incognita

EJEMPLO 12

Este ejemplo ilustra las propiedades fungicidas de compuestos de fórmula (I). Los compuestos se evaluaron contra una variedad de enfermedades foliares de plantas causadas por hongos. La técnica empleada fue como se describe a continuación.

Se cultivaron plantas en John Innes Potting Compost (N° 1 ó 2) en minimacetas de 4 cm de diámetro y 3,5 cm de profundidad. Se formularon las muestras de prueba en forma individual como una solución ya sea en acetona o en acetona/etanol (1:1 en volumen), la cual se diluyó en agua deionizada hasta una concentración de 100 ppm (es decir, 1 mg de compuesto en un volumen final de 10 ml) inmediatamente antes de usarla.

Se aplicaron compuestos individuales de fórmula (I) como una aplicación foliar (Folr) (donde se aplicó la solución química al follaje de las plantas de prueba rociando la planta hasta su retención máxima de gotas). Cuando los asperjados foliares fueron aplicados a cultivos de monocotiledóneas, se adicionó TWEEN™ 20 (0,1 % en volumen).

Se llevaron a cabo estas pruebas contra *Plasmopara viticola* (PLASVI), en vides; contra *Phytophthora infestans lycopersici* (PHYTIN), en tomates; contra *Erysiphe graminis f. sp. tritici* (ERYGST); y contra *Puccinia recondita* (PUCCRT), en trigo. Se aplicó cada tratamiento a dos plantas replicadas para

Plasmodora viticola y *Phytophthora infestans lycopersici*. Para las pruebas en *Erysiphe graminis f. sp. tritici* y *Puccinia recondita*, se usaron dos macetas replicadas que contenían, cada una, de 6 a 10 plantas para cada tratamiento. Las plantas de *Plasmopara viticola, Phytophthora infestans lycopersici* y *Puccinia recondita* se inocularon con una suspensión calibrada de esporas de hongos un día después de (Prev) de la aplicación química. Se inocularon las plantas de *Erysiphe graminis f. sp. tritici* usando una técnica de inoculación por "sacudida", seis horas después (Prev) de la aplicación química.

Después de la aplicación química y la inoculación, se incubaron las plantas de *Plasmopara viticola, Phytophthora infestans lycopersici* y *Puccinia recondita* bajo condiciones de alta humedad y se las colocó luego en un ambiente apropiado para permitir que procediera la infección, hasta que la enfermedad pudiera ser evaluada. Después de la aplicación química y la inoculación, se dispusieron las plantas de *Erysiphe graminis f. sp. tritici* bajo condiciones apropiadas para permitir que procediera la infección. Para *Plasmopara viticola,* las plantas se volvieron a incubar bajo condiciones de elevada humedad por 24 horas previas a la evaluación. El período de tiempo entre la aplicación química y la evaluación varió de cuatro a catorce días de acuerdo con la enfermedad y con el ambiente. Sin embargo, cada enfermedad individual se evaluó después del mismo período de tiempo para todas las muestras.

Se llevaron a cabo las evaluaciones en una sola hoja de cada una de las dos plantas replicadas para *Plasmopara viticola*. Para *Phytophthora infestans lycopersici,* las evaluaciones se llevaron a cabo en dos hojas de cada una de las plantas replicadas y el nivel de enfermedad promedio a lo largo de las dos

hojas se asentó por réplica. Las evaluaciones de *Erysiphe graminis f. sp. tritici* y *Puccinia recondita* se llevaron a cabo colectivamente sobre las plantas en cada maceta replicada.

Se evaluó visualmente el nivel presente de enfermedad (es decir, el porcentaje del área de la hoja cubierto por la enfermedad activamente esporulante) usando la escala de determinación en tiras mostrada más bajo. Para cada tratamiento, se promediaron los valores evaluados en todas las réplicas con el fin de obtener valores promedio de enfermedad presente en las plantas control sin tratar. Este dato calculado se refiere como un valor POCO (Porcentaje de Control).

Un ejemplo de un cálculo típico es como sigue:

Nivel promedio de enfermedad para el tratamiento A = 25 %

Nivel promedio de enfermedad para controles sin tratar = 90 %

$$\text{POCO} = \frac{\{\text{Nivel promedio de enfermedad para el tratamiento A}\}}{\{\text{Nivel promedio de enfermedad para controles sin tratar}\}} \times 100 =$$

$$= \frac{25}{90} \times 100 = 27{,}8$$

Este valor POCO se redondea luego hacia el número entero más cerca en una escala de 0 - 100 %; en este ejemplo particular, el resultado del POCO será 28.

Los resultados de POCO se indican a continuación:

Compuesto Nro. (Tabla)	ERYSGT (foliar)	PHYTIN (foliar)	PLASVI (foliar)	PUCCRT (foliar)
1 (1)	0	3	0	0
3 (1)	0	0	33	0

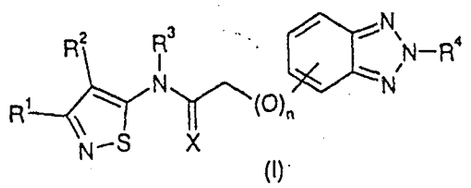
211
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4 (1)	0	100	100	0
5 (1)	0	100	0	0
6 (1)	0	-	0	0
7 (1)	0	100	100	0
8 (1)	0	0	0	0
9 (1)	100	0	3	0

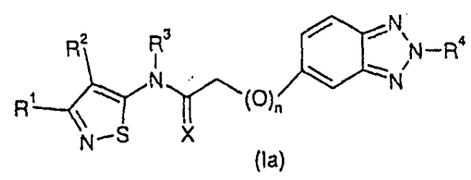
ERYSGT=*Erysiphe graminis tritici* PHYTIN= *Phytophthora infestans lycopersici*

PLASVI=*Plasmopara viticola* PUCCRT= *Puccinia recondita*

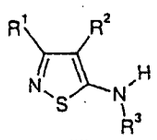
Fórmulas Químicas en la Descripción



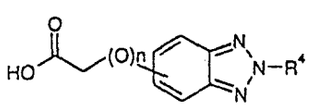
(I)



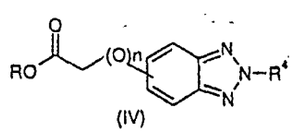
(Ia)



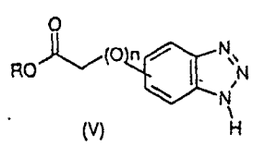
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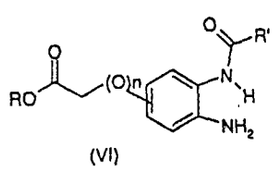
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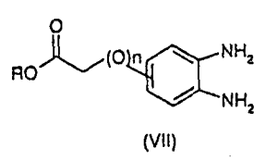
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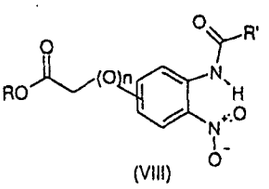
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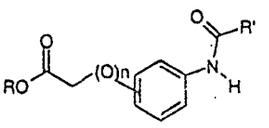
(VI)



(VII)



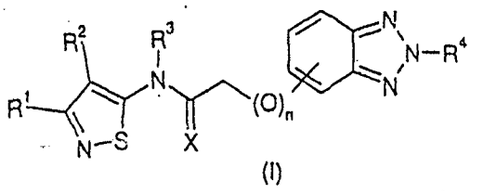
(VIII)



(IX)

REIVINDICACIONES

1. Un compuesto de fórmula (I):



(I)

en donde R^1 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi, C_{1-6} haloalcoxi, C_{1-6} alquiltio, C_{3-7} cicloalquilo o C_{1-6} alcoxi (C_{1-6}) alquilo; R^2 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, ciano, nitro, CHO, $CH=NOR^5$, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo o C_{1-6} alquil$S(O)_q$; o juntos R^1 o R^2 forman un anillo carbocíclico saturado o insaturado de cinco o seis miembros, opcionalmente sustituido por uno o dos grupos C_{1-6} alquilo; R^3 es hidrógeno, C_{1-6} alquilo, CH_2(C_{1-4} haloalquilo), C_{3-6} alquenilo, C_{3-6} alquinilo, C_{1-6} alcoxi(C_{1-6})alquilo, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo, formilo, fenoxicarbonilo opcionalmente sustituido, fenil(C_{1-4})alquilo opcionalmente sustituido o $S(O)_pR^6$; R^4 es hidrógeno, C_{1-8} alquilo, C_{1-6} haloalquilo, C_{1-6} cianoalquilo, C_{3-6} alquenilo, C_{3-6} alquinilo, C_{3-7} cicloalquilo, C_{3-7} cicloalquil (C_{1-6}) alquilo, C_{3-6} haloalquenilo, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{1-6} carboxialquilo, C_{1-6} alquilcarbonil (C_{1-6}) alquilo, C_{1-6} alcoxicarbonil (C_{1-6}) alquilo, C_{1-6} alquiltio (C_{1-6}) alquilo, C_{1-6} alquilsulfinil (C_{1-6}) alquilo, C_{1-6} alquilsulfonil (C_{1-6}) alquilo, aminocarbonil (C_{1-6}) alquilo, C_{1-6} alquilaminocarbonil (C_{1-6}) alquilo, di(C_{1-6}) alquilaminocarbonil (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^5 es

hidrógeno, (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^6 es C_{1-6} alquilo, C_{1-6} haloalquilo, o fenilo opcionalmente sustituido; X es O o S; n es 0 o 1; y p y q son, independientemente, 0, 1 o 2.

2. Procesos para fabricar compuestos de la fórmula (I) como se definen en la reivindicación 1.

3. Una composición fungicida, insecticida, acaricida, molusquicida o nematicida que comprende una cantidad eficaz como fungicida, insecticida, acaricida, molusquicida o nematicida de un compuesto de fórmula (I) y un vehículo o diluyente para el mismo.

4. Un método para combatir y controlar hongos que comprende aplicar a una planta, a una semilla de una planta, o al locus de la planta o semilla o al suelo, una cantidad eficaz como fungicida de un compuesto de fórmula (I) de acuerdo con la cláusula 1, o una composición que contiene un compuesto de fórmula (I) de acuerdo con la cláusula 3.

5. Un método para combatir y controlar insectos, ácaros, nematodos o moluscos que comprende aplicar a una plaga, al locus de una plaga o a una planta susceptible de ser atacada por una plaga una cantidad eficaz como insecticida, acaricida, nematicida o molusquicida de un compuesto de la fórmula (I) de acuerdo con la cláusula 1, o una composición que contiene un compuesto de fórmula (I) de acuerdo con la cláusula 3.

6. Un método de acuerdo con la cláusula 5 en donde las pestes de insectos son pestes de insectos de plantas.

GXP 28953

Tomo 2/2

The Patent Office

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INVESTOR IN PEOPLE

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Concept House
Cardiff Road
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South Wales
NP10 8QQ

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Signed Andrew Cheney

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1. Your reference

PPD 50466/GB/P

31JAN00 E509118-1 D02093
P01/7700 0.00-0002039.6

2. Patent application number
(The Patent Office will fill in this part)

0002039.6

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

ZENECA Limited
15 Stanhope Gate
London W1Y 6LN
UNITED KINGDOM

Patents ADP number *(if you know it)*

6254007002

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention

CHEMICAL COMPOUNDS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

John Richard WATERMAN
Intellectual Property Department
ZENECA Agrochemicals
Jealott's Hill Research Station
P O Box 3538
Bracknell Berkshire RG42 6YA
UNITED KINGDOM

Patents ADP number *(if you know it)*

06791537001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or

b) there is an inventor who is not named as an applicant, or

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11. I/We request the grant of a patent on the basis of this application.

Signature ZENECA LIMITED D. L. Royal Date 28/6/00

Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

VIJAYA KUMARI MALLIPEDDI 01344 414365

DAWN LISA ROYAL 01344 414079

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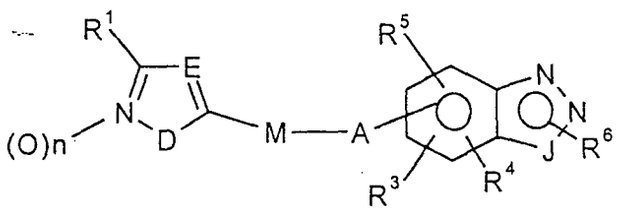
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CHEMICAL COMPOUNDS

The present invention relates to azine and azole derivatives, to processes for preparing them, to fungicidal, insecticidal, acaricidal, molluscicidal and nematicidal compositions comprising them, to methods of using them to combat fungal diseases (especially fungal diseases of plants) and to methods of using them to combat and control insect, acarine, mollusc and nematode pests.

Azole and azine derivatives are disclosed in WO95/31448, WO97/18198, WO98/02424 and WO98/05670.

The present invention provides a compound of formula (I):



(I)

wherein n is 0 or 1; A is optionally substituted C_{1-6} alkylene, optionally substituted C_{2-6} alkenylene, optionally substituted C_{2-6} alkynylene, optionally substituted C_{1-6} alkylenoxy, optionally substituted oxy(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenethio, optionally substituted thio(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenamino, optionally substituted amino(C_{1-6})alkylene, optionally substituted [C_{1-6} alkyleneoxy(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenethio(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfinyl(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfonyl(C_{1-6})alkylene] or optionally substituted [C_{1-6} alkyleneamino(C_{1-6})alkylene];

D is S, NR^{10} $CR^8=CR^9$, $CR^8=N$, $CR^8=N(O)$, $N=CR^9$ or $N(O)=CR^9$;

R^{10} is C_{1-6} alkyl

E is N, N-oxide or CR^{12};

M is $OC(=Y)$, $N(R^{51})C(=Y)$, $N=C(OR^{52})$, $N=C(SR^{53})$ or $N=C(NR^{54}R^{55})$ where O or N is the atom of attachment to the ring containing E and D;

Y is O, S or NR^{13};

J is N or CR^{14}

R^1 is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{3-7} cycloalkyl, cyano, nitro or SF_5;

R^{51} is hydrogen, optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, optionally substituted phenoxycarbonyl, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted C_{1-6} arylthio, optionally substituted C_{1-6} arylsulfinyl, optionally substituted C_{1-6} arylsulfonyl or $R^{20}R^{21}NS$;

R^{52} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, , amino, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted phenoxycarbonyl, tri(C_{1-4})alkylsilyl, aryldi(C_{1-4})alkylsilyl, (C_{1-4})alkyldiarylsilyl or triarylsilyl;

R^{53} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl or optionally substituted phenoxycarbonyl);

R^{54} and R^{55} are, independently optionally substituted C_{1-10} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, hydroxy, amino,

optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, or optionally substituted phenoxycarbonyl;

R^3, R^4 and R^5 are, independently, hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5;

R^6 is hydrogen, cyano, optionally substituted C_{1-20} alkyl, optionally substituted C_{2-20} alkenyl(C_{1-6})alkyl, optionally substituted C_{2-20} alkynyl(C_{1-6})alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{5-6} cycloalkenyl, formyl, optionally substituted C_{1-20} alkoxycarbonyl, optionally substituted C_{1-20} alkylcarbonyl, aminocarbonyl, optionally substituted C_{1-20}alkylaminocarbonyl, optionally substituted di(C_{1-20})alkylaminocarbonyl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyl, optionally substituted arylaminocarbonyl, optionally substituted N-alkyl-N-arylaminocarbonyl, optionally substituted diarylaminocarbonyl, optionally substituted heteroaryloxycarbonyl, optionally substituted heteroarylcarbonyl, optionally substituted heteroarylaminocarbonyl, optionally substituted alkylheteroarylaminocarbonyl, optionally substituted diheteroarylaminocarbonyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted heterocyclyl, optionally substituted C_{1-20} alkylsulfonyl, or optionally substituted arylsulfonyl;

R^8 and R^9 are, independently, hydrogen, halogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl or optionally substituted C_{1-6} alkoxy;

R^{12} is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, formyl, $R^{32}ON=C(R^{30})$, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5; or R^1 and R^{12} together with the atoms to which they are attached may be joined to form a five, six or seven-membered saturated or unsaturated ring carbocylic or heterocyclic ring which may contain one or two hetero atoms

selected from O, N or S and which may be optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen;

R^{13} is hydrogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted (C_{2-6})alkenyl(C_{1-6})alkyl, optionally substituted (C_{2-6})alkynyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted C_{1-6} alkylcarbonylamino, optionally substituted C_{1-6} alkoxycarbonylamino, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted arylthio, optionally substituted arylsulfinyl, optionally substituted arylsulfonyl or C_{1-6} acyloxy;

R^{14} is hydrogen, halogen, nitro, cyano, optionally substituted C_{1-8} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkylaminocarbonyl, optionally substituted di(C_{1-6})alkylaminocarbonyl, optionally substituted phenyl or optionally substituted heteroaryl;

R^{20} and R^{21} are, independently, optionally substituted C_{1-6} alkyl or R^{20} and R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

R^{30} is hydrogen, optionally substituted phenyl or optionally substituted C_{1-6} alkyl; and

R^{32} is hydrogen, optionally substituted phenyl (C_{1-2})alkyl or optionally substituted C_{1-20} alkyl.

The compounds of formula (I) may exist in different geometric or optical isomers or tautomeric forms. This invention covers all such isomers and tautomers and mixtures thereof in all proportions.

When present, optional substituents on alkylene, alkenylene or alkynylene moieties include, subject to valency constraints, one or more of halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{1-6} alkoxy(C_{1-6}) alkyl, C_{1-6} alkoxy, cyano, =O, $=NR^{33}$ and $=CR^{34}R^{35}$, wherein R^{33} is C_{1-6} alkyl, C_{1-6} haloalkyl, OR^{36} or $R^{37}R^{38}N$; where R^{34} and R^{35} are, independently,

hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy, C_{1-6} haloalkyl, cyano, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl or $R^{39}R^{40}N$; R^{36} is C_{1-6} alkyl, C_{1-6} haloalkyl or phenyl(C_{1-2})alkyl; R^{37} and R^{38} are, independently, hydrogen, C_{1-8} alkyl, C_{3-7} cycloalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl(C_{1-6})alkyl, C_{2-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, carboxy(C_{1-6})alkyl or phenyl(C_{1-2})alkyl or R^{37} and R^{38} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups; R^{39} and R^{40} are, independently, hydrogen, C_{1-8} alkyl, C_{3-7} cycloalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl(C_{1-6})alkyl, C_{2-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, carboxy(C_{1-6})alkyl or phenyl(C_{1-2})alkyl; or R^{39} and R^{40} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl or *neo*-pentyl. When present, the optional substituents on alkyl include one or more of halogen, nitro, cyano, HO_2C, C_{1-10} alkoxy (itself optionally substituted by C_{1-10} alkoxy), aryl(C_{1-4})alkoxy, C_{1-10} alkylthio, C_{1-10} alkylcarbonyl, C_{1-10} alkoxycarbonyl, C_{1-6} alkylaminocarbonyl, di(C_{1-6} alkyl)aminocarbonyl, (C_{1-6})alkylcarbonyloxy, optionally substituted phenyl, heteroaryl, aryloxy, arylcarbonyloxy, heteroaryloxy, heterocyclyl, heterocyclyloxy, C_{3-7} cycloalkyl (itself optionally substituted with (C_{1-6})alkyl or halogen), C_{3-7} cycloalkyloxy, C_{5-7} cycloalkenyl, C_{1-6} alkylsulfonyl, C_{1-6} alkylsulfinyl, tri(C_{1-4})alkylsilyl, tri(C_{1-4})alkylsilyl(C_{1-6})alkoxy, aryldi(C_{1-4})alkylsilyl, (C_{1-4})alkyldiarylsilyl and triarylsilyl.

Alkenyl and alkynyl moieties can be in the form of straight or branched chains, and the alkenyl moieties, where appropriate, can be of either the (E)- or (Z)-configuration. Examples are vinyl, allyl and propargyl. When present, the optional substituents on alkenyl or alkynyl include one or more of halogen, aryl and C_{3-7} cycloalkyl.

In the context of this specification acyl is optionally substituted C_{1-6} alkylcarbonyl (for example acetyl), optionally substituted C_{2-6} alkenylcarbonyl, optionally substituted C_{2-6}

alkynylcarbonyl, optionally substituted arylcarbonyl (for example benzoyl) or optionally substituted heteroarylcarbonyl.

Halogen is fluorine, chlorine, bromine or iodine.

Haloalkyl groups are alkyl groups which are optionally substituted with one or more of the same or different halogen atoms and are, for example, CF_3, CF_2Cl, CF_3CH_2 or CHF_2CH_2.

Aryl includes naphthyl, anthracyl, fluorenyl and indenyl but is preferably phenyl.

The term heteroaryl refers to an aromatic ring containing up to 10 atoms including one or more heteroatoms (preferably one or two heteroatoms) selected from O, S and N. Examples of such rings include pyridine, pyrimidine, furan, quinoline, quinazoline, pyrazole, thiophene, thiazole, oxazole and isoxazole.

The terms heterocycle and heterocyclyl refers to a non-aromatic ring containing up to 10 atoms including one or more (preferably one or two) heteroatoms selected from O, S and N. Examples of such rings include 1,3-dioxolane, tetrahydrofuran and morpholine. It is preferred that heterocyclyl is optionally substituted by C_{1-6} alkyl.

Cycloalkyl includes cyclopropyl, cyclopentyl and cyclohexyl. The optional substituents for cycloalkyl include halogen, cyano and C_{1-3} alkyl.

Cycloalkenyl includes cyclopentenyl and cyclohexenyl. The optional substituents for cycloalkenyl include C_{1-3} alkyl, halogen and cyano.

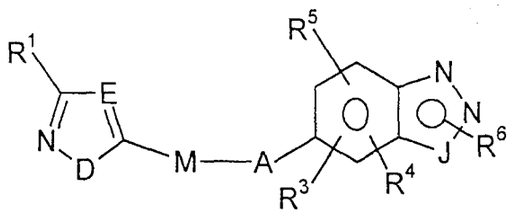
Carbocyclic rings include aryl, cycloalkyl and cycloalkenyl groups.

For substituted phenyl moieties, heterocyclyl and heteroaryl groups it is preferred that one or more substituents are independently selected from halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{2-6} alkenyl, C_{2-6} haloalkenyl, C_{2-6} alkynyl, C_{3-7} cycloalkyl, nitro, cyano, CO_2H, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, $R^{41}R^{42}N$ or $R^{43}R^{44}NC(O)$ wherein R^{41}, R^{42}, R^{43} and R^{44} are, independently, hydrogen or C_{1-6} alkyl.

It is to be understood that dialkylamino substituents include those where the dialkyl groups together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected

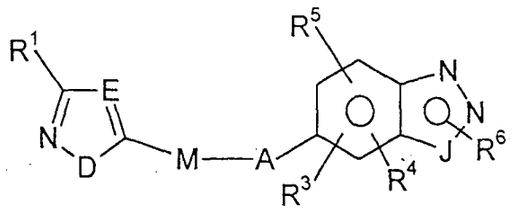
from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups. When heterocyclic rings are formed by joining two groups on an N atom, the resulting rings are suitably pyrrolidine, piperidine, thiomorpholine and morpholine each of which may be substituted by one or two (C_{1-6})alkyl groups.

In a further aspect, the present invention provides a compound of formula (IA):



(IA)

wherein A, D, E, M, Y, J, R^1, R^3, R^4, R^5 and R^6 are as defined above for a compound of formula (I). More preferred compounds of formula (IA) are those of formula (IB)



(IB)

wherein

D is S, NR^{10}, $CR^8{=}CR^9$, $CR^8{=}N$, $CR^8{=}N(O)$, $N{=}CR^9$ or $N(O){=}CR^9$;

E is N or CR^{12};

R^1 is hydrogen, halogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} cyanoalkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{3-6} cycloalkyl, C_{3-7} cycloalkyl(C_{1-4})alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, cyano, nitro or SF_5;

A is C_{1-6} alkylene, C_{1-6} alkenylene, C_{1-6} alkylenoxy, oxy(C_{1-6})alkylene, C_{1-6} alkylenamino or C_{1-6} alkylenethio, each of which is optionally substituted by C_{1-3} alkyl, C_{1-3} haloalkyl, C_{1-3} cyanoalkyl, halogen, C_{1-3} alkoxy, C_{1-6} alkoxycarbonyl, cyano, =O, $=NR^{15}$ or $=CR^{16}R^{17}$;

M is $N(R^{51})C(=Y)$ or $N=C(SR^{53})$ where O or N is the atom of attachment to the ring containing E and D;

Y is O, S or NR^{13};

J is N or CR^{14}

R^{51} is hydrogen, C_{1-10} alkyl, benzyloxymethyl, benzoyloxymethyl, C_{1-6}alkoxy(C_{1-6})alkyl, C_{2-6} alkenyl(C_{1-6})alkyl (especially allyl), C_{2-6} alkynyl(C_{1-6})alkyl (especially propargyl), C_{1-10} alkylcarbonyl or C_{1-10} alkoxycarbonyl (especially *iso*butoxycarbonyl);

R^{53} is C_{1-10} alkyl, benzyloxymethyl, benzoyloxymethyl, C_{1-6}alkoxy(C_{1-6})alkyl, C_{2-6} alkenyl(C_{1-6})alkyl (especially allyl), C_{2-6} alkynyl(C_{1-6})alkyl (especially propargyl), C_{1-10} alkylcarbonyl or C_{1-10} alkoxycarbonyl (especially *iso*butoxycarbonyl);

R^3, R^4 and R^5 are independently selected from hydrogen, halogen, C_{1-6} alkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{1-6} haloalkyl, cyano, nitro, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or SF_5;

R^6 is cyano, C_{1-8} alkyl, C_{2-6} haloalkyl, C_{1-6} cyanoalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl(C_{1-6})alkyl, C_{3-7} cycloalkyl, C_{3-7} halocycloalkyl, C_{3-7} cyanocycloalkyl, C_{1-3} alkyl(C_{3-7})cycloalkyl, C_{1-3} alkyl(C_{3-7})halocycloalkyl, C_{5-6} cycloalkenyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, C_{5-6} cycloalkenyl(C_{1-6})alkyl, C_{2-6} haloalkenyl(C_{1-6})alkyl, C_{1-6} cyanoalkenyl(C_{1-6})alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{3-6} alkenyloxy(C_{1-6})alkyl, C_{3-6} alkynyloxy(C_{1-6})alkyl, aryloxy(C_{1-6})alkyl, formyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{2-6} alkenylcarbonyl(C_{1-6})alkyl, C_{2-6} alkynylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{3-6} alkenyloxycarbonyl(C_{1-6})alkyl, C_{3-6} alkynyloxycarbonyl(C_{1-6})alkyl, aryloxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, aminocarbonyl(C_{2-6})alkenyl, aminocarbonyl(C_{2-6})alkynyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{2-6})alkenyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{2-6})alkenyl(C_{1-6})alkyl, alkylaminocarbonyl(C_{2-6})alkynyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkynyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl, aminocarbonyl, C_{1-6} alkylaminocarbonyl, di(C_{1-6})alkylaminocarbonyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{1-4})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano,

C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{2-4})alkenyl(C_{1-6})alkyl, (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy), heteroaryl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy), heterocyclyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heteroaryl(C_{1-4})alkyl (where the heteroaryl may be substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy),or heterocyclyl(C_{1-4})alkyl (where the heterocyclyl may be substituted by halo, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy);

R^8 and R^9 independently are, hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl C_{2-6} alkenyl, C_{1-6} alkynyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy;

R^{12} is hydrogen, halogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{1-6} alkynyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkoxy (C_{1-6})alkyl, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{1-6} haloalkyl, cyano, nitro, formyl, CH=NOR^{32}, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or SF_5; or together R^1 and R^{12} together with the atoms to which they are attached may be joined to form a five, six or seven-membered saturated or unsaturated ring carbocylic or heterocyclic ring which may contain one or two hetero atoms selected from O, N or S and which may be optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen;

R^{13} is cyano, nitro, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{3-7} cycloalkyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, CH_2(C_{2-6})alkenyl, CH_2(C_{2-6})alkynyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy) heteroaryl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, C_{1-6} alkylamino, di(C_{1-6})alkylamino, C_{1-6} alkylcarbonylamino, C_{1-6} alkoxycarbonylamino, C_{1-6} alkoxy, C_{1-6} alkylthio, C_{1-6} alkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylthio, C_{1-6} haloalkylsulfinyl, C_{1-6} haloalkylsulfonyl, arylthio, arylsulfinyl, arylsulfonyl or OCO(C_{1-6})alkyl;

R^{14} is hydrogen, halogen, nitro, cyano, C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{3-7} cycloalkyl, C_{2-6} haloalkenyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, C_{1-6}alkox(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl, C_{1-6} alkylaminocarbonyl, di(C_{1-}

$_6$alkylaminocarbonyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} +haloalkoxy) or heteroaryl (optionally substituted by halo,nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy).

R^{15} is C_{1-6} alkyl, OR^{22} or $NR^{23}R^{24}$;

R^{16} is hydrogen, C_{1-6} alkyl or C_{1-6} haloalkyl;

R^{17} is hydrogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, cyano, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl or $NR^{46}R^{47}$;

R^{20} and R^{21} independently are, hydrogen, C_{1-6} alkyl, $CH_2(C_{1-4}$ haloalkyl), C_{1-6} cyanoalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkoxy(C_{1-6})alkoxy(C_{1-6})alkyl, phenyl(C_{1-4})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heteroaryl(C_{1-4})alkyl (wherein the heteroaryl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heterocyclyl(C_{1-4})alkyl (wherein the heterocyclyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), or R^{20} and R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

R^{22} is C_{1-6} alkyl or optionally substituted phenyl(C_{1-2})alkyl;

R^{23} and R^{24} independently are, hydrogen, C_{1-8} alkyl or phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy);

R^{30} is hydrogen or C_{1-3} alkyl;

R^{32} is C_{1-6} alkyl or phenyl(C_{1-2})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy); and

R^{46} and R^{47} independently, are, hydrogen, C_{1-8} alkyl, C_{3-7} cycloalkyl, C_{3-6} alkenyl, C_{3-6} alkynyl, C_{2-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, carboxy(C_{1-6})alkyl or phenyl(C_{1-2})alkyl; or R^{46} and R^{47} R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two

further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

Preferably A is C_{1-4} alkylene -C(O)- or C_{1-4} alkyleneoxy.

Preferably D is S or $CR^8=CR^9$, where R^8 and R^9 are, independently, hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl C_{2-6} alkenyl, C_{1-6} alkynyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy.

Preferably E is N or CR^{12} where R^{12} is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkoxy (C_{1-6})alkyl, C_{1-6} alkylthio or SF_5; or R^1 and R^{12} together with the atoms to which they are attached form a benzene ring optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen.

A preferred value of M is $N(R^{51})C(=O)$ where N is the atom of attachment to the ring containing E and D; and R^{51} is hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, benzyloxymethyl or benzoyloxymethyl.

Preferably Y is O

Preferably J is N or CR^{14} where R^{14} is hydrogen, C_{1-6} alkyl, C_{1-6} haloalkyl, cyano, halogen or nitro.

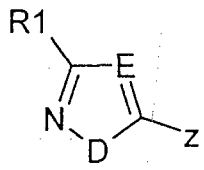
R^1 is preferably hydrogen, halogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{3-6} cycloalkyl, cyano, nitro or SF_5;

Preferably R^3, R^4 and R^5 are independently hydrogen, C_{1-3} alkyl or halogen.

R^6 is preferably C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl (C_{1-6})alkyl, C_{3-7} cycloalkyl, C_{3-7} halocycloalkyl, C_{3-7} cyanocycloalkyl, C_{1-3} alkyl(C_{3-7})cycloalkyl, C_{1-3} alkyl(C_{3-7})halocycloalkyl, C_{5-6} cycloalkenyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, C_{5-6} cycloalkenyl(C_{1-6})alkyl, C_{2-6} haloalkenyl(C_{1-6})alkyl, C_{1-6} cyanoalkenyl(C_{1-6})alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{3-6} alkenyloxy(C_{1-6})alkyl, C_{3-6} alkynyloxy(C_{1-6})alkyl, aryloxy(C_{1-6})alkyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{2-6} alkenylcarbonyl(C_{1-6})alkyl, C_{2-6} alkynylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{3-6} alkenyloxycarbonyl(C_{1-6})alkyl, C_{3-6} alkynyloxycarbonyl(C_{1-6})alkyl, aryloxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, aminocarbonyl(C_{2-6})alkenyl, aminocarbonyl(C_{2-6})alkynyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkenyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkenyl(C_{1-6})alkyl, alkylaminocarbonyl(C_{1-6})alkynyl(C_{1-6})alkyl,

di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkynyl(C_{1-6})alkyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{1-4})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{2-4})alkenyl(C_{1-6})alkyl, (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy), heteroaryl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heterocyclyl (wherein the heterocyclyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heteroaryl(C_{1-4})alkyl (wherein the heteroaryl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy)or heterocyclyl(C_{1-4})alkyl (wherein the heterocyclyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy);

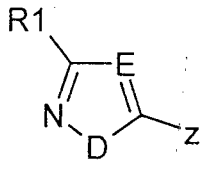
More preferred optionally substituted rings of formula



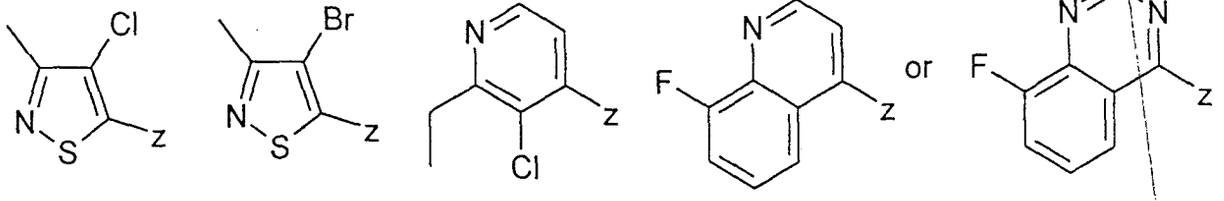
where Z represents the point of attachment to M

include optionally substituted isothiazolyl, optionally substituted pyridyl, optionally substituted pyrimidinyl, optionally substituted quinazolinyl and optionally substituted quinolinyl groups in which the optional substituents are chosen from halo, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkoxy(C_{1-6})alkyl or C_{1-6} haloalkoxy.

Most preferred optionally substituted rings of formula



are



More preferably A is CH_2, or CH_2O, even more preferably CH_2.

It is more preferred that M is $NR^{51}C(=O)$, where R^{51} is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy (C_{1-4})alkyl, benzyloxymethyl or benzoyloxymethyl. It is especially preferred that R^{51} is hydrogen, ethyl, ethoxymethyl, allyl or propargyl

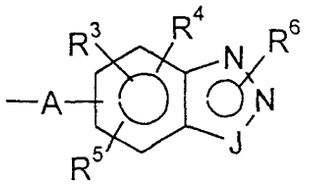
It is more preferred that R^3, R^4 and R^5 are independently, hydrogen, or halogen (especially fluorine); it is especially preferred that each of R^3, R^4 and R^5 is hydrogen.

More preferably J is N or CR^{14} where R^{14} is hydrogen, methyl, or halogen

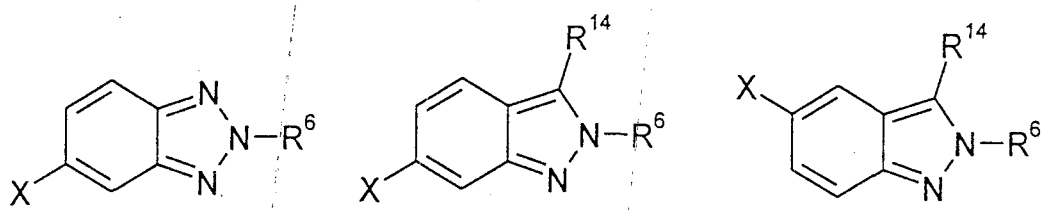
More preferably R^6 is C_{1-8} alkyl, C_{2-8} haloalkyl, C_{1-8} cyanoalkyl, C_{3-7} cycloalkyl, C_{1-3} alkyl (C_{3-7}) cycloalkyl, C_{1-6} alkoxy (C_{1-6}) alkyl, heterocyclic (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl (optionally substituted by halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, nitro, cyano or C_{1-6} alkylsulfonyl) or heteroaryl (optionally substituted by halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, nitro, cyano or C_{1-6} alkylsulfonyl)

Particularly preferred values of R_6 are C_{1-8} alkyl, C_{2-6} haloalkyl, C_{1-6}alkoxy(C_{1-6})alkyl, C_{3-7}cycloalkyl or C_{3-7} cycloalkyl(C_{1-6})alkyl.

Particularly preferred values of the group:

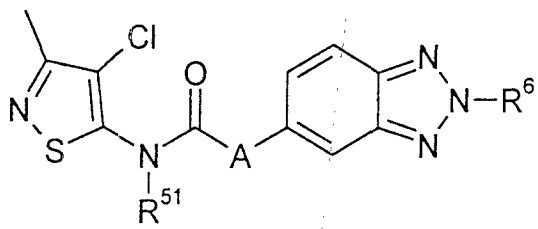


are



where X represents the position of attachment of A to the ring.

The compounds of the following Tables illustrate compounds of the invention. Table 1 provides compounds of the formula (1A'):



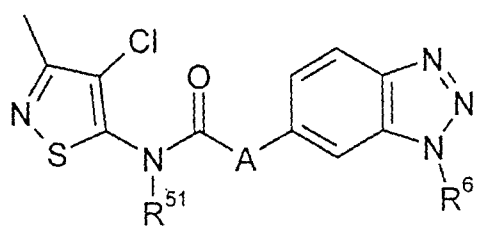
(1A')

where R^{51}, A and R^6 are as defined in Table 1.

TABLE 1

Compound No.	R^{51}	A	R^6
1.1	H	CH_2	$CH_2CH_2CH_3$
1.2	H	CH_2	CH_3
1.3	H	CH_2	*para*-fluorobenzyl
1.4	H	CH_2	CH_2CF_2
1.5	H	CH_2	$(CH_2)_4CH_3$
1.6	H	CH_2	2-chloro-4-trifluoro-methylphenyl
1.7	H	CH_2	$CH(CH_3)CH_2CH_3$
1.8	H	CH_2	CH_2CH_3
1.9	H	CH_2	$CH_2C(CH_3)_3$
1.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
1.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
1.12	H	CH_2	4-trifluoromethylphenyl
1.13	H	$CH(CH_2CH_2CH(CH_3)2)$	$CH_2CH_2CH(CH_3)_2$
1.14	H	CH_2	$CH_2CF_2OCH_3$
1.15	H	CH_2	$CH_2CH_2CH(CH_3)_2$
1.16	H	CH_2	$CH_2CH(CH_3)_2$

Table 2 provides compounds of the formula (1B')

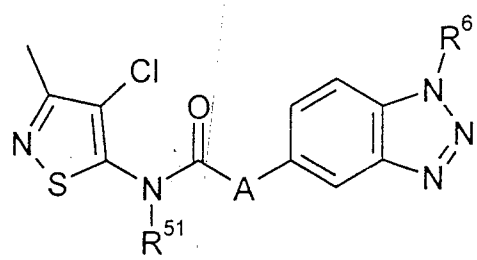


(1B')

TABLE 2

Compound No.	R^{51}	A	R^6
2.1	H	CH_2	$CH_2CH_2CH_3$
2.2	H	CH_2	CH_3
2.3	H	CH_2	*para*-fluorobenzyl
2.4	H	CH_2	CH_2CF_3
2.5	H	CH_2	$(CH_2)_4CH_3$
2.6	H	CH_2	2-chloro-4-trifluoro-methylphenyl
2.7	H	CH_2	$CH(CH_3)CH_2CH_3$
2.8	H	CH_2	CH_2CH_3
2.9	H	CH_2	$CH_2C(CH_3)_3$
2.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
2.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
2.12	H	CH_2	4-trifluoromethylphenyl
2.13	H	$CH(CH_2CH_2CH(CH_3)2)$	$CH_2CH_2CH(CH_3)_2$
2.14	H	CH_2	$CH_2CF_2OCH_3$
2.15	H	CH_2	$CH_2CH_2CH(CH_3)$
2.16	H	CH_2	$CH_2CH(CH_3)_2$
2.17	H	CH_2	$COCH_2$

Table 3 provides compounds of the formula (1C'):

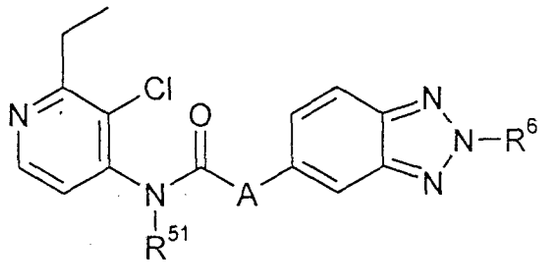


(IC')

TABLE 3

Compound No.	R^{51}	A	R^6
3.1	H	CH_2	$CH_2CH_2CH_3$
3.2	H	CH_2	CH_3
3.3	H	CH_2	*para*-fluorobenzyl
3.4	H	CH_2	CH_2CF_3
3.5	H	CH_2	$(CH_2)_4CH_3$
3.6	H	CH_2	2-chloro-4-trifluro-methylphenyl
3.7	H	CH_2	$CH(CH_3)CH2CH3$
3.8	H	CH_2	CH_2CH_3
3.9	H	CH_2	$CH_2C(CH_3)_3$
3.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
3.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
3.12	H	CH_2	4-trifluoromethyl-phenyl
3.13	H	$CH(CH_2CH_2CH(CH_3)_2)$	$CH_2CH_2CH(CH_3)_2$
3.14	H	CH_2	$CH_2CF_2OCH_3$
3.15	H	CH_2	$CH_2CH_2CH(CH_3)_3$
3.16	H	CH_2	$CH_2CH(CH_3)_2$
3.17	H	CH_2	$COCH_3$

Table 4 provides compounds of the formula (1D')

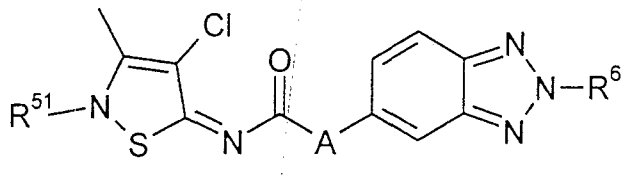


(ID')

TABLE 4

Compound No.	R^{51}	A	R^6
4.1	H	CH_2	$CH_2CH_2CH_3$
4.2	H	CH_2	CH_3
4.3	H	CH_2	*para*-fluorobenzyl
4.4	H	CH_2	CH_2CH_3
4.5	H	CH_2	$(CH_2)_4CH_3$
4.6	H	CH_2	2-chloro-4-trifluoromethylphenyl
4.7	H	CH_2	$CH(CH_3)CH_2CH_3$
4.8	H	CH_2	CH_2CH_3
4.9	H	CH_2	$CH_2C(CH_3)_3$
4.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
4.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
4.12	H	CH_2	4-trifluoromethylphenyl
4.13	H	$CH(CH_2CH_2CH(CH_3)2)$	$CH_2CH_2CH(CH_3)_2$
4.14	H	CH_2	$CH_2CF_2OCH_3$
4.15	H	CH_2	$CH_2CH_2CH(CH_3)_2$
4.16	H	CH_2	$CH_2CH(CH_3)_2$

Table 5 provides compounds of the formula (IE')



(IE')

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TABLE 5

Compound No.	R^{51}	A	R^{6}
5.1	CH_2CH_3	H	$CH_2CH_2CH_3$
5.2	$CH_2OCH_2CH_3$	H	$CH_2CH_2CH_3$

The following abbreviations are used throughout this description:

m.p. = melting point
ppm = parts per million
s = singlet
br = broad
d = doublet
dd = doublet of doublets
t = triplet
q = quartet
m = multiplet

Table 6 shows selected NMR data, all with $CDCl_3$, as the solvent (unless otherwise stated; if a mixture of solvents is present, this is indicated as, for example ($CDCl_3$ / *d6*-DMSO)), (no attempt is made to list all characterising data in all cases) for compounds of tables 1 - 5

TABLE 6

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
1.1	1.0 (t, 3H); 2.15 (m, 2H);2.35 (s, 3H); 4.0 (s, 2H); 4.7(t, 2H); 7.35 (dd, 1H); 7.85 (d, 1H); 7.95 (d, 1H); 8.15 (br, 1H)
1.2	2.35 (s, 3H); 4.0 (s, 2H); 4.5 (s, 3H); 7.35 (dd, 1H); 7.8 (d, 1H); 7.9 (d, 1H); 8.05 (br, 1H)
1.3	(*d6*-DMSO): 2.35 (s, 3H); 4.05 (s, 2H); 5.8 (s, 2H) 7.0 (m, 2H); 7.4 (m, 3H); 7.8 (m, 2H): 10.9 (br, 1H)

TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
1.4	2.4 (s, 3H); 4.0 (s, 2H); 5.3 (q, 2H); 7.4 (dd, 1H) 7.85 (d, 1H); 7.95 (d, 1H); 8.15 (br, 1H)
1.5	0.9 (t, 3H); 1.35 (m, 4H); 2.15 (m, 2H); 2.4 (s, 3H): 4.05 (s, 2H); 4.7 (t, 2H); 7.35 (dd, 1H); 7.85 (d, 2H); 7.9 (d, 2H); 8.15 (br, 1H)
1.6	2.4 (s, 3H); 4.05 (s, 2H); 7.45 (dd, 1H); 7.75 (dd, 1H); 7.95 (m, 3H); 8.05 (m, 1H); 8.2 (br, 1H)
1.7	0.85 (t, 3H); 1.7 (d, 3H); 2.0-2.2 (m, 2H); 2.35 (s, 3H); 4.0(s, 2H); 4.9 (m, 1H); 7.3 (dd, 1H); 7.85 (d, 1H); 7.9 (d, 1H); 8.15 (br, 1H)
1.8	1.75 (t, 3H); 2.35 (s, 3H); 4.0 (s, 2H); 4.8(q, 2H); 7.35 (dd, 1H); 7.8 (br, 1H); 7.9 (d, 1H); 8.1 (br, 1H)
1.9	1.05 (s, 9H); 2.4(s, 3H); 4.05 (s, 2H); 4.55 (s, 2H); 7.35 (dd, 1H); 7.85 (br, 1H); 7.95(d, 1H); 8.15 (br, 1H)
1.10	0.95 (t, 3H); 1.2 (t, 3H); 2.13 (m, 2H); 2.5 (s, 3H) 3.65 (br, 2H); 3.8 (br, 2H); 4.65 (t, 2H); 7.15 (br, 1H); 7.5 (br, 1H); 7.78 (dd, 1H)
1.11	0.95 (t, 3H); 1.2 (t, 3H); 2.1 (m, 2H); 2.5 (s, 3H); 3.6 (q, 2H) 3.7 (br, 2H); 4.7 (t, 2H); 5.2 (br, 2H); 7.15 (br, 1H); 7.55 (br, 1H); 7.8 (d, 1H)
1.12	2.4 (s, 3H); 4.1 (s, 2H); 7.5 (m, 1H); 7.8-7.9 (m, 4H); 8.5(br, 2H); 10.35 (s, 1H)
1.13	0.88 (dd, 6H); 1.0 (d, 6H); 1.62 (m, 4H); 2.0 (m, 2H); 2.32 (m 2H); 2.36 (s, 3H); 3.77 (dd, 1H); 4.77 (dd, 2H); 7.37 (dd, 1H); 7.83 (s, 1H); 7.9 (d, 1H); 8.06 (s, 1H)
1.14	2.39 (s, 3H); 3.61 (s, 3H); 4.03 (s, 2H); 5.19 (t, 2H) 7.40 (dd, 1H); 7.88 (s, 1H); 7.97 (d, 1H); 8.16 (s, 1H)

TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$, unless stated)
1.15	1.0 (d, 6H); 2.03 (q, 2H); 2.17 (s, 3H); 2.37 (m, 1H); 4.0 (s, 2H); 4.77 (dd, 2H); 7.34 (dd, 1H); 7.83 (s, 1H); 7.92 (d, 1H); 8.16 (s, 1H)
1.16	1.0 (d, 6H); 2.37 (s, 3H); 2.54 (m, 1H); 4.03 (s, 2H); 4.56 (d, 2H); 7.36 (dd, 1H); 7.84 (s, 1H); 7.94 (d, 1H)
2.1	
2.2	2.35 (s, 3H); 4.1 (s, 2H); 4.23 (s, 3H); 7.3(d, 1H); 7.55 (d, 1H): 8.1 (d, 1H); 8.3 (br, 1H)
2.3	
2.4	2.4 (s, 3H); 4.1 (s, 2H); 5.25 (q, 1H); 7.6 (m, 2H); 8.1 (br, 1H); 8.25 (br, 1H)
2.5	
2.6	
2.7	
2.8	
2.9	
2.10	
2.11	
2.12	
2.13	
2.14	
2.15	
2.16	
2.17	2.40(s, 3H); 3.03 (s, 3H); 4.09 (s, 2H); 7.66 (dd, 2H); 8.10 (d, 1H); 8.2 (br, 1H); 8.34 (d, 1H)
3.1	

TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
3.2	2.35 (s, 3H); 4.1 (s, 2H); 4.3 (s, 3H); 7.55 (m, 2H); 8.0 (d, 1H); 8.3(br, 1H)
3.3	
3.4	2.4 (s, 3H); 4.05 (s, 2H); 7.4 (dd, 1H); 7.6 (d, 1H); 8.15 (d, 1H); 8.3 (br, 1H)
3.5	
3.6	
3.7	
3.8	
3.9	
3.10	
3.11	
3.12	
3.13	
3.14	
3.15	
3.16	
3.17	2.40 (s, 3H); 3.03 (s, 3H); 4.10 (s, 2H); 7.52 (dd, 2H); 8.19 (d, 1H); 8.2 (br, 1 H); 8.3 (d, 1H)
4.1	1.0 (t, 3H); 1.25 (t, 3H); 2.15 (m, 2H); 2.85 (q, 2H); 3.95 (s, 2H); 4.7 (t, 2H); 7.35 (m, 1H) 7.85 (br, 1H); 7.95 (d, 1H); 7.95 (br, 1H); 8.2 (d, 1H); 8.35 (d, 1H)
4.2	
4.3	
4.4	

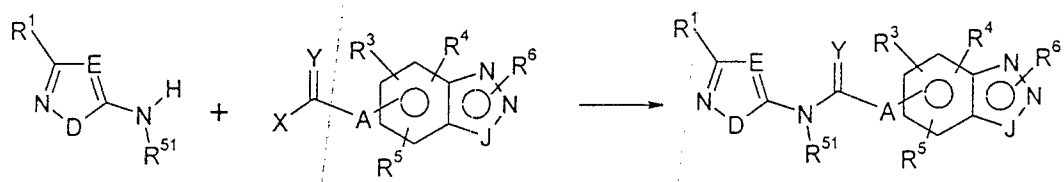
TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
4.5	
4.6	
4.7	
4.8	
4.9	
4.10	
4.11	
4.12	
4.13	
4.14	
4.15	
4.16	
5.1	0.95 (t, 3H); 1.4 (t, 3H); 2.12 (m, 2H); 2.5 (s, 3H); 3.9 (q, 2H); 4.2 (s, 2H), 4.65 (t, 2H); 7.42 (dd, 1H); 7.8 (br, 1H); 7.81 (br, 1H)
5.2	0.95 (t, 3H); 1.15 (t, 3H); 2.1 (m, 2H); 2.55 (s, 3H); 3.5 (q, 2H); 4.2 (s, 2H); 4.7 (t, 2H); 5.2 (s, 2H); 7.4 (dd, 1H); 7.8 (m, 2H)

The compounds of the invention may be made in a variety of ways. For example, as shown in Scheme 1, compounds (I) wherein Y is O and A is alkylene, alkenylene, alkylenoxy, alkylenamino or alkylenethio may be prepared by reacting amine (II) with an appropriate carboxylic ester (III) (X = alkoxy or aryloxy) or with a carboxylic acid (III, X = OH) in the presence of a known coupling agent such as 1,3-dicyclohexylcarbodiimide or 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide. Alternatively the carboxylic acid may first be converted to an acid chloride, anhydride or chloroformate suitable for reaction with an amine to form an amide; such procedures are well known to those skilled in the art and are

described, for example in J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985, pps 370-376 and references therein.

Scheme 1



(II) (III) (I)

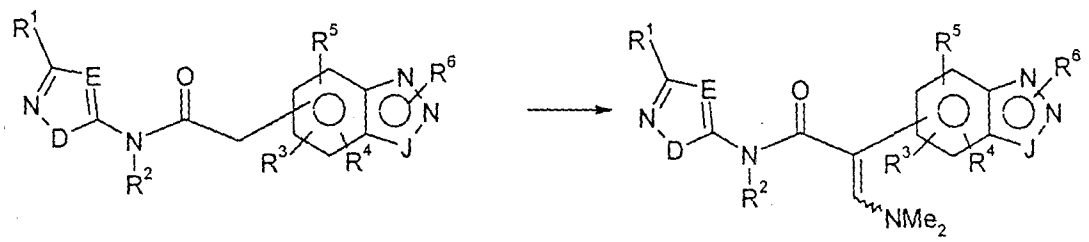
Amines (II) are known compounds, or may be prepared from commercially available starting materials by methods described in the literature (see, for example, C. Oliver Kappe, Robert Flammang, and Curt Wentrup, Heterocycles, Vol. 37, No. 3, 1615, (1994), A. Adams and R. Slack, J. Chem. Soc., 3061, (1959) and Ronald E Hackler, Kenneth W. Burow, Jr., Sylvester V. Kaster and David I. Wickiser, J. Heterocyclic Chem, 26, 1575, (1989), Ronald E Hackler, Glen P Jourdan, Peter L Johnson, Brian R Thoreen and Jack G Samaritoni, PCT Int. Appl., WO9304580 A1, and references therein).

The syntheses of substituted benzotriazoles and indazoles is described in the chemical literature (see, for example Alan R. Katritsky and Charles W. Rees, Comprehensive Heterocyclic Chemistry, Pergamon Press, 1984; Christoph Ruchardt and Volker Hassmann, Liebis Ann. Chem., 1980, 908; Jean-Jacques Vandenbossche and Alain Lagrange, Eur. Pat. Appl., EP904769; F. Halley and X. Sava, Synth. Commun. 1997, 27 (7), 1199; Donald R. James, Don R. Baker, Steven D. Mielich, William J. Michaely, Steven Fitzjohn, Christopher G. Knudsen, Christopher Mathews and John M. Gerdes, PCT Int. Appl., WO9318008 A1, Donald Richard James and Raymond Anthony Felix, PCT Int. Appl., WO9425446 A1) and similar methods may be used to prepare Compounds (III) starting from appropriately substituted anilines, as detailed in the experimental section. Alternatively, halobenzotriazoles and haloindazoles (especially where the halogen is bromo or iodo), which may be prepared by the above methods, may be converted into Compounds (III) via procedures involving transition-metal catalysed transformations analogous to those described by Nitya G. Kundu

et al., Tetrahedron, 53 (39), 13397, (1997), Takao Sakamoto et al. Heterocycles, 36 (11), 2509 (1993), Motoi Kawatsura and John F. Hartwig, JACS, 1999, 121, 1473, and others.

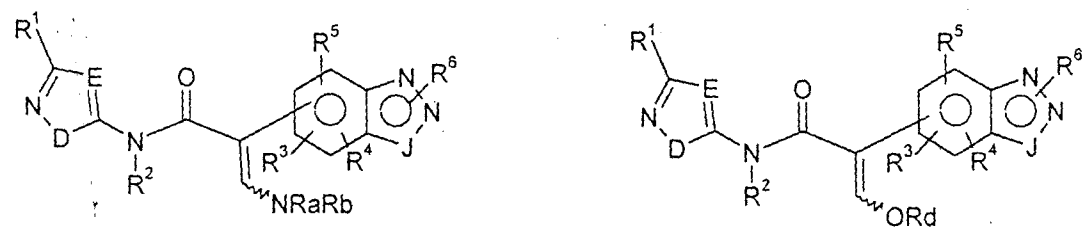
A compound of formula (I), wherein Y is sulphur, may be prepared by reacting a compound of formula (I), wherein Y is oxygen, with a suitable thionating agent such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent), 2,4-bis(methylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy reagent methyl), 2,4-bis(*para*-tolyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy reagent *p*-tolyl) or phosphorus pentasulfide in a suitable solvent such as toluene or fluorobenzene.

Compounds of formula (IV) may be made from (V) by treatment with N,N-dimethylformamide dialkyl acetal in a suitable solvent such as toluene or N,N-dimethylformamide. Frequently this reaction produces a mixture of E and Z isomers which are sometimes separable by standard techniques such as flash column chromatography and recrystallisation. This invention covers isolated isomers together with mixtures of isomers.



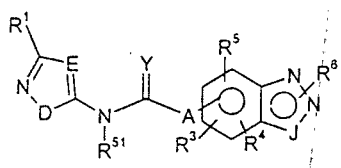
(V) (IV)

Compounds (IV) may be treated subsequently with amines (HNRaRb) to give Compounds (VI); compounds (V) may be treated in an analogous manner with trialkylorthoformates ($HC(ORd)_3$) to afford Compounds (VII):

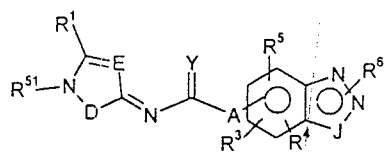


(VI) (VII)

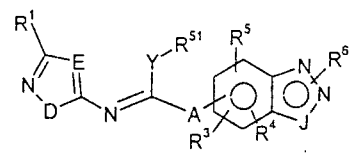
Compounds (I), wherein R^{51} is hydrogen, may be treated with an optionally substituted alkylating agent (such as an alkyl halide, chloromethylether, dialkyl sulfate or trialkyloxonium salt) optionally in the presence of a base to give additional compounds (I) wherein R^{51} is optionally substituted alkyl which form a further part of this invention. When Y is O, this reaction usually produces a mixture of isomeric products (I) and (VIII). In contrast, when Y is S, (IX) is the predominant product



(I)



(VIII)



(IX)

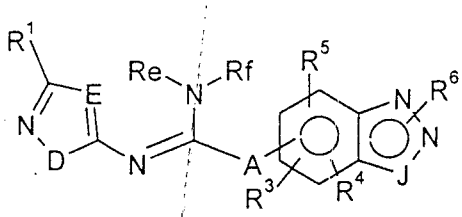
Compounds of formula (VIII) are novel, and as such form a further aspect of the invention. Certain of these compounds also possess insecticidal and fungicidal activity

Those skilled in the art will recognise that analogous reactions involving sulfenylation, sulfonylation and acylation are possible when Y is O.

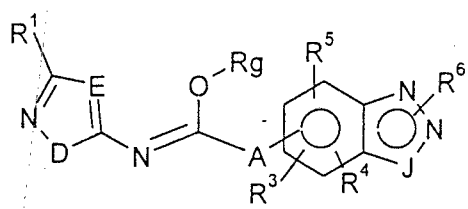
Compounds (I) where R^{51} is alkoxymethyl or acyloxymethyl, may also be prepared from Compound (I) where R^{51} is hydrogen by sequential reaction with formaldehyde and an alkylating or acylating agent.

Additional compounds (I) may be prepared from (I) where R^{51} is hydrogen by reaction with hydroxymethylbenzotriazole or benzotriazoles and aldehydes according to the method of A. R. Katritzky et al., J. Org. Chem., (1993), 58, 2086.

Compounds (IX), Y = S may be reacted with alcohols, amines, O-alkylhydroxyl-amines and hydrazines, optionally in the presence of a mercuric salt (such as mercuric chloride), according to known procedures to give compounds (X) and (XI) respectively:



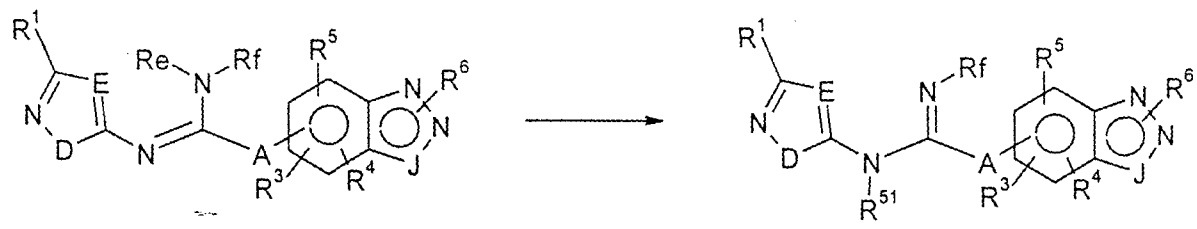
(X)



(XI)

where Re is H, optionally substituted alkyl, alkenyl or alkynyl, Rf is substituted alkyl, alkenyl alkynyl, amino, substituted amino or alkoxy and Rg is optionally substituted alkyl, alkenyl or alkynyl.

Compounds (X) where Re is hydrogen may be treated with an optionally substituted alkylating agent (such as an alkyl halide, chloromethylether, dialkyl sulfate or trialkyloxonium salt) optionally in the presence of a base to give further Compounds (I)



(X)

Heteroaryl N-Oxides can be produced by methods known to the skilled person.

The compounds of formula (I) can be used to combat and control infestations of insect pests such as Lepidoptera, Diptera, Hemiptera, Thysanoptera, Orthoptera, Dictyoptera, Coleoptera, Siphonaptera, Hymenoptera and Isoptera and also other invertebrate pests, for example, acarine, nematode and mollusc pests. Insects, acarines, nematodes and molluscs are hereinafter collectively referred to as pests. The pests which may be combated and controlled by the use of the invention compounds include those pests associated with agriculture (which term includes the growing of crops for food and fibre products), horticulture and animal husbandry, companion animals, forestry and the storage of products of vegetable origin (such as fruit, grain and timber); those pests associated with the damage of man-made structures and the transmission of diseases of man and animals; and also nuisance pests (such as flies).

Examples of pest species which may be controlled by the compounds of formula (I) include: *Myzus persicae* (aphid), *Aphis gossypii* (aphid), *Aphis fabae* (aphid), *Lygus* spp. (capsids), *Dysdercus* spp. (capsids), *Nilaparvata lugens* (planthopper), *Nephotettixc incticeps* (leafhopper), *Nezara* spp. (stinkbugs), *Euschistus* spp. (stinkbugs), *Leptocorisa* spp. (stinkbugs), *Frankliniella occidentalis* (thrip), Thrips spp. (thrips), *Leptinotarsa*

decemlineata (Colorado potato beetle), *Anthonomus grandis* (boll weevil), *Aonidiella* spp. (scale insects), *Trialeurodes* spp. (white flies), *Bemisia tabaci* (white fly), *Ostrinia nubilalis* (European corn borer), *Spodoptera littoralis* (cotton leafworm), *Heliothis virescens* (tobacco budworm), *Helicoverpa armigera* (cotton bollworm), *Helicoverpa zea* (cotton bollworm), *Sylepta derogata* (cotton leaf roller), *Pieris brassicae* (white butterfly), *Plutella xylostella* (diamond back moth), *Agrotis* spp. (cutworms), *Chilo suppressalis* (rice stem borer), *Locusta migratoria* (locust), *Chortiocetes terminifera* (locust), *Diabrotica* spp. (rootworms), *Panonychus ulmi* (European red mite), *Panonychus citri* (citrus red mite), *Tetranychus urticae* (two-spotted spider mite), *Tetranychus cinnabarinus* (carmine spider mite), *Phyllocoptruta oleivora* (citrus rust mite), *Polyphagotarsonemus latus* (broad mite), *Brevipalpus* spp. (flat mites), *Boophilus microplus* (cattle tick), *Dermacentor variabilis* (American dog tick), *Ctenocephalides felis* (cat flea), *Liriomyza* spp. (leafminer), *Musca domestica* (housefly), *Aedes aegypti* (mosquito), *Anopheles* spp. (mosquitoes), *Culex* spp. (mosquitoes), *Lucillia* spp. (blowflies), *Blattella germanica* (cockroach), *Periplaneta americana* (cockroach), *Blatta orientalis* (cockroach), termites of the Mastotermitidae (for example *Mastotermes* spp.), the Kalotermitidae (for example *Neotermes* spp.), the Rhinotermitidae (for example *Coptotermes formosanus*, *Reticulitermes flavipes*, *R. speratu*, *R. virginicus*, *R. hesperus*, and *R. santonensis*) and the Termitidae (for example *Globitermes sulphureus*), *Solenopsis geminata* (fire ant), *Monomorium pharaonis* (pharaoh's ant), *Damalinia* spp. and *Linognathus* spp. (biting and sucking lice), *Meloidogyne* spp. (root knot nematodes), *Globodera* spp. and *Heterodera* spp. (cyst nematodes), *Pratylenchus* spp. (lesion nematodes), *Rhodopholus* spp. (banana burrowing nematodes), *Tylenchulus* spp.(citrus nematodes), *Haemonchus contortus* (barber pole worm), *Caenorhabditis elegans* (vinegar eelworm), *Trichostrongylus* spp. (gastro intestinal nematodes) and *Deroceras reticulatum* (slug).

The compounds of formula (I) are also active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia recondita*, *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet,

vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Erysiphe graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici)* and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercosporella herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frogeye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; *Plasmopara viticola* on vines; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco,

cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon, pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes; *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium* spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarus*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seditiosum*) or lumber, notably *Cephaloascus fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

A compound of formula (I) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (I) may be volatile enough to be active in the vapour phase against one or more fungi on the plant.

The invention therefore provides a method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a pest, a locus of pest, or to a plant

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susceptible to attack by a pest, and a method of combating and controlling fungi which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a plant, to a seed of a plant, to the locus of the plant or seed, to soil or to any other growth medium (for example a nutrient solution). The compounds of formula (I) are preferably used against insects, acarines, nematodes or fungi.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicant and antisporulant treatments.

As fungicides, the compounds of formula (I) are preferably used for agricultural, horticultural and turfgrass purposes in the form of a composition.

In order to apply a compound of formula (I) as an insecticide, acaricide, nematicide or molluscicide to a pest, a locus of pest, or to a plant susceptible to attack by a pest, or, as a fungicide to a plant, to a seed of a plant, to the locus of the plant or seed, to soil or to any other growth medium, a compound of formula (I) is usually formulated into a composition which includes, in addition to the compound of formula (I), a suitable inert diluent or carrier and, optionally, a surface active agent (SFA). SFAs are chemicals which are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (I). The composition is generally used for the control of pests or fungi such that a compound of formula (I) is applied at a rate of from 0.1g to10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (I) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides an insecticidal, acaricidal, nematicidal, molluscicidal or fungicidal composition comprising an insecticidally,

acaricidally, nematicidally, molluscicidally or fungicidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor. The composition is preferably an insecticidal, acaricidal, nematicidal or fungicidal composition.

In a still further aspect the invention provides a method of combating and controlling pests or fungi at a locus which comprises treating the pests or fungi or the locus of the pests or fungi with an insecticidally, acaricidally, nematicidally, molluscicidally or fungicidally effective amount of a composition comprising a compound of formula (I). The compounds of formula (I) are preferably used against insects, acarines, nematodes or fungi.

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (I).

Dustable powders (DP) may be prepared by mixing a compound of formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder. Soluble powders (SP) may be prepared by mixing a compound of formula (I) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing a compound of formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrins, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Dispersible Concentrates (DC) may be prepared by dissolving a compound of formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as C_8-C_{10} fatty acid dimethylamide) and chlorinated hydrocarbons. An

EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment. Preparation of an EW involves obtaining a compound of formula (I) either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifiying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents which have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of formula (I) is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (I). SCs may be prepared by ball or bead milling the solid compound of formula (I) in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle. Alternatively, a compound of formula (I) may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Aerosol formulations comprise a compound of formula (I) and a suitable propellant (for example *n*-butane). A compound of formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula (I) may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (I) and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the compound of formula (I) and they may be used for seed treatment. A compound of formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A composition may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (I)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of formula (I)).

A compound of formula (I) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and DC compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

Wetting agents, dispersing agents and emulsifying agents may be surface SFAs of the cationic, anionic, amphoteric or non-ionic type.

Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-*iso*propyl- and tri-*iso*propyl-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycinates.

Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (I) may be applied by any of the known means of applying pesticidal or fungicidal compounds. For example, it may be applied, formulated or unformulated, to the pests or to a locus of the pests (such as a habitat of the pests, or a growing plant liable to infestation by the pests) or to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which

plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (I) may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ECs, EWs, MEs SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula (I) (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of formula (I) may be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula (I).

The invention therefore also provides a fertiliser composition comprising a fertiliser and a compound of formula (I).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematicidal or acaricidal activity.

By including another fungicide, the resulting composition may have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (I)

alone. Further the other fungicide may have a synergistic effect on the fungicidal activity of the compound of formula (I).

The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of formula (I); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition. Examples of suitable pesticides include the following:

a) Pyrethroids, such as permethrin, cypermethrin, fenvalerate, esfenvalerate, deltamethrin, cyhalothrin (in particular lambda-cyhalothrin), bifenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids (for example ethofenprox), natural pyrethrin, tetramethrin, s-bioallethrin, fenfluthrin, prallethrin or 5-benzyl-3-furylmethyl-(E)-(1R,3S)-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl)cyclopropane carboxylate;

b) Organophosphates, such as, profenofos, sulprofos, acephate, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, profenofos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chlorpyrifos, phosalone, terbufos, fensulfothion, fonofos, phorate, phoxim, pirimiphos-methyl, pirimiphos-ethyl, fenitrothion, fosthiazate or diazinon;

c) Carbamates (including aryl carbamates), such as pirimicarb, triazamate, cloethocarb, carbofuran, furathiocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur, methomyl or oxamyl;

d) Benzoyl ureas, such as diflubenzuron, triflumuron, hexaflumuron, flufenoxuron or chlorfluazuron;

e) Organic tin compounds, such as cyhexatin, fenbutatin oxide or azocyclotin;

f) Pyrazoles, such as tebufenpyrad and fenpyroximate;

g) Macrolides, such as avermectins or milbemycins, for example abamectin, emamectin benzoate, ivermectin, milbemycin, spinosad or azadirachtin;

h) Hormones or pheromones;

i) Organochlorine compounds such as endosulfan, benzene hexachloride, DDT, chlordane or dieldrin;

j) Amidines, such as chlordimeform or amitraz;

k) Fumigant agents, such as chloropicrin, dichloropropane, methyl bromide or metam;

l) Chloronicotinyl compounds such as imidacloprid, thiacloprid, acetamiprid, nitenpyram or thiamethoxam;

m) Diacylhydrazines, such as tebufenozide, chromafenozide or methoxyfenozide;

n) Diphenyl ethers, such as diofenolan or pyriproxifen;

o) Indoxacarb;

p) Chlorfenapyr; or

q) Pymetrozine.

In addition to the major chemical classes of pesticide listed above, other pesticides having particular targets may be employed in the composition, if appropriate for the intended utility of the composition. For instance, selective insecticides for particular crops, for example stemborer specific insecticides (such as cartap) or hopper specific insecticides (such as buprofezin) for use in rice may be employed. Alternatively insecticides or acaricides specific for particular insect species/stages may also be included in the compositions (for example acaricidal ovo-larvicides, such as clofentezine, flubenzimine, hexythiazox or tetradifon; acaricidal motilicides, such as dicofol or propargite; acaricides, such as bromopropylate or chlorobenzilate; or growth regulators, such as hydramethylnon, cyromazine, methoprene, chlorfluazuron or diflubenzuron).

Examples of fungicidal compounds which may be included in the composition of the invention are (*E*)-*N*-methyl-2-[2-(2,5-dimethylphenoxymethyl)phenyl]-2-methoxy-iminoacetamide (SSF-129), 4-bromo-2-cyano-*N*,*N*-dimethyl-6-trifluoromethyl-benzimidazole-1-sulphonamide, α-[*N*-(3-chloro-2,6-xylyl)-2-methoxy-acetamido]-γ-butyrolactone, 4-chloro-2-cyano-*N*,*N*-dimethyl-5-*p*-tolylimidazole-1-sulfonamide (IKF-916, cyamidazosulfamid), 3-5-dichloro-*N*-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-4-methylbenzamide (RH-7281, zoxamide), *N*-allyl-4,5,-dimethyl-2-trimethylsilylthiophene-3-carboxamide (MON65500), *N*-(1-cyano-1,2-dimethylpropyl)-2-

(2,4-dichlorophenoxy)propionamide (AC382042), *N*-(2-methoxy-5-pyridyl)-cyclopropane carboxamide, acibenzolar (CGA245704), alanycarb, aldimorph, anilazine, azaconazole, azoxystrobin, benalaxyl, benomyl, biloxazol, bitertanol, blasticidin S, bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA41396, CGA41397, chinomethionate, chlorothalonil, chlorozolinate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate and Bordeaux mixture, cymoxanil, cyproconazole, cyprodinil, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O,O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethomorph, dimethirimol, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethirimol, ethyl(*Z*)-*N*-benzyl-*N*([methyl(methyl-thioethylideneaminooxycarbonyl)amino]thio)-β-alaninate, etridiazole, famoxadone, fenamidone (RPA407213), fenarimol, fenbuconazole, fenfuram, fenhexamid (KBR2738), fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, fluoroimide, fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos, iprodione, iprovalicarb (SZX0722), isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metconazole, metiram, metiram-zinc, metominostrobin, myclobutanil, neoasozin, nickel dimethyldithio-carbamate, nitrothal-*iso*propyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosetyl-Al, phosphorus acids, phthalide, picoxystrobin (ZA1963), polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, prop-iconazole, propineb, propionic acid, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyr-oxyfur, pyrrolnitrin, quaternary ammonium compounds, quinomethionate, quinoxyfen, quintozene, sipconazole (F-155), sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamid,

2-(thiocyanomethylthio)benzothiazole, thiophanate-methyl, thiram, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin (CGA279202), triforine, triflumizole, triticonazole, validamycin A, vapam, vinclozolin, zineb and ziram.

The compounds of formula (I) may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Examples of suitable synergists for use in the compositions include piperonyl butoxide, sesamex, safroxan and dodecyl imidazole.

Suitable herbicides and plant-growth regulators for inclusion in the compositions will depend upon the intended target and the effect required.

An example of a rice selective herbicide which may be included is propanil. An example of a plant growth regulator for use in cotton is PIX™.

Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The invention is illustrated by the following examples.

Example 1

Preparation of Compound 1.1, N-(4-chloro-3-methylisothiazol-5-yl)-(2-propyl-benzotriazol-5-yl)acetamide

Step 1

Preparation of methyl 4-aminophenylacetate

4-Aminophenylacetic acid (100g) was suspended in methanol (1000ml) and gaseous hydrogen chloride was passed through until the mixture was saturated. The mixture was heated at 50°C for 2 hours and was then allowed to cool to room temperature. The solvent

was evaporated *in vacuo*, the residue taken up aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl 4-aminophenylacetate as a pale brown liquid.

^{1}H NMR ($CDCl_3$) δ ppm: 3.5 (s, 2H); 3.7 (s, 3H); 6.65 (m, 2H); 7.05 (m, 2H).

Step 2

Preparation of methyl 4-acetamido-3-nitrophenylacetate

Methyl 4-aminophenylacetate (110g, 0.667mol) was added dropwise to acetic anhydride (600ml), maintaining the temperature of the reaction mixture below 30°C by external cooling. Once the addition was complete the mixture was cooled to below 10°C and concentrated nitric acid (85 ml) was added dropwise. Once the addition of the acid was complete, the mixture was allowed to warm to room temperature and poured onto a mixture of ice and water. The precipitated solid was collected by filtration and dried to give methyl 4-acetamido-3-nitrophenylacetate (120g) as a pale yellow solid.

^{1}H NMR ($CDCl_3$) δ ppm: 2.3 (s, 3H); 3.65 (s, 2H); 3.7 (s, 3H); 7.55 (dd, 1H); 8.1 (d, 1H); 8.7 (d, 1H); 10.3 (b, 1H).

Step 3

Preparation of methyl 4-acetamido-3-aminophenylacetate

Methyl 4-acetamido-3-nitrophenylacetate (40g, 0.159mol)) was dissolved in methanol (400ml) and hydrogenated at 5bar over a 5% palladium on carbon catalyst. The catalyst was removed by filtration and the filtrate evaporated *in vacuo* to give methyl 4-acetamido-3-aminophenylacetate.

Step 4

Preparation of methyl (benzotriazol-5-yl)acetate

Methyl 4-acetamido-3-aminophenylacetate (77g, 0.373mol) was taken up in a mixture of acetic acid (210ml) and water (210ml) and cooled to below 5°C. A solution of sodium nitrite (38.63g, 0.559mol) in water (200ml) was added dropwise, and once the

addition was complete the mixture was stirred for 4hours, warming slowly to room temperature. The mixture was diluted with ethyl acetate and the insoluble material removed by filtration. The filtrate was washed with brine, dried over anhydrous magnesium sulfate, filtered and the solvent evaporated *in vacuo*, to give a viscous residue (51g). The residue was dissolved in a solution of methanol (400ml) previously saturated with hydrogen chloride and the mixture stirred for 2hours. The solvent was removed *in vacuo*, the residue taken up in water, neutralised with saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl (benzotriazol-5-yl)acetate (35g) as a reddish liquid which crystallised on standing.

^{1}H NMR ($CDCl_3$) δ ppm: 3.7 (s, 3H); 3.8 (s, 2H); 7.35 (d, 1H); 7.8 (b, 2H); 13.6 (b, 1H).

Step 5

Preparation of methyl (2-propylbenzotriazol-5-yl)acetate

A solution of methyl (benzotriazol-5-yl)acetate (10g, 0.0523mol) in N,N-dimethylformamide was added dropwise to a chilled (ice-bath) suspension of sodium hydride (60% dispersion in oil, 2.3g, 0.0575mol) in N,N-dimethylformamide. When the addition was complete, the ice-bath was removed and the mixture stirred for 1hour. N-Propyl iodide (9.78g, 0.0575mol) was added dropwise, and once the addition was complete the mixture was stirred at room temperature for 3hours. The reaction mixture was poured onto ice/water, and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by column chromatography to afford methyl (2-propylbenzotriazol-5-yl)acetate (4.8g).

^{1}H NMR ($CDCl_3$) δ ppm: 0.9 (t, 3H); 2.1 (m, 2H); 3.7 (s, 3H); 3.8 (s, 2H); 4.65 (t, 2H); 7.3 (dd, 1H); 7.7 (d, 1H); 7.8 (d, 1H).

This step also generates methyl (1-propylbenzotriazol-6-yl)acetate and methyl (1-propylbenzotriazol-5-yl)acetate which may be isolated and converted to Compounds (2.1) and (3.1) respectively by procedures similar to those detailed below.

Step 6

Preparation of (2-propylbenzotriazol-5-yl)acetic acid

The acetate prepared in Step 6 above (4.8g, 0.0206mol) was dissolved in methanol (60ml) and potassium hydroxide flakes (1.27g, 0.0226mol) added. The mixture was refluxed for 2hours, then cooled and the solvent evaporated *in vacuo*. The residual solid was dissolved in water and extracted with diethyl ether. The aqueous solution was acidified to pH 1 by addition of dilute aqueous hydrochloric acid and extracted with ethyl acetate. The ethyl acetate extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford (2-propylbenzotriazol-5-yl)acetic acid (3.6g) as a colourless solid.

Step 7

Preparation of N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)-acetamide

The acid prepared in Step 7 (0.438g, 0.002mol) was dissolved in dichloromethane (5ml) and one drop of N,N-dimethyl formamide was added. Oxalyl chloride (0.307g, 0.0022mol) was added dropwise, and the mixture stirred at room temperature for 2hours. The solvent was removed *in vacuo*, the residue taken up in xylene and added to a mixture of 5-amino-4-chloro-3-methylisothiazole (0.446g, 0.003mol) in xylene and heated at reflux for 2hours. The mixture was cooled to room temperature and the solvent evaporated *in vacuo*. The residue was taken up in ethyl acetate, washed sequentially with saturated aqueous sodium bicarbonate solution and brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by flash column chromatography, eluting with 2:1 hexane : ethyl acetate, to give N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)-acetamide (0.34g) as a sandy-coloured solid.

^{1}H NMR ($CDCl_3$) δ ppm: 1.0 (t, 3H); 2.15 (m, 2H); 2.35 (s, 3H); 4.0 (s, 2H); 4.7 (t, 2H); 7.35 (dd, 1H); 7.85 (d, 1H); 7.95 (d, 1H); 8.15 (br, 1H).

Example 2.

Preparation of Compound 1.11, N-(4-chloro-3-methylisothiazol-5-yl)-N-(ethoxymethyl)-(2-propylbenzotriazol-5-yl)acetamide and Compound 5.2, N-[2-ethoxyoxymethyl-4-chloro-3-methylisothiazolin-5-ylidene]-(2-propylbenzo-triazol-5-yl) acetamide

Lithium bis(trimethylsilyl)amide (1.0 M solution in tetrahydrofuran, 3.3 ml, 0.0033 mol) was added dropwise to a solution of N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)acetamide (Compound 1.1) (0.699 g, 0.002 mol) in tetrahydrofuran (10 ml) and once the addition was complete the mixture was stirred at room temperature for 30 minutes. Chloromethylethyl ether (0.620 g, 0.0066 mol) was added and the mixture stirred at room temperature for 2 hours. The mixture was poured into water, neutralised, and extracted with ethyl acetate. The organic extract was dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated *in vacuo*. The residue was further purified by flash column chromatography, eluting initially with 2:1 hexane : ethyl acetate and then with ethyl acetate to give N-(4-chloro-3-methylisothiazol-5-yl)-N-(ethoxymethyl)-(2-propylbenzotriazol-5-yl)acetamide (Compound 1.11) (0.135 g) as an orange gum and N-[2-ethoxyoxymethyl-4-chloro-3-methylisothiazolin-5-ylidene]-(2-propylbenzotriazol-5-yl) acetamide (Compound 5.2) (0.128 g) as a colourless solid, m.p. 108-109 °C

Compound 1.11

^{1}H NMR ($CDCl_3$) δ ppm: 0.95 (t, 3H); 1.2 (t, 3H); 2.1 (m, 2H); 2.5 (s, 3H); 3.6 (q, 2H), 3.7 (br, 2H); 4.7 (t, 2H); 5.1 (br, 2H); 7.15 (br, 1H); 7.55 (br, 1H); 7.8 (d, 1H)

Compound 5.2

^{1}H NMR ($CDCl_3$) δ ppm: 0.95 (t, 3H); 1.15 (t, 3H); 2.1 (m, 2H); 2.55 (s, 3H); 3.5 (q, 2H); 4.2 (s, 2H); 4.7 (t, 2H), 5.2 (s, 2H); 7.4 (dd, 1H); 7.8 (m, 2H)

EXAMPLE 3

This Example illustrates the pesticidal/insecticidal properties of compounds of formula (I). The activities of samples of individual compounds and mixtures of compounds of formula (I) were determined using a variety of pests., The pests were treated with a liquid

composition containing 500 parts per million (ppm) by weight of a compound . Each composition was made by dissolving the compound in an acetone and ethanol (50:50 by volume) mixture and diluting the solution with water containing 0.05% by volume of a wetting agent, SYNPERONIC NP8, until the liquid composition contained the required concentration of the compound.

Samples used were as follows:

Sample No.	Component A	Component B	Ratio A : B
1	Compound 1.1		
2	Compound 1.2		
3	Compound 2.2	Compound 3.2	1 : 3
4	Compound 1.3		
5	Compound 2.3	Compound 3.3	1 : 1
6	Compound 2.4	Compound 3.4	8 : 92
7	Compound 2.4	Compound 3.4	1 : 2
8	Compound 1.4		
9	Compound 1.5		
10	Compound 2.5	Compound 3.5	1 : 1
11	Compound 1.6		
12	Compound 2.6	Compound 3.6	1 : 1
13	Compound 1.7		
14	Compound 2.7	Compound 3.7	1 : 1
15	Compound 1.8		
16	Compound 2.8	Compound 3.8	1 : 1
17	Compound 1.9		
18	Compound 2.9	Compound 3.9	3 : 2
19	Compound 1.10		
20	Compound 1.11		
21	Compound 1.12		
22	Compound 3.12		

23	Compound 2.12	Compound 3.12	1 : 1
24	Compound 2.1	Compound 3.1	1 : 1
25	Compound 2.12	Compound 3.12	9 : 1
26	Compound 2.17		
27	Compound 3.17		
28	Compound 1.13		
29	Compound 1.14		
30	Compound 1.15		
31	Compound 1.16		
32	Compound 4.1		
33	Compound 5.1		
34	Compound 5.2		

The test procedure adopted with regard to each pest, was essentially the same and comprised supporting a number of the pests on a medium which was usually a substrate, a host plant or a foodstuff on which the pests feed, and treating either or both the medium and the pests with a composition. Pest mortality was assessed usually between two and five days after treatment.

The results of the tests against peach aphid (*Myzus persicae*) are presented below. In this test Chinese cabbage leaves were infested with aphids, the infested leaves were sprayed with the test composition, and the mortality assessed after three days. The results indicate a grading of mortality (score) designated as 9, 5 or 0 wherein 9 indicates 80-100% mortality, 5 indicates 40-79% mortality and 0 indicates less than 40% mortality.

Sample Nos. 2, 13, 15, 19, 20, 30, 31 and 32 each gave a mortality score of 9 whilst Sample Nos. 8, 9, 11, 17, 29 and 34 gave a score of 5

In addition, in a similar test against two-spotted spider mites (*Tetranychus urticae*) Sample Nos. 1, 8, 11, 12, 13, 17, 18, 19, 20 and 30 each gave a mortality score of 9 whilst Sample No. 9 gave a score of 5.

EXAMPLE 4

This Example illustrates the fungicidal properties of compounds of formula (I). The compounds were tested against a variety of foliar fungal diseases of plants. The technique employed was as follows.

Plants were grown in John Innes Potting Compost (No.1 or 2) in 4cm diameter, 3.5cm depth minipots. The test samples were individually formulated as a solution either in acetone or acetone/ethanol (1:1 by volume) which was diluted in deionised water to a concentration of 100ppm (that is, 1mg of compound in a final volume of 10ml) immediately before use. When foliar sprays were applied to monocotyledonous crops, TWEEN 20 (0.1% by volume) was added. TWEEN is a registered trade mark.

Individual compounds of formula (I), or mixtures of compounds of formula (1), were applied as a foliar (Folr) application (where the chemical solution was applied to the foliage of the test plants by spraying the plant to maximum droplet retention.)

These tests were carried out against *Uncinula necator* (UNCINE), on vines; *Phytophthora infestans lycopersici* (PHYTIN) on tomatoes; *Puccinia recondita* (PUCCRT), on wheat; and *Pyricularia oryzae* (PYRIOR) on rice. Each treatment was applied to two or more replicate plants for *Phytophthora infestans lycopersici* and *Uncinula necator*. For tests on *Puccinia recondita* and *Pyricularia oryzae* two replicate pots each containing 6 to10 plants were used for each treatment. The plants were inoculated one day before (Erad) or one day after (Prot) chemical application. The *Phytophthora infestans lycopersici, Puccinia recondita* and *Pyricularia oryzae* plants were inoculated with a calibrated fungal spore suspension. The *Uncinula necator* plants were inoculated using a 'blowing' inoculation technique.

After chemical application and inoculation, the plants were incubated under high humidity conditions and then put into an appropriate environment to allow infection to proceed, until the disease was ready for assessment. The time period between chemical application and assessment varied from five to fourteen days according to the disease and

270
255

environment. However, each individual disease was assessed after the same time period for all samples.

Assessments were performed on each of two leaves on each of the replicate plants for *Phytophthora infestans lycopersici*. Assessments were performed on a single leaf of each of the replicate plants for *Uncinula necator*. For *Puccinia recondita and Pyricularia recondita* assessments were carried out collectively on the plants in each replicate pot.

The disease level present (that is, the percentage leaf area covered by actively sporulating disease) was assessed visually. For each treatment, the assessed values for all its replicates were meaned to provide mean disease values. Untreated control plants were assessed in the same manner. The data were then processed by the method, described hereinafter, to provide PRCO (Percentage Reduction from Control) values.

An example of a typical calculation is as follows:

Mean disease level for treatment A = 25%

Mean disease level on untreated controls = 85%

$$PRCO = 100 - \left\{ \frac{\text{Mean disease level for treatment A}}{\text{Mean disease level on untreated controls}} \right\} \times 100$$

$$= 100 - \left(\frac{25}{85} \times 100\right) = 70.6$$

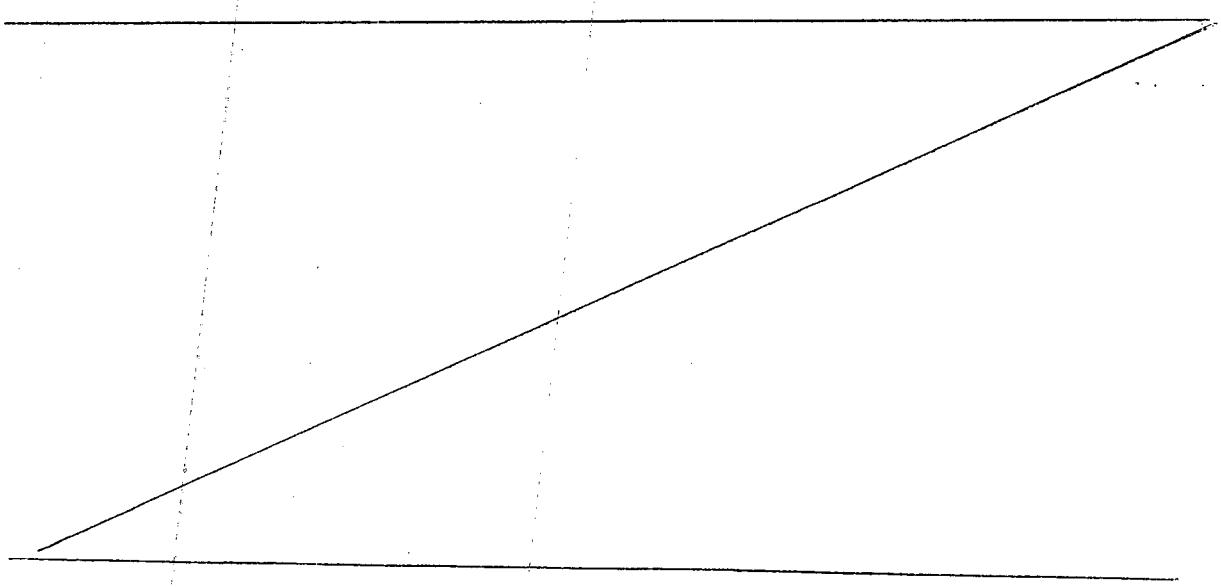
The PRCO is then rounded to the nearest whole number; therefore, in this particular example, the PRCO result is 71.

It is possible for negative PRCO values to be obtained.

PRCO results are shown below in Table 7.

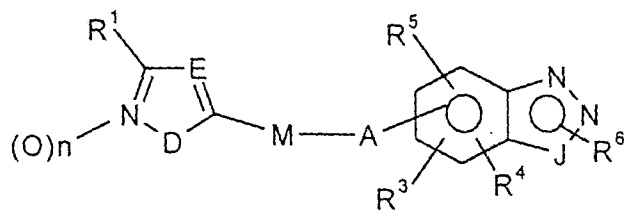
TABLE 7

Sample No.	PHYTIN Prot	PUCCRT Prot	PYRIOR Prot	UNCINE Erad
1	100	100	100	
2			87	
3			40	
4			92	
6	75	16	6	11
7			96	
8			100	
9	100	99	100	
11			100	
12			98	
19	81	87		
30	100	100		100
31	100	100		100
33	30	36		
34	81		93	100



Claims

1. A compound of formula (I):



(I)

wherein n is 0 or 1; A is optionally substituted C_{1-6} alkylene, optionally substituted C_{2-6} alkenylene, optionally substituted C_{2-6} alkynylene, optionally substituted C_{1-6} alkylenoxy, optionally substituted oxy(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenethio, optionally substituted thio(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenamino, optionally substituted amino(C_{1-6})alkylene, optionally substituted [C_{1-6} alkyleneoxy(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenethio(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfinyl(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfonyl(C_{1-6})alkylene] or optionally substituted [C_{1-6} alkyleneamino(C_{1-6})alkylene];

D is S, NR^{10} CR^8=CR^9, CR^8=N, CR^8=N(O), N=CR^9 or N(O)=CR^9;

R^{10} is C_{1-6} alkyl;

E is N, N-oxide or CR^{12};

M is OC(=Y), N(R^{51})C(=Y), N=C(OR^{52}), N=C(SR^{53}) or N=C($NR^{54}R^{55}$) where O or N is the atom of attachment to the ring containing E and D;

Y is O, S or NR^{13};

J is N or CR^{14};

R^1 is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{3-7} cycloalkyl, cyano, nitro or SF_5;

R^{51} is hydrogen, optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, optionally substituted phenoxycarbonyl, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted C_{1-6} arylthio, optionally substituted C_{1-6} arylsulfinyl, optionally substituted C_{1-6} arylsulfonyl or $R^{20}R^{21}NS$;

R^{52} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, , amino, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted phenoxycarbonyl, tri(C_{1-4})alkylsilyl, aryldi(C_{1-4})alkylsilyl, (C_{1-4})alkyldiarylsilyl or triarylsilyl;

R^{53} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl or optionally substituted phenoxycarbonyl);

R^{54} and R^{55} are, independently optionally substituted C_{1-10} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, hydroxy, amino, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, or optionally substituted phenoxycarbonyl;

R^3, R^4 and R^5 are, independently, hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally

substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5;

R^6 is hydrogen, cyano, optionally substituted C_{1-20} alkyl, optionally substituted C_{2-20} alkenyl(C_{1-6})alkyl, optionally substituted C_{2-20} alkynyl(C_{1-6})alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{5-6} cycloalkenyl, formyl, optionally substituted C_{1-20} alkoxycarbonyl, optionally substituted C_{1-20} alkylcarbonyl, aminocarbonyl, optionally substituted C_{1-20} alkylaminocarbonyl, optionally substituted di(C_{1-20})alkylaminocarbonyl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyl, optionally substituted arylaminocarbonyl, optionally substituted N-alkyl-N-arylaminocarbonyl, optionally substituted diarylaminocarbonyl, optionally substituted heteroaryloxycarbonyl, optionally substituted heteroarylcarbonyl, optionally substituted heteroarylaminocarbonyl, optionally substituted alkylheteroarylaminocarbonyl, optionally substituted diheteroarylaminocarbonyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted heterocyclyl, optionally substituted C_{1-20} alkylsulfonyl, or optionally substituted arylsulfonyl;

R^8 and R^9 are, independently, hydrogen, halogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl or optionally substituted C_{1-6} alkoxy;

R^{12} is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, formyl, $R^{32}ON=C(R^{30})$, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5; or R^1 and R^{12} together with the atoms to which they are attached may be joined to form a five, six or seven-membered saturated or unsaturated ring carbocylic or heterocyclic ring which may contain one or two hetero atoms selected from O, N or S and which may be optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen;

R^{13} is hydrogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted (C_{2-6})alkenyl(C_{1-6})alkyl, optionally substituted (C_{2-6})alkynyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted C_{1-6} alkylcarbonylamino, optionally substituted C_{1-6} alkoxycarbonylamino, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted arylthio, optionally substituted arylsulfinyl, optionally substituted arylsulfonyl or C_{1-6} acyloxy;

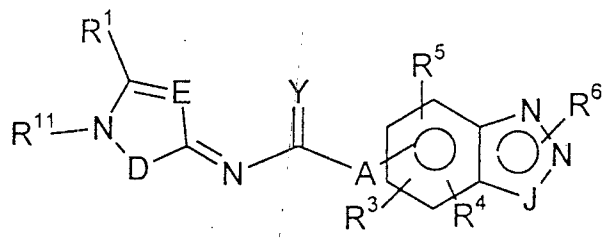
R^{14} is hydrogen, halogen, nitro, cyano, optionally substituted C_{1-8} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkylaminocarbonyl, optionally substituted di(C_{1-6})alkylaminocarbonyl, optionally substituted phenyl or optionally substituted heteroaryl;

R^{20} and R^{21} are, independently, optionally substituted C_{1-6} alkyl or R^{20} and R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

R^{30} is hydrogen, optionally substituted phenyl or optionally substituted C_{1-6} alkyl; and

R^{32} is hydrogen, optionally substituted phenyl (C_{1-2})alkyl or optionally substituted C_{1-20} alkyl;

2. A compound of formula (VIII):



(VIII)

wherein A, D, E, Y, J, R^1, R^3, R^4, R^5 and R^6 are as defined in claim 1 and R^{11} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, optionally substituted phenoxycarbonyl, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted C_{1-6} arylthio, optionally substituted C_{1-6} arylsulfinyl, optionally substituted C_{1-6} arylsulfonyl or $R^{20}R^{21}NS$.

3 A fungicidal, insecticidal, acaricidal, molluscicidal or nematicidal composition comprising a fungicidally, insecticidally, acaricidally, molluscicidally or nematicidally effective amount of a compound of formula (I) as claimed in claim 1 or a compound of formula (VIII) as claimed in claim 2 and a carrier or diluent therefor.

4 A method of combating and controlling fungi comprising applying to a plant, to a seed of a plant, to the locus of the plant or seed or to the soil a fungicidally effective amount of a compound of formula (I) as claimed in claim 1 or a compound of formula (VIII) as claimed in claim 2.

5 A method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I) as claimed in claim 1 or a compound of formula (VIII) as claimed in claim 2.

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TRADUCCION

Oficina de Patentes - Autoridad Ejecutiva del Departamento de Comercio e Industria.

Oficina de Patentes - Cardiff Road, Newport, South Wales NP10 8QQ

El que suscribe, funcionario debidamente autorizado para firmar y expedir certificados en representación del Controlador General, en virtud de Artículo 74(1) y (4) de la Ley de Desregulación y Contrataciones de 1994, certifica por la presente que los documentos adjuntos son copia fiel de la documentación presentada originariamente en relación con la solicitud de patente identificada en el presente certificado.

De acuerdo con el Reglamento de Patentes (Reinscripción de Sociedades) de 1982, si una compañía mencionada en este certificado y los documentos adjuntos ha sido reinscripta de acuerdo a la Ley de Sociedades de 1980 con el mismo nombre que aquél con el cual estaba inscripta inmediatamente antes de la reinscripción, excepto la sustitución o inclusión en la última parte del nombre de las palabras "public limited company" o su equivalente en galés, las referencias al nombre de la sociedad que figuren en este certificado y cualesquiera documentos adjuntos se considerarán como referidas al nombre con el cual ha sido reinscripta.

De acuerdo con la norma, las palabras "public limited company" pueden ser sustituidas por p.l.c., plc, P.L.C. o PLC.

Con la reinscripción de acuerdo a la Ley de Sociedades no se constituye una nueva entidad legal, sino que simplemente se somete a la sociedad a determinadas reglas legales societarias adicionales.

Firmado, ilegible. Fecha: 14 de marzo del 2000

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(Sello en relieve sobre oblea y cinta)

En la hoja siguiente dice:

Formulario de Patente 1/77

OFICINA DE PATENTES Oficina de Patentes - Cardiff Road, Newport, Gwent NP9 1RH

Solicitud de Patente

Recibido en mano el 28 de enero del 2000

31 enero 00 E509118-1 D02093 P01/7700 0.00-0002039.6

1. Su referencia: PPD 50466/ GB/ P

2. Solicitud de patente número: **0002039.6**

3. Nombre completo, domicilio y código postal del o los solicitantes:

ZENECA Limited, 15 Stanhope Gate, LONDON WIY 6LN, REINO UNIDO

Número ADP de patentes: 6254007002

Si el solicitante es una corporación, indicar el país/estado : REINO UNIDO

4. Título de la Invención : **COMPUESTOS QUIMICOS**

5. Nombre del agente (si corresponde) :

John Richard Waterman

Domicilio de servicio en el Reino Unido al cual se debe enviar la correspondencia:

Intellectual Property Dept., ZENECA Agrochemicals, Jealott's Hill Research Station, PO Box 3538, Bracknell Berkshire RG42 6YA, Mereside, REINO UNIDO

Número de ADP de patentes: 06791537001

9. Indique la cantidad de hojas de todos los siguientes adjuntos que ingresa con este formulario. No cuente copias de un mismo documento.

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275

Hojas de continuación de este formulario :

Memoria descriptiva: 50

Reivindicaciones: 5

11. Solicito/solicitamos el otorgamiento de una patente sobre la base de esta solicitud. Firmado. Fecha: 28/1/00

12. Nombre y número telefónico del representante en el Reino Unido:

VIJAYA KUMARI MALLIPEDDI - 01344 414365

DAWN LISA ROYAL - 01344 414079

Otros items en blanco.

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UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

No. **D613061**

Date **20 March, 2000**

This document bears
the signature / seal of **A Cressey**

Acting in the capacity of **Official Of The Patent Office Newport**

Signed by: **B. Amarteifio**

FOREIGN AND COMMONWEALTH OFFICE
LONDON

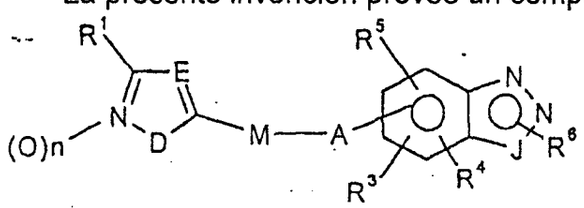
For Her Majesty's Principal Secretary of State
For Foreign and Commonwealth Affairs

COMPUESTOS QUÍMICOS

La presente invención se relaciona con derivados azina y azol, con procesos para prepararlos, con composiciones fungicidas, insecticidas, acaricidas, molusquicidas y nematicidas que los comprenden, con métodos para usarlos para combatir enfermedades provocadas por hongos (especialmente enfermedades provocadas por hongos en las plantas) y con métodos para usarlos para combatir y controlar plagas de insectos, ácaros, moluscos y nematodos.

En WO95/31448, WO97/18198, WO98/02424 y WO98/05670 se describen derivados azina y azol.

La presente invención provee un compuesto de fórmula (I):



(I)

en donde n es 0 o 1; A es C_{1-6} alquileno opcionalmente sustituido, C_{2-6} alquenileno opcionalmente sustituido, C_{2-6} alquinileno opcionalmente sustituido, C_{1-6} alquilenoxi opcionalmente sustituido, oxi (C_{1-6}) alquileno opcionalmente sustituido, C_{1-6} alquilentio opcionalmente sustituido, tio (C_{1-6}) alquileno opcionalmente sustituido, C_{1-6} alquilenamino opcionalmente sustituido, amino (C_{1-6}) alquileno opcionalmente sustituido, [C_{1-6}alquilenoxi (C_{1-6}) alquileno] opcionalmente sustituido, [C_{1-6} alquilentio (C_{1-6}) alquileno] opcionalmente sustituido, [C_{1-6} alquilensulfinil (C_{1-6}) alquileno] opcionalmente sustituido, [C_{1-6} alquilensulfonil (C_{1-6}) alquileno] opcionalmente sustituido o [C_{1-6}alquilenamino (C_{1-6}) alquileno] opcionalmente sustituido;

D es S, NR^{10}, $CR^8=CR^9$, $CR^8=N$, $CR^8=N(O)$, $N=CR^9$ o $N(O)=CR^9$;

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R^{10} es C_{1-6} alquilo;

E es N,N-óxido o CR^{12};

M es $OC(=Y)$, $N(R^{51})C(=Y)$, $N=C(OR^{52})$, $N=C(SR^{53})$ o $N=C(NR^{54}R^{55})$ donde O o N es el átomo de unión al anillo que contiene E y D;

Y es O, S o NR^{13};

J es N o CR^{14};

R^1 es hidrógeno, halógeno, C_{1-6} alquilo opcionalmente sustituido, C_{2-6} alquenilo opcionalmente sustituido, C_{2-6} alquinilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, ciano, nitro o SF_5;

R^{51} es hidrógeno, C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinilo (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, fenoxicarbonilo opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, C_{1-6} ariltio opcionalmente sustituido, C_{1-6} arilsulfinilo opcionalmente sustituido, C_{1-6} arilsulfonilo opcionalmente sustituido o $R^{20}R^{21}NS$;

R^{52} es C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, 1-10 alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(1-10)alquilaminocarbonilo

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opcionalmente sustituido, amino, C_{1-6} alquilamino opcionalmente sustituido, di (C_{1-6}) alquilamino opcionalmente sustituido, fenoxicarbonilo opcionalmente sustituido, tri(C_{1-4})alquilsililo, arildi (C_{1-4})alquilsililo, (C_{1-4})alquildiarilsililo o triarilsililo;

R^{53} es C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquil] opcionalmente sustituido, [C_{2-6} alquinil-(C_{1-6})alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido o fenoxicarbonilo opcionalmente sustituido);

R^{54} y R^{55} son, independientemente C_{1-10} alquilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, hidroxi, amino, C_{1-6} alquilamino opcionalmente sustituido, di (C_{1-6}) alquilamino opcionalmente sustituido, o fenoxicarbonilo opcionalmente sustituido;

R^3, R^4 y R^5 son, independientemente, hidrógeno, halógeno, C_{1-6}alquilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, ciano, nitro, C_{1-6} alquilcarbonilo opcionalmente sustituido, C_{1-6} alcoxicarbonilo opcionalmente sustituido o SF_5;

R^6 es hidrógeno, ciano, C_{1-20} alquilo opcionalmente sustituido, C_{2-20}

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de fórmula (I)). Tales aditivos incluyen agentes activos en superficie, agregados de rocío basados en aceites, por ejemplo, algunos aceites minerales o aceites vegetales naturales (tales como aceite de soja y aceite de semilla de colza), y mezclas de éstos con otros coadyuvantes bio - mejoradores (ingredientes que pueden ayudar o modificar la acción de un compuesto de fórmula (I)).

Puede formularse también un compuesto de fórmula (I) para su uso en el tratamiento de semillas, por ejemplo, como una composición en polvo, incluyendo un polvo para el tratamiento seco de semillas (DS), un polvo soluble en agua (SS) o un polvo dispersable en agua para un tratamiento con jarabe (WS), o como una composición líquida, incluyendo un concentrado fluido (FS), una solución (LS) o una suspensión en cápsula (CS). Las preparaciones de DS, SS, WS, FS y las composiciones de LS son muy similares, respectivamente, a las preparaciones de DP, SP, WP, SC y a las composiciones de DC descriptas con anterioridad. Las composiciones para el tratamiento de semillas pueden incluir un agente para asistir en la adhesión de la composición a la semilla (por ejemplo, un aceite mineral o una barrera formadora de película).

Los agentes humectantes, dispersantes y emulsificadores pueden ser SFA de superficie de tipo catiónico, anfotérico o no iónico.

Los SFA adecuados de tipo catiónico incluyen compuestos de amonio cuaternario (por ejemplo, bromuro de cetiltrimetil amonio), imidazolinas y sales de amina.

Los SFA aniónicos adecuados incluyen metales alcalinos, sales de ácidos grasos, sales de monoésteres alifáticos de ácido sulfúrico (por ejemplo, lauril sulfato de sodio), sales de compuestos aromáticos sulfonados (por

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ejemplo, dodecilbencensulfonato de sodio, dodecilbencensulfonato de calcio, sulfonato de butilnaftaleno y mezclas de sulfonatos de sodio de diisopropil y trimetil naftaleno), sulfatos de éter, sulfatos de alcoholes de éteres (por ejemplo, sulfato de lauret-3 sodio), carboxilatos de éter (por ejemplo, carboxilato de lauret-3 sodio), ésteres de fosfato (productos de la reacción entre uno o más alcoholes grasos y ácido fosfórico (predominantemente mono - ésteres) o pentóxido de fósforo (predominantemente di - ésteres), por ejemplo, la reacción entre alcohol laurílico y ácido tetrafosfónico, adicionalmente puede etoxilarse estos productos), sulfosuccinamatos, sulfonatos de parafina o de olefina, tauratos y lignosulfonatos.

Los SFA adecuados de tipo anfotérico incluyen las betaínas, los propionatos y los glicinatos.

Los SFA adecuados de tipo no iónico incluyen los productos de la condensación de los óxidos de alquileno, del óxido de propileno del óxido de butileno o de mezclas de los mismos, con alcoholes grasos (tales como alcohol oleílico o alcohol cetílico) o con alquilfenoles (tales como octilfenol, nonilfenol u octilcresol), ésteres parciales derivados de ácidos grasos de cadena larga o de anhídridos de hexitol, productos de la condensación de dichos ésteres parciales con óxido de etileno, polímeros en bloque (que comprenden óxido de etileno y óxido de propileno), alcanolamidas, ésteres simples (por ejemplo, ésteres de polietilen glicol de ácidos grasos); óxidos de amina (por ejemplo, óxido de lauril dimetil amina); y lecitinas.

Los agentes suspensores adecuados incluyen coloides hidrofílicos (tales como polisacáridos, polivinilpirrolidona o carboximetilcelulosa de sodio) y arcillas de condensación (tales como bentonita o atapulgita).

Puede aplicarse un compuesto de fórmula (I) por medio de cualquiera de los métodos de aplicación conocidos para aplicar compuestos pesticidas o fungicidas. Por ejemplo, puede aplicárselo formulado o sin formular, a las plagas o a los sitios de las plagas (tales como un hábitat de las plagas, o a una planta en crecimiento que puede se afectada por las plagas) o a cualquier parte de la planta, incluyendo el follaje, los tallos, las ramas o las raíces, a la semilla ante de plantarla, o a otro medio en el cual estén creciendo las plantas o donde se las vaya a plantar (tal como el suelo que rodea las raíces, el suelo en general, el agua de riego o los sistemas hidropónicos de cultivo), en forma directa o por medio de rocío, de polvo, por volcado, como crema o como una formulación de pasta, como vapor o a través de su distribución y de su incorporación a una composición (tal como una composición granular o como una composición empaquetada en una bolsa soluble en agua) en el ambiente del suelo o en el agua.

Puede inyectarse también un compuesto de fórmula (I) en las plantas o puede rociárselo sobre la vegetación usando técnicas electrodinámicas de rocío u otros métodos de bajo volumen, o aplicárselo por medio de sistemas de irrigación terrestre o aérea.

Las composiciones para su uso como preparaciones acuosas (soluciones o dispersiones acuosas) se suplen generalmente bajo la forma de un concentrado que contiene una alta proporción del ingrediente activo, agregándose el concentrado al agua antes de usarlo. Se requiere comúnmente que estos concentrados, que pueden incluir DC, SC, EC, EW, ME, SO, SP, WP, WO y CS, resistan el almacenamiento por períodos prolongados y, después de tal almacenamiento, que sean capaces de mezclarse con agua

para formar preparaciones acuosas que permanezcan homogéneas por un tiempo suficiente como para permitirles ser aplicadas por medio de un equipo convencional de rocío. Tales preparaciones acuosas pueden contener cantidades variables de un compuesto de fórmula (I) (por ejemplo, de 0,0001 a 10% en peso), dependiendo del propósito para el cual quiera usárselas.

Puede usarse un compuesto de fórmula (I) en mezclas con fertilizadores (por ejemplo, fertilizadores con nitrógeno, con potasio o con fósforo). Los tipos adecuados de formulación incluyen gránulos de fertilizador. Las mezclas contienen adecuadamente hasta un 25% en peso del compuesto de fórmula (I).

La invención provee entonces una composición fertilizadora que comprende un fertilizador y un compuesto de fórmula (I).

Las composiciones de esta invención pueden contener otros compuestos que tengan actividad biológica, por ejemplo, micronutrientes o compuestos que tengan una actividad fungicida complementaria o que posean actividad de regulación del crecimiento vegetal, herbicida, insecticida, nematicida o acaricida.

Mediante la inclusión de otro fungicida, la composición resultante puede tener un mayor espectro de actividad o un mayor nivel de actividad intrínseca que el compuesto de fórmula (I) por sí solo. Además, el otro fungicida puede tener un efecto sinergístico sobre la actividad fungicida del compuesto de fórmula (I).

El compuesto de fórmula (I) puede ser el único ingrediente activo de la composición o puede estar mezclado con uno o más ingredientes activos adicionales tales como un pesticida, un fungicida, un sinergista, un herbicida o un regulador del crecimiento vegetal, cuando resulte apropiado. Un ingrediente

activo adicional puede proveer una composición que tenga un mayor espectro de actividad o una mayor persistencia e un lugar, que sinergice la actividad o complemente la actividad (por ejemplo, aumentando la velocidad del efecto o sobrepasando la repelencia) del compuesto de fórmula (I), o puede ayudar a evitar o prevenir el desarrollo de resistencia a componentes individuales. El ingrediente activo particular dependerá de la utilidad pretendida de la composición. Los ejemplos de pesticidas adecuados incluyen los siguientes:

a) Piretroides, tales como permetrina, cipermetrina, fenvalerato, esfenvalerato, deltametrina, cihalotrina (en particular, lambda - cihalotrina), bifentrina, fenpropatrina, ciflutrina, teflutrina, piretroides seguros para peces (por ejemplo, etofenprox), piretrinas naturales, tetrametrina, s - bioaletrina, fenflutrina, praletrina o carboxilato de 5- bencil -3- furilmetil - (E) - (1R, 3S) -2,2- dimetil -3- (2-oxotiolan -3- ilidenmetil) ciclopropano;

b) Organofosfatos tales como, profenofos, sulprofos, acefato, metil paratión, metil - azinfos, metil – demeton - s, heptenofos, tiometon, fenamifos, monocrotofos, profenofos, triazofos, metamidofos, dimetoato, fosfamidón, malatión, clorpirifos, fosalona, terbufos, fensulfotión, fonofos, forate, foxim, metil - pirimifos, etil - pirimifos, fenitrotión, fostiazato o diazinón;

c) Carbamatos (incluyendo carbamatos de arilo) tales como pirimicarb, triazamato, cloetocarb, carbofurano, furatiocarb, etiofencarb, aldicarb, tiofurox, carbosulfano, bendiocarb, fenobucarb, propoxur, metomil u oxamil;

d) Benzoil ureas tales como diflubenzurona, triflumurona, hexaflumurona, fllifenoxurona o clorfluazurona;

e) Compuestos orgánicos de estaño tales como cihexatina, óxido de fenbutatina o azociclotina;

f) Pirazoles tales como teblifenpirad y fenpiroximato;

g) Macrólidos tales como avermectinas o milbernicinas, por ejemplo, abamectina, benzoato de emamectina, ivermectina, milbernicina, spinosad o azadiractina;

h) Hormonas o feromonas;

i) Compuestos organoclorados tales como endosulfano, hexacloruro de benceno, DDT, clordano o dieldrina;

j) Amidinas tales como clordimeform o amitraz;

k) Agentes fumigadores tales como cloropicrina, dicloropropano, bromuro de metilo o metam;

l) Compuestos de cloronicotinilo tales como imidacloprid, tiacloprid, acetamiprid, nitenpiram o tiiametoxam;

m) Diacilhidrazines, tales como tebufenozida, cromafenozida o metoxifenozida;

n) Ésteres de difenilo tales como diofenolan o piriproxifeno;

o) Indoxacarb;

p) Clorfenapyr; o

q) Pimetrozina.

Además de las clases mayores de pesticidas que se indicaron anteriormente, pueden emplearse en al composición otros pesticidas que tengan blancos particulares, si resultan apropiados para la utilidad pretendida de la composición. Por ejemplo, pueden emplearse insecticidas selectivos para cultivos particulares, por ejemplo, insecticidas específicos para taladros (tales como cartap) o insecticidas específicos para saltamontes para su uso sobre arroz. Como alternativa, pueden incluirse insecticidas o acaricidas específicos para especies/estadíos específicos de insectos en las composciones (por

ejemplo, ovo – larvicidas acaricidas tales como clofentezina, flubencimina, hexitaiazox o tetradifon; motilicidas acaricidas tales como dicofol o propargita; acaricides tales como bromopropilato o clorobencilato; o reguladores del crecimiento tales como hidrametilnon, ciromazina, metopreno, cllorfluazuro o difllibenzuro).

Los ejemplos de compuestos fungicidas que pueden incluirse en la aomposición de la invención son (E) - N – metill -2- [2- (2,5- dimetiilfenoximetil) fenil] -2- metoxi - iminoacetamida (SSF -129), 4- bromo -2- ciano -N, N- dimetil - 6- trifltiorometil bencimidazol -1- sulfonamida, α - [N- (3- cloro-2, 6- xilil) -2- rnetoxi acetamido] -γ- butirolactona, 4- cloro -2- ciano -N, N- dimetil -5- p – tolilimidazol –1- sulfonamida (IKF-916, ciamidazosulfamida), 3,5- dicloro -N- (3- cloro -1- etil -1- metil –2- oxopropil) -4-rnetilbenzamida (RH- 7281, zoxamida), N- allil -4, 5- dimetil –2- trimetilsililtiofen –3- carboxamida (MON65500), N - (1- ciano -1, 2- dimetilpropil) –2- (2, 4- diclorofenoxi) propionamida (AC382042), N - (2- metoxi -5- piridil) - ciclopropan carboxamida, acibenzolar (COA245704), alanicarb, aldimorph, anilazina, azaconazol, azoxistrobina, benalaxil, benomil, biloxazol, bitertanol, blasticidina S, bromuconazol, bupirimato, captafol, captan, carbendazim, clorhidrato de carbendazim, carboxina, carpropamid, carvona, COA41396, COA41397, quiinometionato, clorotalonilo, clorozolinato, clozilacon, compuestos que contienen cobre tales como oxicloruro de cobre, oxiquinolato de cobre, sulfato de cobre, talato de cobre y mezcla de Bordeaux, cymoxanilo, ciproconazol, ciprodinilo, debacarb, 1,1'- dióxido de di -2- piridil disulfuro, diclofluanid, diclomezina, dicloran, dietofencarb, difenoconazol, difenzoquat, diflumetorim, tiofosfato de O, O – di – iso – propil – S - bencilo, dimefluazol, dimetconazol, dimetomorf, dimetirimol, diniconazol, dinocap, ditianon, cloruro

de dodecil dimetil ammonio, dodemorf, dodina, dogliadina, edifenfos, epoxiconazol, etirimol, etil (Z) – N – bencil – N- ([metil (metil - tioetilidenaminoxicarbonil) amino] tio) -β- alaninato, etridiazol, famoxadona, fenamidona (RPA407213), fenarimol, fenbuconazol, fenfuram, fenhexamid (KBR2738), fenpiclonil, fenpropidin, fenpropimorf, fentin acetato, fentin hidróxido, ferbam, ferirnzone, fluazinam, fludioxonil, flumetover, fluoroimida, fluquinconazol, flusilazol, flutolanil, fllitriafol, folpet, fuberidazol, furalaxil, furametpyr, guazatine, hexaconazol, hidroxiisoxazol, himexazol, imazalilo, imibenconazol, iminoctadina, triacetato de iminoctadina, ipconazol, iprobenfos, iprodiona, iprovalicarb (SZX0722), isopropanil butil carbamato, isoprotiolano, kasugamicina, metil - kresoxim, L Y186054, L Y211795, L Y248908, mancozeb, maneb, mefenoxam, mepanipirim, mepronil, metalaxil, metconazol, metiram, metiram - cinc, metominostrobin, miclobutanil, neoasozina, dimetilditio-carbamato de níquel, nitrotal - isopropilo, nuarimol, ofurace, compuestos de organomercurio, oxadixil, oxastilfuro, ácido oxolínico, oxpoconazol, oxicarboxina, pefurazoato, penconazol, pencicuro, óxido de fenazin, fosetil – A1, ácidos de fósforo, ftaluro, picoxistrobin (ZA1963), polioxina D, poliram, probenazol, procloraz, procimidona, propamocarb, propiconazol, propineb, ácido propionico, pyrazofos, pirifenox, pirimetanil, piroquilon, piroxifur, pirrolnitrina, compuestos de amonio cuaternario, quinometionato, quinoxifen, quintozeno, sipconazol (F -155), pentaclorofenato de sodio, espiroxamina, estreptomicina, azufre, tebuconazol, tecloftalam, tecnazeno, tetraconazol, tiabendazol, tifluzamid, 2- (tiocianometiltio) benzotiazol, metil - tiofanate, tiram, timibenconazol, metil - tolclofos, tolilfluanid, triadimefon, triadimenol, triazbutilo,

triazóxido, triciclazol, tridemorf, trifloxistrobin (COA279202), triforina, triflumizol, triticonazol, validamicina A, vapam, vinclozolin, zineb y ziram.

Los compuestos de fórmula (I) pueden mezclarse con el suelo, con la turba o con el medio de generación de raíces para la protección de las plantas contra enfermedades propias de las raíces, propias del suelo o foliares.

Los ejemplos de sinergistas adecuados para su uso en las composiciones incluyen butóxido de piperonilo, sesamex, safroxan y dodecil imidazol.

Los herbicidas y los reguladores del crecimiento vegetal que pueden incluirse en las composiciones dependerán del blanco pretendido y del efecto requerido.

Un ejemplo de herbicida selectivo para arroz que puede incluirse es el propanilo. Un ejemplo de regulador del crecimiento vegetal que puede usarse sobre algodón es PIX™.

Algunas mezclas pueden comprender ingredientes activos que tengan diferentes propiedades físicas, químicas o biológicas, de manera que no se presten al mismo tipo de formulaciones. En estas circunstancias, pueden prepararse otros tipos de formulaciones. Por ejemplo, cuando un ingrediente activo es un sólido insoluble en agua y el otro es un líquido insoluble en agua, puede ser aún posible dispersar cada ingrediente activo en la misma fase acuosa dispersando el ingrediente activo sólido como una suspensión (usando una preparación análoga a la de un SC) pero dispersando el ingrediente activo líquido como una emulsión (usando una preparación análoga a la de un EW). La composición resultante es una formulación de estispoemulsión (SE).

La invención está ilustrada por los siguientes Ejemplos.

EJEMPLO 1

Este ejemplo ilustra la preparación de N - (4- cloro -3- metilisotiazol -5- il) - (2- propilbenzotriazol -5- il) acetamida (Compuesto N° A.3.1).

Paso 1 - Preparación de 4- aminofenilacetato de metilo.

Se suspendió ácido 4- aminofenilacético (100 g) en metanol (1000 ml) y se hizo pasar cloruro de hidrógeno gaseoso hasta que se saturó la mezcla. La mezcla se calentó a 50°C durante 2 horas y luego se la dejó enfriar hasta temperatura ambiente. El solvente se evaporó al vacío, el residuo se capturó en una solución acuosa de bicarbonato de sodio y se lo extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío para dar 4- aminofenilacetato de metilo bajo la forma de un líquido marrón claro.

^{1}H NMR ($CDCl_3$) δ ppm: 3.5 (s,2H); 3.7 (s,3H); 6.65 (m,2H); 7.05 (m,2H).Paso 2 - Preparación de 4- acetamido -3 - nitrofenilacetato de metilo.

Se agregó por goteo 4- aminofenilacetato de metilo (110 g, 0,667 mol) a anhídrido acético (600 ml), manteniendo la temperatura de la mezcla de reacción por debajo de 30°C por enfriamiento externo. Una vez finalizada la adición la mezcla se enfrió a menos de 10°C y se agregó por goteo ácido nítrico concentrado (85 ml). Una vez finalizada la adición de ácido nítrico, la mezcla se dejó calentar hasta temperatura ambiente y se la vertió sobre una mezcla de hielo y agua. El sólido precipitado se recolectó por filtrado y se los secó para dar 4- acetamido -3 - Nitrofenilacetato de metilo (120 g) bajo la forma de un sólido amarillo pálido.

^{1}H NMR ($CDCl_3$) δ ppm: 2,3 (s,3H); 3,65 (s,2H); 3,7 (s,3H); 7,55 (dd,1H); 8,1 (d,1H); 8,7 (d,1H); 10,3 (b,1H).

Paso 3 - Preparación de 4- acetamido -3- aminofenilacetato de metilo.

Se disolvió 4- acetamido -3 - nitrofenilacetato de metilo (40 g, 0,159 mol) en metanol (400 ml) y se hidrogenó a 5 bar sobre un catalizador de paladio sobre carbón al 5%. El catalizador se eliminó por filtración y el filtrado se evaporó al vacío para dar 4- acetamido -3- aminofenilacetato de metilo.

Paso 4 - Preparación de (benzotriazol -5- il) acetato de metilo

Se capturó 4- acetamido -3- aminofenilacetato de metilo (77 g, 0,373 mol) en una mezcla de ácido acético (210 ml) y agua (210 ml), y se lo enfrió a menos de 5°C. Se agregó una solución de nitrito de sodio (38,63 g, 0,559 mol) en agua (200 ml) por goteo, y, una vez finalizada la adición, la mezcla se agitó durante 4 horas, calentando lentamente hasta temperatura ambiente. La mezcla se diluyó con acetato de etilo y el material insoluble se eliminó por filtrado. El filtrado se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el solvente se evaporó al vacío para dar un residuo viscoso (51 g) que luego se disolvió en una solución de metanol (400 ml) previamente saturada con cloruro de hidrógeno, y la mezcla se agitó durante 2 horas. El solvente se eliminó al vacío, el residuo se capturó en agua, se lo neutralizó con solución saturada acuosa de bicarbonato de sodio y se lo extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío para dar 5- benzotriazoleacetato de metilo (35 g) bajo la forma de un líquido rojizo que se cristalizó con el reposo.

^{1}H NMR ($CDCl_3$) D ppm: 3,7 (s,3H); 3,8 (s, 2H); 7,35 (d,1H); 7,8 (b,2H); 13.6 (b,1H).

Paso 5 - Preparación de (2- propil - benzotriazol -5- il) acetato de metilo.

Se agregó una solución de 5- benzotriazoleacetato de metilo (10 g, 0,0523 mol) en N, N - dimetilformamida por goteo a una suspensión enfriada (baño de hielo) de hidruro de sodio (dispersión al 60% en aceite, 2,3 g, 0,0575 mol) en N, N - dimetilformamida. Cuando se completó la adición, el baño de hielo se eliminó y la mezcla se agitó durante 1 hora. Se agregó ioduro de N - propilo (9,78 g, 0,0575 mol) por goteo, y, una vez finalizada la adición, la mezcla se agitó a temperatura ambiente durante 3 horas. La mezcla de reacción se vertió en hielo/agua, y se la extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío, El residuo se purificó adicionalmente por cromatografía de columna para dar (2- propilbenzotriazol - 5- il) acetato de metilo (4,8 g).

^{1}H NMR ($CDCl_3$) D ppm: 0,9 (t,3H); 2,1 (m,2H); 3,7 (s,3H); 3,8 (s,2H); 4.65 (t,2H); 7.3 (dd,1H); 7,7 (d,1H); 7.8 (d,1H).

Paso 6 - Preparación de ácido (2- Propilbenzotriazol -5- il) acético.

El acetato preparado en el paso 5 anterior (4.8 g, 0.0206 mol) se disolvió en metanol (60 ml) y se agregaron escamas de hidróxido de potasio (1,27 g, 0,0226 mol). La mezcla se calentó a reflujo durante 2 horas, luego se enfrió y el solvente se evaporó al vacío. El sólido residual se disolvió en agua y se extrajo con éter dietílico. La solución acuosa se acidificó a pH 1 mediante el agregado de ácido clorhídrico diluido acuoso y se la extrajo con acetato de etilo. El extracto de acetato de etilo se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío para dar ácido (2- propilbenzotriazol -5- il) acético (3,6 g) bajo la forma de un sólido incoloro.

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El ácido preparado en el paso 6 (0,438 g, 0,002 mol) se disolvió en diclorometano (5 ml) y se agregó una gota de N - dimetilformamida (0,307 g, 0,0022 mol), se agregó cloruro de oxalilo por goteo, y la mezcla se agitó a temperatura ambiente durante 2 horas. El solvente se eliminó al vacío, el residuo se capturó en xileno, se lo agregó a una mezcla de 5- amino -4- cloro - 3- metilisotiazol (0,446 g, 0,003 mol) en xileno y se calentó a reflujo durante 2 horas.

La mezcla se enfrió a temperatura ambiente y el solvente se evaporó al vacío. El residuo se capturó en acetato de etilo, se lo lavó secuencialmente con solución saturada acuosa de bicarbonato de sodio y con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío. El residuo se purificó adicionalmente por cromatografía instantánea en columna, eluyendo con 2: 1 hexano: etilo acetato, para dar el compuesto del título (0,34 g) bajo la forma de un sólido color arena.

EJEMPLO 2

Este ejemplo ilustra la preparación de N - (4- cloro -3- metilisotiazol -5- il) - N - (etoximetil) - (2- propilbenzotriazol -5- il) acetamida (Compuesto N° A3.6) y N - [2- etoximetil -4- cloro -3- metilisotiazolin - 5- iliden] - (2- propilbenzo - triazol -5- il) acetamida (Compuesto N° 13.6).

Se agregó bis (trimetilsilil) amida de litio (solución 1,0 M en tetrahidrofurano, 3,3 ml, 0,0033 mol) por goteo a una solución de N - (4- cloro - 3- metilisotiazol -5- il) - (2- propilbenzotriazol -5- il) acetamida (Compuesto N° A3.1) (0,699 g, 0,002 mol) en tetrahidrofurano (10 ml) y, una vez finalizada la adición, la mezcla se agitó a temperatura ambiente durante 30 minutos. Se agregó clorometiléter (0,620 g, 0,0066 mol) y la mezcla se agitó a temperatura

ambiente durante 2 horas. La mezcla se vertió en agua, se la neutralizó, y se la extrajo con acetato de etilo. El extracto orgánico se secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío. El residuo se purificó adicionalmente por cromatografía de columna instantánea, eluyendo inicialmente con 2: 1 hexano: acetato de etilo y luego con acetato de etilo para dar N - (4- cloro -3- metilisotiazol -5- il) - N - (etoximetil) - (2- propilbenzotriazol - 5- il) acetamida (0.135 g) bajo la forma de una goma anaranjada y N - [2- etoximetil -4- cloro -3- metilisotiazol en -5- ilideno] - (2- propilbenzotriazol -5- il) acetamida (0,128 g) bajo la forma de sólido incoloro, p f, 108 a 109 °C.

EJEMPLO 3

Este ejemplo ilustra la preparación de (4- cloro -3- metilisotiazol -5- il) -[2- (2- metilpropil) indazol -5- il] acetamida (Compuesto N° A6.145).

Paso 1 - Preparación de 4- bromo -2- metilacetanilida.

Se agregó anhídrido acético (15,2 ml, 0,16 mol) por goteo a una mezcla agitada de 4- bromo -2- metilanilina (10,0 g, 0,054 mol) y acetato de sodio (2,52 g, 0,056 mol) en tolueno (150 ml). Una vez finalizada la adición la mezcla se calentó a 85°C y se agitó durante 40 minutos. La mezcla se enfrió a temperatura ambiente, se la diluyó con acetato de etilo y se lavó con agua. La solución orgánica se evaporó al vacío, se agregó una cantidad adicional de tolueno y luego el solvente se evaporó para dar 4- bromo -2- metilacetanilida (12,3 g), bajo la forma de un sólido incoloro.

Paso 2 - Preparación de 5- bromoindazol.

Se agregó por goteo nitrito de ter - butilo (8,34 g, 0,081 mol), a lo largo de 30 minutos, a una suspensión de 4- bromo -2- metilacetanilida (12,3 g) en tolueno (300 ml) a 65°C y se agitó la mezcla a 65°C por 45 minutos, y luego a

90°C por 3 horas. La mezcla se enfrió a temperatura ambiente y el solvente se eliminó al vacío. Se purificó el residuo por cromatografía de columna instantánea en gel de sílica gel eluyendo con 2: 1 éter dietílico: hexano para dar 5- bromoindazol (4, 12 g), como un sólido color arena.

^{1}H NMR ($CDCl_3$) δ: 7,27 (m,1H); 7,40- 7,54 (m,2H); 7,94 (m,1H); 8,06 (br,1 H) ppm.

Paso 3 - Preparación de 5- bromo -1- (2- metilpropil) indazol y 5- bromo - 2- (2- metilpropil) indazol.

Se suspendió hidruro de sodio (80% de suspensión en aceite, 0,7 g, 0,023 mol) en N, N - dimetilformamida (DMF) (10 ml) y luego se agregó por goteo una solución de 5- bromoindazol (4,1 g, 0,021 mol) en DMF (40 ml) a lo largo de 30 minutos. Una vez finalizada la adición, la mezcla se agitó a temperatura ambiente por 75 minutos y luego se agregó una solución de 1- bromo -2- metilpropano (3,7 g; 0,027 mol) en DMF (25 ml) durante 10 minutos. La mezcla se agitó durante 5 horas y se la dejó reposar luego a temperatura ambiente durante la noche. La mezcla se vertió en agua, se la extrajo con éter dietílico y luego se lavó el extracto orgánico adicionalmente con agua, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío. Se purificó el residuo por cromatografía de columna instantánea en gel de sílica eluyendo con 1: 1 éter dietílico: hexano para dar 5- bromo -1- (2- metilpropil) indazol (2,67 g) y 5- bromo -2- (2- metilpropil) indazol (1,49 g), cada uno como una aceite anaranjado.

5- Bromo -1- (2- metilpropil) indazol:

^{1}H NMR ($CDCl_3$) 8: 0,92 (d,6H); 2,32 (m,1H); 4,16 (d,2H); 7,28 (m,1H); 7,44 (m,1H); 7,86 (m,1H); 7,92 (s,1H) ppm.

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5- Bromo -2- (2- metilpropil) indazol:

^{1}H NMR ($CDCl_3$) 8: 0,94 (d,6H); 2,38 (m,1H); 4,18 (d,2H); 7,32 (m,1H); 7,58 (m,1H); 7,82 (m,2H) ppm.

Paso 4 - Preparación de [2- (2- metilpropil) indazol -5- illacetato de etilo.

Se revolvieron 5- bromo -2- (2- metilpropil) indazol (1,41 g, 0,0056 mol) y acetato de paladio (0,063 g, 0,00028 mol) en tolueno (10 ml) bajo una atmósfera de nitrógeno. Se agregaron trimetilsililacetato de etilo (2,35 ml, 0,0115 mol), ter - butóxido de potasio (0,66 g, 0,059 mol) y una solución al 10% peso en volumen de tri-ter-butilfosfina en tolueno (0,97 ml, 0,00048 mol) en forma secuencial, y luego se calentó la mezcla a 90°C por 105 minutos. La mezcla se enfrió a temperatura ambiente, se la diluyó con éter dietílico, se la filtró a través de tierras de diatomeas y el filtrado se evaporó al vacío. Se purificó el residuo por cromatografía de columna instantánea en gel de sílica eluyendo con 2: 1 éter dietílico: hexano para dar [2- (2- metilpropil) indazol -5- il] acetato de etil (1,85 g), como un aceite amarillo.

^{1}H NMR ($CDCl_3$) 8: 0,96 (d,6H); 1,27 (t,3H); 2,39 (m,1H); 3,68 (s,2H); 4,12- 4,22 (m,4H); 7,22 (m,1H); 7,54 (m,1H); 7,68 (m,1H); 7,84 (s,1H) ppm.

Paso 5 - Preparación de N - 4- cloro -3- metilisotiazol -5- il) -[2- (2- metilpropil) indazol -5- il] acetamida.

Se agregó metóxido de sodio (0,42 g, 0,0078 mol) a una solución de 5- amino -4- cloro -3- metilisotiazol (0,46 g, 0,0031 mol) en tetrahidrofurano (THF) (15 ml) y se agitó la mezcla a temperatura ambiente por 15 minutos. Se agregó una solución de [2- (2- metilpropil) indazol -5- il] acetato de etilo (0,80 g, 0,0031 mol) en THF por goteo y, una vez finalizada la adición, la mezcla se agitó a temperatura ambiente por 3 horas. La mezcla se particionó entre acetato de

etilo y una solución acuosa saturada de cloruro de amonio, y luego se secó el extracto orgánico sobre sulfato de magnesio anhidro, se lo filtró y se evaporó el filtrado al vacío. Se tituló el residuo con éter dietílico para dar N - (4- cloro -3- metilisotiazol -5- il) -[2- (2- metilpropil) indazol -5- il] acetamida (0,78 g) como un sólido marrón pálido (p f, 133 a 135°C).

EJEMPLO 4

Este ejemplo ilustra la preparación de N - (4- cloro -3- metilisotiazol -5- il) - N - (etoximetil) -[2- (2- metilpropil) indazol -5- il] acetamida (Compuesto N° A6.150) y N - [2- etoximetil -4- cloro -3- metilisotiazoliN - 5- iliden] -[2- (2- metilpropil) indazol -5- il) acetamida (Compuesto N° 16.102).

Se disolvió N - (4- cloro -3- metilisotiazol -5- il) -[2- (2- metilpropil) indazol - 5- il] acetamida (0,50 g, 0,0014 mol) en diclorometano (15 ml) y se enfrió la solución hasta 5°C. Se agregaron secuencialmente éter de clorometil etilo (0,32 ml, 0,0035 mol), una solución acuosa saturada de hidróxido de sodio al 50% (0,56 ml) y cloruro de benciltrietilammonio (0,018 g) y luego la mezcla se agitó durante 2 horas. La mezcla se diluyó con diclorometano, se la lavó con agua, se la secó sobre sulfato de magnesio anhidro, se la filtró y el filtrado se evaporó al vacío. Se purificó el residuo por cromatografía de columna instantánea en gel de sílica, inicialmente eluyendo con 3: 1 éter dietílico: hexano, luego con éter dietílico y finalmente con acetato de etilo para dar N - (4- cloro -3- metilisotiazol -5- il) - N - (etoximetil) -[2- (2- methylpropil) indazol -5- il] acetamida (0,16 g) como un aceite amarillo y N - [2- etoximetil -4- cloro -3- metilisotiazolin - 5- iliden] -[2- (2- metilpropil) indazol -5- il) acetamida (0,20 g) como un sólido color crema (p f, 105 a 106°C).

EJEMPLO 5

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Este ejemplo ilustra las propiedades pesticidas/insecticidas de los compuestos de fórmula (I). Se determinaron las actividades de muestras compuestos de fórmula (I) individuales o de mezclas de compuestos de fórmula (I) usando una variedad de plagas. Se trataron las plagas con una composición líquida que contenía 500 partes por millón (ppm) en peso de un compuesto. Cada composición se hizo disolviendo el compuesto en una mezcla de acetona y etanol (50: 50 en volumen) y diluyendo la solución con agua que contenía 0,05% en volumen de un agente humectante, SYNPERONIC NP8, hasta que la composición líquida contuvo la concentración deseada de compuesto.

Las muestras usadas se indican en la Tabla 2.

Tabla 2

Muestra N°	Componente A (Compuesto N°)	Componente B (Compuesto N°)	Relación Molar A: B
1	A3.1		
2	A1.1		
3	F1.1	E1.1	1: 3
4	A18.1		
5	E18.1	F18.1	1: 1
6	F15.1	E15.1	8: 92
7	F15.1	E15.1	1: 2
8	A15.1		
9	A9,1		
10	E9.1	F9.1	1: 1
11	A20.1		
12	E20.1	F20.1	1: 1

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13	A7.1		
14	E7.1	F7.1	1: 1
15	A2.1		
16	E2.1	F2.1	1: 1
17	A13.1		
18	E13.1	F13.1	3: 2
19	A3.2		
20	A3.6		
21	A21.1		
22	F21.1		
23	E21.1	F21.1	1: 1
24	E3.1	F3.1	1: 1
25	E21.1	F21.1	9: 1
26	F21.1		
27	E22.1		
29	A16.1		
30	A10.1		
31	A6.1		
32	A3.103		
33	13.2		
34	13.6		
35	E6.145		
36	A6.145		
37	E6.150		
38	J6.102		

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39	A6.150		
40	16.102		

El procedimiento de prueba adoptado respecto de cada plaga fue esencialmente el mismo y comprendió apoyar una cantidad en un medio que era comúnmente un sustrato, una planta hospedadora o un alimento sobre el cual se alimentaban las plagas, y tratar el medio y/o las plagas con una composición. Se evaluó la mortalidad de las plagas usualmente entre dos y cinco días después del tratamiento.

Los resultados de las pruebas contra el pulgón del durazno (*Myzus persicae*) se presentan a continuación. En esta prueba, se infestaron hojas de prueba de repollo chino con pulgones, se las roció con la composición de prueba y se evaluó la mortalidad luego de tres días. Los resultados indican un grado de mortalidad (puntuación) designado como 9, 5 ó 0, donde 9 indica un 90 a 100% de mortalidad, 5 indica un 40 a 79% de mortalidad y 0 indica menos de 40% de mortalidad.

Las muestras N° 2, 13, 15, 19, 20, 30, 31, 32, 36, 37, 39 y 40 brindaron, cada una, una puntuación de mortalidad de 9, mientras que las muestras N° 8, 9, 11, 17, 29, 34, 35 y 38 brindaron, cada una, una puntuación de mortalidad de 5.

Además, en una prueba similar contra dos ácaros de dos manchas (*Tetranychus urticae*, las muestras N° 1, 8, 11, 12, 13, 17, 18, 19, 20 y 30 brindaron, cada una, una puntuación de mortalidad de 9, mientras que la muestra N° 9 brindó una puntuación de 5.

EJEMPLO 6

Este ejemplo ilustra las propiedades fungicidas de compuestos de fórmula (I). Los compuestos se evaluaron contra una variedad de enfermedades foliares de plantas causadas por hongos. La técnica empleada fue como se describe a continuación.

Se cultivaron plantas en John Innes Potting Compost (N° 1 ó 2) en minimacetas de 4 cm de diámetro y 3,5 cm de profundidad. Se formularon las muestras de prueba en forma individual como una solución ya sea en acetona o en acetona/etanol (1: 1 en volumen), la cual se diluyó en agua deionizada hasta una concentración de 100 ppm (es decir, 1 mg de compuesto en un volumen final de 10 ml) inmediatamente antes de usarla. Cuando se aplicaron rocíos foliares a cultivos de monocotiledóneas, se agregó TWEEN 20 (0,1% en volumen). TWEEN es una marca registrada.

Se aplicaron compuestos individuales de fórmula (I), o mezclas de compuestos de fórmula (I), como una aplicación foliar (Folr) (donde se aplicó la solución química al follaje de las plantas de prueba rociando la planta hasta su retención máxima de gotas).

Se llevaron a cabo estas pruebas contra *Uncinula necator* (UNCINE), en enredaderas; contra *Phytophthora infestans lycopersici* (PHYTIN) en tomates; contra *Puccinia recondita* (PUCCRT), en trigo; y contra *Piricularia oryzae* (PYRIOR) en arroz. Se aplicó cada tratamiento a dos o más plantas replicadas para *Phytophthora infestans lycopersici* y para *Uncinula necator*. Para las pruebas en *Puccinia recondita* y *Piricularia oryzae*, se usaron dos macetas replicadas que contenían, cada una, de 6 a 10 plantas para cada tratamiento. Se inocularon las plantas un día antes (Erad) o un día después (Prot) de la aplicación química. Las plantas de *Phytophthora infestans lycopersici*, *Puccinia*

recondita y *Piricularia oryzae* se inocularon con una suspensión calibrada de esporas de hongos. Se inocularon las plantas de *Uncinula necator* usando una técnica de inoculación de "soplado".

Después de la aplicación y la inoculación química, se incubaron las plantas bajo condiciones de alta humedad y se las colocó luego en un ambiente apropiado para permitir que procediera la infección, hasta que la enfermedad pudiera ser evaluada. El período de tiempo entre la aplicación química y la evaluación varió de cinco a catorce días de acuerdo con la enfermedad y con el ambiente. Sin embargo, cada enfermedad individual se evaluó después del mismo período de tiempo para todas las muestras.

Se llevaron a cabo las evaluaciones en una de cada dos hojas sobre cada una de las plantas replicadas para *Phytophthora infestans lycopersici*. Las evaluaciones se llevaron a cabo en una única hoja de cada una de las plantas replicadas para *Uncinula necator*. Las evaluaciones de *Puccinia recondita* y *Piricularia recondita* se llevaron a cabo colectivamente sobre las plantas en cada maceta replicada.

Se evaluó visualmente el nivel presente de enfermedad (es decir, el porcentaje del área de la hoja cubierto por la enfermedad activamente esporulante). Para cada tratamiento, se promediaron los valores evaluados en todas las réplicas con el fin de obtener valores promedio de enfermedad. Las plantas control sin tratar se evaluaron de la misma manera. Los datos se procesaron luego por el método que se describe a continuación para proveer valores de PRCO (Porcentaje de Reducción respecto del Control).

Un ejemplo de un cálculo típico es como sigue:

Nivel promedio de enfermedad para el tratamiento A = 25%

Nivel promedio de enfermedad para controles sin tratar = 85%

PRCO = 100 - {Nivel promedio de enfermedad para el A} x 100

{ Nivel promedio de enfermedad para controles sin tratar}

= 100 - (25 x 100) = 70,6

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El PRCO se redondea luego hacia el número entero más cercaN° Entonces, en este ejemplo particular, el resultado del PRCO es 71.

Es posible obtener valores negativos de PRCO.

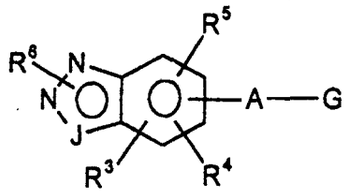
Los resultados de PRCO se indican a continuación en la Tabla 3, donde los números de muestra son como se los definió en el Ejemplo 5.

Tabla 3

Muestra N°	PHYTIN Prot	PUCCRT Prot	PYRIOR Prot	UNCINE Erad
1	100	100	100	
2			87	
3			40	
4			92	
6	75	16	6	11
7			96	
8			100	
9	100	99	100	
11			100	
12			98	
19	81	87		
30	100	100		100
31	100	100		100
33	30	36		
34	81		93	100

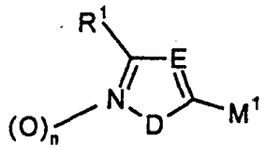
REIVINDICACIONES

1. Un compuesto CARACTERIZADO PORQUE es de fórmula (I):



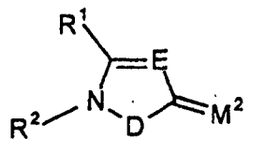
(I)

donde G se selecciona entre



(i)

or



(ii)

donde M^1 o M^2 está unido a A; n es 0 ó 1; A es C_{1-6} alquileno, C_{2-6} alquenileno opcionalmente sustituido, C_{2-6} alquinileno opcionalmente sustituido, C_{1-6} alquilenoxi opcionalmente sustituido, Oxi (C_{1-6}) alquileno opcionalmente sustituido, C_{1-6} alquilenotio opcionalmente sustituido, opcionalmente sustituido tio (C_{1-6}) alquileno, C_{1-6} alquilenamino opcionalmente sustituido, amino (C_{1-6}) alquileno opcionalmente sustituido, [C_{1-6} alquilenoxi (C_{1-6}) alquileno] opcionalmente sustituido [C_{1-6} alquilenotio (C_{1-6}) alquileno] , opcionalmente sustituido, [C_{1-6} alquilenosulfinil (C_{1-6}) alquileno] opcionalmente sustituido, [C_{1-6} alquilenosulfonil (C_{1-6}) alquileno] opcionalmente sustituido o [C_{1-6} alquilenoamino (C_{1-6}) alquileno] opcionalmente sustituido; cuando G es (i), D es S, NR^7, $CR^8=CR^9$, $CR^8=N$, $CR^8=N(O)$, $N=CR^9$ o $N(O)=CR^9$; cuando G es (ii), D es S o NR^7; E es N, N-óxido o CR^{10}; M^1 es $OC(=Y)$, $N(R^{11})C(=Y)$, $N=C(OR^{12})$, $N=C(SR^{13})$ o $N=C(NR^{14}R^{15})$ donde O o N es el átomo de unión al anillo que contiene D y E; M^2 es N-C(=Y) donde N es el átomo de unión al anillo que contiene D y E; Y es O, S o NR^{16}; J es N o CR^{17}; R^1 es hidrógeno, halógeno, C_{1-6}alquilo opcionalmente sustituido, C_{2-6} alquenilo opcionalmente sustituido, C_{2-6} alquinilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido,

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ciano, nitro o SF_5; R^2 es C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, fenoxicarbonilo opcionalmente sustituido, C_{1-6}alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, ariltio opcionalmente sustituido, arilsulfinilo opcionalmente sustituido, arilsulfonilo opcionalmente sustituido o $R^{18}R^{19}NS$; R^3, R^4 y R^5 son, independientemente, hidrógeno, halógeno, C_{1-6}alquilo opcionalmente sustituido, C_{1-6}alcoxi opcionalmente sustituido, C_{1-6}alquiltio opcionalmente sustituido, C_{1-6}alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, ciano, nitro, C_{1-6}alquilcarbonilo opcionalmente sustituido, C_{1-6} alcoxicarbonilo opcionalmente sustituido o SF_5; R^6 es hidrógeno, ciano, C_{1-20} alquilo opcionalmente sustituido, C_{2-20} alquenil- sustituido (C_{1-6}) alquilo opcionalmente sustituido, C_{2-20} alquinil (C_{1-6}) alquilo opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{5-6} cicloalquenilo opcionalmente sustituido, formilo, C_{1-20} alcoxicarbonilo opcionalmente sustituido, C_{1-20} alquilcarbonilo opcionalmente sustituido, aminocarbonilo, C_{1-20} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-20})alquilaminocarbonilo opcionalmente sustituido, ariloxicarbonilo opcionalmente sustituido, arilcarbonilo opcionalmente sustituido, arilaminocarbonilo opcionalmente sustituido, N-alquil-N-arilaminocarbonilo opcionalmente sustituido, diarilaminocarbonilo opcionalmente sustituido, heteroariloxicarbonilo opcionalmente sustituido, heteroarilcarbonilo opcionalmente sustituido, heteroarilaminocarbonilo opcionalmente sustituido, alquilheteroarilaminocarbonilo opcionalmente sustituido, diheteroarilaminocarbonilo opcionalmente sustituido, fenilo opcionalmente

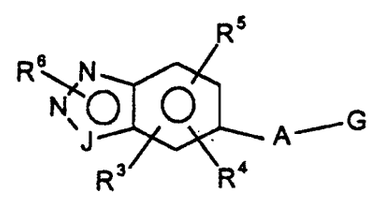
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sustituido, heteroarilo opcionalmente sustituido, heterociclilo opcionalmente sustituido, C_{1-20} alquilsulfonilo opcionalmente sustituido o arilsulfonilo opcionalmente sustituido; R^7 es C_{1-6} alquilo; R^8 y R^9 son, independientemente, hidrógeno, halógeno, ciano, nitro, C_{1-6} alquilo opcionalmente sustituido, C_{2-6} alquenilo opcionalmente sustituido, C_{2-6} alquinilo opcionalmente sustituido o C_{1-6} alcoxi opcionalmente sustituido; R^{10} es hidrógeno, halógeno, C_{1-6} alquilo opcionalmente sustituido, C_{2-6} alquenilo opcionalmente sustituido, C_{2-6} alquinilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6}alquilsulfonilo opcionalmente sustituido, ciano, nitro, formilo, $R^{20}N=C(R^{21})$, C_{1-6} alquilcarbonilo opcionalmente sustituido, C_{1-6} alcoxicarbonilo opcionalmente sustituido o SF_5; o R^1 y R^{10} junto con los átomos a los cuales están unidos pueden unirse para formar un anillo carbocíclico o heterocíclico saturado o insaturado de cinco, seis o siete miembros que puede contener entre uno y dos heteroátomos seleccionados entre O, N o S y que puede ser opcionalmente sustituido por C_{1-6} alquilo, C_{1-6} haloalquilo o halógeno; R^{11} es hidrógeno, C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, fenoxicarbonilo opcionalmente sustituido, C_{1-6}alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, ariltio opcionalmente sustituido, arilsulfinilo opcionalmente sustituido, arilsulfonilo opcionalmente sustituido o $R^{22}R^{23}NS$; R^{12} es C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido,

formilo, C_{1-10} alquilaminocarbonilo, opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, amino, C_{1-6} alquilamino opcionalmente sustituido, di (C_{1-6}) alquilamino opcionalmente sustituido, fenoxicarbonilo opcionalmente sustituido, tri(C_{1-4})alquilsililo, arildi(C_{1-4})alquilsililo, (C_{1-4})alquildiarilsililo o triarilsililo; R^{13} es C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquil] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido o fenoxicarbonilo opcionalmente sustituido); R^{14} y R^{15} son, independientemente C_{1-10} alquilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, hidroxi, amino, C_{1-6} alquilamino opcionalmente sustituido, di (C_{1-6}) alquilamino opcionalmente sustituido, o fenoxicarbonilo opcionalmente sustituido; R^{16} es hidrógeno, ciano, nitro, C_{1-6} alquilo opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, (C_{2-6})alquenil (C_{1-6}) alquilo opcionalmente sustituido, (C_{2-6})alquinil (C_{1-6}) alquilo opcionalmente sustituido, fenilo opcionalmente sustituido, heteroarilo opcionalmente sustituido, C_{1-6} alquilcarbonilo opcionalmente sustituido, C_{1-6} alcoxicarbonilo opcionalmente sustituido, C_{1-6} alquilamino opcionalmente sustituido, di (C_{1-6}) alquilamino opcionalmente sustituido, C_{1-6} alquilcarbonilamino opcionalmente sustituido, C_{1-6} alcoxicarbonilamino opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, ariltio opcionalmente sustituido,

arilsulfinilo opcionalmente sustituido, arilsulfonilo opcionalmente sustituido o C_{1-6} aciloxi; R^{17} es hidrógeno, halógeno, nitro, ciano, C_{1-8} alquilo opcionalmente sustituido, C_{2-6} alquenilo opcionalmente sustituido, C_{2-6} alquinilo opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-6} alcoxicarbonilo opcionalmente sustituido, C_{1-6} alquilcarbonilo opcionalmente sustituido, C_{1-6} alquilaminocarbonilo opcionalmente sustituido, di (C_{1-6}) alquilaminocarbonilo opcionalmente sustituido, fenilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^{18} y R^{19} son, independientemente, C_{1-6} alquilo opcionalmente sustituido o R^{18} y R^{19} junto con el átomo de N al cual están unidos forman un anillo heterocíclico de cinco, seis o siete miembros que puede contener uno o dos heteroátomos adicionales seleccionados entre O, N o S y que puede ser opcionalmente sustituido por uno o dos grupos C_{1-6} alquilo; R^{20} es hidrógeno, fenilo opcionalmente sustituido, fenil(C_{1-4})alquilo opcionalmente sustituido o C_{1-20} alquilo opcionalmente sustituido; R^{21} es hidrógeno, fenilo opcionalmente sustituido o C_{1-6} alquilo opcionalmente sustituido; y R^{22} y R^{23} son, independientemente, C_{1-6} alquilo opcionalmente sustituido o R^{22} y R^{23} junto con el átomo de N al cual están unidos forman un anillo heterocíclico de cinco, seis o siete miembros que puede contener uno o dos heteroátomos adicionales seleccionados entre O, N o S y que puede estar opcionalmente sustituido por uno o dos grupos C_{1-6} alquilo.

2. Un compuesto CARACTERIZADO PORQUE es de fórmula (IA):



(IA)

donde A, G, J, R^3, R^4, R^5 y R^6 tienen los valores definidos en la cláusula 1.

3. Un compuesto de fórmula (I) de acuerdo con la cláusula 1, o un compuesto de la fórmula (IA) de acuerdo con la cláusula 2, CARACTERIZADO PORQUE

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cuando G es (i) como se define en la cláusula 1, D es S o $CR^8=CR^9$, donde R^8 y R^9 son, independientemente, hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo C_{2-6} alquenilo, C_{1-6} alquinilo, C_{1-6} alcoxi o C_{1-6} haloalcoxi; cuando G es (ii) de acuerdo con la cláusula 1, D es S, E es N o CR^{10} donde R^{10} es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi, C_{1-6} haloalcoxi, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{1-6} alquiltio o SF_5; o R^1 y R^{10} junto con los átomos a los cuales están unidos forman un anillo de benceno opcionalmente sustituido por C_{1-6}alquilo, C_{1-6} haloalquilo o halógeno; y M^1 es $N(R^{11})C(=O)$ donde R^{11} es hidrógeno, C_{1-6} alquilo, C_{1-6} alcoxi (C_{1-6}) alquilo, benciloximetilo o benzoiloximetilo.

4. Un compuesto de fórmula (I) de acuerdo con la cláusula 1 o 3, o un compuesto de fórmula (IA) de acuerdo con la cláusula 2 ó 3, CARACTERIZADO PORQUE A es C_{1-4} alquileno, -C(O). O C_{1-4} alquilenoxi.

5. Un compuesto de fórmula (I) de acuerdo con las cláusulas 1, 3 ó 4, o un compuesto de fórmula (IA) de acuerdo con las cláusulas 2, 3 ó 4, CARACTERIZADO PORQUE G es (i) tal como se define en la cláusula 1 y n es 0.

6. Un compuesto de fórmula (I) de acuerdo con la cláusula 1, 3, 4 ó 5, o un compuesto de fórmula (IA) de acuerdo con las cláusulas 2, 3, 4 ó 5 CARACTERIZADO PORQUE R^3, R^4 y R^5 son independientemente hidrógeno, C_{1-3} alquilo o halógeno.

7 - Un compuesto de fórmula (I) de acuerdo con la cláusula 1, 3, 4, 5, ó 6 o un compuesto de la fórmula (IA) de acuerdo con lá cláusula 2, 3, 4, 5 ó 6 CARACTERIZADO PORQUE R^6 es C_{1-10} alquilo o C_{1-10} haloalquilo (cada uno de los cuales puede ser sustituido con un grupo C_{1-6} alquiloxima, C_{1-6} haloalquiloxima, C_{1-6} alquilhidrazona o C_{1-6} haloalquilhidrazona) o ciano, C_{1-6} cianoalquilo, C_{2-6} alquenil (C_{1-6}) alquilo, C_{2-6} alquinil (C_{1-6}) alquilo, C_{3-7} cicloalquilo, C_{3-7} halocicloalquilo, C_{3-7} cianocicloalquilo, C_{1-3} alquil(C_{3-7})cicloalquilo, C_{1-3} alquil(C_{3-7})halocicloalquilo, C_{5-6} cicloalquenilo, C_{3-7} cicloalquil

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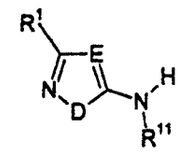
(C_{1-6}) alquilo, CS-6 cicloalquenil (C_{1-6}) alquilo, C_{2-6} haloalquenilo (C_{1-6}) alquilo, C_{1-6} cianoalquenil (C_{1-6}) alquilo, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{3-6} alqueniloxi (C_{1-6}) alquilo, C_{3-6} alquiniloxi (C_{1-6}) alquilo, ariloxi (C_{1-6}) alquilo, formilo, C_{1-6} carboxialquilo, C_{1-6} alquilcarbonil (C_{1-6}) alquilo, C_{2-6} alquenilcarbonil (C_{1-6}) alquilo, C_{2-6} alquinilcarbonil (C_{1-6}) alquilo, C_{1-6} alcoxicarbonil (C_{1-6}) alquilo, C_{3-6} alqueniloxicarbonil (C_{1-6}) alquilo, C_{3-6} alquiniloxicarbonil (C_{1-6}) alquilo, ariloxicarbonil (C_{1-6}) alquilo, C_{1-6} alquiltio (C_{1-6}) alquilo, C_{1-6} alquilsulfinil (C_{1-6}) alquilo, C_{1-6} alquilsulfonil (C_{1-6}) alquilo, aminocarbonil (C_{1-6}) alquilo, aminocarbonil(C_{2-6})alquenilo, aminocarbonil(C_{2-6})alquinilo, C_{1-6} alquilaminocarbonil (C_{1-6}) alquilo, di (C_{1-6}) alquilaminocarbonil (C_{1-6}) alquilo, C_{1-6} alquilaminocarbonil(C_{2-6})alquenil (C_{1-6}) alquilo, di (C_{1-6}) alquilaminocarbonil(C_{2-6})alquenil (C_{1-6}) alquilo, alquilaminocarbonyl (C_{2-6})alquinil(C_{1-6})alquilo, di (C_{1-6}) alquilaminocarbonil (C_{1-6}) alquinil (C_{1-6}) alquilo, C_{1-6} alcoxicarbonilo, C_{1-6} alquilcarbonilo, aminocarbonilo, C_{1-6} alquilaminocarbonilo, di (C_{1-6}) alquilaminocarbonilo, fenilo (opcionalmente sustituido por halo, nitro, ciano, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi o C_{1-6} haloalcoxi), fenil(C_{1-4})alquilo (donde el grupo fenilo es opcionalmente sustituido por halo, nitro, ciano, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi o C_{1-6} haloalcoxi), fenil(C_{2-4})alquenil (C_{1-6}) alquilo, (donde el grupo fenilo es opcionalmente sustituido por halo, nitro, ciano, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi, C_{1-6}alquilsulfonilo o C_{1-6} haloalcoxi), heteroarilo (opcionalmente sustituido por halo, nitro, ciano, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi, C_{1-6} alquilsulfonilo o C_{1-6} haloalcoxi), heterociclilo (opcionalmente sustituido por halo, nitro, ciano, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi o C_{1-6} haloalcoxi), heteroaril(C_{1-4})alquilo (donde el heteroarilo puede ser sustituido por halo, nitro, ciano, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi o C_{1-6} haloalcoxi),o heterociclilo(C_{1-4})alquilo (donde el heterociclilo puede ser sustituido por halo, ciano, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi o C_{1-6} haloalcoxi).

8. Un compuesto de fórmula (I) de acuerdo con la cláusula 1, 3, 4, 5, 6 ó 7 o un compuesto de fórmula IA de la cláusula 2, 3, 4, 5, 6 ó 7 donde J es N o

CR^{17} donde R^{17} es hidrógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, ciano, halógeno o nitro.

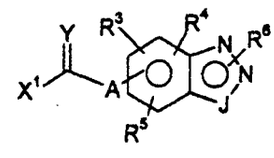
9. Un proceso para preparar un compuesto de fórmula (I) de acuerdo con la cláusula 1, CARACTERIZADO PORQUE comprende los pasos de:

(a) cuando Y es oxígeno, hacer reaccionar un compuesto de fórmula (II)



(II)

donde D, E, R^1 y R^{11} tienen los valores definidos en la cláusula 1 con un compuesto de fórmula (III)



(III)

donde Y es oxígeno, X^1 es un grupo saliente y A, J, R^3, R^4 , R^5 y R^6 tienen los valores definidos en la fórmula 1, o

(b) cuando Y es azufre, preparando un compuesto de fórmula (I) de acuerdo con la cláusula 1, donde Y es oxígeno usando el método descripto en (a) y luego hacer reaccionar este compuesto con un agente tionizador.

10. Una composición fungicida, insecticida, acaricida, molusquicida o nematicida CARACTERIZADA PORQUE comprende una cantidad eficaz como fungicida, insecticida, acaricida, molusquicida o nematicida de un compuesto de fórmula (I) de acuerdo con la cláusula 1 y un vehículo o diluyente para el mismo.

11. Un método para combatir y controlar hongos CARACTERIZADO PORQUE comprende aplicar a una planta, a una semilla de una planta, o al locus de la planta o semilla o al suelo, una cantidad eficaz como fungicida de

Ver 155

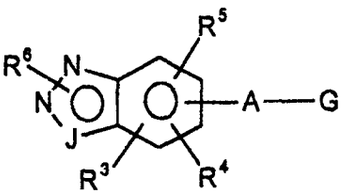
un compuesto de fórmula (I) de acuerdo con la cláusula 1.

12. Un método para combatir y controlar insectos, ácaros, nematodos o moluscos CARACTERIZADO PORQUE comprende aplicar a una plaga, al locus de una plaga o a una planta susceptible de ser atacada por una plaga una cantidad eficaz como insecticida, acaricida, nematicida o molusquicida de un compuesto de la fórmula (I) de acuerdo con la cláusula 1.

COMPUESTOS QUÍMICOS

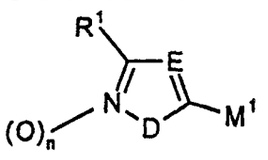
RESUMEN

Un compuesto de fórmula (I):



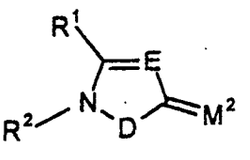
(I)

donde G se selecciona entre



(i)

ó



(ii)

donde M^1 o M^2 está unido a A; n es 0 ó 1; cuando G es (i), D es S, NR^7, $CR^8=CR^9$, $CR^8=N$, $CR^8=N(O)$, $N=CR^9$ o $N(O)=CR^9$; cuando G es (ii), D es S o NR^7; E es N, N-óxido o CR^{10}; M^1 es $OC(=Y)$, $N(R^{11})C(=Y)$, $N=C(OR^{12})$, $N=C(SR^{13})$ o $N=C(NR^{14}R^{15})$ donde O o N es el átomo de unión al anillo que contiene D y E; M^2 es N-C(=Y) donde N es el átomo de unión al anillo que contiene D y E; Y es O, S o NR^{16}; J es N o CR^{17}; y A, R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, y R^{15} son cada uno determinados grupos orgánicos o inorgánicos.

160

Industria y Comercio
SUPERINTENDENCIA

SUPERINDUSTRIA Y COMERCIO
Radicacion : 00028953 00000000 Folios: 162
Fecha (AMD): 2000-04-19 14:24:49
Tramite : 002 PATENTES D 1 REGISTRO/ 411 PRESENTAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

REQUISITOS MINIMOS PARA A

PATENTE DE INVENCIÓN [✓] **MODELO DE UTILIDAD [ ]**

- Nombre e identificación del Solicitante [ ]
- Nombre e identificación del Inventor [ ]
- Título o nombre de la Invención [ ]
- Descripción [ ]
- Reivindicaciones [ ]
- Resumen [ ]
- Comprobante de Pago [ ]

COMPLETA [ ] INCOMPLETA [ ]

DISEÑO INDUSTRIAL [ ]

- Nombre e identificación del peticionario [ ]
- Nombre e identificación del inventor o diseñador [ ]
- Indicación del género de productos para los cuales debe utilizarse [ ]
- Representación gráfica [ ]
- Comprobante de pago [ ]

COMPLETA [ ] INCOMPLETA [ ]

_____.
Firma Responsable

Fecha:_____.

Carrera 13 No. 27-00 Piso 5 y 10
Conmutador: 334 12 21-2-3-4
Fax: 281 31 25 e-mail: info@sic.gov.co
Santa Fe de Bogotá D.C. - Colombia

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

INFORME DE PROTOCOLO

Expediente 00-028953

Fecha: 24 de abril del 2000

Se certifica que:

Desde fecha 14 de mayo de 1993, del folio 71.481 al folio 71.493 del libro de Protocolo N° 236, obra el poder N° 14458 conferido por ZENECA LIMITED

domiciliado(a) en Londres - Inglaterra

al doctor RAMIRO CASTRO DUQUE y/o HECTOR GOMEZ MEJIA.

Representante en Santafé de Bogotá D.C. Los mismos.

Facultad para desistir si.

Revisado.

Carrera 13 N° 27-00 Pisos 5° y 10°
Conmutador 334 1221-2-3-4
Fax 281 3125
Santafé de Bogotá, D.C. - Colombia

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

152

DIVISION DE NUEVAS CREACIONES
PRIMER EXAMEN DE FORMA

165
2000-04-24
430

EXPEDIENTE 00-028953
Practicado el examen jurídico de acuerdo con lo establecido en el art. 21 de la Decisión 344 se determinó que esta solicitud de **Patente de Invención:**

SI [x] **NO [ ]** **NO APLICABLE [ ]** Presentó los poderes necesarios en forma correcta (Decisión 344, art. 14-a).

SI [x] **NO [ ]** **NO APLICABLE [ ]** Acreditó, en forma correcta, la existencia y representación de la persona jurídica solicitante (art. 14-c de la Decisión 344; literal g) del art. 4 del Decreto 117/94).

SI [x] **NO [ ]** **NO APLICABLE [ ]** Presentó, en forma correcta el comprobante de pago por la tasa de presentación establecida (art. 13-f de la Decisión 344 y la Resolución 02 del 4 de enero del 2000).

SI [x] **NO [ ]** **EXTEMPORANEAMENTE [ ]** Reivindicó prioridad, dentro del plazo y de acuerdo con lo previsto en el Artículo 4 del Convenio de Paris.

SI [ ] **NO [x]** **NO APLICABLE [ ]** Presentó copia, certificada su conformidad por la Administración que recibió la solicitud de la cual reivindica prioridad, al momento de radicar la solicitud nacional.

SI [ ] **NO [x]** **NO APLICABLE [ ]** Presentó la traducción del capítulo reivindicatorio de la solicitud de la cual se reivindica prioridad (Art. 4, D-3 Convenio de París; Concepto: 5 de enero de 1999 S.I.C.).

SI [ ] **NO [x]** **CUMPLE LOS REQUISITOS JURIDICOS**

OBSERVACIONES JURIDICAS CONVENIO DE PARIS: En todo caso, deberá presentar copia certificada su conformidad por la Administración que recibió la solicitud de la cual reivindica prioridad, **en cualquier momento dentro del plazo de tres (3) meses**, contados a partir de la fecha de depósito de la solicitud posterior. La omisión de esta formalidad implicará la perdida del derecho de prioridad.

En consecuencia, se conceptúa que esta solicitud:

SI [ ] **NO [X]** Se ajusta a los aspectos **FORMALES** indicados en la Decisión 344 y por tanto,

SI [ ] **NO [x]** Se recomienda **PUBLICAR** el extracto correspondiente.

Santafé de Bogotá, D.C., 24 de abril del 2000.

EXAMINADOR JURIDICO

Carrera 13 Nº 27-00 Pisos 5° y 10°
Conmutador 334 1221-2-3-4
Fax 281 3125
Santafé de Bogotá, D.C. - Colombia

166

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2000-06-04
430

PRIMER EXAMEN DE FORMA

Radicación no 0-28953

Concepto Técnico no 828 Clasificación Internacional de Patentes A01N 43/56

Practicado el examen de acuerdo a lo establecido en el Art. 21 de la Decisión 344 se determinó que esta solicitud de **Patente de Invención:**

SI [X] NO [ ]	Contiene la identificación correcta del inventor (Art.8, Art.13-a).
SI [X] NO [ ]	Contiene la identificación correcta del solicitante (Artículo 13-a).
SI [X] NO [ ]	Contiene el resumen con el objeto y finalidad de la invención en forma correcta (Art.13-e).
SI [ ] NO [X]	Contiene el título o nombre de la invención en forma correcta (Art.13-b).
SI [X] NO [ ]	Contiene la descripción clara y completa de la invención (Art.13-c).
SI [ ] NO [ ]	Contiene los dibujos correctos (Art.14-c junto con el literal d) del Art. 4 del Dto. 117 del 94).
SI [X] NO [ ]	Contiene las unidades de medida en el sistema exigido (Art.14-c junto con el Decreto 3464 del 26 de diciembre de 1980).
SI [ ] NO [X]	Contiene una o más reivindicaciones, en forma correcta, que precisen la materia para la cual se solicita la protección mediante la patente (Art.13-d).
SI [ ] NO [X]	Contiene el extracto de acuerdo con el literal c) del artículo 4 del Dto. 117 /94.
SI [ ] NO [X]	Contiene el arte final del dibujo característico de acuerdo con el literal c) del artículo 4 y el artículo 27 del Dto. 117 /94.
SI [ ] NO [X]	Contiene la tarjeta del Archivo Temático [formato P-104] en forma correcta (Art.14-c junto con el literal b) del artículo 4 del Dto. 117 /94).
SI [X] NO [ ]	Contiene la tarjeta del Archivo de Propietarios [formato P-105] en forma correcta (Art.14-c junto con el literal b) del artículo 4 del Dto. 117 /94).
SI [ ] NO [X]	**CUMPLE LOS REQUISITOS TÉCNICOS**

OBSERVACIONES Y OTROS: SI [X] NO [ ] ver hoja(s) anexa(s)

Santa Fe de Bogotá, D.C., 9 DE JUNIO DE 2000

EXAMINADOR TÉCNICO
Código 202001

167
104

DIVISIÓN DE NUEVAS CREACIONES
1er examen de forma

EXPEDIENTE No. **0-28953**

CONCEPTO TÉCNICO No. **828**
CLASIFICACIÓN INTERNACIONAL DE PATENTES: **A01N43/56**

El título debe complementarse indicando que se trata de compuestos químicos del tipo azoles y su proceso de obtención.

La reivindicación 9 debe indicar cuál es el agente tionizador del inciso b.
La reivindicación 10 para que defina correctamente la composición debe indicar en forma precisa la proporción en que se encuentra el principio activo, puesto que la expresión " cantidad eficaz " resulta ambigua.

De acuerdo con las observaciones realizar las correcciones necesarias presentando NUEVO CAPÍTULO REIVINDICATORIO COMPLETO, de tal forma que sea claro y preciso.

Anexar nueva tarjeta de archivo propietario y Falta tarjeta temático y el extracto para publicación con su correspondiente resumen en el cual se debería indicar las reivindicaciones principales. Si el resumen del extracto sobrepasa el límite del número de palabras establecidas se debe pagar el valor correspondiente asignado por la oficina por cada palabra adicional que se quiera publicar.

Falta arte final de la fórmula estructural tamaño 12x12 cm por duplicado para efecto de la publicación y uno de 6x6 cm.

202001
Examinador Técnico de Patentes

Santa Fe de Bogotá, D.C. 9 de junio de 2000

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

168
165
2000-06-15
420

EXPEDIENTE 00-028953

AUTO 1146

LA JEFE DE LA DIVISION DE NUEVAS CREACIONES

DISPONE

ARTICULO PRIMERO: Reconocer personería al doctor Ramiro Castro Duque, como apoderado del solicitante, en los términos y para los efectos del poder conferido

ARTICULO SEGUNDO: Conforme lo establece el artículo 22 de la Decisión 344 de la Comisión del Acuerdo de Cartagena, requiérese al solicitante, para que dentro del plazo de treinta (30) días hábiles siguientes a la fecha de notificación del auto, presente respuesta a las observaciones o complemente los antecedentes señalados en el examen de forma.

ARTICULO TERCERO: Notificar por estado el presente auto, advirtiendo que contra el no procede recurso alguno en la vía gubernativa.

NOTIFIQUESE Y CUMPLASE
Dado en Santafé de Bogotá D.C., a los 13 JUN 2000

LA JEFE DE LA DIVISION DE NUEVAS CREACIONES,

ALIX CARMENZA CESPEDES DE VERGEL

NOTIFICADO POR ESTADO

Santafé de Bogotá D.C., 15 JUN 2000 notificado por anotación en estado de esta misma fecha.

VENCIMIENTO NOTIFICACION ESTADO

SOLICITO PRORROGA TERMINO SI____ NO____

VENCIMIENTO TERMINO PRORROGA

Carrera 13 Nº 27-00 Pisos 5° y 10°
Conmutador 334 1221-2-3-4
Fax 281 3125
Santafé de Bogotá, D.C. - Colombia

04.273

REPUBLICA DE COLOMBIA

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

DIVISION DE NUEVAS CREACIONES

CONTESTACION A REPAROS - OBSERVACIONES
APORTACION DE NUEVA DOCUMENTACION A
UNA SOLICITUD DE PATENTE DE INVENCION O
MODELO DE UTILIDAD O DISEÑO INDUSTRIAL

SUPERINDUSTRIA Y COMERCIO
Radicación : 00028953 00000001 Folios: 199
Fecha (AMD): 2000-06-12 17:07:03
Tramite : 332 PATENTES D 1 REGISTRO/ 329 COMPLEMEN
Competencia: 8700 DIVISION DE NUEVAS CREACIONES

Solicitud de Patente
Expediente No.00 028.953

CONTESTACION: Reparos ☐
Observaciones ☐
Otros ☐
NUEVA DOCUMENTACION APORTADA ☒

☒ PATENTE ☐ MODELO DE UTILIDAD ☐ DISEÑO INDUSTRIAL

TITULO: **COMPUESTOS QUIMICOS**

SOLICITANTE: **ZENECA LIMITED**

INDICE DE DOCUMENTOS QUE SE ACOMPAÑAN

1	Copias certificadas por la Oficina de Patentes del	☐	a favor del solicitante, junto con su correspondien-
1	Reino Unido de las dos primeras solicitudes pre-	☐	te traducción oficial al español.
2	sentadas para la misma invención, de las cuales	☐	
☐	REIVINDICAMOS PRIORIDAD, junto con sus correspon-	☐	
1	dientes traducciones al español.	☐	
2	Documento de cesión de derechos sobre la invención	☐	

APODERADO: RAMIRO CASTRO DUQUE Código 340

DOMICILIO: Cra. 7 No. 16-56 Piso 9 TEL: 2-812424

FIRMA:

NUMERO DE HOJAS 199

RADICADO POR: Nombres y Apellidos

Junio 12, 2000
CPB/hsr.

Impresos Calidad 2833953

Colombia

The Patent Office

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed Andrew Cressy

Dated 16 March 2000

Patents Form 1/77

Pa[illegible] 1 Act 1977
(Re[illegible] 3)

THE PATENT OFFICE
20 APR 1999
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PPD 50402/GB/P

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3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

ZENECA Limited
15 Stanhope Gate
London W1Y 6LN
UNITED KINGDOM

Patents ADP number *(if you know it)*

6254007002 ✓

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention

CHEMICAL COMPOUNDS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Francis John TIERNEY
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Patents ADP number *(if you know it)*

06786941001

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ZENECA LIMITED
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Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

VIJAYA KUMARI MALLIPEDDI 01344 414365
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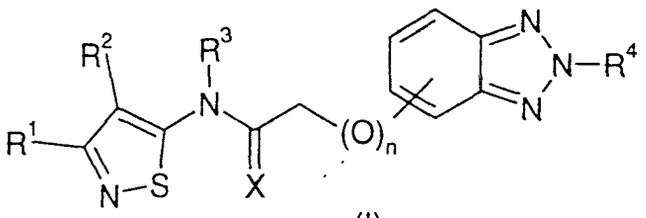
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CHEMICAL COMPOUNDS

The present invention relates to isothiazole derivatives, to processes for preparing them, to fungicidal, insecticidal, acaricidal, molluscicidal and nematicidal compositions comprising them, to methods of using them to combat fungal diseases (especially fungal diseases of plants) and to methods of using them to combat and control insect, acarine, mollusc and nematode pests.

Isothiazole derivatives are disclosed in WO 95/31448, WO 97/18198, WO 98/02424 and WO 98/05670.

The present invention provides a compound of formula (I):



(I)

wherein R^1 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{3-6} cycloalkyl or C_{1-6} alkoxy(C_{1-6})alkyl; R^2 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, cyano, nitro, CHO, CH=NOR^5, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or C_{1-6} alkyl$S(O)_q$; or together R^1 and R^2 form a five or six membered saturated or unsaturated carbocyclic ring, optionally substituted by one or two C_{1-6} alkyl groups; R^3 is hydrogen, C_{1-6} alkyl, CH_2(C_{1-4} haloalkyl), C_{3-6} alkenyl, C_{3-6} alkynyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, formyl, optionally substituted phenoxycarbonyl, optionally substituted phenyl(C_{1-4})alkyl or $S(O)_pR^6$; R^4 is hydrogen, C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{3-6} alkenyl, C_{3-6} alkynyl, C_{3-7} cycloalkyl, C_{3-6} cycloalkyl(C_{1-6})alkyl, C_{3-6} haloalkenyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted phenyl(C_{1-4})alkyl or optionally substituted heteroaryl; R^5 is hydrogen, C_{1-6} alkyl, optionally substituted phenyl or optionally substituted phenyl(C_{1-4})alkyl; R^6 is C_{1-6} alkyl, C_{1-6} haloalkyl or optionally substituted phenyl; X is O or S; n is 0 or 1; and p and q are, independently, 0, 1 or 2.

Alkyl is straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl or *neo*-pentyl.

Halogen is fluorine, chlorine, bromine or iodine.

Haloalkyl groups are optionally substituted with one or more of the same or different halogen atoms and are, for example, CF_3, CH_2CF_3 or CH_2CHF_2.

Phenyl(C_{1-4})alkyl is, for example, 1-phenyleth-1-yl, 2-phenyleth-1-yl, 2-phenylprop-2-yl, 3-phenylprop-1-yl, but is preferably benzyl.

The term heteroaryl refers to an aromatic ring containing one or more heteroatoms (preferably one or two heteroatoms) selected from O, S and N. Examples of such rings include pyridine, pyrimidine, furan, thiophene, thiazole, oxazole and isoxazole.

It is preferred that phenyl moieties and heteroaryl groups are optionally substituted by one or more substituents independently selected from halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{2-6} alkenyl, C_{2-6} haloalkenyl, C_{2-6} alkynyl, C_{3-6} cycloalkyl, nitro, cyano, CO_2H, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, R^8R^9N or $R^{10}R^{11}NC(O)$; wherein R^8, R^9, R^{10} and R^{11} are, independently, hydrogen or C_{1-6} alkyl.

It is preferred that R^1 is ethyl or, especially, methyl.

It is preferred that R^2 is hydrogen, halogen (especially chloro) or cyano.

It is preferred that n is 0.

It is preferred that the compounds of the invention are of formula (Ia).

In one particular aspect the present invention provides a compound of formula (Ia) wherein R^1 is C_{1-4} alkyl (especially methyl or ethyl); R^2 is hydrogen, halogen (especially chloro or bromo) or cyano; or R^1 and R^2 together form a cyclopentyl, cyclohexyl or phenyl ring; R^3 is hydrogen, C_{1-4} alkyl (especially methyl or ethyl), phenyl(C_{1-4})alkyl (especially benzyl), C_{1-4} alkylcarbonyl (especially acetyl) or C_{1-4} alkylsulfonyl (especially methanesulfonyl); n is 0; X is oxygen; and R^4 is C1-6 alkyl [optionally substituted with halogen, C_{1-4} alkoxy, phenyl (itself optionally substituted with halogen), CO_2H, $CONH_2$ (itself optionally substituted with C_{1-4} alkyl), cyano, C_{3-6} cycloalkyl or $CO(C_{1-4}$ alkoxy)], C_{3-6} alkenyl, C_{3-6} alkynyl, C_{3-6} cycloalkyl, phenyl [optionally substituted with halogen, C_{1-4} haloalkyl (especially CF_3), nitro, CO_2H, or cyano] or heteroaryl (especially pyridyl or pyrimidinyl) [optionally substituted with C_{1-4} alkyl or C_{1-4} haloalkyl].

The compounds in the following Tables illustrate compounds of the invention.

TABLE 1

The compounds of Table 1 are compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 is as given in the table below.

Compound No.	R^4	^{1}H NMR δ ppm ($CDCl_3$ unless stated)
1	*n*-propyl	1.0(t,3H); 2.15(m,2H); 2.35(s,3H); 4.0(s,2H); 4.7(t,2H); 7.35(dd,1H); 7.85(d,1H); 7.95(d,1H); 8.15(b,1H)
2	4-CF_3-C_6H_4	2.4(s,3H); 4.1(s,2H); 7.5(m,1H), 7.8-7.9(m,4H); 8.5(bd,2H); 10.35(s,1H)
3	methyl	2.35(s,3H); 4.0(s,2H); 4.5(s,3H); 7.35(dd,1H), 7.8(d,1H); 7.9(d,1H); 8.05(b,1H)
4	4-F-$C_6H_4CH_2$	(DMSO-d_6): 2.35(s,3H); 4.05(s,2H); 5.8(s,2H); 7.0(m,2H); 7.4(m,3H); 7.8(m,2H); 10.9(b,1H)
5	CF_3CH_2	2.4(s,3H); 4.0(s,2H); 5.3(q,2H); 7.4(dd,1H); 7.85(d,1H); 7.95(d,1H); 8.15(b,1H)
6	*n*-pentyl	0.9(t,3H); 1.35(m,4H); 2.15(m,2H); 2.4(s,3H); 4.05(s,2H); 4.7(t,2H); 7.35(dd,1H); 7.85(d,1H); 7.9(d,1H); 8.15(b,1H)
7	2-Cl-3-CF_3-C_6H_3	2.4(s,3H); 4.05(s,2H); 7.45(dd,1H); 7.75(dd,1H); 7.95(m,3H); 8.05(m,1H); 8.2(b,1H)
8	1-methylpropyl	0.85(t,3H); 1.7(d,3H); 2.0-2.2(m,2H); 2.35(s,3H); 4.0(s,2H); 4.9(m,1H); 7.3(dd,1H); 7.85(d,1H); 7.9(d,1H); 8.15(b,1H)
9	ethyl	1.75(t,3H); 2.35(s,3H); 4.0(s,2H); 4.8(q,2H); 7.35(dd,1H); 7.8(b,1H); 7.9(d,1H); 8.1(b,1H)
10	2,2-dimethylpropyl	1.05(s,9H); 2.4(s,3H); 4.05(s,2H); 4.55(s,2H); 7.35(dd,1H); 7.85(b,1H); 7.95(d,1H); 8.15(b,1H)
11	*n*-butyl	
12	2-methylpropyl	
13	2-methoxyethyl	

14	methoxymethyl
15	$CH_2CH=C(CH_3)_2$
16	2-chloroethyl
17	allyl
18	propargyl
19	CH_2CO_2H
20	$CH_2CO_2CH_3$
21	$CH_2CO_2C_2H_5$
22	$CH(CH_3)CO_2H$
23	$CH(CH_3)CO_2CH_3$
24	$CH(CH_3)CO_2C_2H_5$
25	$C(CH_3)_2CO_2H$
26	$C(CH_3)_2CO_2CH_3$
27	$C(CH_3)_2CO_2C_2H_5$
28	CH_2CONH_2
29	$CH(CH_3)CONH_2$
30	$C(CH_3)_2CONH_2$
31	$CH_2CONHCH_3$
32	$CH_2CON(CH_3)_2$
33	$CH(CH_3)CONHCH_3$
34	$CH(CH_3)CON(CH_3)_2$
34	$CH_2CO_2C(CH_3)_3$
35	cyanomethyl
36	pentafluoroethyl
37	cyclopentyl
38	2-fluoroethyl
39	difluoromethyl
40	2-thioethoxyethyl
41	CH_2-cyclopropyl
42	CH_2-cyclopentyl
43	CH_2-cyclohexyl
44	$2\text{-}NO_2\text{-}C_6H_4$

45	2-pyridyl
46	5-CF_3-2-pyridyl
47	C_6F_5
48	4-CO_2H-C_6H_4
49	2-Cl-4-CN-C_6H_3
50	3,5-dimethyl-pyrimidin-2-yl

TABLE 2

Table 2 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 3

Table 3 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 4

Table 4 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 5

Table 5 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 6

Table 6 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 7

Table 7 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is hydrogen, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 8

Table 8 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is fluoro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 9

Table 9 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is bromo, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 10

Table 10 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is cyano, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 11

Table 11 contains 50 compounds of formula (Ia) wherein R^1 is methyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 1 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 12

Table 12 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 13

Table 13 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 14

Table 14 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 15

Table 15 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 16

Table 16 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 17

Table 17 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 18

Table 18 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is hydrogen, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 19

Table 19 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is fluoro, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 20

Table 20 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is bromo, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 21

Table 21 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is cyano, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 22

Table 22 contains 50 compounds of formula (Ia) wherein R^1 is ethyl, R^2 is chloro, R^3 is hydrogen, X is oxygen, n is 1 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 23

Table 23 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 24

Table 24 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 25

Table 25 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 26

Table 26 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 27

Table 27 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 28

Table 28 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclopentyl ring, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 29

Table 29 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 30

Table 30 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 31

Table 31 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 32

Table 32 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 33

Table 33 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 34

Table 34 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a cyclohexyl ring, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 35

Table 35 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is hydrogen, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 36

Table 36 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is methyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 37

Table 37 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is ethyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 38

Table 38 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is benzyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 39

Table 39 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is acetyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

TABLE 40

Table 40 contains 50 compounds of formula (Ia) wherein R^1 and R^2 together form a phenyl ring, R^3 is methanesulfonyl, X is oxygen, n is 0 and R^4 has the value for the correspondingly numbered compound in Table 1.

Compounds of formula (I) can be prepared by acylation of an appropriate 5-aminoisothiazole (II) with an appropriate carboxylic acid (III), preferably in the presence of a known coupling agent such as 1,3-dicyclohexylcarbodiimide or 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide. Alternatively the carboxylic acid (III) may first be converted to an acid chloride, anhydride or chloroformate suitable for reaction with an amine to form an amide; such procedures are described, for example in J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985, pps 370-376 and references therein.

5-Aminoisothiazoles (II) are either available commercially, or can be prepared from commercially available starting materials by methods described in the literature. (See, for example, C. Oliver Kappe, Robert Flammang, and Curt Wentrup, Heterocycles, Vol. 37, No. 3, 1615, (1994); A. Adams and R. Slack, J. Chem. Soc., 3061, (1959); and Ronald E Hackler, Kenneth W. Burow, Jr., Sylvester V. Kaster and David I. Wickiser, J. Heterocyclic Chem, 26, 1575, (1989))

Carboxylic acids (III) can be prepared by hydroylsis of their corresponding esters (IV) by methods described in the art. The esters can be chosen to be hydrolysed under neutral, basic or acidic conditions, and the conditions are chosen such that the substituent R^4 is not affected by the hydrolysis reaction. Esters capable of ready hydrolysis under different conditions are known in the literature, and suitable esters may be selected, for example, by reference to Theodora W. Greene, Protective Groups in Organic Synthesis, Chapter 5, John Wiley and Sons, New York, 1981.

Esters (IV) can be prepared by reacting a benzotriazoles (V) with a compound R^4L, wherein L is a suitable leaving group such as halogen. (For suitable coupling reactions see, for example, Comprehensive Heterocyclic Chemistry, ed. Alan R Katritzky and Charles W Rees, Volume 5, pps 669-732 Pergamon Press, 1984 and references therein.) Reactions such as these can give rise to isomeric products. The desired isomer (IV) can usually be separated from any others present by standard techniques such as flash column chromatography or crystallisation from a solution containing one or more suitable solvents.

Benzotriazoles (V) may be prepared by the sequential diazotisation and hydrolysis of an acylated diamine (VI), or by hydrolysis of an acylated diamine (VI) to give a diamine (VII) which is then diazotised. Procedures for forming benzotriazoles (V) from such precursors are well known in the literature. (See, for example, Comprehensive Heterocyclic Chemistry, ed. Alan R Katritzky and Charles W Rees, Volume 5, pps 722-723 Pergamon Press, 1984 and references therein.)

Acylated diamines (VI) can be prepared by the reduction of a corresponding nitroanilide (VIII), which in turn is prepared by the nitration of an anilide (IX). Procedures for effecting these transformations are well known in the literature. (See, for example, references given in J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985). Anilides (IX) are known in the art and can be prepared from known compounds using procedures described in the art.

Compounds of formula (I) wherein R^3 is other than hydrogen can be prepared by reacting a compound of formula (I) wherein R^3 is hydrogen with a compound R^3L^*, wherein L* is a leaving group (such as halogen), optionally in the presence of a base and a phase transfer catalyst. Examples of suitable alkylating agents include, alkyl halides such as methyl iodide and alkyl sulfates such as dimethylsulfate. Suitable acylating agents include anhydrides such as acetic anhydride, acid chlorides such as acetyl chloride or benzoyl chloride and chloroformates such as ethyl chloroformate. Suitable bases include organic bases such as triethylamine, pyridine, alkali metal alkoxides such as potassium *tert*-butoxide and inorganic bases such as sodium hydride and sodium hydroxide. Suitable phase transfer catalysts may be selected by reference to the literature (see, for example, J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985, pps 320-322 and references therein).

A compound of formula (I) wherein X is sulfur can be prepared from a compound of formula (I) wherein X is oxygen by reacting that compound with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent) or phophorus pentasulfide in a solvent (such as toluene).

The compounds of formula (I) can be used to combat and control infestations of insect pests such as Lepidoptera, Diptera, Homoptera and Coleoptera and also other invertebrate pests, for example, acarine, nematode and mollusc pests. Insects, acarines, nematodes and molluscs are hereinafter collectively referred to as pests. The pests which

may be combated and controlled by the use of the invention compounds include those pests associated with agriculture (which term includes the growing of crops for food and fibre products), horticulture and animal husbandry, companion animals, forestry and the storage of products of vegetable origin (such as fruit, grain and timber) and also those pests associated with the transmission of diseases of man and animals.

Examples of pest species which may be controlled by the compounds of formula (I) include: *Myzus persicae* (aphid), *Aphis gossypii* (aphid), *Aphis fabae* (aphid), *Lygus* spp. (capsids), *Dysdercus* spp. (capsids), *Nilaparvata lugens* (planthopper), *Nephotettix cincticeps* (leafhopper), *Nezara* spp. (stinkbug), *Euschistus* spp. (stinkbugs), *Leptocorisa* spp. (stinkbugs), *Frankliniella occidentalis* (thrip), *Thrips* spp. (thrips), *Leptinotarsa decemlineata* (Colorado potato beetle), *Anthonomus grandis* (boll weevil), *Aonidiella* spp. (scale insects), *Trialeurodes* spp. (white flies), *Bemisia tabaci* (white fly), *Spodoptera littoralis* (cotton leafworm), *Heliothis virescens* (tobacco budworm), *Helicoverpa armigera* (cotton bollworm), *Pieris brassicae* (white butterfly), *Plutella xylostella* (diamond back moth), *Agrotis* spp. (cutworms), *Chilo suppressalis* (rice stem borer), *Chortiocetes terminifera* (locust), *Diabrotica* spp. (rootworms), *Panonychus ulmi* (European red mite), *Panonychus citri* (citrus red mite), *Tetranychus urticae* (two-spotted spider mite), *Tetranychus cinnabarinus* (carmine spider mite), *Phyllocoptruta oleivora* (citrus rust mite), *Polyphagotarsonemus latus* (broad mite), *Brevipalpus* spp. (flat mites), *Liriomyza* spp. (leafminers), *Musca domestica* (housefly), *Aedes aegypti* (mosquito), *Anopheles* spp. (mosquitoes), *Culex* spp. (mosquitoes), *Blattella germanica* (cockroach), *Periplaneta americana* (cockroach), *Blatta orientalis* (cockroach), *Ostrinia nubilalis* (European corn borer), *Meloidogyne* spp. (root knot nematodes), *Globodera* spp. and *Heterodera* spp. (cyst nematodes), *Pratylenchus* spp. (lesion nematodes) and *Deroceras reticulatum* (slug). Further examples include insects which adversely affect the health of the public or of animals.

The compounds of formula (I) are also active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia recondita*, *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet, vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Erysiphe graminis* (powdery mildew) on barley, wheat, rye and turf and other

powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fuliginea* on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici*) and *Phaeosphaeria nodorum* (*Stagonospora nodorum*), *Pseudocercosporella herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frogeye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; *Plasmopara viticola* on vines; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco, cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas,

peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon, pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes; *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium* spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarus*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seditiosum*) or lumber, notably *Cephaloascus fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

A compound of formula (I) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (I) may be volatile enough to be active in the vapour phase against one or more fungi on the plant.

The invention therefore provides a method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a pest, a locus of pest, or to a plant susceptible to attack by a pest, and a method of combating and controlling fungi which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a plant, to a seed of a plant, to the locus of the plant or seed or to soil. The compounds of formula (I) are preferably used against insects, acarines, nematodes or fungi.

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The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicant and antisporulant treatments.

As fungicides, the compounds of formula (I) are preferably used for agricultural, horticultural and turfgrass purposes in the form of a composition.

In order to apply a compound of formula (I) as an insecticide, acaricide, nematicide or molluscicide to a pest, a locus of pest, or to a plant susceptible to attack by a pest, or, as a fungicide to a plant, to a seed of a plant, to the locus of the plant or seed or to soil, a compound of formula (I) is usually formulated into a composition which includes, in addition to the compound of formula (I), a suitable inert diluent or carrier and, optionally, a surface active agent. Surface active agents are chemicals which are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersibility and wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (I). The composition is generally used for the control of pests or fungi such that a compound of formula (I) is applied at a rate of from 0.1g to10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (I) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides an insecticidal, acaricidal, nematicidal, molluscicidal or fungicidal composition comprising an insecticidally, acaricidally, nematicidally, molluscicidally or fungicidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor. The composition is preferably an insecticidal, acaricidal, nematicidal or fungicidal composition.

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), emulsions (both oil in water (EW) and water in oil (EO)), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed

dressings. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (I).

Dustable powders (DP) may be prepared by mixing a compound of formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder.

Soluble powders (SP) can be prepared by mixing a compound of formula (I) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) can be prepared by mixing a compound of formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include aliphatic and aromatic petroleum solvents, alcohols, polyvinyl acetates, polyvinyl alcohols, ethers, ketones, esters, dextrins, sugars and vegetable oils. One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Soluble concentrates (SL) can be prepared by dissolving a compound of formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may

contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil in water emulsions (EW) may be prepared by dissolving a compound of formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents) and, for an emulsion, subsequently adding, under high shear agitation, the mixture to water (which may contain one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol). Suitable organic solvents for use in ECs or EWs include vegetable oils, *N*-substituted pyrrolidones, glycol ethers, chlorinated hydrocarbons (such as chlorobenzenes) and aromatic solvents (such as alkylbenzenes or alkylnaphthalenes).

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (I). SCs may be prepared by ball or bead milling the solid compound of formula (I) in a suitable medium with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle.

Aerosol formulations comprise a compound of formula (I) and a suitable propellant (for example *n*-butane). A compound of formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula (I) can be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

Capsule suspensions (CS) can be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (I) and, optionally, a carrier or diluent therefor. The compositions may provide for controlled release of the compound of formula (I) and they can be used for seed treatment. A compound of formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A composition may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (I)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soya bean and rape seed oil), and blends of these with other bio-enhancing adjuvants.

A compound of formula (I) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and SL compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil).

Wetting agents, dispersing agents and emulsifying agents may be of the cationic, anionic, amphoteric or non-ionic type.

Suitable agents of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic agents include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-*iso*propyl- and tri-*iso*propyl-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid, additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable agents of the amphoteric type include betaines, propionates and glycinates.

Suitable agents of the non-ionic type include condensation products of ethylene oxide with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or

hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters) or their ethoxylated derivatives; amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (I) can be applied by any of the known means of applying pesticidal or fungicidal compounds. For example, it can be applied, formulated or unformulated, to the pests or to a locus of the pests (such as a habitat of the pests, or a growing plant liable to infestation by the pests) or to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it can be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (I) may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include SLs, SCs, ECs, EWs, SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula (I) (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of formula (I) can be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types

include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula (I).

The invention therefore also provides a fertiliser composition comprising a fertiliser and a compound of formula (I).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematicidal or acaricidal activity.

By including another fungicide, the resulting composition can have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (I) alone. Further the other fungicide can have a synergistic effect on the fungicidal activity of the compound of formula (I).

The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of formula (I); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition.

Examples of suitable pesticides include the following:

a) Pyrethroids, such as permethrin, cypermethrin, fenvalerate, esfenvalerate, deltamethrin, cyhalothrin (in particular lambda-cyhalothrin), bifenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids (for example ethofenprox), natural pyrethrin, tetramethrin, s-bioallethrin, fenfluthrin, prallethrin or 5-benzyl-3-furylmethyl-(*E*)-(1*R*,3*S*)-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl)cyclopropane carboxylate;

b) Organophosphates, such as profenofos, sulprofos, acephate, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, profenofos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chlorpyrifos, phosalone, terbufos, fensulfothion, fonofos, phorate, phoxim, pirimiphos-methyl, pirimiphos-ethyl, fenitrothion, fosthiazate or diazinon;

c) Carbamates (including aryl carbamates), such as pirimicarb, triazamate, cloethocarb, carbofuran, furathiocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur, methomyl or oxamyl;

d) Benzoyl ureas, such as diflubenzuron, triflumuron, hexaflumuron, flufenoxuron or chlorfluazuron;

e) Organic tin compounds, such as cyhexatin, fenbutatin oxide or azocyclotin;

f) Pyrazoles, such as fipronil, tebufenpyrad and fenpyroximate;

g) Macrolides, such as avermectins or milbemycins, for example abamectin, emamectin benzoate, ivermectin, milbemycin, spinosad or azadirachtin;

h) Hormones or pheromones;

i) Organochlorine compounds such as endosulfan, benzene hexachloride, DDT, chlordane or dieldrin;

j) Amidines, such as chlordimeform or amitraz;

k) Fumigant agents, such as chloropicrin, dichloropropane, methyl bromide or metam;

l) Chloronicotinyl compounds such as imidacloprid, acetamiprid, nitenpyram or thiomethoxam;

m) Diacylhydrazines, such as tebufenozide;

n) Diphenyl ethers, such as diofenolan or pyriproxifen;

o) Indoxacarb;

p) Chlorfenapyr; or

q) Pymetrozine.

In addition to the major chemical classes of pesticide listed above, other pesticides having particular targets may be employed in the composition, if appropriate for the intended utility of the composition. For instance, selective insecticides for particular crops, for example stemborer specific insecticides for use in rice (such as cartap or buprofezin) can be employed. Alternatively insecticides or acaricides specific for particular insect species/stages may also be included in the compositions (for example acaricidal ovo-larvicides, such as clofentezine, flubenzimine, hexythiazox or tetradifon; acaricidal motilicides, such as dicofol or propargite; acaricides, such as bromopropylate or chlorobenzilate; or growth regulators, such as hydramethylnon, cyromazine, methoprene, chlorfluazuron or diflubenzuron).

Examples of fungicidal compounds which may be included in the composition of the invention are (*E*)-*N*-methyl-2-(2-phenoxyphenyl)-2-methoxyiminoacetamide, (*E*)-*N*-methyl-

2-[2-(2,5-dimethylphenoxymethyl)phenyl]-2-methoxy-iminoacetamide, (*RS*)-1-aminopropylphosphonic acid, (*RS*)-4-(4-chlorophenyl)-2-phenyl-2-(1*H*-1,2,4-triazol-1-ylmethyl)butyronitrile, (Z)-*N*-but-2-enyloxymethyl-2-chloro-2',6'-diethylacetanilide, 1-(2-cyano-2--methoxyiminoacetyl)-3-ethyl urea, 4-(2,2-difluoro-1,3-benzodioxol-4-yl)-pyrrole-3-carbonitrile, 4-bromo-2-cyano-*N*,*N*-dimethyl-6-trifluoromethylbenzimidazole-1-sulphonamide, 5-ethyl-5,8-dihydro-8-oxo(1,3)-dioxol-(4,5-g)quinoline-7-carboxylic acid, α-[*N*-(3-chloro-2,6-xylyl)-2-methoxyacetamido]-γ-butyrolactone, *N*-(2-methoxy-5-pyridyl)-cyclopropane carboxamide, acibenzolar (CGA245704), alanycarb, aldimorph, ampropylfos, anilazine, azaconazole, azoxystrobin, benalaxyl, benomyl, biloxazol, binapacryl, bitertanol, blasticidin S, bromuconazole, bupirimate, butenachlor, buthiobate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA41396, CGA41397, chinomethionate, chloroneb, chlorothalonil, chlorozolinate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate, and Bordeaux mixture, cycloheximide, cymoxanil, cyproconazole, cyprodinyl, cyprofuram, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, dichlone, diclobutrazol, diclomezine, dicloran, didecyl dimethyl ammonium chloride, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O*,*O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethomorph, dimethirimol, diniconazole, dinocap, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, etaconazole, ethirimol, ethoxyquin, ethyl (*Z*)-*N*-benzyl-*N*-([methyl(methyl-thioethylideneamino-oxycarbonyl)amino]thio)-β-alaninate, etridiazole, famoxadone, fenaminosulph, fenapanil, fenarimol, fenbuconazole, fenfuram, fenhexamid (KBR 2738), fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, fluoroimide, fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fuberidazole, furalaxyl, furametpyr, furconazole-cis, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, ipconazole, iprobenfos, iprodione, isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metconazole, methfuroxam, metiram, metiram-zinc, metominostrobin, metsulfovax, myclobutanil, neoasozin, nickel dimethyldithiocarbamate, nitrothal-*iso*propyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole,

oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosetyl-Al, phosphorus acids, phthalide, picoxystrobin (ZA1963), polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propiconazole, propineb, propionic acid, prothiocarb, pyracarbolid, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinconazole, quinomethionate, quinoxyfen. quintozene, rabenazole, sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thicyofen, thifluzamide, 2-(thiocyanomethylthio)benzothiazole, thiophanatemethyl, thiram, timibenconazole, tolclofos-methyl, tolylfluanid, triacetate salt of 1,1'-iminodi(octamethylene)diguanidine, triadimefon, triadimenol, triazbutyl, triazoxide, tricyclazole, tridemorph, trifloxystrobin, triforine, triflumizole, triticonazole, validamycin A, vapam, vinclozolin, XRD-563, zineb and ziram. The compounds of formula (I) can be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Examples of suitable synergists for use in the compositions include piperonyl butoxide, sesamex, safroxan and dodecyl imidazole.

Suitable herbicides and plant-growth regulators for inclusion in the compositions will depend upon the intended target and the effect required.

An example of a rice selective herbicide which can be included is propanil. An example of a plant growth regulator for use in cotton is PIX™.

Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The invention is illustrated by the following Examples, in which the ingredients below are referred to by their Registered Trade Marks and have the following compositions.

Registered Trade Mark	Composition
SYNPERONIC NP8 } SYNPERONIC NP13 }	Nonylphenol-ethylene oxide condensate
SYNPERONIC A7	Synthetic primary alcohol-ethylene oxide condensate
AROMASOL H	Alkylbenzene solvent
SOLVESSO 200	Inert organic diluent
KELTROL	Polysaccharide
PROXEL	Bactericide

The following abbreviations are used throughout:

s = singlet	b = broad	q = quartet
d = doublet	m = multiplet	dd = double doublet
t = triplet	bd = broad doublet	

EXAMPLE 1

This Example illustrates the preparation of N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)acetamide (Compound No. 1 of Table I).

Step 1

4-Aminophenylacetic acid (100g) was suspended in methanol (1000ml) and gaseous hydrogen chloride was passed through until the mixture was saturated. The mixture was heated at 50°C for 2 hours and was then allowed to cool to room temperature. The solvent was evaporated *in vacuo*, the residue taken up aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl 4-aminophenylacetate as a pale brown liquid.

^{1}H NMR ($CDCl_3$) δ ppm: 3.5(s,2H); 3.7(s,3H); 6.65(m,2H); 7.05(m,2H).

Step 2

Methyl 4-aminophenylacetate (110g, 0.667mol) was added dropwise to acetic anhydride (600ml), maintaining the temperature of the reaction mixture below 30°C by external cooling. Once the addition was complete the mixture was cooled to below 10°C and concentrated nitric acid (85 ml) was added dropwise. Once the addition of the acid was

complete, the mixture was allowed to warm to room temperature and poured onto a mixture of ice and water. The precipitated solid was collected by filtration and dried to give methyl 4-acetamido-3-nitrophenylacetate (120g) as a pale yellow solid.

^{1}H NMR ($CDCl_3$) δ ppm: 2.3(s,3H); 3.65(s,2H); 3.7(s,3H); 7.55(dd,1H); 8.1(d,1H); 8.7(d,1H); 10.3(b,1H).

Step 3

Methyl 4-acetamido-3-nitrophenylacetate (40g, 0.159mol)) was dissolved in methanol (400ml) and hydrogenated at 5bar over a 5% palladium on carbon catalyst. The catalyst was removed by filtration and the filtrate evaporated *in vacuo* to give methyl 4-acetamido-3-aminophenylacetate.

Step 4

Methyl 4-acetamido-3-aminophenylacetate (77g, 0.373mol) was taken up in a mixture of acetic acid (210ml) and water (210ml) and cooled to below 5°C. A solution of sodium nitrite (38.63g, 0.559mol) in water (200ml) was added dropwise, and once the addition was complete the mixture was stirred for 4hours, warming slowly to room temperature. The mixture was diluted with ethyl acetate and the insoluble material removed by filtration. The filtrate was washed with brine, dried over anhydrous magnesium sulfate, filtered and the solvent evaporated *in vacuo*, to give a viscous residue (51g) used directly in the next step.

Step 5

The product obtained in Step 4 above was dissolved in a solution of methanol (400ml) previously saturated with hydrogen chloride and the mixture stirred for 2hours. The solvent was removed *in vacuo*, the residue taken up in water, neutralised with saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl 5-benzotriazoleacetate (35g) as a reddish liquid which crystallised on standing.

^{1}H NMR ($CDCl_3$) δ ppm: 3.7(s,3H); 3.8(s, 2H); 7.35(d,1H); 7.8(b,2H); 13.6(b,1H).

Step 6

A solution of methyl 5-benzotriazoleacetate (10g, 0.0523mol) in N,N-dimethylformamide was added dropwise to a chilled (ice-bath) suspension of sodium hydride (60% dispersion in oil, 2.3g, 0.0575mol) in N,N-dimethylformamide. When the addition was

complete, the ice-bath was removed and the mixture stirred for 1hour. N-Propyl iodide (9.78g, 0.0575mol) was added dropwise, and once the addition was complete the mixture was stirred at room temperature for 3hours. The reaction mixture was poured onto ice/water, and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by column chromatography to afford methyl (2-propylbenzotriazol-5-yl)acetate (4.8g).

^{1}H NMR ($CDCl_3$) δ ppm: 0.9(t,3H); 2.1(m,2H); 3.7(s,3H); 3.8(s,2H); 4.65(t,2H); 7.3(dd,1H); 7.7(d,1H); 7.8(d,1H).

Step 7

The acetate prepared in Step 6 above (4.8g, 0.0206mol) was dissolved in methanol (60ml) and potassium hydroxide flakes (1.27g, 0.0226mol) added. The mixture was refluxed for 2hours, then cooled and the solvent evaporated *in vacuo*. The residual solid was dissolved in water and extracted with diethyl ether. The aqueous solution was acidified to pH 1 by addition of dilute aqueous hydrochloric acid and extracted with ethyl acetate. The ethyl acetate extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford (2-propylbenzotriazol-5-yl)acetic acid (3.6g) as a colourless solid.

Step 8

The acid prepared in Step 7 (0.438g, 0.002mol) was dissolved in dichloromethane (5ml) and one drop of N,N-dimethyl formamide was added. Oxalyl chloride (0.307g, 0.0022mol) was added dropwise, and the mixture stirred at room temperature for 2hours. The solvent was removed *in vacuo*, the residue taken up in xylene and added to a mixture of 5-amino-4-chloro-3-methylisothiazole (0.446g, 0.003mol) in xylene and heated at reflux for 2hours. The mixture was cooled to room temperature and the solvent evaporated *in vacuo*. The residue was taken up in ethyl acetate, washed sequentially with saturated aqueous sodium bicarbonate solution and brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by flash column chromatography, eluting with 2:1 hexane : ethyl acetate, to give the title compound (0.34g) as a sandy-coloured solid.

^{1}H NMR ($CDCl_3$) δ ppm: 1.0(t,3H); 2.15(m,2H); 2.35(s,3H); 4.0(s,2H); 4.7(t,2H); 7.35(dd,1H); 7.85(d,1H); 7.95(d,1H); 8.15(b,1H).

EXAMPLE 2

This Example illustrates an emulsifiable concentrate composition which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The emulsifiable concentrate has the following composition:

	% by weight
Compound No. 1	25.0
SYNPERONIC NP13	2.5
Calcium dodecylbenzenesulphonate	2.5
AROMASOL H	70.0

EXAMPLE 3

This Example illustrates a wettable powder composition which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The wettable powder has the following composition:

	% by weight
Compound No. 1	25.0
Silica	25.0
Sodium lignosulphonate	5.0
Sodium lauryl sulphate	2.0
Kaolin	43.0

EXAMPLE 4

This Example illustrates a dustable powder which may be applied directly to plants or other surfaces. The dustable powder has the following composition:

	% by weight
Compound No. 1	1.0
Talc	99.0

EXAMPLE 5

This Example illustrates an oil miscible liquid formulation suitable for application by ultra low volume techniques after mixing with an organic diluent. The formulation has the following composition:

	% by weight
Compound No. 1	10.0
SOLVESSO 200	90.0

EXAMPLE 6

This Example illustrates a capsule suspension concentrate which is readily convertible, by addition to water, into a preparation suitable for application as an aqueous spray. The capsule suspension concentrate has the following composition:

	% by weight
Compound No. 1	10.0
AROMASOL H	10.0
Toluene di-isocyanate	3.0
SYNPERONIC A7	1.0
Polyvinyl alcohol	2.0
Bentonite	1.5
KELTROL	0.1
Water	72.4

EXAMPLE 7

This Example illustrates a ready for use granular formulation that is prepared from a preformed granular carrier. The granular formulation has the following composition:

	% by weight
Compound No. 1	0.5
SOLVESSO 200	0.2
SYNPERONIC A7	0.1
Calcium carbonate granules (diameter 0.3-0.7mm)	99.2

EXAMPLE 8

This Example illustrates a ready for use granular formulation that is prepared by granulation of the powdered components. The granular formulation has the following composition:

	% by weight
Compound No. 1	0.5
Sodium lignosulphonate	5.0
Kaolin	94.5

EXAMPLE 9

This Example illustrates an aqueous suspension concentrate composition which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The suspension concentrate has the following composition:

	% by weight
Compound No. 1	25.0
Sodium lignosulphonate	3.0
Propylene glycol	10.0
Bentonite	2.0
KELTROL	0.1
PROXEL	0.1
Water	59.8

EXAMPLE 10

This Example illustrates a water dispersible granule formulation which is readily convertible, by addition to water, into a preparation suitable for spraying purposes. The water dispersible granule has the following composition:

	% by weight
Compound No. 1	25.0
Silica	5.0
Sodium lignosulphonate	10.0
Sodium lauryl sulphate	5.0
Sodium acetate	10.0
Montmorillonite powder	45.0

EXAMPLE 11

This Example illustrates the pesticidal/insecticidal properties of compounds of formula (I). The activities of individual compounds of formula (I) were determined using a variety of pests. With the exception of nematodes, the pests were treated with a liquid composition containing 500 parts per million (ppm) by weight of a compound unless otherwise stated. Each composition was made by dissolving the compound in an acetone and ethanol (50:50 by volume) mixture and diluting the solution with water containing 0.05% by volume of a wetting agent, SYNPERONIC NP8, until the liquid composition contained the required concentration of the compound.

The test procedure adopted with regard to each pest, except nematodes, was essentially the same and comprised supporting a number of the pests on a medium which was usually a substrate, a host plant or a foodstuff on which the pests feed, and treating either or both the medium and the pests with a composition. Pest mortality was assessed usually between [redacted] and five days after treatment. Knockdown of housefly (*Musca domestica*) was assessed 15 minutes after treatment.

The test procedure for nematodes involved dissolving the compound in an acetone and ethanol (50:50 by volume) mixture and diluting the solution with water to obtain a final concentration of the compound of 12.5ppm. J2 infective juveniles of *Meloidogyne incognita* were suspended in the solution in a glass vial and mortality assessed after a period of three days.

The results of the tests are presented below. The results indicate a grading of mortality (score) designated as 99, 55 or 0 wherein 99 indicates 80-100% mortality, 55 indicates 40-79% mortality and 0 indicates less than 40% mortality.

Compound No. (Table)	TETRUR	MYZUPE	MUSCDO AK	MUSCDO AC	HELIVI	LAPHEG	MELGIN
1 (1)	99	0	-	-	99	99	55
3 (1)	0	99	0	55	55	55	0
4 (1)	0	0	0	0	55	0	0
5 (1)	99	0	99	99	0	55	99
6 (1)	55	55	0	55	0	99	99
7 (1)	99	55	0	99	99	99	0
8 (1)	99	99	99	99	55	99	55
9 (1)	0	99	99	99	55	0	0
10 (1)	99	55	99	99	99	99	0

187
155

TETRUR = *Tetranychus urticae* MYZUPE = *Myzus persicae*

MUSCDO AK = *Musca domestica* (kill) MUSCDO AC = *Musca domestica* (knockdown)

HELIVI = *Heliothis virescens* LAPHEG = [redacted]

MELGIN = *Meloidogyne incognita*

EXAMPLE 12

This Example illustrates the fungicidal properties of compounds of formula (I). The compounds were tested against a variety of foliar fungal diseases of plants. The technique employed was as follows.

Plants were grown in John Innes Potting Compost (No. 1 or 2) in 4cm diameter, 3.5cm depth minipots. The test compounds were individually formulated as a solution either in acetone or acetone/ethanol (1:1 by volume) which was diluted in deionised water to a concentration of 100ppm (that is, 1mg of compound in a final volume of 10ml) immediately before use.

Individual compounds of formula (I) were applied as a foliar (Folr) application (where the chemical solution was applied to the foliage of the test plants by spraying the plant to maximum droplet retention). When foliar sprays were applied to monocotyledonous crops, TWEEN™ 20 (0.1% by volume) was added.

These tests were carried out against *Plasmopara viticola* (PLASVI), on vines; *Phytophthora infestans lycopersici* (PHYTIN), on tomatoes; *Erysiphe graminis f.sp. tritici* (ERYGST) and *Puccinia recondita* (PUCCRT), on wheat. Each treatment was applied to two replicate plants for *Plasmopara viticola* and *Phytophthora infestans lycopersici.* In tests on *Erysiphe graminis f.sp. tritici* and *Puccinia recondita* two replicate pots each containing 6 to10 plants were used for each treatment. The *Plasmopara viticola*, *Phytophthora infestans lycopersici* and *Puccinia recondita* plants were inoculated with a calibrated fungal spore suspension one day after (Prev) chemical application. The *Erysiphe graminis f.sp. tritici* were inoculated using a 'shake' inoculation technique, six hours after (Prev) chemical application.

After chemical application and inoculation, the *Plasmopara viticola*, *Phytophthora infestans lycopersici* and *Puccinia recondita* plants were incubated under high humidity conditions and then put into an appropriate environment to allow infection to proceed, until

the disease was ready for assessment. After chemical application and inoculation, the *Erysiphe graminis f.sp. tritici* plants were put directly into an appropriate environment to allow infection to proceed. For *Plasmopara viticola*, the plants were reincubated under high humidity conditions for 24hours prior to assessment. The time period between inoculation and assessment varied from four to fourteen days according to the disease and environment. However, each individual disease was assessed after the same time period for all compounds.

Assessments were performed on a single leaf of each of the two replicate plants for *Plasmopara viticola*. For *Phytophthora infestans lycopersici,* assessments were carried out on two leaves on each of the replicate plants and a mean disease level across the two leaves was recorded per replicate. For *Erysiphe graminis f.sp. tritici* and *Puccinia recondita* assessments were carried out collectively on the plants in each replicate pot.

The disease level present (that is, the percentage leaf area covered by actively sporulating disease) was assessed visually using the banded assessment scale shown below). For each treatment, the assessed value for each replicate was then meaned before being expressed as a percentage of the mean level of disease present on the untreated control plants. This calculated value is referred to as a POCO (Percentage of Control) value.

An example of a typical calculation is as follows:

Mean disease level for treatment A = 25

Mean disease level on untreated controls = 90

$$\text{POCO} = \frac{\text{Mean disease level for treatment A}}{\text{Mean disease level on untreated controls}} \times 100 = \frac{25}{90} \times 100 = 27.8$$

This POCO value is then rounded to the nearest whole number on a 0-100% scale; in this particular example, the POCO result will be 28.

The POCO results are shown below.

Compound Number (Table)	ERYSGT (foliar)	PHYTIN (foliar)	PLASVI (foliar)	PUCCRT (foliar)
1 (1)	0	3	0	0
3 (1)	0	0	33	0
4 (1)	0	100	100	0
5 (1)	0	100	0	0
6 (1)	0	-	0	0
7 (1)	0	100	100	0
8 (1)	0	0	0	0
9 (1)	100	0	3	0

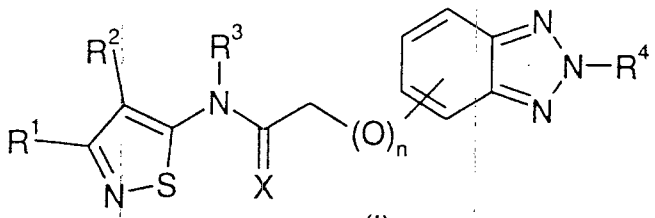
ERYSGT = *Erysiphe graminis tritici*

PHYTIN = *Phytophthora infestans lycopersici*

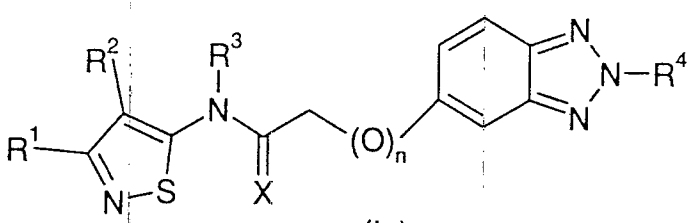
PLASVI = *Plasmopara viticola*

PUCCRT = *Puccinia recondita*

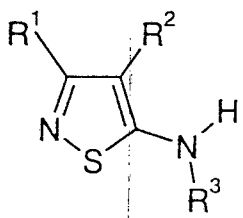
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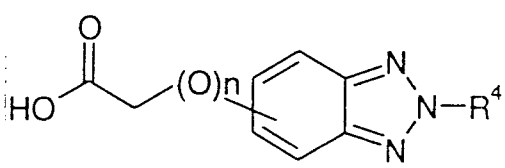
(I)



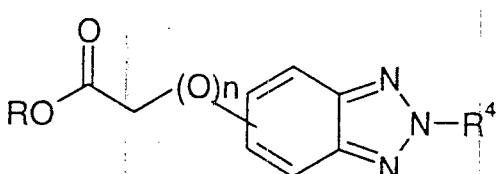
(Ia)



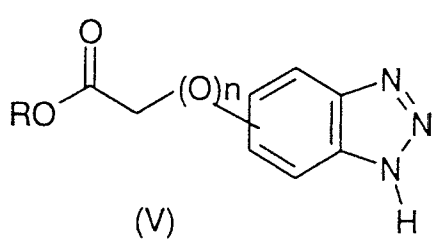
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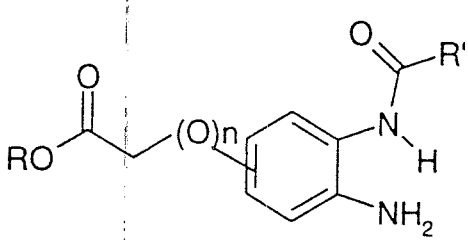
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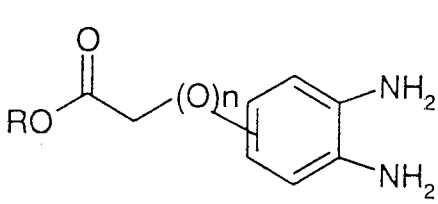
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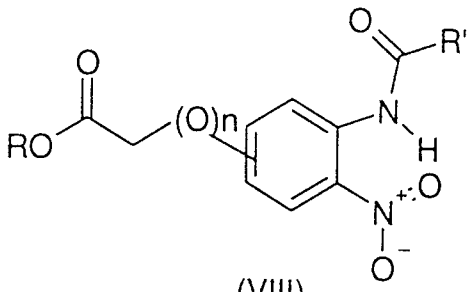
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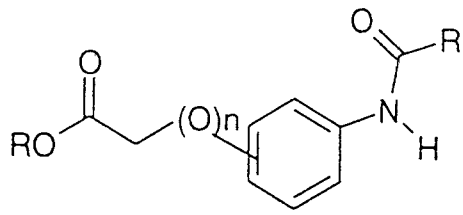
(VI)



(VII)



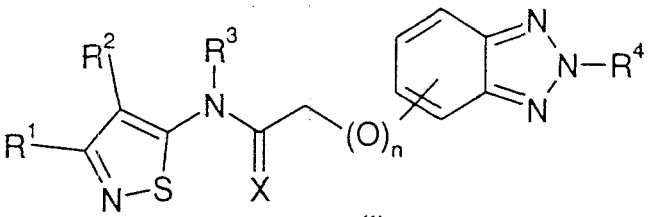
(VIII)



(IX)

CLAIMS

1. A compound of formula (I):



(I)

wherein R^1 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{3-6} cycloalkyl or C_{1-6} alkoxy(C_{1-6})alkyl; R^2 is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, cyano, nitro, CHO, CH=NOR^5, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or C_{1-6} alkyl$S(O)_q$; or together R^1 and R^2 form a five or six membered saturated or unsaturated carbocyclic ring, optionally substituted by one or two C_{1-6} alkyl groups; R^3 is hydrogen, C_{1-6} alkyl, CH_2(C_{1-4} haloalkyl), C_{3-6} alkenyl, C_{3-6} alkynyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, formyl, optionally substituted phenoxycarbonyl, optionally substituted phenyl(C_{1-4})alkyl or $S(O)_pR^6$; R^4 is hydrogen, C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{3-6} alkenyl, C_{3-6} alkynyl, C_{3-7} cycloalkyl, C_{3-6} cycloalkyl(C_{1-6})alkyl, C_{3-6} haloalkenyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted phenyl(C_{1-4})alkyl or optionally substituted heteroaryl; R^5 is hydrogen, C_{1-6} alkyl, optionally substituted phenyl or optionally substituted phenyl(C_{1-4})alkyl; R^6 is C_{1-6} alkyl, C_{1-6} haloalkyl or optionally substituted phenyl; X is O or S; n is 0 or 1; and p and q are, independently, 0, 1 or 2.

2. Processes for making compounds of formula (I) as defined in claim 1.

3. A fungicidal, insecticidal, acaricidal, molluscicidal or nematicidal composition comprising a fungicidally, insecticidally, acaricidally, molluscicidally or nematicidally effective amount of a compound of formula (I) and a carrier or diluent therefor.

4. A method of combating and controlling fungi comprising applying to a plant, to a seed of a plant, to the locus of the plant or seed or to the soil a fungicidally effective amount of a compound of formula (I) as claimed in claim 1, or a composition containing a compound of formula (I) as claimed in claim 3.

5. A method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I) as claimed in claim 1, or a composition containing a compound of formula (I) as claimed in claim 3.

6. A method as claimed in claim 5 wherein the insect pests are insect pests of plants.

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TRADUCCION

Oficina de Patentes - Autoridad Ejecutiva del Departamento de Comercio e Industria.

Oficina de Patentes - Cardiff Road, Newport, South Wales NP10 8QQ

El que suscribe, funcionario debidamente autorizado para firmar y expedir certificados en representación del Controlador General, en virtud de Artículo 74(1) y (4) de la Ley de Desregulación y Contrataciones de 1994, certifica por la presente que los documentos adjuntos son copia fiel de la documentación presentada originariamente en relación con la solicitud de patente identificada en el presente certificado.

De acuerdo con el Reglamento de Patentes (Reinscripción de Sociedades) de 1982, si una compañía mencionada en este certificado y los documentos adjuntos ha sido reinscripta de acuerdo a la Ley de Sociedades de 1980 con el mismo nombre que aquél con el cual estaba inscripta inmediatamente antes de la reinscripción, excepto la sustitución o inclusión en la última parte del nombre de las palabras "public limited company" o su equivalente en galés, las referencias al nombre de la sociedad que figuren en este certificado y cualesquiera documentos adjuntos se considerarán como referidas al nombre con el cual ha sido reinscripta.

De acuerdo con la norma, las palabras "public limited company" pueden ser sustituidas por p.l.c., plc, P.L.C. o PLC.

Con la reinscripción de acuerdo a la Ley de Sociedades no se constituye una nueva entidad legal, sino que simplemente se somete a la sociedad a determinadas reglas legales societarias adicionales.

Firmado, ilegible. Fecha: 16 de marzo del 2000

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(Sello en relieve sobre oblea y cinta)

En la hoja siguiente dice:

Formulario de Patente 1/77

OFICINA DE PATENTES Oficina de Patentes - Cardiff Road, Newport, Gwent NP9 1RH

Solicitud de Patente

Recibido en mano el 20 de abril de 1999

1. Su referencia: PPD 50402/ GB/ P

2. Solicitud de patente número: **9909062.3**

3. Nombre completo, domicilio y código postal del o los solicitantes:

ZENECA Limited, 15 Stanhope Gate, LONDON WIY 6LN, REINO UNIDO

Número ADP de patentes: 6254007002

Si el solicitante es una corporación, indicar el país/estado : REINO UNIDO

4. Título de la Invención : **COMPUESTOS QUIMICOS**

5. Nombre del agente (si corresponde) :

FRANCIS JOHN TIERNEY

Domicilio de servicio en el Reino Unido al cual se debe enviar la correspondencia:

Intellectual Property Dept., ZENECA Pharmaceuticals, Jealott's Hill Research Station, PO Box 3538, Bracknell Berkshire RG42 6YA, Mereside, REINO UNIDO

Número de ADP de patentes: 06786941001

9. Indique la cantidad de hojas de todos los siguientes adjuntos que ingresa con este formulario. No cuente copias de un mismo documento.

Hojas de continuación de este formulario :

Memoria descriptiva: 35

Reivindicaciones: 2

11. Solicito/solicitamos el otorgamiento de una patente sobre la base de esta solicitud. Firmado. Fecha: 20/04/99

12. Nombre y número telefónico del representante en el Reino Unido:

VIJAYA KUMARI MALLIPEDDI - 01344 414365

DAWN LISA ROYAL - 01344 414079

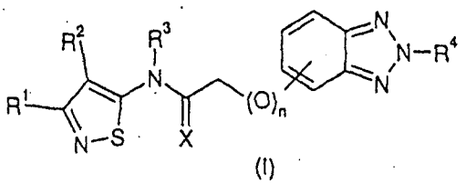
Otros items en blanco.

COMPUESTOS QUÍMICOS

La presente invención se relaciona con derivados isotiazol, con procesos para prepararlos, con composiciones fungicidas, insecticidas, acaricidas, molusquicidas y nematicidas que los comprenden, con métodos para usarlos para combatir enfermedades provocadas por hongos (especialmente enfermedades provocadas por hongos en las plantas) y con métodos para usarlos para combatir y controlar plagas de insectos, ácaros, moluscos y nematodos.

En WO95/31448, WO97/18198, WO98/02424 y WO98/05670 se describen derivados isotiazol.

La presente invención provee un compuesto de fórmula (I):



(I)

en donde R^1 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi, C_{1-6} haloalcoxi, C_{1-6} alquiltio, C_{3-7} cicloalquilo o C_{1-6} alcoxi (C_{1-6}) alquilo; R^2 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, ciano, nitro, CHO, $CH=NOR^5$, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo o C_{1-6} alquil$S(O)_q$; o juntos R^1 o R^2 forman un anillo carbocíclico saturado o insaturado de cinco o seis miembros, opcionalmente sustituido por uno o dos grupos C_{1-6} alquilo; R^3 es hidrógeno, C_{1-6} alquilo, CH_2(C_{1-4} haloalquilo), C_{3-6} alquenilo, C_{3-6} alquinilo, C_{1-6} alcoxi(C_{1-6})alquilo, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo, formilo, fenoxicarbonilo opcionalmente sustituido, fenil(C_{1-4})alquilo opcionalmente sustituido o $S(O)_pR^6$; R^4 es hidrógeno, C_{1-8} alquilo, C_{1-6} haloalquilo, C_{1-6} cianoalquilo, C_{3-6} alquenilo, C_{3-6} alquinilo, C_{3-7} cicloalquilo, C_{3-7} cicloalquil (C_{1-6})

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alquilo, C_{3-6} haloalquenilo, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{1-6} carboxialquilo, C_{1-6} alquilcarbonil (C_{1-6}) alquilo, C_{1-6} alcoxicarbonil (C_{1-6}) alquilo, C_{1-6} alquiltio (C_{1-6}) alquilo, C_{1-6} alquilsulfinil (C_{1-6}) alquilo, C_{1-6} alquilsulfonil (C_{1-6}) alquilo, aminocarbonil (C_{1-6}) alquilo, C_{1-6} alquilaminocarbonil (C_{1-6}) alquilo, di(C_{1-6}) alquilaminocarbonil (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^5 es hidrógeno, (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^6 es C_{1-6} alquilo, C_{1-6} haloalquilo, o fenilo opcionalmente sustituido; X es O o S; n es 0 o 1; y p y q son, independientemente, 0, 1 o 2.

Cada porción alquilo es una cadena lineal o ramificada y es, por ejemplo, metilo, etilo, n-propilo, n-butilo, n-pentilo, n-hexilo, iso-propilo, n-butilo, sec-butilo, iso-butilo, tert-butilo o neo-pentilo.

Halógeno es flúor, cloro, bromo o yodo.

Los grupos haloalquilo son grupos alquilo que son opcionalmente sustituidos con uno o más entre los mismos u otros átomos de halógeno y son, por ejemplo, CF_3, CH_2CF_3 o CH_2CHF_2.

Fenil (C1-4) alquilo es, por ejemplo, 1-fenilet-1-il, 2-fenilet-1-il, 2-fenilprop-2-il, 3-fenilprop-1-il, pero es preferentemente bencilo.

El término heteroarilo se refiere a un anillo aromático que contiene uno o más heteroátomos (preferentemente uno o dos heteroátomos) seleccionados entre O, S y N. Entre los ejemplos de tales anillos se incluyen piridina, pirimidina, furano, tiofeno, tiazol, oxazol e isoxazol.

Para porciones de fenilo o grupos heteroarilo se prefiere que estén opcionalmente sustituidos por uno o más sustituyentes seleccionados

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independientemente entre halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{1-6} alcoxi, C_{1-6} haloalcoxi, C_{1-6} alquiltio, C_{1-6} haloalquiltio, C_{1-6} alquilsulfinilo, C_{1-6} haloalquilsulfinilo, C_{1-6} alquilsulfonilo, C_{1-6} haloalquilsulfonilo, C_{2-6} alquenilo, C_{2-6} haloalquenilo, C_{2-6} alquinilo, C_{3-7} cicloalquilo, nitro, ciano, CO_2H, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo, R^8R^9N o $R^{10}R^{11}NC(O)$; en donde R^8, R^9, R^{10} y R^{11} son, independientemente, hidrógeno o C_{1-6} alquilo.

Se prefiere que R1 sea etilo o, especialmente, metilo.

Se prefiere que R2 sea hidrógeno, halógeno (especialmente cloro) o ciano.

Se prefiere que n sea 0.

Se prefiere que los compuestos de la invención sean de la fórmula (Ia).

En un aspecto adicional, la presente invención provee un compuesto de fórmula (Ia), en donde R^1 es C_{1-4} alquilo (especialmente metilo o etilo); R^2 es hidrógeno, halógeno (especialmente cloro o bromo) o ciano; o juntos R^1 y R^2 forman un anillo ciclopentilo, ciclohexilo o fenilo; R^3 es hidrógeno, C_{1-4} alquilo (especialmente metilo o etilo), fenil (C_{1-4}) alquilo (especialmente bencilo), C_{1-4} alquilcarbonilo (especialmente acetilo) o C_{1-4} alquilsulfonilo (especialmente metansulfonilo); R^4 es C_{1-6} alquilo [opcionalmente sustituido con halógeno, C_{1-4} alcoxi, fenilo (el mismo opcionalmente sustituido con halógeno), CO_2H, $CONH_2$ (el mismo opcionalmente sustituido con C_{1-4} alquilo), ciano, C_{3-6} cicloalquilo o $CO(C_{1-4}$ alcoxi)], C_{3-6} alquenilo, C_{3-6} alquinilo, C_{3-6} cicloalquilo, fenilo [opcionalmente sustituido con halógeno, C_{1-4} haloalquilo (especialmente CF_3), nitro, CO_2H, o ciano] o heteroarilo (especialmente piridilo o pirimidinilo) [opcionalmente sustituido con C_{1-4} alquilo o C_{1-4} haloalquilo].

Los compuestos en la siguientes Tablas ilustran los compuestos de la

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invención.

TABLA 1

Los compuestos de la Tabla 1 son compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es hidrógeno. X es oxígeno, n es 0 y R^4 es como se describe en la Tabla de más abajo.

Compuesto Nro. R^4 ^1H NMR □ ppm ($CDCl_3$ salvo que se establezca lo contrario)

1 n-propilo 1.0 (t, 3H); 2,15 (m, 2H); 2,35 (s, 3H); 4,0 (s, 2H); 4,7 (t, 2H); 7,35 (dd, 1H); 7,85 (d, 1H); 7,95 (d, 1H); 8,15 (b, 1H)

2 4-CF_3-C_6H_4 2,4 (s, 3H); 4,1 (s, 2H); 7,5 (m, 1H), 7,8-7,9 (m, 4H); 8,5 (bd, 2H); 10,35 (s, 1H)

3 metilo 2,35 (s, 3H); 4,0 (s, 2H); 4,5 (s, 3H); 7,35 dd, 1H), 7,8 (d, 1H); 7,9 (d, 1H); 8,05 (b, 1H)

4 4-F-$C_6H_4CH_2$ (DMSO-d6): 2,35 (s, 3H); 4,05 (s, 2H); 5,8 (s, 2H); 7,0 (m, 2H); 7,4 (m, 3H); 7,8 (m, 2H); 10,9 (b, 1H)

5 CF_3CH_2 2,4 (s, 3H); 4,0 (s, 2H); 5,3 (q, 2H); 7,4 (dd, 1H), 7,85 (d, 1H); 7,95 (d, 1H); 8,15 (b, 1H)

6 n-pentilo 0,9 (t, 3H); 1,35 (m, 4H); 2,15 (m, 2H); 2,4 (s, 3H); 4,05 (s, 2H); 4,7 (t, 2H); 7,35 (dd, 1H); 7,85 (d, 1H); 7,9 (d, 1H); 8,15 (b, 1H)

7 2-Cl-3-CF_3-C_6H_3 2,4 (s, 3H); 4,05 (s, 2H); 7,45 (dd, 1H); 7,75 (dd, 1H); 7,95 (m, 3H); 8,05 (m, 1H); 8,2 (b, 1H)

8 1-metilpropil 0,85 (t, 3H); 1,7 (d, 3H); 2,0-2,2 (m, 2H); 2,35 (s, 3H); 4,0 (s, 2H); 4,9 (m, 1H); 7,3 (dd, 1H); 7,85 (d, 1H); 7,9 (d, 1H); 8,15 (b, 1H)

9 etil 1,75 (t,3H); 2,35 (s, 3H); 4,0 (s, 2H); 4,8 (q, 2H); 7,35 (dd, 1H); 7,8 (b, 1H); 7,9 (d, 1H); 8,1 (b, 1H)

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10 2,2-dimetilpropilo 1,05 (s, 9H); 2,4 (s, 3H); 4,05 (s, 2H); 4,55 (s, 2H); 7,35 (dd, 1H); 7,85 (b, 1H); 7,95 (d, 1H); 8,15 (b, 1H)

11 n-butilo

12 2-metilpropilo

13 2-metoxietilo

14 metoximetilo

15 $CH_2CH=C(CH_3)_2$

16 2-cloroetilo

17 alilo

18 propargilo

19 CH_2CO_2H

20 $CH_2CO_2CH_3$

21 $CH_2CO_2C_2H_5$

22 $CH(CH_3)CO_2H$

23 $CH(CH_3)CO_2CH_3$

24 $CH(CH_3)CO_2C_2H_5$

25 $C(CH_3)_2CO_2H$

26 $C(CH_3)_2CO_2CH_3$

27 $C(CH_3)_2CO_2C_2H_5$

28 CH_2CONH_2

29 $CH(CH_3)CONH_2$

30 $C(CH_3)_2CONH_2$

31 $CH_2CONHCH_3$

32 $CH_2CON(CH_3)_2$

33 $CH(CH_3)CONHCH_3$

34	$CH(CH_3)CON(CH_3)_2$
34	$CH_2CO_2C(CH_3)_3$
35	cianometilo
36	pentafluoroetilo
37	ciclopentilo
38	2-fluoroetilo
39	difluorometilo
40	2-tioetoxietilo
41	CH_2-ciclopropilo
42	CH_2-ciclopentilo
43	CH_2-ciclohexilo
44	2-NO_2-C_6H_4
45	piridilo
46	5-CF_3-2-piridilo
47	C_6F_5
48	4-CO_2H-C_6H_4
49	2-Cl-4-CN-C_6H_3
50	3,5-dimetil-pirimidin-2-ilo

TABLA 2

La Tabla 2 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 3

La Tabla 3 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el

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compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 4

La Tabla 4 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 5

La Tabla 5 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 6

La Tabla 6 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 7

La Tabla 7 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es hidrógeno, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 8

La Tabla 8 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es flúor, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 9

La Tabla 9 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es bromo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

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TABLA 10

La Tabla 10 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es ciano, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 11

La Tabla 11 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es metilo, R^2 es cloro, R^3 es hidrógeno, X es oxígeno, n es 1 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 12

La Tabla 12 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 13

La Tabla 13 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 14

La Tabla 14 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 15

La Tabla 15 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 16

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La Tabla 16 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 17

La Tabla 17 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es cloro, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 18

La Tabla 18 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es hidrógeno, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 19

La Tabla 19 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es flúor, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 20

La Tabla 20 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es bromo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 21

La Tabla 21 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es etilo, R^2 es ciano, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 22

La Tabla 22 contiene 50 compuestos de la fórmula (Ia) en donde R^1 es

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etilo, R^2 es cloro, R^3 es hidrógeno, X es oxígeno, n es 1 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 23

La Tabla 23 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 24

La Tabla 24 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 25

La Tabla 25 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 26

La Tabla 26 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 27

La Tabla 27 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclopentilo, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 28

La Tabla 28 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1

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y R^2 forman un anillo ciclopentilo, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 29

La Tabla 29 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 30

La Tabla 30 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 31

La Tabla 31 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 32

La Tabla 32 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 33

La Tabla 33 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 34

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La Tabla 34 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo ciclohexilo, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 35

La Tabla 35 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es hidrógeno, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 36

La Tabla 36 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es metilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 37

La Tabla 37 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es etilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 38

La Tabla 38 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es bencilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 39

La Tabla 39 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es acetilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

TABLA 40

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La Tabla 40 contiene 50 compuestos de la fórmula (Ia) en donde juntos R^1 y R^2 forman un anillo fenilo, R^3 es metansulfonilo, X es oxígeno, n es 0 y R^4 tiene el valor para el compuesto numerado en forma correspondiente en la Tabla 1.

Los compuestos de la fórmula (I) pueden hacerse por acilación de un 5-aminoisotiazol (II) con un ácido carboxílico apropiado (III), preferentemente en presencia de un agente conocido de unión tal como la 1,3-diciclohexilcarbodiimida o la 1-(3-dimetilaminopropil)-3-etilcarbodiimida. Como alternativa, el ácido carboxílico (III) puede convertirse primero en un cloruro ácido, un anhídrido o un cloroformiato adecuado para su reacción con una amina con el fin de dar una amida; tales procedimientos se describen, por ejemplo, en J March, Advanced Organic Chemistry, Tercera Edición, John Wiley and Sons, Nueva York, 1985, páginas 370-376, y en las referencias presentes en el mismo.

Los 5-aminoisotiazoles (II) son compuestos que se pueden conseguir comercialmente o pueden ser preparados a partir de materiales iniciales disponibles comercialmente por métodos descriptos en la literatura (véanse, por ejemplo, C Oliver Kappe, Robert Flammang y Curt Wentrup, Heterocycles, Vol 37 Nº 3, 1616 (1994), A Adams y R Slack, J Chem Soc, 3061 (1959), y Ronald E Hackler, Kennet W Burow Jr, Sylvester V Kaster y David I Wickisier, J Heterocyclic Chem, 26, 1575, (1989).

Los ácidos carboxílicos (III) pueden ser preparados pos hidrólisis de sus correspondientes ésteres (IV) por los métodos descriptos en el arte. Los ésteres pueden ser elegidos para ser hidrolizados bajo condiciones neutras, básicas o acídicas, y las condiciones se eligen de tal forma que el sustituyente

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R^4 no sea afectado por la reacción de hidrólisis. Los ésteres capaces de ser hidrolizados en forma rápida en cualquier condición se conocen en la literatura, y ésteres adecuados se pueden seleccionar, por ejemplo, de la siguiente referencia: Theodor W. Greene, Protective Groups in Organic Synthesis, Capítulo 5, John Wiley & Sons, New York, 1981.

Los ésteres (IV) pueden prepararse por reacción de benzotriazoles (V) con un compuesto R^4L, en donde L es un grupo saliente adecuado tal como un halógeno. (Para reacciones de acoplamiento adecuadas véase, por ejemplo, Alan R Katritzky y Charles W Rees, Comprehensive Heterocyclic Chemistry, Pergamon Press, 1984 y las referencias allí presentes). Las reacciones tales como éstas pueden dar lugar a productos isoméricos. El isómero (IV) deseado usualmente se separa de los otros presentes por medio de técnicas estándar tales como cromatografía en columna rápida o por cristalización de una solución conteniendo uno o más solventes adecuados.

Los benzotriazoles (V) se pueden preparar por la diazotación secuencial y la hidrólisis de la diamina acilada (VI), o por hidrólisis de una diamina acilada (VI) para dar una diamina (VII) que puede ser entonces diazotada. Los procedimientos para la formación de benzotriazoles (V) de tales precursores son bien conocidos en la literatura. (véase, por ejemplo, Alan R Katritzky y Charles W Rees, Comprehensive Heterocyclic Chemistry, Pergamon Press, 1984 y las referencias allí incluidas)

Las diaminas aciladas (VI) se pueden preparar por la reducción de la correspondiente nitroanilida (VIII), que a su vez se prepara por nitración de una anilida (IX). Los procedimientos para realizar estas transformaciones son bien conocidos en la literatura. (Ver, por ejemplo, las referencias dadas en J March,

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Advanced Organic Chemistry, Tercera Edición, John Wiley and Sons, Nueva York, 1985). Las anilidas (IX) son conocidas en el arte y se pueden preparar a partir de compuestos conocidos usando procedimientos descriptos en el arte.

Los compuestos de fórmula (I) en donde R^3 es diferente a hidrógeno, se pueden preparar por medio de la reacción de un compuesto de fórmula (I) en donde R^3 es hidrógeno con un compuesto R^3L^*, en donde L^* es un grupo saliente (tal como halógeno), en forma opcional en la presencia de una base y un catalizador de transferencia de fase. Ejemplos de agentes alquilantes adecuados incluyen, haluros de alquilo tales como ioduro de metilo y sulfatos de alquilo tales como dimetilsulfato. Agentes acilantes adecuados incluyen anhídridos tales como anhídrido acético, cloruros de ácido tales como cloruro de acetilo o cloruro de benzoílo y cloroformiatos tales como etil cloroformiato. Bases adecuadas incluyen bases orgánicas tales como trietilamina, piridina, alcóxidos de metales alcalinos tales como ter-butóxido de potasio y bases inorgánicas tales como hidruro de sodio y hidróxido de sodio. Catalizadores de transferencia de fase adecuados pueden seleccionarse usando las referencias de la literatura (ver, por ejemplo, en J March, Advanced Organic Chemistry, Tercera Edición, John Wiley and Sons, Nueva York, 1985, págs. 320-322 y las referencias allí incluidas).

Un compuesto de fórmula (I) cuando X es azufre puede prepararse a partir de un compuesto de fórmula (I), cuando X es oxígeno, mediante la reacción de dicho compuesto con 2,4-bis(4-metoxifenil)–1,3-ditia–2,4-difosfetan–2,4-disulfuro (reactivo de Lawesson) o pentasulfuro de fósforo en un solvente (tal como tolueno).

Los compuestos de fórmula (I) pueden usarse para combatir y controlar

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infestaciones de plagas de insectos tales como Lepidoptera, Diptera, Homoptera y Coleoptera, y también otros invertebrados plagas, por ejemplo, plagas de ácaros, de nematodos y de moluscos. Los insectos, los ácaros, los nematodos y los moluscos se indican colectivamente de aquí en más como plagas. Las plagas que pueden ser combatidas y controladas mediante el uso de los compuestos de la invención incluyen aquellas plagas asociadas con la agricultura (término que incluye el crecimiento de cultivos para productos de comida y de fibra), con la horticultura y con la cría de animales, con los animales de compañía, con la forestación y con el almacenamiento de productos de origen vegetal (tales como la fruta, el grano y la madera), aquellas plagas asociadas con el daño a estructuras hechas por el hombre y con la transmisión de enfermedades al hombre y a los animales.

Los ejemplos de especies que pueden ser controladas por los compuestos de fórmula (I) incluyen: *Myzus persicae* (pulgón), *Aphis gossypii* (pulgón), *Aphis fabae* (pulgón), *Lygus* spp (chinche), *Dysdercus* spp (chinche del algodón), *Nilaparvata lugens* (saltamontes), *Nephotettixc incticeps* (saltamontes), *Nezara* spp (chinche de olor), *Euschistus* spp (chinche de olor), *Leptocorisa* spp (chinche de olor), *Frankliniella occidentalis* (trip), Thrips spp (trip), *Leptinotarsa decemlineata* (escarabajo de la papa de Colorado), *Anthonomus grandis* (gorgojo), *Aonidiella* spp (cochinilla), *Trialeurodes* spp (mosca blanca), *Bemisia tabaci* (mosca blanca), *Spodoptera littoralis* (oruga marchadora del algodón), *Heliothis virescens* (oruga del tabaco), *Helicoverpa armigera* (oruga del algodón), *Pieris brassicae* (mariposa blanca), *Plutella xylostella* (polilla espalda de diamante), *Agrotis* spp (oruga cortadora), *Chilo suppressalis* (taladro del arroz), *Chortiocetes terminifera* (langosta), *Diabrotica*

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spp (taladros de las raíces), *Panonychus ulmi* (ácaro rojo europeo), *Panonychus citri* (ácaro rojo de los cítricos), *Tetranychus urticae* (ácaro de dos manchas), *Tetranychus cinnabarinus* (ácaro carmín), *Phyllocoptruta oleivora* (ácaro pardo de los cítricos), *Polyphagotarsonemus latus* (ácaro ancho), *Brevipalpus* spp (ácaro chato), *Liriomyza* spp (oruga minadora de las hojas), *Musca domestica* (mosca doméstica), *Aedes aegypti* (mosquito), *Anopheles* spp (mosquito), *Culex* spp (mosquito), *Blattella germanica* (cucaracha), *Periplaneta americana* (cucaracha), *Blatta orientalis* (cucaracha), *Ostrinia nubilalis* (taladro europeo del maíz), *Meloidogyne* spp (nematode de los nudos de las raíces), *Globodera* spp y *Heterodera* spp (nematode de cistos), *Pratylenchus* spp (nematode de las lesiones) y *Deroceras reticulatum* (babosa). Ejemplos adicionales incluyen insectos que afectan en forma adversa la salud del público y de los animales.

Los compuestos de fórmula (I) son también fungicidas activos y pueden usarse para controlar uno o más de los siguientes patógenos: *Pyricularia oryzae* (*Magnaporthe grisea*) en arroz y trigo y otras *Pyricularia* spp en otros hospedadores; *Puccinia recondita*, *Puccinia striiformis* y otros hongos en trigo, *Puccinia hordei*, *Puccinia striiformis* y otros hongos en cebada, y hongos en otros hospedadores (por ejemplo, pasto, avena, café, peras, manzanas, maníes, remolacha, verduras y plantas ornamentales); *Erysiphe cichoracearum* en cucúrbitas (por ejemplo, melón); *Erysiphe graminis* (musgo polvoriento) en cebada, trigo, avena y pasto, y otros musgos polvorientos en varios hospedadores, tales como *Sphaerotheca macularis* en lúpulo, *Sphaerotheca fuliginea* en cucúrbitas (por ejemplo, pepino), *Leveillula taurica* en tomates, radicheta y pimienta verde, *Podosphaera leucotricha* en manzanas y *Uncinula*

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necator en enredaderas; *Cochliobolus* spp, *Helminthosporium* spp, *Drechslera* spp (*Pyrenophora* spp), *Rhynchosporium* spp, *Mycosphaerella graminicola* (*Septoria tritici*) y *Phaeosphaeria nodorum* (*Stagonospora nodorum*), *Pseudocercosporella herpotrichoides* y *Gaeumannomyces graminis* en cereales (por ejemplo, trigo, centeno, avena), pasto y otros hospedadores; *Cercospora arachidicola* y *Cercosporidium personatum* en maníes y otras *Cercospora* spp en otros hospedadores, por ejemplo, remolacha, bananas, soja y arroz; *Botrytis cinerea* (moho gris) en tomates, frutillas, verduras, enredaderas y otros hospedadores, y otras *Botrytis* spp en otros hospedadores; *Alternaria* spp en verduras (por ejemplo, zanahorias), aceite de colza, manzanas, tomates, papas, cereales (por ejemplo, trigo) y otros hospedadores; *Venturia* spp (incluyendo *Venturia inaequalis* (costra)) en manzanas, peras, fruta de hueso, nueces de los árboles y otros hospedadores; *Cladosporium* spp en una variedad de hospedadores, incluyendo cereales (por ejemplo, trigo) y tomates; *Monilinia* spp en fruta de hueso, nueces de los árboles y otros hospedadores; *Didymella* spp en tomates, pasto, trigo, cucúrbitas y otros hospedadores; *Phoma* spp en aceite de colza, pasto, arroz, papas, trigo y otros hospedadores; *Aspergillus* spp y *Aureobasidium* spp en trigo, plantas leñosas y otros hospedadores; *Ascochyta* spp en arvejas, trigo, centeno y otros hospedadores; *Stemphylium* spp (*Pleospora* spp) en manzanas, peras, cebollas y otros hospedadores; enfermedades de verano (por ejemplo, hongo amargo (*Glomerella cingulata*), hongo negro o hongo manchador de hojas (*Botryosphaeria obtusa*), hongo manchador de la fruta de Brooks (*Mycosphaerella pomi*), moho Cedar de la manzana (*Gymnosporangium juniperi-virginianae*), moho manchado (*Gloeodes pomigena*), mancha de mosca

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(*Schizothyrium pomi*) y hongo blanco (*Botryosphaeria dothidea*)) en manzanas y peras; *Plasmopara viticola* en enredaderas; otros mohos infecciosos, tales como *Bremia lactucae* en lechuga, *Peronospora* spp en soja, tabaco, cebollas y otros hospedadores, *Pseudoperonospora humuli* en lúpulo y *Pseudoperonospora cubensis* en cucúrbitas; *Pythium* spp (incluyendo *Pythium ultimum*) en pasto y otros hospedadores; *Phytophthora infestans* en papas y tomates, y otras *Phytophthora* spp en verduras, frutillas, palta, pimienta, ornamentales, tabaco, cacao y otros hospedadores; *Thanatephorus cucumeris* en arroz y pasto, y oras *Rhizoctonia* spp en varios hospedadores tales como trigo y centeno, maníes, verduras, algodón y pasto; *Sclerotinia* spp en pasto, maníes, papas, aceite de colza y otros hospedadores; *Sclerotium* spp en pasto, maníes y otros hospedadores; *Gibberella fujikuroi* en arroz; *Colletotrichum* spp en una variedad de hospedadores, incluyendo pasto, café y verduras; *Laetisaria fuciformis* en pasto; *Mycosphaerella* spp en bananas, maníes, cítricos, pecanas, papaya y otros hospedadores; *Diaporthe* spp en cítricos, soja, melón, peras, lupino y otros hospedadores; *Elsinoe* spp en cítricos, enredaderas, aceitunas, pecanas, rosas y otros hospedadores; *Verticillium* spp en una variedad de hospedadores, incluyendo lúpulo, papas y tomates; *Pyrenopeziza* spp en aceite de colza y otros hospedadores; *Oncobasidium theobromae* en cacao causando muerte vascular; *Fusarium* spp, *Typhula* spp, *Microdochium nivale*, *Ustilago* spp, *Urocystis* spp, *Tilletia* spp y *Claviceps purpurea* en una variedad de hospedadores, pero en particular en trigo, centeno, pasto y maíz; *Ramularia* spp en remolacha, centeno y otros hospedadores; enfermedades pos cosecha, particularmente sobre fruta (por ejemplo, *Penicillium digitatum*, *Penicillium italicum* y *Trichoderma viride* en

naranjas, *Colletotrichum musae* y *Gloeosporium musarum* en bananas y *Botrytis cinerea* en uvas); otros patógenos en enredaderas, notablemente *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarus*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* y *Stereum hirsutum;* otros patógenos en árboles (por ejemplo, *Lophodermium seditiosum*) o de leña, notablemente *Cephaloascus fragrans*, *Ceratocystis* spp, *Ophiostoma piceae*, *Penicillium* spp, *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* y *Aureobasidium pullulans;* y vectores fúngicos de enfermedades virales (por ejemplo, *Polymyxa graminis* en cereales como el vector del virus mosaico amarillo del centeno (BYMV) y *Polymyxa betae* en remolacha como el vector de rhizomania).

Un compuesto de fórmula (I) puede estar localizado acropética, basipética o localmente en un tejido vegetal para que sea activo contra uno o más hongos. Aún más, un compuesto de fórmula (I) puede ser lo suficientemente volátil como para ser activo en la fase vapor contra uno o más hongos en la planta.

La invención provee entonces un método para combatir y controlar insectos, ácaros, nematodos o moluscos que comprende aplicar una cantidad efectiva para la eliminación de insectos, de ácaros, de nematodos o de moluscos de un compuesto de fórmula (I), o de una composición que contiene un compuesto de fórmula (I), a una plaga, al sitio de una plaga o a una planta susceptible de ser atacada por una plaga, un método para combatir y controlar hongos que comprende aplicar una cantidad efectiva para la eliminación de hongos de compuesto de fórmula (I), o de una composición que contiene un compuesto de fórmula (I), a una planta, a la semilla de una planta, al sitio de la

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planta o de la semilla, al suelo o a cualquier medio de crecimiento (por ejemplo, una solución nutritiva). Los compuestos de fórmula (I) se usan preferiblemente contra insectos, ácaros, nematodos u hongos.

El término "planta", como se lo usa en la presente documentación, incluye retoños, arbustos y árboles. Además, el método fungicida de la invención incluye tratamientos protectores, curativos, sistémicos, erradicadores y antiesporulantes.

Como fungicidas, los compuestos de fórmula (I) se usan preferiblemente para propósitos agrícolas, hortícolas o decorativos bajo la forma de una composición.

Para aplicar un compuesto de fórmula (I) como un insecticida, un acaricida, un nematicida o un molusquicida a una plaga, al sitio de una plaga o a una planta susceptible de ser atacada por una plaga, o como un fungicida a una planta, a la semilla de una planta, al sitio de la planta o de la semilla, al suelo o a cualquier otro medio de crecimiento, se formula comúnmente un compuesto de fórmula (I), un diluyente o un vehículo adecuado inerte, y, opcionalmente, un agente activo en superficie. Los agentes activos en superficie son sustancias químicas que son capaces de modificar las propiedades de una interfase (por ejemplo, de una interfase sólido/líquido, líquido/aire o líquido/líquido) disminuyendo la tensión interfacial y conduciendo así a cambios en otras propiedades (por ejemplo, la dispersión, la emulsificación y el humedecimiento). Se prefiere que todas las composiciones (tanto las formulaciones sólidas como las líquidas) comprendan, en peso, de 0,0001 a 95 %, más preferiblemente de 1 a 85 %, por ejemplo, de 5 a 60 %, de un compuesto de fórmula (I). La composición de usa generalmente para el

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control de plagas o de hongos, de manera que el compuesto de fórmula (I) se aplica a una tasa de 0,1 g a 10 kg por hectárea, preferiblemente de 1 g a 6 kg por hectárea, más preferiblemente de 1 g a 1 kg por hectárea.

Cuando se lo emplea en una cobertura para semillas, se usa el compuesto de fórmula (I) a una tasa de 0,0001 g a 10 g (por ejemplo, de 0,001 g a 0,05 g), preferiblemente de 0,005 g a 10 g, más preferiblemente de 0,005 g a 4 g, por kilogramo de semilla.

En otro aspecto, la presente invención provee una composición insecticida, acaricida, nematicida, moluscicida o fungicida que comprende una cantidad efectiva para la eliminación de insectos, de ácaros, de nematodos, de moluscos o de hongos de un compuesto de fórmula (I), y un vehículo o un diluyente para el mismo. La composición es preferiblemente una composición insecticida, acaricida, nematicida o fungicida.

Las composiciones pueden elegirse entre una cantidad de tipos de formulación, incluyendo polvos esparcibles (DP), polvos solubles (SP), gránulos solubles en agua (SG), gránulos dispersables en agua (WG), polvos humedecibles (WP), gránulos (GR) (de liberación rápida o lenta), concentrados solubles (SL), líquidos miscibles con aceites (OL), líquidos de volumen ultra bajo (UL), concentrados emulsificables (EC), emulsiones (tanto de aceite en agua (EW) como de agua en aceite (EO)), concentrados en suspensión (SC), aerosoles, composiciones de niebla/humo, suspensiones en cápsulas (CS) y formulaciones para el tratamiento de semillas. El tipo de formulación elegido en cada caso dependerá del propósito particular planeado y de las propiedades biológicas del compuesto de fórmula (I).

Los polvos esparcibles (DP) pueden prepararse mezclando un

compuesto de fórmula (I) con uno o más diluyentes sólidos (por ejemplo, arcillas naturales, caolina, pirofilita, bentonita, alúmina, montmorillonita, kieselguhr, tiza, tierras de diatomeas, fosfatos de calcio, carbonatos de calcio y de magnesio, azufre, cal, harinas, talco y otros vehículos sólidos orgánicos e inorgánicos), y moliendo mecánicamente la mezcla hasta dar un polvo fino.

Los polvos solubles (SP) pueden prepararse mezclando un compuesto de fórmula (I) con una o más sales inorgánicas solubles en agua (tales como bicarbonato de sodio, carbonato de sodio y sulfato de magnesio), o con uno o más sólidos orgánicos solubles en agua (tales como los polisacáridos), y, opcionalmente, con uno o más agentes humectantes, con uno o más agentes dispersantes o con una mezcla de dichos agentes para mejorar la dispersibilidad/solubilidad en agua. La mezcla se muele luego para dar un polvo fino. Pueden granularse también composiciones similares para dar gránulos solubles en agua (SG).

Los polvos humedecibles (WP) pueden prepararse mezclando un compuesto de fórmula (I) con uno o más diluyentes o vehículos sólidos, con uno o más agentes humectantes y, preferiblemente, con uno o más agentes dispersantes, y, opcionalmente, con uno o más agentes suspensores para facilitar la dispersión en líquidos. La mezcla se muele luego para dar un polvo fino. Pueden granularse también composiciones similares para dar gránulos dispersables en agua (WG).

Los gránulos (GR) pueden formarse granulando una mezcla de un compuesto de fórmula (I) y uno o más diluyentes o vehículos sólidos en polvo, o a partir de gránulos vacíos previamente formados, absorbiendo un compuesto de fórmula (I) (o una solución del mismo en un agente adecuado)

en un material granular poroso (tal como pumita, arcillas de atapulgita, tierra de Fuller, kieselguhr, tierras de diatomeas o granos de maíz molidos) o adsorbiendo un compuesto de fórmula (I) (o una solución del mismo en un agente adecuado) en un tercer material de núcleo duro (tal como arena, silicato, carbonatos, sulfatos o fosfatos minerales), y secando si resulta necesario. Los agentes que se usan comúnmente para ayudar en la absorción o en la adsorción incluyen solventes (tales como solventes aromáticos y alifáticos de petróleo, alcoholes, éteres, cetonas y ésteres) y agentes adhesivos (tales como polivinil acetatos, polivinil alcoholes, dextrinas, azúcares y aceites vegetales). Pueden incluirse también uno o más aditivos diferentes en los gránulos (por ejemplo, un agente emulsificador, un agente humectante o un agente dispersante).

Los concentrados dispersables (DC) pueden prepararse disolviendo un compuesto de fórmula (I) en agua o en un solvente orgánico, tal como una cetona, un alcohol o un éter de glicol. Estas soluciones pueden contener un agente activo en superficie (por ejemplo, para mejorar la dilución en agua o para evitar la cristalización en un tanque de rociado).

Los concentrados emulsificables (EC) o las emulsiones de aceite en agua (EW) pueden prepararse disolviendo un compuesto de fórmula (I) en un solvente orgánico (que contiene opcionalmente uno o más agentes humectantes, uno o más agentes emulsificadores o una mezcla de dichos agentes) y, para una emulsión, adicionando sucesivamente, con agitación de corte fuerte, la mezcla a agua (que puede contener uno o más agentes humectantes, uno o más agentes emulsificadores o una mezcla de dichos agentes). Los solventes orgánicos adecuados para su uso en los ECs incluyen

cetonas (tales como ciclohexanona o metilciclohexanona) y alcoholes (tales como alcohol bencílico, alcohol furfurílico o butanol). Los solventes adecuados para su uso en los ECs o EWs incluyen aceites vegetales, pirrolidonas N-sustituidas, éteres glicólicos, hidrocarburos clorados (tales como clorobencenos) y solventes aromáticos (tales como alquilbencenos o alquilnaftalenos).

Los concentrados en suspensión (SC) pueden comprender suspensiones acuosas o no acuosas de partículas sólidas insolubles finamente divididas de un compuesto de fórmula (I). Los SCs pueden prepararse moliendo con balón o con esferas el compuesto sólido de fórmula (I) en un medio adecuado, opcionalmente con uno o más agentes dispersantes, para producir una suspensión fina de partículas del compuesto. Pueden incluirse en la composición uno o más agentes humectantes y puede incluirse un agente suspensor para reducir la tasa a la cual se establecen las partículas.

Las formulaciones de aerosol comprenden un compuesto de fórmula (I) y un propelente adecuado (por ejemplo, n-butano). Puede disolverse o dispersarse también un compuesto de fórmula (I) en un medio adecuado (por ejemplo, agua o un líquido miscible con agua, tal como n-propanol) para proveer composiciones que pueden ser usadas en bombas de rocío no presurizadas de acción manual.

Puede mezclarse un compuesto de fórmula (I) en estado seco con una mezcla pirotécnica con el fin de formar una composición adecuada para generar, en un espacio cerrado, un humo que contenga el compuesto.

Las suspensiones de cápsulas (CS) pueden prepararse de una forma similar a la preparación de formulaciones EW con un estado adicional de

polimerización, de manera que se obtiene una suspensión acuosa de gotas de aceite, en la cual cada gota de aceite está encapsulada por una cubierta polimérica y contiene un compuesto de fórmula (I) y, opcionalmente, un vehículo o un diluyente del mismo. Las composiciones pueden proveer la liberación controlada del compuesto de fórmula (I) y pueden usarse para el tratamiento de semillas. Puede formularse también un compuesto de fórmula (I) en una matriz polimérica biodegradable para proveer una liberación lenta y controlada del compuesto.

Una composición puede incluir uno o más aditivos para mejorar el desempeño biológico de la composición (por ejemplo, mejorando el humedecimiento, la retención o la distribución en superficies, la resistencia a la lluvia en superficies tratadas, o la asimilación y la movilidad de un compuesto de fórmula (I)). Tales aditivos incluyen agentes activos en superficie, agregados de rocío basados en aceites, por ejemplo, algunos aceites minerales o aceites vegetales naturales (tales como aceite de soja y aceite de semilla de colza), y mezclas de éstos con otros coadyuvantes bio-mejoradores.

Puede formularse también un compuesto de fórmula (I) para su uso en el tratamiento de semillas, por ejemplo, como una composición en polvo, incluyendo un polvo para el tratamiento seco de semillas (DS), un polvo soluble en agua (SS) o un polvo dispersable en agua para un tratamiento con jarabe (WS), o como una composición líquida, incluyendo un concentrado fluido (FS), una solución (LS) o una suspensión en cápsula (CS). Las preparaciones de DS, SS, WS, FS y las composiciones de LS son muy similares, respectivamente, a las preparaciones de DP, SP, WP, SC y a las composiciones de DC descriptas con anterioridad. Las composiciones para el

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tratamiento de semillas pueden incluir un agente para asistir en la adhesión de la composición a la semilla (por ejemplo, un aceite mineral).

Los agentes humectantes, dispersantes y emulsificadores pueden ser de tipo catiónico, anfotérico o no iónico.

Los agentes adecuados de tipo catiónico incluyen compuestos de amonio cuaternario (por ejemplo, bromuro de cetiltrimetil amonio), imidazolinas y sales de amina.

Los agentes aniónicos adecuados incluyen sales de metales alcalinos de ácidos grasos, sales de monoésteres alifáticos de ácido sulfúrico (por ejemplo, lauril sulfato de sodio), sales de compuestos aromáticos sulfonados (por ejemplo, dodecilbencensulfonato de sodio, sulfonato de butilnaftaleno y mezclas de sulfonatos de sodio de diisopropil y trimetil naftaleno), sulfatos de éter, sulfatos de alcoholes de éteres (por ejemplo, sulfato de lauret-3 sodio), carboxilatos de éter (por ejemplo, carboxilato de lauret-3 sodio), ésteres de fosfato (productos de la reacción entre uno o más alcoholes grasos y ácido fosfórico (predominantemente monoésteres) o pentóxido de fósforo (predominantemente diésteres), por ejemplo, la reacción entre alcohol laurílico y ácido tetrafosfórico, adicionalmente puede etoxilarse estos productos), sulfosuccinamatos, sulfonatos de parafina o de olefina, tauratos y lignosulfonatos.

Los agentes adecuados de tipo anfotérico incluyen las betaínas, los propionatos y los glicinatos.

Los agentes adecuados de tipo no iónico incluyen los productos de la condensación de óxido de etileno con alcoholes grasos (tales como alcohol oleílico o alcohol cetílico) o con alquilfenoles (tales como octilfenol, nonilfenol u

octilcresol), ésteres parciales derivados de ácidos grasos de cadena larga o de anhídridos de hexitol, productos de la condensación de dichos ésteres parciales con óxido de etileno, polímeros en bloque (que comprenden óxido de etileno y óxido de propileno), alcanolamidas, ésteres simples (por ejemplo, ésteres de polietilen glicol de ácidos grasos) o sus derivados etoxilados; óxidos de amina (por ejemplo, óxido de lauril dimetil amina); y lecitinas.

Los agentes suspensores adecuados incluyen coloides hidrofílicos (tales como polisacáridos, polivinilpirrolidona o carboximetilcelulosa de sodio) y arcillas de condensación (tales como bentonita o atapulgita).

Puede aplicarse un compuesto de fórmula (I) por medio de cualquiera de los métodos de aplicación conocidos para aplicar compuestos pesticidas o fungicidas: Por ejemplo, puede aplicárselo formulado o sin formular, a las plagas o a los sitios de las plagas (tales como un hábitat de las plagas, o a una planta en crecimiento que puede se afectada por las plagas) o a cualquier parte de la planta, incluyendo el follaje, los tallos, las ramas o las raíces, a la semilla ante de plantarla, o a otro medio en el cual estén creciendo las plantas o donde se las vaya a plantar (tal como el suelo que rodea las raíces, el suelo en general, el agua de riego o los sistemas hidropónicos de cultivo), en forma directa o por medio de rocío, de polvo, por volcado, como crema o como una formulación de pasta, como vapor o a través de su distribución y de su incorporación a una composición (tal como una composición granular o como una composición empaquetada en una bolsa soluble en agua) en el ambiente del suelo o en el agua.

Puede inyectarse también un compuesto de fórmula (I) en las plantas o puede rociárselo sobre la vegetación usando técnicas electrodinámicas de

rocío u otros métodos de bajo volumen, o aplicárselo por medio de sistemas de irrigación terrestre o aérea.

Las composiciones para su uso como preparaciones acuosas (soluciones o dispersiones acuosas) se suplen generalmente bajo la forma de un concentrado que contiene una alta proporción del ingrediente activo, agregándose el concentrado al agua antes de usarlo. Se requiere comúnmente que estos concentrados, que pueden incluir SLs, SCs, ECs, EWs, SGs, SPs, WPs, WGs y CSs, resistan el almacenamiento por períodos prolongados y, después de tal almacenamiento, que sean capaces de mezclarse con agua para formar preparaciones acuosas que permanezcan homogéneas por un tiempo suficiente como para permitirles ser aplicadas por medio de un equipo convencional de rocío. Tales preparaciones acuosas pueden contener cantidades variables de un compuesto de fórmula (I) (por ejemplo, de 0,0001 a 10 % en peso), dependiendo del propósito para el cual quiera usárselas.

Puede usarse un compuesto de fórmula (I) en mezclas con fertilizadores (por ejemplo, fertilizadores con nitrógeno, con potasio o con fósforo). Los tipos adecuados de formulación incluyen gránulos de fertilizador. Las mezclas contienen adecuadamente hasta un 25 % en peso del compuesto de fórmula (I).

La invención provee entonces una composición fertilizadora que comprende un fertilizador y un compuesto de fórmula (I).

Las composiciones de esta invención pueden contener otros compuestos que tengan actividad biológica, por ejemplo, micronutrientes o compuestos que tengan una actividad fungicida complementaria o que posean actividad de regulación del crecimiento vegetal, herbicida, insecticida,

nematicida o acaricida.

Mediante la inclusión de otro fungicida, la composición resultante puede tener un mayor espectro de actividad o un mayor nivel de actividad intrínseca que el compuesto de fórmula (I) por sí solo. Además, el otro fungicida puede tener un efecto sinergístico sobre la actividad fungicida del compuesto de fórmula (I).

El compuesto de fórmula (I) puede ser el único ingrediente activo de la composición o puede estar mezclado con uno o más ingredientes activos adicionales tales como un pesticida, un fungicida, un sinergista, un herbicida o un regulador del crecimiento vegetal, cuando resulte apropiado. Un ingrediente activo adicional puede proveer una composición que tenga un mayor espectro de actividad o una mayor persistencia e un lugar, que sinergice la actividad o complemente la actividad (por ejemplo, aumentando la velocidad del efecto o sobrepasando la repelencia) del compuesto de fórmula (I), o puede ayudar a evitar o prevenir el desarrollo de resistencia a componentes individuales. El ingrediente activo particular dependerá de la utilidad pretendida de la composición.

Los ejemplos de pesticidas adecuados incluyen los siguientes:

a) Piretroides, tales como permetrina, cipermetrina, fenvalerato, esfenvalerato, deltametrina, cihalotrina (en particular, lambda-cihalotrina), bifentrina, fenpropatrina, ciflutrina, teflutrina, piretroides seguros para peces (por ejemplo, etofenprox), piretrinas naturales, tetrametrina, s-bioaletrina, fenflutrina, praletrina o carboxilato de 5-bencil-3-furilmetil-(E)-(1R, 3S)-2,2-dimetil-3-(2-oxotiolan-3-ilidenmetil) ciclopropano;

b) Organofosfatos tales como, profenofos, sulprofos, acefato, metil paratión,

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metil-azinfos, s-metil demeton, heptenofos, tiometon, fenamifos, monocrotofos, profenofos, triazofos, metamidofos, dimetoato, fosfamidón, malatión, clorpirifos, fosalona, terbufos, fensulfotión, fonofos, forate, foxim, metil-pirimifos, etil-pirimifos, fenitrotión, fostiazato o diazinón;

c) Carbamatos (incluyendo carbamatos de arilo) tales como pirimicarb, triazamato, cloetocarb, carbofurano, furatiocarb, etiofencarb, aldicarb, tiofurox, carbosulfano, bendiocarb, fenobucarb, propoxur, metomil u oxamil;

d) Benzoil ureas tales como diflubenzurona, triflumurona, hexaflumurona, fllifenoxurona o clorfluazurona;

e) Compuestos orgánicos de estaño tales como cihexatina, óxido de fenbutatina o azociclotina;

f) Pirazoles tales como fipronil, tebufenpirad y fenpiroximato;

g) Macrólidos tales como avermectinas o milbernicinas, por ejemplo, abamectina, benzoato de emamectina, ivermectina, milbernicina, spinosad o azadiractina;

h) Hormonas o feromonas;

i) Compuestos organoclorados tales como endosulfano, hexacloruro de benceno, DDT, clordano o dieldrina;

j) Amidinas tales como clordimeform o amitraz;

k) Agentes fumigadores tales como cloropicrina, dicloropropano, bromuro de metilo o metam;

l) Compuestos de cloronicotinilo tales como imidacloprid, acetamiprid, nitenpiram o tiiametoxam;

m) Diacilhidrazines, tales como tebufenozida;

n) Ésteres de difenilo tales como diofenolan o piriproxifeno;

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o) Indoxacarb;

p) Clorfenapir; o

q) Pimetrozina.

Además de las clases mayores de pesticidas que se indicaron anteriormente, pueden emplearse en al composición otros pesticidas que tengan blancos particulares, si resultan apropiados para la utilidad pretendida de la composición. Por ejemplo, pueden emplearse insecticidas selectivos para cultivos particulares, por ejemplo, insecticidas específicos para taladros (tales como cartap) o insecticidas específicos para saltamontes para su uso sobre arroz. Como alternativa, pueden incluirse insecticidas o acaricidas específicos para especies/estadíos específicos de insectos en las composiciones (por ejemplo, ovo-larvicidas acaricidas tales como clofentezina, flubencimina, hexitaiazox o tetradifon; motilicidas acaricidas tales como dicofol o propargita; acaricidas tales como bromopropilato o clorobencilato; o reguladores del crecimiento tales como hidrametilnon, ciromazina, metopreno, clorfluazuro o difllibenzuro).

Los ejemplos de compuestos fungicidas que pueden incluirse en la composición de la invención son (E)-N–metil-2-(2-fenoxifenil)-2-metoxiiminoacetamida, (E)-N-metil-2-[2-(2,5- dimetiilfenoximetil) fenil]-2-metoxi-iminoacetamida, ácido (RS)-1-aminopropil-fosfónico, (RS)-4-(4-clorofenil)-2-fenil-2-(1H-1,2,4-triazol-1-ilmetil)butironitrilo, (Z)-N-but-2-eniloximetil-2-cloro-2',6'-dietilacetanilida, 1-(2-ciano-2-metoxiiminoacetil)-3-etil urea, 4-(2,2-difluoro-1,3-benzodioxol-4-il)-pirrol-3-carbonitrilo, 4-bromo-2-ciano-N,N-dimetil-6-trifluorometil-bencimidazol-1-sulfonamida, ácido 5-etil-5,8-dihidro-8-oxo(1,3)-dioxol-(4,5-g)quinolina-7-carboxílico, α-[N-(3-cloro-2,6-xilil)-2-metoxi-

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acetamido]-γ-butirolactona, N-(2-metoxi-5-piridil)-ciclopropan carboxamida, acibenzolar (CGA245704), alanicarb, aldimorph, anilazina, azaconazol, azoxistrobina, benalaxil, benomil, biloxazol, bitertanol, blasticidina S, bromuconazol, bupirimato, butenacor, butiobate, captafol, captan, carbendazim, clorhidrato de carbendazim, carboxina, carpropamid, carvona, CGA41396, CGA41397, chinometionato, cloroneb, clorotalonilo, clorozolinato, clozilacon, compuestos que contienen cobre tales como oxicloruro de cobre, oxiquinolato de cobre, sulfato de cobre, talato de cobre y mezcla de Bordeaux, cicloheximida, cymoxanilo, ciproconazol, ciprodinilo, ciprofuram, debacarb, 1,1'-dióxido de di-2-piridil disulfuro, diclofluanid, diclone, diclobutrazol, diclomezina, dicloran, cloruro de didecil dimetil amonio, dietofencarb, difenoconazol, difenzoquat, diflumetorim, tiofosfato de O, O–di–iso–propil–S-bencilo, dimefluazol, dimetconazol, dimetomorf, dimetirimol, diniconazol, dinocap, dipiritiona, ditalimfos, ditianon, dodemorf, dodina, doguadina, edifenfos, epoxiconazol, etaconazol, etirimol, etoxiquin, etil (Z)–N–bencil–N-([metil(metil-tioetilidenamino-oxicarbonil)amino]tio)-β-alaninato, etridiazol, famoxadona, fenaminosulf, fenapanil, fenarimol, fenbuconazol, fenfuram, fenhexamid (KBR2738), fenpiclonil, fenpropidin, fenpropimorf, fentin acetato, fentin hidróxido, ferbam, ferirnzone, fluazinam, fludioxonil, flumetover, fluoroimida, fluquinconazol, flusilazol, flutolanil, flutriafol, folpet, fuberidazol, furalaxil, furametpir, furconazole-cis, guazatine, hexaconazol, hidroxiisoxazol, himexazol, imazalil, imibenconazol, ipconazol, iprobenfos, iprodiona, isopropanil butil carbamato, isoprotiolano, kasugamicina, metil-kresoxim, LY186054, LY211795, LY248908, mancozeb, maneb, mefenoxam, mepanipirim, mepronil, metalaxil, metconazol, metiram, metiram-cinc, metominostrobin, metsulfovax,

miclobutanil, neoasozina, dimetilditiocarbamato de níquel, nitrotal-isopropilo, nuarimol, ofurace, compuestos de organomercurio, oxadixil, oxasulfuron, ácido oxolínico, oxpoconazol, oxicarboxina, pefurazoato, penconazol, pencicuron, óxido de fenazin, fosetil–Al, ácidos fosforosos, ftalida, picoxistrobin (ZA1963), polioxina D, poliram, probenazol, procloraz, procimidona, propamocarb, propiconazol, propineb, ácido propiónico, pyrazofos, pirifenox, pirimetanil, piroquilon, piroxifur, pirrolnitrina, compuestos de amonio cuaternario, quinconazole, quinometionato, quinoxifen, rabenazole, pentaclorofenato de sodio, espiroxamina, estreptomicina, azufre, tebuconazol, tecloftalam, tecnazeno, tetraconazol, tiabendazol, tifluzamida, 2-(tiocianometiltio)benzotiazol, metil-tiofanato, tiram, timibenconazol, metil-tolclofos, tolilfluanid, sal triacética de 1,1'-iminodi(octametilene)diguanidina, triadimefon, triadimenol, triazbutilo, triazóxido, triciclazol, tridemorf, trifloxistrobin, triforina, triflumizol, triticonazol, validamicina A, vapam, vinclozolin, XRD-563, zineb y ziram. Los compuestos de fórmula (I) pueden mezclarse con el suelo, con la turba o con el medio de generación de raíces para la protección de las plantas contra enfermedades fúngicas propias de las raíces, propias del suelo o foliares.

Los ejemplos de sinergistas adecuados para su uso en las composiciones incluyen butóxido de piperonilo, sesamex, safroxan y dodecil imidazol.

Los herbicidas y los reguladores del crecimiento vegetal que pueden incluirse en las composiciones dependerán del blanco pretendido y del efecto requerido.

Un ejemplo de herbicida selectivo para arroz que puede incluirse es el

propanilo. Un ejemplo de regulador del crecimiento vegetal que puede usarse sobre algodón es PIX™.

Algunas mezclas pueden comprender ingredientes activos que tengan diferentes propiedades físicas, químicas o biológicas, de manera que no se presten al mismo tipo de formulaciones. En estas circunstancias, pueden prepararse otros tipos de formulaciones. Por ejemplo, cuando un ingrediente activo es un sólido insoluble en agua y el otro es un líquido insoluble en agua, puede ser aún posible dispersar cada ingrediente activo en la misma fase acuosa dispersando el ingrediente activo sólido como una suspensión (usando una preparación análoga a la de un SC) pero dispersando el ingrediente activo líquido como una emulsión (usando una preparación análoga a la de un EW). La composición resultante es una formulación de suspoemulsión (SE).

La invención está ilustrada por los siguientes Ejemplos, en los que los ingredientes de más abajo son nombrados por medio de su marca comercial registrada y tienen las siguientes composiciones.

Marca Comercial Registrada	**Composición**
SYNPERONIC NP8 } SYNPERONIC NP13 }	Condensado de nonilfenol y óxido de etileno
SYNPERONIC A7	Condensado sintético de alcohol primario y óxido de etileno
AROMASOL H	Solvente de alquilbenceno
SOLVESSO 200	Diluyente orgánico inerte
KELTROL	Polisacárido
PROXEL	Bactericada

Las siguientes abreviaturas se usan a lo largo de la descripción:

s = singulete b = ancho q = cuarteto

d = doblete m = multiplete dd = doble doblete

t = triplete bd = doblete ancho

EJEMPLO 1

Este ejemplo ilustra la preparación de N-(4-cloro-3-metilisotiazol-5-il)-(2-propilbenzotriazol-5-il)acetamida (Compuesto N° 1 de la Tabla I).

Paso 1

Se suspendió ácido 4-aminofenilacético (100 g) en metanol (1000 ml) y se hizo pasar cloruro de hidrógeno gaseoso hasta que se saturó la mezcla. La mezcla se calentó a 50 °C durante 2 horas y luego se la dejó enfriar hasta temperatura ambiente. El solvente se evaporó al vacío, el residuo se capturó en una solución acuosa de bicarbonato de sodio y se lo extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío para dar 4-aminofenilacetato de metilo bajo la forma de un líquido marrón claro.

^{1}H NMR ($CDCl_3$) δ ppm: 3.5 (s,2H); 3.7 (s,3H); 6.65 (m,2H); 7.05 (m,2H).

Paso 2

Se agregó por goteo 4-aminofenilacetato de metilo (110 g, 0,667 mol) a anhídrido acético (600 ml), manteniendo la temperatura de la mezcla de reacción por debajo de 30 °C por enfriamiento externo. Una vez finalizada la adición la mezcla se enfrió a menos de 10 °C y se agregó por goteo ácido nítrico concentrado (85 ml). Una vez finalizada la adición de ácido nítrico, la mezcla se dejó calentar hasta temperatura ambiente y se la vertió sobre una mezcla de hielo y agua. El sólido precipitado se recolectó por filtrado y se los secó para dar 4- acetamido -3 - Nitrofenilacetato de metilo (120 g) bajo la forma

de un sólido amarillo pálido.

^{1}H NMR ($CDCl_3$) δ ppm: 2,3 (s,3H); 3,65 (s,2H); 3,7 (s,3H); 7,55 (dd,1H); 8,1 (d,1H); 8,7 (d,1H); 10,3 (b,1H).

Paso 3

Se disolvió 4-acetamido-3-nitrofenilacetato de metilo (40 g, 0,159 mol) en metanol (400 ml) y se hidrogenó a 5 bar sobre un catalizador de paladio sobre carbón al 5 %. El catalizador se eliminó por filtración y el filtrado se evaporó al vacío para dar 4-acetamido-3-aminofenilacetato de metilo.

Paso 4

Se capturó 4-acetamido-3-aminofenilacetato de metilo (77 g, 0,373 mol) en una mezcla de ácido acético (210 ml) y agua (210 ml), y se lo enfrió a menos de 5 °C. Se agregó una solución de nitrito de sodio (38,63 g, 0,559 mol) en agua (200 ml) por goteo, y, una vez finalizada la adición, la mezcla se agitó durante 4 horas, calentando lentamente hasta temperatura ambiente. La mezcla se diluyó con acetato de etilo y el material insoluble se eliminó por filtrado. El filtrado se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el solvente se evaporó al vacío para dar un residuo viscoso (51 g) que se empleó en el siguiente paso.

Paso 5

El producto obtenido en el Paso 4 anterior se disolvió en una solución de metanol (400 ml) previamente saturada con cloruro de hidrógeno, y la mezcla se agitó durante 2 horas. El solvente se eliminó al vacío, el residuo se capturó en agua, se lo neutralizó con solución saturada acuosa de bicarbonato de sodio y se lo extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se

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evaporó al vacío para dar 5-benzotriazoleacetato de metilo (35 g) bajo la forma de un líquido rojizo que se cristalizó con el reposo.

^{1}H NMR ($CDCl_3$) □ ppm: 3,7 (s,3H); 3,8 (s, 2H); 7,35 (d,1H); 7,8 (b,2H); 13.6 (b,1H).

Paso 6

Se agregó una solución de 5-benzotriazolacetato de metilo (10 g, 0,0523 mol) en N, N-dimetilformamida por goteo a una suspensión enfriada (baño de hielo) de hidruro de sodio (dispersión al 60% en aceite, 2,3 g, 0,0575 mol) en N, N - dimetilformamida. Cuando se completó la adición, el baño de hielo se eliminó y la mezcla se agitó durante 1 hora. Se agregó ioduro de N - propilo (9,78 g, 0,0575 mol) por goteo, y, una vez finalizada la adición, la mezcla se agitó a temperatura ambiente durante 3 horas. La mezcla de reacción se vertió en hielo/agua, y se la extrajo con acetato de etilo. El extracto orgánico se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío, El residuo se purificó adicionalmente por cromatografía de columna para dar (2- propilbenzotriazol -5- il) acetato de metilo (4,8 g).

^{1}H NMR ($CDCl_3$) □ ppm: 0,9 (t,3H); 2,1 (m,2H); 3,7 (s,3H); 3,8 (s,2H); 4.65 (t,2H); 7.3 (dd,1H); 7,7 (d,1H); 7.8 (d,1H).

Paso 7

El acetato preparado en el paso 6 anterior (4.8 g, 0.0206 mol) se disolvió en metanol (60 ml) y se agregaron escamas de hidróxido de potasio (1,27 g, 0,0226 mol). La mezcla se calentó a reflujo durante 2 horas, luego se enfrió y el solvente se evaporó al vacío. El sólido residual se disolvió en agua y se extrajo con éter dietílico. La solución acuosa se acidificó a pH 1 mediante el agregado

de ácido clorhídrico diluido acuoso y se la extrajo con acetato de etilo. El extracto de acetato de etilo se lavó con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío para dar ácido (2- propilbenzotriazol -5- il) acético (3,6 g) bajo la forma de un sólido incoloro.

Paso 8

El ácido preparado en el paso 7 (0,438 g, 0,002 mol) se disolvió en diclorometano (5 ml) y se agregó una gota de N,N-dimetilformamida (0,307 g, 0,0022 mol), se agregó cloruro de oxalilo por goteo, y la mezcla se agitó a temperatura ambiente durante 2 horas. El solvente se eliminó al vacío, el residuo se capturó en xileno, se lo agregó a una mezcla de 5- amino -4- cloro - 3- metilisotiazol (0,446 g, 0,003 mol) en xileno y se calentó a reflujo durante 2 horas. La mezcla se enfrió a temperatura ambiente y el solvente se evaporó al vacío. El residuo se capturó en acetato de etilo, se lo lavó secuencialmente con solución saturada acuosa de bicarbonato de sodio y con solución salina, se lo secó sobre sulfato de magnesio anhidro, se lo filtró y el filtrado se evaporó al vacío. El residuo se purificó adicionalmente por cromatografía instantánea en columna, eluyendo con 2:1 hexano:acetato de etilo, para dar el compuesto del título (0,34 g) bajo la forma de un sólido color arena.

^{1}H NMR ($CDCl_3$) □ ppm: 1,0 (t,3H); 2,15 (m,2H); 2,35 (s,3H); 4,0 (s,2H); 4.7 (t,2H); 7.35 (dd,1H); 7,85 (d,1H); 7.95 (d,1H); 8,15 (b,1H).

EJEMPLO 2

Este Ejemplo ilustra una composición concentrada emulsificable que es convertida con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. El concentrado emulsificable tiene la siguiente composición.

	% en peso
Compuesto Nro. 1	25,0
SYNPERONIC NP13	2,5
Dodecilbencensulfonato de calcio	2,5
AROMASOL H	70,0

EJEMPLO 3

Este Ejemplo ilustra una composición en polvo mojable que es convertida con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. El polvo mojable tiene la siguiente composición.

	% en peso
Compuesto Nro. 1	25,0
Sílica	25,0
Lignosulfonato de sodio	5,0
Laurilsulfato de sodio	2,0
Caolín	43,0

EJEMPLO 4

Este ejemplo ilustra un polvo capaz de ser espolvoreado que puede ser aplicado directamente a las plantas u otras superficies. El polvo espolvoreable tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	1,0
Talco	99,0

EJEMPLO 5

Este Ejemplo ilustra una formulación líquida miscible en aceite adecuada para la aplicación por técnicas de volúmenes ultra bajos después de mezclar

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con un diluyente orgánico. La formulación tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	10,0
SOLVESSO 200	90,0

EJEMPLO 6

Este Ejemplo ilustra un concentrado en suspensión en cápsulas que es convertido con facilidad, por adición en agua, en una preparación adecuada para su aplicación como un asperjado acuoso. El concentrado en suspensión en cápsulas tiene la siguiente composición.

	% en peso
Compuesto Nro. 1	10,0
AROMASOL H	70,0
Di-isocianato de tolueno	2,5
SYNPERONIC A7	1,0
Alcohol polivinílico	2,0
Bentonita	1,5
KELTROL	0,1
Agua	72,4

EJEMPLO 7

Este Ejemplo ilustra una formulación granular lista para usar que se prepara a partir de un portador granular preformado. La formulación granular tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	0,5
SOLVESSO 200	0,2

SYNPERONIC A7	0,1

Gránulos de carbonato de calcio (diámetro 0,3 - 0,7 mm) 99,2

EJEMPLO 8

Este Ejemplo ilustra una formulación granular lista para usar que se prepara por granulación de los componentes convertidos en polvo. La formulación granular tiene la siguiente composición:

	% en peso
Compuesto Nro. 1	0,5
Lignosulfonato de sodio	5,0
Caolín	94,5

EJEMPLO 9

Este Ejemplo ilustra un concentrado en suspensión acuoso que es convertido con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. El concentrado en suspensión tiene la siguiente composición.

	% en peso
Compuesto Nro. 1	25,0
Lignosulfonato de sodio	3,0
Propilénglicol	10,0
Bentonita	2,0
KELTROL	0,1
PROXEL	0,1
Agua	59,8

EJEMPLO 10

Este Ejemplo ilustra una formulación en gránulos dispersable en agua que

es convertida con facilidad, por adición en agua, en una preparación adecuada para propósitos de asperjado. Los gránulos dispersables en agua tienen la siguiente composición.

	% en peso
Compuesto Nro. 1	25,0
Sílica	5,0
Lignosulfonato de sodio	10,0
Laurilsulfato de sodio	5,0
Montmorillonita en polvo	45,0

EJEMPLO 11

Este ejemplo ilustra las propiedades pesticidas/insecticidas de los compuestos de fórmula (I). Se determinaron las actividades de compuestos de fórmula (I) individuales usando una variedad de plagas. Con excepción de los nematodos, las plagas se trataron con una composición líquida que contenía 500 partes por millón (ppm) en peso de un compuesto, salvo indicación en contrario. Cada composición se hizo disolviendo el compuesto en una mezcla de acetona y etanol (50:50 en volumen) y diluyendo la solución con agua que contenía 0,05 % en volumen de un agente humectante, SYNPERONIC NP8, hasta que la composición líquida contuvo la concentración deseada de compuesto.

El procedimiento de prueba adoptado respecto de cada plaga, excepto para nematodos, fue esencialmente el mismo y comprendió apoyar una cantidad de la peste en un medio que era comúnmente un sustrato, una planta hospedadora o un alimento sobre el cual se alimentaban las plagas, y tratar el medio y/o las plagas con una composición. Se evaluó la mortalidad de las

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plagas usualmente entre tres y cinco días después del tratamiento. La capacidad de volteo de la mosca doméstica (*Musca domestica*) se evaluó 15 minutos después del tratamiento.

El procedimiento de prueba para nematodos involucró la disolución del compuesto en una mezcla de acetona y etanol (50:50 en volumen) y diluyendo la solución con agua para obtener una concentración final del compuesto de 12,5 ppm. 12 ejemplares juveniles infecciosos de *Meloidogyne incognita* se suspendieron en la solución en un recipiente de vidrio y se calculó la mortalidad después de un período de tres días.

Los resultados de las pruebas se presentan a continuación. Los resultados indican un grado de mortalidad (puntuación) designado como 99, 55 ó 0, en donde 99 indica un 80 a 100 % de mortalidad, 55 indica un 40 a 79 % de mortalidad y 0 indica menos de 40 % de mortalidad.

Compuesto Nro. (Tabla)	TETRUR	MYZUPE	MUSCDOA	MUSCDOAC	HELIVI	LAPHEG	MELGIN
1 (1)	99	0	-	-	99	99	55
3 (1)	0	99	0	55	55	55	0
4 (1)	0	0	0	0	55	0	0
5 (1)	99	0	99	99	0	55	99
6 (1)	55	55	0	55	0	99	99
7 (1)	99	55	0	99	99	99	0
8 (1)	99	99	99	99	55	99	55
9 (1)	0	99	99	99	55	0	0
10 (1)	99	55	99	99	99	99	0

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TETRUR = Tetranycus urticae MYZUPE = Myzus persicae

MUSCO AK=Musca domestica (muerte) MUSCDO AC=Musca domestica (volteo)

HELIVI=Heliotis viriscens LAPHEG=

MELGIN=Meloidogyne incognita

EJEMPLO 12

Este ejemplo ilustra las propiedades fungicidas de compuestos de fórmula (I). Los compuestos se evaluaron contra una variedad de enfermedades foliares de plantas causadas por hongos. La técnica empleada fue como se describe a continuación.

Se cultivaron plantas en John Innes Potting Compost (N° 1 ó 2) en minimacetas de 4 cm de diámetro y 3,5 cm de profundidad. Se formularon las muestras de prueba en forma individual como una solución ya sea en acetona o en acetona/etanol (1:1 en volumen), la cual se diluyó en agua deionizada hasta una concentración de 100 ppm (es decir, 1 mg de compuesto en un volumen final de 10 ml) inmediatamente antes de usarla.

Se aplicaron compuestos individuales de fórmula (I) como una aplicación foliar (Folr) (donde se aplicó la solución química al follaje de las plantas de prueba rociando la planta hasta su retención máxima de gotas). Cuando los asperjados foliares fueron aplicados a cultivos de monocotiledóneas, se adicionó TWEEN™ 20 (0,1 % en volumen).

Se llevaron a cabo estas pruebas contra *Plasmopara viticola* (PLASVI), en vides; contra *Phytophthora infestans lycopersici* (PHYTIN), en tomates; contra *Erysiphe graminis f. sp. tritici* (ERYGST); y contra *Puccinia recondita* (PUCCRT), en trigo. Se aplicó cada tratamiento a dos plantas replicadas para

Plasmodora viticola y *Phytophthora infestans lycopersici.* Para las pruebas en *Erysiphe graminis f. sp. tritici* y *Puccinia recondita*, se usaron dos macetas replicadas que contenían, cada una, de 6 a 10 plantas para cada tratamiento. Las plantas de *Plasmopara viticola, Phytophthora infestans lycopersici* y *Puccinia recondita* se inocularon con una suspensión calibrada de esporas de hongos un día después de (Prev) de la aplicación química. Se inocularon las plantas de *Erysiphe graminis f. sp. tritici* usando una técnica de inoculación por "sacudida", seis horas después (Prev) de la aplicación química.

Después de la aplicación química y la inoculación, se incubaron las plantas de *Plasmopara viticola, Phytophthora infestans lycopersici* y *Puccinia recondita* bajo condiciones de alta humedad y se las colocó luego en un ambiente apropiado para permitir que procediera la infección, hasta que la enfermedad pudiera ser evaluada. Después de la aplicación química y la inoculación, se dispusieron las plantas de *Erysiphe graminis f. sp. tritici* bajo condiciones apropiadas para permitir que procediera la infección. Para *Plasmopara viticola,* las plantas se volvieron a incubar bajo condiciones de elevada humedad por 24 horas previas a la evaluación. El período de tiempo entre la aplicación química y la evaluación varió de cuatro a catorce días de acuerdo con la enfermedad y con el ambiente. Sin embargo, cada enfermedad individual se evaluó después del mismo período de tiempo para todas las muestras.

Se llevaron a cabo las evaluaciones en una sola hoja de cada una de las dos plantas replicadas para *Plasmopara viticola*. Para *Phytophthora infestans lycopersici,* las evaluaciones se llevaron a cabo en dos hojas de cada una de las plantas replicadas y el nivel de enfermedad promedio a lo largo de las dos

hojas se asentó por réplica. Las evaluaciones de *Erysiphe graminis f. sp. tritici* y *Puccinia recondita* se llevaron a cabo colectivamente sobre las plantas en cada maceta replicada.

Se evaluó visualmente el nivel presente de enfermedad (es decir, el porcentaje del área de la hoja cubierto por la enfermedad activamente esporulante) usando la escala de determinación en tiras mostrada más bajo. Para cada tratamiento, se promediaron los valores evaluados en todas las réplicas con el fin de obtener valores promedio de enfermedad presente en las plantas control sin tratar. Este dato calculado se refiere como un valor POCO (Porcentaje de Control).

Un ejemplo de un cálculo típico es como sigue:

Nivel promedio de enfermedad para el tratamiento A = 25 %

Nivel promedio de enfermedad para controles sin tratar = 90 %

$$\text{POCO} = \frac{\{\text{Nivel promedio de enfermedad para el tratamiento A}\}}{\{\text{Nivel promedio de enfermedad para controles sin tratar}\}} \times 100 =$$

$$= \frac{25}{90} \times 100 = 27{,}8$$

Este valor POCO se redondea luego hacia el número entero más cerca en una escala de 0 - 100 %; en este ejemplo particular, el resultado del POCO será 28.

Los resultados de POCO se indican a continuación:

Compuesto Nro. (Tabla)	ERYSGT (foliar)	PHYTIN (foliar)	PLASVI (foliar)	PUCCRT (foliar)
1 (1)	0	3	0	0
3 (1)	0	0	33	0

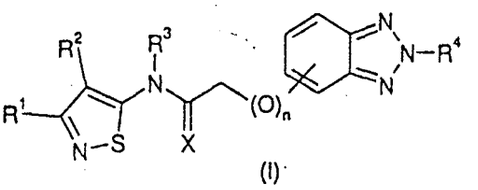
241
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4 (1)	0	100	100	0
5 (1)	0	100	0	0
6 (1)	0	-	0	0
7 (1)	0	100	100	0
8 (1)	0	0	0	0
9 (1)	100	0	3	0

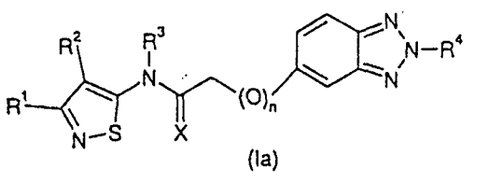
ERYSGT=*Erysiphe graminis tritici* PHYTIN= *Phytophthora infestans lycopersici*

PLASVI=*Plasmopara viticola* PUCCRT= *Puccinia recondita*

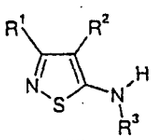
Fórmulas Químicas en la Descripción



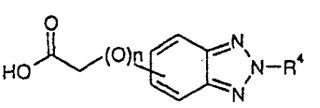
(I)



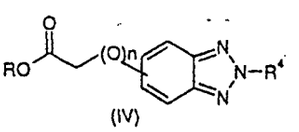
(Ia)



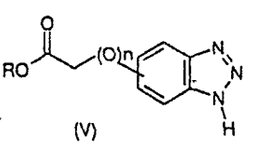
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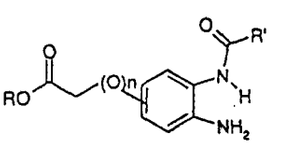
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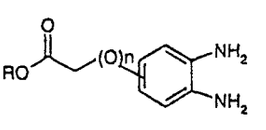
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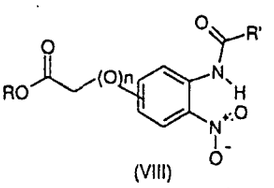
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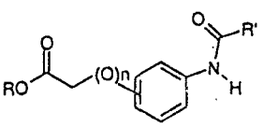
(VI)



(VII)



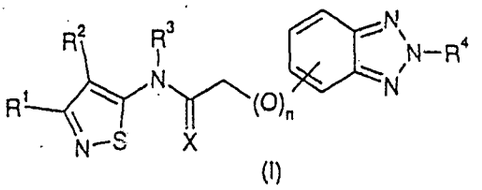
(VIII)



(IX)

REIVINDICACIONES

1. Un compuesto de fórmula (I):



(I)

en donde R^1 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, C_{1-6} alcoxi, C_{1-6} haloalcoxi, C_{1-6} alquiltio, C_{3-7} cicloalquilo o C_{1-6} alcoxi (C_{1-6}) alquilo; R^2 es hidrógeno, halógeno, C_{1-6} alquilo, C_{1-6} haloalquilo, ciano, nitro, CHO, $CH=NOR^5$, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo o C_{1-6} alquil$S(O)_q$; o juntos R^1 o R^2 forman un anillo carbocíclico saturado o insaturado de cinco o seis miembros, opcionalmente sustituido por uno o dos grupos C_{1-6} alquilo; R^3 es hidrógeno, C_{1-6} alquilo, CH_2(C_{1-4} haloalquilo), C_{3-6} alquenilo, C_{3-6} alquinilo, C_{1-6} alcoxi(C_{1-6})alquilo, C_{1-6} alquilcarbonilo, C_{1-6} alcoxicarbonilo, formilo, fenoxicarbonilo opcionalmente sustituido, fenil(C_{1-4})alquilo opcionalmente sustituido o $S(O)_pR^6$; R^4 es hidrógeno, C_{1-8} alquilo, C_{1-6} haloalquilo, C_{1-6} cianoalquilo, C_{3-6} alquenilo, C_{3-6} alquinilo, C_{3-7} cicloalquilo, C_{3-7} cicloalquil (C_{1-6}) alquilo, C_{3-6} haloalquenilo, C_{1-6} alcoxi (C_{1-6}) alquilo, C_{1-6} carboxialquilo, C_{1-6} alquilcarbonil (C_{1-6}) alquilo, C_{1-6} alcoxicarbonil (C_{1-6}) alquilo, C_{1-6} alquiltio (C_{1-6}) alquilo, C_{1-6} alquilsulfinil (C_{1-6}) alquilo, C_{1-6} alquilsulfonil (C_{1-6}) alquilo, aminocarbonil (C_{1-6}) alquilo, C_{1-6} alquilaminocarbonil (C_{1-6}) alquilo, di(C_{1-6}) alquilaminocarbonil (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^5 es

hidrógeno, (C_{1-6}) alquilo, fenilo opcionalmente sustituido, fenil (C_{1-4}) alquilo opcionalmente sustituido o heteroarilo opcionalmente sustituido; R^6 es C_{1-6} alquilo, C_{1-6} haloalquilo, o fenilo opcionalmente sustituido; X es O o S; n es 0 o 1; y p y q son, independientemente, 0, 1 o 2.

2. Procesos para fabricar compuestos de la fórmula (I) como se definen en la reivindicación 1.

3. Una composición fungicida, insecticida, acaricida, molusquicida o nematicida que comprende una cantidad eficaz como fungicida, insecticida, acaricida, molusquicida o nematicida de un compuesto de fórmula (I) y un vehículo o diluyente para el mismo.

4. Un método para combatir y controlar hongos que comprende aplicar a una planta, a una semilla de una planta, o al locus de la planta o semilla o al suelo, una cantidad eficaz como fungicida de un compuesto de fórmula (I) de acuerdo con la cláusula 1, o una composición que contiene un compuesto de fórmula (I) de acuerdo con la cláusula 3.

5. Un método para combatir y controlar insectos, ácaros, nematodos o moluscos que comprende aplicar a una plaga, al locus de una plaga o a una planta susceptible de ser atacada por una plaga una cantidad eficaz como insecticida, acaricida, nematicida o molusquicida de un compuesto de la fórmula (I) de acuerdo con la cláusula 1, o una composición que contiene un compuesto de fórmula (I) de acuerdo con la cláusula 3.

6. Un método de acuerdo con la cláusula 5 en donde las pestes de insectos son pestes de insectos de plantas.

GXP 28953

Tomo 2/2

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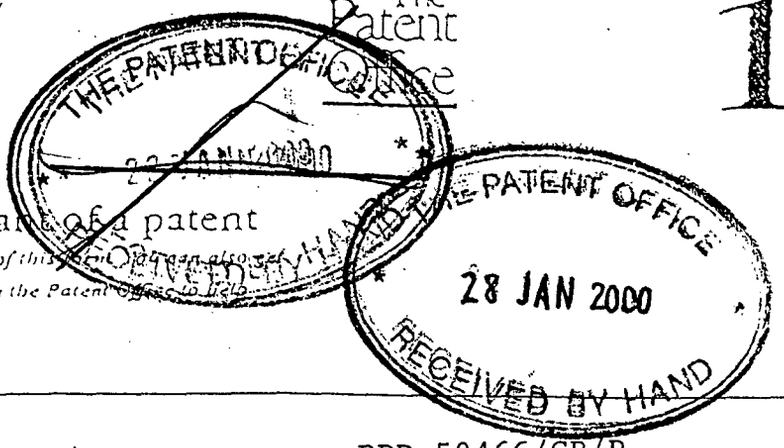
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Request for grant of a patent

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1. Your reference

PPD 50466/GB/P

31JAN00 E509118-1 D02093
P01/7700 0.00-0002039.6

2. Patent application number
(The Patent Office will fill in this part)

0002039.6

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

ZENECA Limited
15 Stanhope Gate
London W1Y 6LN
UNITED KINGDOM

Patents ADP number *(if you know it)*

6254007002

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention

CHEMICAL COMPOUNDS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

John Richard WATERMAN
Intellectual Property Department
ZENECA Agrochemicals
Jealott's Hill Research Station
P O Box 3538
Bracknell Berkshire RG42 6YA
UNITED KINGDOM

Patents ADP number *(if you know it)*

06791537001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
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11. I/We request the grant of a patent on the basis of this application.

ZENECA LIMITED

Signature D. L. Royal Date 28/6/00

Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

VIJAYA KUMARI MALLIPEDDI 01344 414365

DAWN LISA ROYAL 01344 414079

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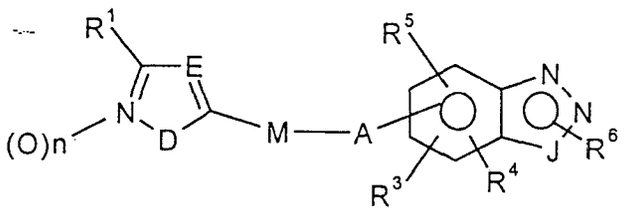
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CHEMICAL COMPOUNDS

The present invention relates to azine and azole derivatives, to processes for preparing them, to fungicidal, insecticidal, acaricidal, molluscicidal and nematicidal compositions comprising them, to methods of using them to combat fungal diseases (especially fungal diseases of plants) and to methods of using them to combat and control insect, acarine, mollusc and nematode pests.

Azole and azine derivatives are disclosed in WO95/31448, WO97/18198, WO98/02424 and WO98/05670.

The present invention provides a compound of formula (I):



(I)

wherein n is 0 or 1; A is optionally substituted C_{1-6} alkylene, optionally substituted C_{2-6} alkenylene, optionally substituted C_{2-6} alkynylene, optionally substituted C_{1-6} alkylenoxy, optionally substituted oxy(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenethio, optionally substituted thio(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenamino, optionally substituted amino(C_{1-6})alkylene, optionally substituted [C_{1-6} alkyleneoxy(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenethio(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfinyl(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfonyl(C_{1-6})alkylene] or optionally substituted [C_{1-6} alkyleneamino(C_{1-6})alkylene];

D is S, NR^{10} $CR^8=CR^9$, $CR^8=N$, $CR^8=N(O)$, $N=CR^9$ or $N(O)=CR^9$;

R^{10} is C_{1-6} alkyl

E is N, N-oxide or CR^{12};

M is $OC(=Y)$, $N(R^{51})C(=Y)$, $N=C(OR^{52})$, $N=C(SR^{53})$ or $N=C(NR^{54}R^{55})$ where O or N is the atom of attachment to the ring containing E and D;

Y is O, S or NR^{13};

J is N or CR^{14}

R^1 is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{3-7} cycloalkyl, cyano, nitro or SF_5;

R^{51} is hydrogen, optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, optionally substituted phenoxycarbonyl, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted C_{1-6} arylthio, optionally substituted C_{1-6} arylsulfinyl, optionally substituted C_{1-6} arylsulfonyl or $R^{20}R^{21}NS$;

R^{52} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, , amino, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted phenoxycarbonyl, tri(C_{1-4})alkylsilyl, aryldi(C_{1-4})alkylsilyl, (C_{1-4})alkyldiarylsilyl or triarylsilyl;

R^{53} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl or optionally substituted phenoxycarbonyl);

R^{54} and R^{55} are, independently optionally substituted C_{1-10} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, hydroxy, amino,

optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, or optionally substituted phenoxycarbonyl;

R^3, R^4 and R^5 are, independently, hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5;

R^6 is hydrogen, cyano, optionally substituted C_{1-20} alkyl, optionally substituted C_{2-20} alkenyl(C_{1-6})alkyl, optionally substituted C_{2-20} alkynyl(C_{1-6})alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{5-6} cycloalkenyl, formyl, optionally substituted C_{1-20} alkoxycarbonyl, optionally substituted C_{1-20} alkylcarbonyl, aminocarbonyl, optionally substituted C_{1-20}alkylaminocarbonyl, optionally substituted di(C_{1-20})alkylaminocarbonyl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyl, optionally substituted arylaminocarbonyl, optionally substituted N-alkyl-N-arylaminocarbonyl, optionally substituted diarylaminocarbonyl, optionally substituted heteroaryloxycarbonyl, optionally substituted heteroarylcarbonyl, optionally substituted heteroarylaminocarbonyl, optionally substituted alkylheteroarylaminocarbonyl, optionally substituted diheteroarylaminocarbonyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted heterocyclyl, optionally substituted C_{1-20} alkylsulfonyl, or optionally substituted arylsulfonyl;

R^8 and R^9 are, independently, hydrogen, halogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl or optionally substituted C_{1-6} alkoxy;

R^{12} is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, formyl, $R^{32}ON=C(R^{30})$, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5; or R^1 and R^{12} together with the atoms to which they are attached may be joined to form a five, six or seven-membered saturated or unsaturated ring carbocylic or heterocyclic ring which may contain one or two hetero atoms

selected from O, N or S and which may be optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen;

R^{13} is hydrogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted (C_{2-6})alkenyl(C_{1-6})alkyl, optionally substituted (C_{2-6})alkynyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted C_{1-6} alkylcarbonylamino, optionally substituted C_{1-6} alkoxycarbonylamino, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted arylthio, optionally substituted arylsulfinyl, optionally substituted arylsulfonyl or C_{1-6} acyloxy;

R^{14} is hydrogen, halogen, nitro, cyano, optionally substituted C_{1-8} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkylaminocarbonyl, optionally substituted di(C_{1-6})alkylaminocarbonyl, optionally substituted phenyl or optionally substituted heteroaryl;

R^{20} and R^{21} are, independently, optionally substituted C_{1-6} alkyl or R^{20} and R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

R^{30} is hydrogen, optionally substituted phenyl or optionally substituted C_{1-6} alkyl; and

R^{32} is hydrogen, optionally substituted phenyl (C_{1-2})alkyl or optionally substituted C_{1-20} alkyl.

The compounds of formula (I) may exist in different geometric or optical isomers or tautomeric forms. This invention covers all such isomers and tautomers and mixtures thereof in all proportions.

When present, optional substituents on alkylene, alkenylene or alkynylene moieties include, subject to valency constraints, one or more of halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{1-6} alkoxy(C_{1-6}) alkyl, C_{1-6} alkoxy, cyano, =O, $=NR^{33}$ and $=CR^{34}R^{35}$, wherein R^{33} is C_{1-6} alkyl, C_{1-6} haloalkyl, OR^{36} or $R^{37}R^{38}N$; where R^{34} and R^{35} are, independently,

hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy, C_{1-6} haloalkyl, cyano, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl or $R^{39}R^{40}N$; R^{36} is C_{1-6} alkyl, C_{1-6} haloalkyl or phenyl(C_{1-2})alkyl; R^{37} and R^{38} are, independently, hydrogen, C_{1-8} alkyl, C_{3-7} cycloalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl(C_{1-6})alkyl, C_{2-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, carboxy(C_{1-6})alkyl or phenyl(C_{1-2})alkyl or R^{37} and R^{38} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups; R^{39} and R^{40} are, independently, hydrogen, C_{1-8} alkyl, C_{3-7} cycloalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl(C_{1-6})alkyl, C_{2-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, carboxy(C_{1-6})alkyl or phenyl(C_{1-2})alkyl; or R^{39} and R^{40} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl or *neo*-pentyl. When present, the optional substituents on alkyl include one or more of halogen, nitro, cyano, HO_2C, C_{1-10} alkoxy (itself optionally substituted by C_{1-10} alkoxy), aryl(C_{1-4})alkoxy, C_{1-10} alkylthio, C_{1-10} alkylcarbonyl, C_{1-10} alkoxycarbonyl, C_{1-6} alkylaminocarbonyl, di(C_{1-6} alkyl)aminocarbonyl, (C_{1-6})alkylcarbonyloxy, optionally substituted phenyl, heteroaryl, aryloxy, arylcarbonyloxy, heteroaryloxy, heterocyclyl, heterocyclyloxy, C_{3-7} cycloalkyl (itself optionally substituted with (C_{1-6})alkyl or halogen), C_{3-7} cycloalkyloxy, C_{5-7} cycloalkenyl, C_{1-6} alkylsulfonyl, C_{1-6} alkylsulfinyl, tri(C_{1-4})alkylsilyl, tri(C_{1-4})alkylsilyl(C_{1-6})alkoxy, aryldi(C_{1-4})alkylsilyl, (C_{1-4})alkyldiarylsilyl and triarylsilyl.

Alkenyl and alkynyl moieties can be in the form of straight or branched chains, and the alkenyl moieties, where appropriate, can be of either the (E)- or (Z)-configuration. Examples are vinyl, allyl and propargyl. When present, the optional substituents on alkenyl or alkynyl include one or more of halogen, aryl and C_{3-7} cycloalkyl.

In the context of this specification acyl is optionally substituted C_{1-6} alkylcarbonyl (for example acetyl), optionally substituted C_{2-6} alkenylcarbonyl, optionally substituted C_{2-6}

alkynylcarbonyl, optionally substituted arylcarbonyl (for example benzoyl) or optionally substituted heteroarylcarbonyl.

Halogen is fluorine, chlorine, bromine or iodine.

Haloalkyl groups are alkyl groups which are optionally substituted with one or more of the same or different halogen atoms and are, for example, CF_3, CF_2Cl, CF_3CH_2 or CHF_2CH_2.

Aryl includes naphthyl, anthracyl, fluorenyl and indenyl but is preferably phenyl.

The term heteroaryl refers to an aromatic ring containing up to 10 atoms including one or more heteroatoms (preferably one or two heteroatoms) selected from O, S and N. Examples of such rings include pyridine, pyrimidine, furan, quinoline, quinazoline, pyrazole, thiophene, thiazole, oxazole and isoxazole.

The terms heterocycle and heterocyclyl refers to a non-aromatic ring containing up to 10 atoms including one or more (preferably one or two) heteroatoms selected from O, S and N. Examples of such rings include 1,3-dioxolane, tetrahydrofuran and morpholine. It is preferred that heterocyclyl is optionally substituted by C_{1-6} alkyl.

Cycloalkyl includes cyclopropyl, cyclopentyl and cyclohexyl. The optional substituents for cycloalkyl include halogen, cyano and C_{1-3} alkyl.

Cycloalkenyl includes cyclopentenyl and cyclohexenyl. The optional substituents for cycloalkenyl include C_{1-3} alkyl, halogen and cyano.

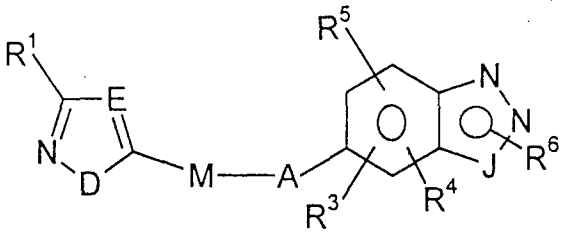
Carbocyclic rings include aryl, cycloalkyl and cycloalkenyl groups.

For substituted phenyl moieties, heterocyclyl and heteroaryl groups it is preferred that one or more substituents are independently selected from halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{2-6} alkenyl, C_{2-6} haloalkenyl, C_{2-6} alkynyl, C_{3-7} cycloalkyl, nitro, cyano, CO_2H, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, $R^{41}R^{42}N$ or $R^{43}R^{44}NC(O)$ wherein R^{41}, R^{42}, R^{43} and R^{44} are, independently, hydrogen or C_{1-6} alkyl.

It is to be understood that dialkylamino substituents include those where the dialkyl groups together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected

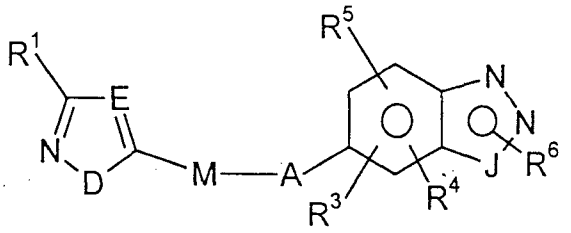
from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups. When heterocyclic rings are formed by joining two groups on an N atom, the resulting rings are suitably pyrrolidine, piperidine, thiomorpholine and morpholine each of which may be substituted by one or two (C_{1-6})alkyl groups.

In a further aspect, the present invention provides a compound of formula (IA):



(IA)

wherein A, D, E, M, Y, J, R^1, R^3, R^4, R^5 and R^6 are as defined above for a compound of formula (I). More preferred compounds of formula (IA) are those of formula (IB)



(IB)

wherein

D is S, NR^{10}, $CR^8{=}CR^9$, $CR^8{=}N$, $CR^8{=}N(O)$, $N{=}CR^9$ or $N(O){=}CR^9$;

E is N or CR^{12};

R^1 is hydrogen, halogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{1-6} cyanoalkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{3-6} cycloalkyl, C_{3-7} cycloalkyl(C_{1-4})alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, cyano, nitro or SF_5;

A is C_{1-6} alkylene, C_{1-6} alkenylene, C_{1-6} alkylenoxy, oxy(C_{1-6})alkylene, C_{1-6} alkylenamino or C_{1-6} alkylenethio, each of which is optionally substituted by C_{1-3} alkyl, C_{1-3} haloalkyl, C_{1-3} cyanoalkyl, halogen, C_{1-3} alkoxy, C_{1-6} alkoxycarbonyl, cyano, =O, $=NR^{15}$ or $=CR^{16}R^{17}$;

M is $N(R^{51})C(=Y)$ or $N=C(SR^{53})$ where O or N is the atom of attachment to the ring containing E and D;

Y is O, S or NR^{13};

J is N or CR^{14}

R^{51} is hydrogen, C_{1-10} alkyl, benzyloxymethyl, benzoyloxymethyl, C_{1-6}alkoxy(C_{1-6})alkyl, C_{2-6} alkenyl(C_{1-6})alkyl (especially allyl), C_{2-6} alkynyl(C_{1-6})alkyl (especially propargyl), C_{1-10} alkylcarbonyl or C_{1-10} alkoxycarbonyl (especially *iso*butoxycarbonyl);

R^{53} is C_{1-10} alkyl, benzyloxymethyl, benzoyloxymethyl, C_{1-6}alkoxy(C_{1-6})alkyl, C_{2-6} alkenyl(C_{1-6})alkyl (especially allyl), C_{2-6} alkynyl(C_{1-6})alkyl (especially propargyl), C_{1-10} alkylcarbonyl or C_{1-10} alkoxycarbonyl (especially *iso*butoxycarbonyl);

R^3, R^4 and R^5 are independently selected from hydrogen, halogen, C_{1-6} alkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{1-6} haloalkyl, cyano, nitro, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or SF_5;

R^6 is cyano, C_{1-8} alkyl, C_{2-6} haloalkyl, C_{1-6} cyanoalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl(C_{1-6})alkyl, C_{3-7} cycloalkyl, C_{3-7} halocycloalkyl, C_{3-7} cyanocycloalkyl, C_{1-3} alkyl(C_{3-7})cycloalkyl, C_{1-3} alkyl(C_{3-7})halocycloalkyl, C_{5-6} cycloalkenyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, C_{5-6} cycloalkenyl(C_{1-6})alkyl, C_{2-6} haloalkenyl(C_{1-6})alkyl, C_{1-6} cyanoalkenyl(C_{1-6})alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{3-6} alkenyloxy(C_{1-6})alkyl, C_{3-6} alkynyloxy(C_{1-6})alkyl, aryloxy(C_{1-6})alkyl, formyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{2-6} alkenylcarbonyl(C_{1-6})alkyl, C_{2-6} alkynylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{3-6} alkenyloxycarbonyl(C_{1-6})alkyl, C_{3-6} alkynyloxycarbonyl(C_{1-6})alkyl, aryloxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, aminocarbonyl(C_{2-6})alkenyl, aminocarbonyl(C_{2-6})alkynyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{2-6})alkenyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{2-6})alkenyl(C_{1-6})alkyl, alkylaminocarbonyl(C_{2-6})alkynyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkynyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl, aminocarbonyl, C_{1-6} alkylaminocarbonyl, di(C_{1-6})alkylaminocarbonyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{1-4})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano,

C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{2-4})alkenyl(C_{1-6})alkyl, (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy), heteroaryl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy), heterocyclyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heteroaryl(C_{1-4})alkyl (where the heteroaryl may be substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy),or heterocyclyl(C_{1-4})alkyl (where the heterocyclyl may be substituted by halo, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy);

R^8 and R^9 independently are, hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl C_{2-6} alkenyl, C_{1-6} alkynyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy;

R^{12} is hydrogen, halogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{1-6} alkynyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkoxy (C_{1-6})alkyl, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{1-6} alkylsulfinyl, C_{1-6} haloalkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylsulfonyl, C_{1-6} haloalkyl, cyano, nitro, formyl, CH=NOR^{32}, C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl or SF_5; or together R^1 and R^{12} together with the atoms to which they are attached may be joined to form a five, six or seven-membered saturated or unsaturated ring carbocylic or heterocyclic ring which may contain one or two hetero atoms selected from O, N or S and which may be optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen;

R^{13} is cyano, nitro, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{3-7} cycloalkyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, $CH_2(C_{2-6})$alkenyl, $CH_2(C_{2-6})$alkynyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy) heteroaryl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), C_{1-6} alkylcarbonyl, C_{1-6} alkoxycarbonyl, C_{1-6} alkylamino, di(C_{1-6})alkylamino, C_{1-6} alkylcarbonylamino, C_{1-6} alkoxycarbonylamino, C_{1-6} alkoxy, C_{1-6} alkylthio, C_{1-6} alkylsulfinyl, C_{1-6} alkylsulfonyl, C_{1-6} haloalkylthio, C_{1-6} haloalkylsulfinyl, C_{1-6} haloalkylsulfonyl, arylthio, arylsulfinyl, arylsulfonyl or OCO(C_{1-6})alkyl;

R^{14} is hydrogen, halogen, nitro, cyano, C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{2-6} alkenyl, C_{2-6} alkynyl, C_{3-7} cycloalkyl, C_{2-6} haloalkenyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, C_{1-6}alkox(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl, C_{1-6} alkylaminocarbonyl, di(C_{1-}

$_6$alkylaminocarbonyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} +haloalkoxy) or heteroaryl (optionally substituted by halo,nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy).

R^{15} is C_{1-6} alkyl, OR^{22} or $NR^{23}R^{24}$;

R^{16} is hydrogen, C_{1-6} alkyl or C_{1-6} haloalkyl;

R^{17} is hydrogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, cyano, C_{1-6} alkoxycarbonyl, C_{1-6} alkylcarbonyl or $NR^{46}R^{47}$;

R^{20} and R^{21} independently are, hydrogen, C_{1-6} alkyl, $CH_2(C_{1-4}$ haloalkyl), C_{1-6} cyanoalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkoxy(C_{1-6})alkoxy(C_{1-6})alkyl, phenyl(C_{1-4})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heteroaryl(C_{1-4})alkyl (wherein the heteroaryl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heterocyclyl(C_{1-4})alkyl (wherein the heterocyclyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), or R^{20} and R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

R^{22} is C_{1-6} alkyl or optionally substituted phenyl(C_{1-2})alkyl;

R^{23} and R^{24} independently are, hydrogen, C_{1-8} alkyl or phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy);

R^{30} is hydrogen or C_{1-3} alkyl;

R^{32} is C_{1-6} alkyl or phenyl(C_{1-2})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy); and

R^{46} and R^{47} independently, are, hydrogen, C_{1-8} alkyl, C_{3-7} cycloalkyl, C_{3-6} alkenyl, C_{3-6} alkynyl, C_{2-6} haloalkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, carboxy(C_{1-6})alkyl or phenyl(C_{1-2})alkyl; or R^{46} and R^{47} R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two

further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

Preferably A is C_{1-4} alkylene -C(O)- or C_{1-4} alkyleneoxy.

Preferably D is S or $CR^8=CR^9$, where R^8 and R^9 are, independently, hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl C_{2-6} alkenyl, C_{1-6} alkynyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy.

Preferably E is N or CR^{12} where R^{12} is hydrogen, halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkoxy (C_{1-6})alkyl, C_{1-6} alkylthio or SF_5; or R^1 and R^{12} together with the atoms to which they are attached form a benzene ring optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen.

A preferred value of M is $N(R^{51})C(=O)$ where N is the atom of attachment to the ring containing E and D; and R^{51} is hydrogen, C_{1-6} alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, benzyloxymethyl or benzoyloxymethyl.

Preferably Y is O

Preferably J is N or CR^{14} where R^{14} is hydrogen, C_{1-6} alkyl, C_{1-6} haloalkyl, cyano, halogen or nitro.

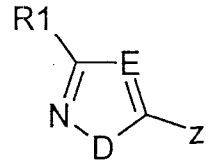
R^1 is preferably hydrogen, halogen, C_{1-6} alkyl, C_{2-6} alkenyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} haloalkoxy, C_{1-6} alkylthio, C_{1-6} haloalkylthio, C_{3-6} cycloalkyl, cyano, nitro or SF_5;

Preferably R^3, R^4 and R^5 are independently hydrogen, C_{1-3} alkyl or halogen.

R^6 is preferably C_{1-8} alkyl, C_{1-6} haloalkyl, C_{1-6} cyanoalkyl, C_{2-6} alkenyl(C_{1-6})alkyl, C_{2-6} alkynyl (C_{1-6})alkyl, C_{3-7} cycloalkyl, C_{3-7} halocycloalkyl, C_{3-7} cyanocycloalkyl, C_{1-3} alkyl(C_{3-7})cycloalkyl, C_{1-3} alkyl(C_{3-7})halocycloalkyl, C_{5-6} cycloalkenyl, C_{3-7} cycloalkyl(C_{1-6})alkyl, C_{5-6} cycloalkenyl(C_{1-6})alkyl, C_{2-6} haloalkenyl(C_{1-6})alkyl, C_{1-6} cyanoalkenyl(C_{1-6})alkyl, C_{1-6} alkoxy(C_{1-6})alkyl, C_{3-6} alkenyloxy(C_{1-6})alkyl, C_{3-6} alkynyloxy(C_{1-6})alkyl, aryloxy(C_{1-6})alkyl, C_{1-6} carboxyalkyl, C_{1-6} alkylcarbonyl(C_{1-6})alkyl, C_{2-6} alkenylcarbonyl(C_{1-6})alkyl, C_{2-6} alkynylcarbonyl(C_{1-6})alkyl, C_{1-6} alkoxycarbonyl(C_{1-6})alkyl, C_{3-6} alkenyloxycarbonyl(C_{1-6})alkyl, C_{3-6} alkynyloxycarbonyl(C_{1-6})alkyl, aryloxycarbonyl(C_{1-6})alkyl, C_{1-6} alkylthio(C_{1-6})alkyl, C_{1-6} alkylsulfinyl(C_{1-6})alkyl, C_{1-6} alkylsulfonyl(C_{1-6})alkyl, aminocarbonyl(C_{1-6})alkyl, aminocarbonyl(C_{2-6})alkenyl, aminocarbonyl(C_{2-6})alkynyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkyl, C_{1-6} alkylaminocarbonyl(C_{1-6})alkenyl(C_{1-6})alkyl, di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkenyl(C_{1-6})alkyl, alkylaminocarbonyl(C_{1-6})alkynyl(C_{1-6})alkyl,

di(C_{1-6})alkylaminocarbonyl(C_{1-6})alkynyl(C_{1-6})alkyl, phenyl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{1-4})alkyl (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl(C_{2-4})alkenyl(C_{1-6})alkyl, (wherein the phenyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy), heteroaryl (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heterocyclyl (wherein the heterocyclyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), heteroaryl(C_{1-4})alkyl (wherein the heteroaryl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkylsulfonyl or C_{1-6} haloalkoxy)or heterocyclyl(C_{1-4})alkyl (wherein the heterocyclyl group is optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy);

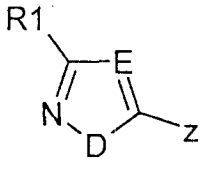
More preferred optionally substituted rings of formula



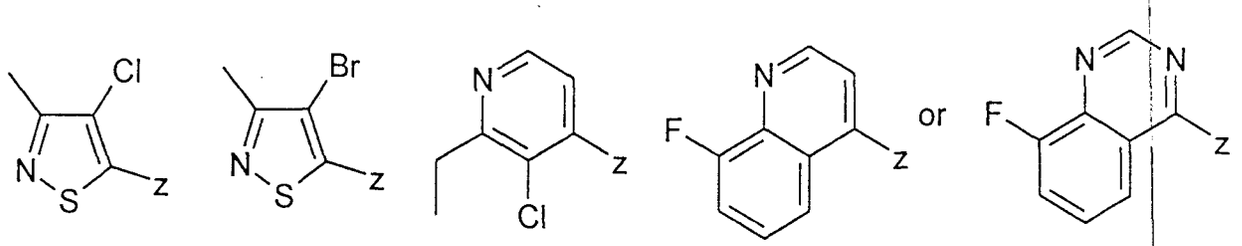
where Z represents the point of attachment to M

include optionally substituted isothiazolyl, optionally substituted pyridyl, optionally substituted pyrimidinyl, optionally substituted quinazolinyl and optionally substituted quinolinyl groups in which the optional substituents are chosen from halo, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, C_{1-6} alkoxy(C_{1-6})alkyl or C_{1-6} haloalkoxy.

Most preferred optionally substituted rings of formula



are



More preferably A is CH_2, or CH_2O, even more preferably CH_2.

It is more preferred that M is $NR^{51}C(=O)$, where R^{51} is hydrogen, C_{1-4} alkyl, C_{1-4} alkoxy (C_{1-4})alkyl, benzyloxymethyl or benzoyloxymethyl. It is especially preferred that R^{51} is hydrogen, ethyl, ethoxymethyl, allyl or propargyl

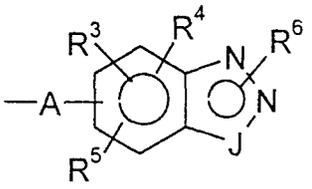
It is more preferred that R^3, R^4 and R^5 are independently, hydrogen, or halogen (especially fluorine); it is especially preferred that each of R^3, R^4 and R^5 is hydrogen.

More preferably J is N or CR^{14} where R^{14} is hydrogen, methyl, or halogen

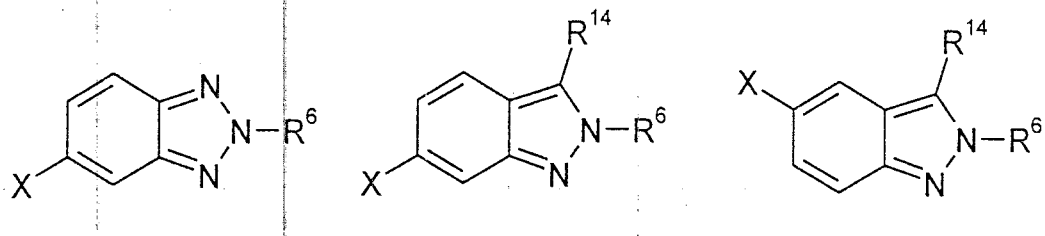
More preferably R^6 is C_{1-8} alkyl, C_{2-8} haloalkyl, C_{1-8} cyanoalkyl, C_{3-7} cycloalkyl, C_{1-3} alkyl (C_{3-7}) cycloalkyl, C_{1-6} alkoxy (C_{1-6}) alkyl, heterocyclic (optionally substituted by halo, nitro, cyano, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy or C_{1-6} haloalkoxy), phenyl (optionally substituted by halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, nitro, cyano or C_{1-6} alkylsulfonyl) or heteroaryl (optionally substituted by halogen, C_{1-6} alkyl, C_{1-6} haloalkyl, C_{1-6} alkoxy, nitro, cyano or C_{1-6} alkylsulfonyl)

Particularly preferred values of R_6 are C_{1-8} alkyl, C_{2-6} haloalkyl, C_{1-6}alkoxy(C_{1-6})alkyl, C_{3-7}cycloalkyl or C_{3-7} cycloalkyl(C_{1-6})alkyl.

Particularly preferred values of the group:

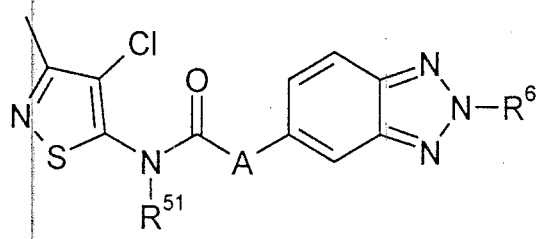


are



where X represents the position of attachment of A to the ring.

The compounds of the following Tables illustrate compounds of the invention. Table 1 provides compounds of the formula (1A'):



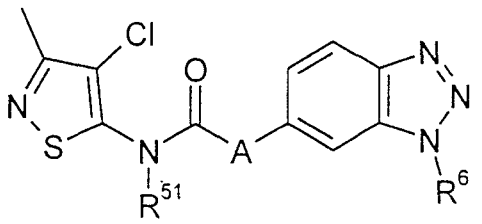
(1A')

where R^{51}, A and R^6 are as defined in Table 1.

TABLE 1

Compound No.	R^{51}	A	R^6
1.1	H	CH_2	$CH_2CH_2CH_3$
1.2	H	CH_2	CH_3
1.3	H	CH_2	*para*-fluorobenzyl
1.4	H	CH_2	CH_2CF_2
1.5	H	CH_2	$(CH_2)_4CH_3$
1.6	H	CH_2	2-chloro-4-trifluoro-methylphenyl
1.7	H	CH_2	$CH(CH_3)CH_2CH_3$
1.8	H	CH_2	CH_2CH_3
1.9	H	CH_2	$CH_2C(CH_3)_3$
1.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
1.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
1.12	H	CH_2	4-trifluoromethylphenyl
1.13	H	$CH(CH_2CH_2CH(CH_3)2)$	$CH_2CH_2CH(CH_3)_2$
1.14	H	CH_2	$CH_2CF_2OCH_3$
1.15	H	CH_2	$CH_2CH_2CH(CH_3)_2$
1.16	H	CH_2	$CH_2CH(CH_3)_2$

Table 2 provides compounds of the formula (1B')

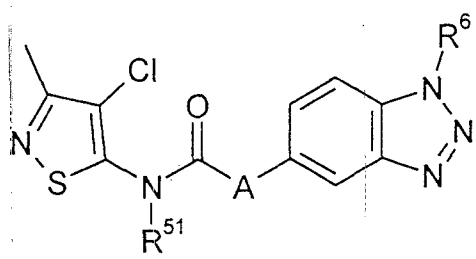


(1B')

TABLE 2

Compound No.	R^{51}	A	R^6
2.1	H	CH_2	$CH_2CH_2CH_3$
2.2	H	CH_2	CH_3
2.3	H	CH_2	*para*-fluorobenzyl
2.4	H	CH_2	CH_2CF_3
2.5	H	CH_2	$(CH_2)_4CH_3$
2.6	H	CH_2	2-chloro-4-trifluoro-methylphenyl
2.7	H	CH_2	$CH(CH_3)CH_2CH_3$
2.8	H	CH_2	CH_2CH_3
2.9	H	CH_2	$CH_2C(CH_3)_3$
2.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
2.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
2.12	H	CH_2	4-trifluoromethylphenyl
2.13	H	$CH(CH_2CH_2CH(CH_3)2)$	$CH_2CH_2CH(CH_3)_2$
2.14	H	CH_2	$CH_2CF_2OCH_3$
2.15	H	CH_2	$CH_2CH_2CH(CH_3)$
2.16	H	CH_2	$CH_2CH(CH_3)_2$
2.17	H	CH_2	$COCH_2$

Table 3 provides compounds of the formula (1C'):

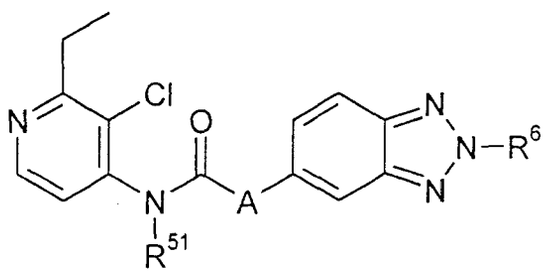


(IC')

TABLE 3

Compound No.	R^{51}	A	R^6
3.1	H	CH_2	$CH_2CH_2CH_3$
3.2	H	CH_2	CH_3
3.3	H	CH_2	*para*-fluorobenzyl
3.4	H	CH_2	CH_2CF_3
3.5	H	CH_2	$(CH_2)_4CH_3$
3.6	H	CH_2	2-chloro-4-trifluro-methylphenyl
3.7	H	CH_2	$CH(CH_3)CH2CH3$
3.8	H	CH_2	CH_2CH_3
3.9	H	CH_2	$CH_2C(CH_3)_3$
3.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
3.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
3.12	H	CH_2	4-trifluoromethyl-phenyl
3.13	H	$CH(CH_2CH_2CH(CH_3)_2)$	$CH_2CH_2CH(CH_3)_2$
3.14	H	CH_2	$CH_2CF_2OCH_3$
3.15	H	CH_2	$CH_2CH_2CH(CH_3)_3$
3.16	H	CH_2	$CH_2CH(CH_3)_2$
3.17	H	CH_2	$COCH_3$

Table 4 provides compounds of the formula (1D')

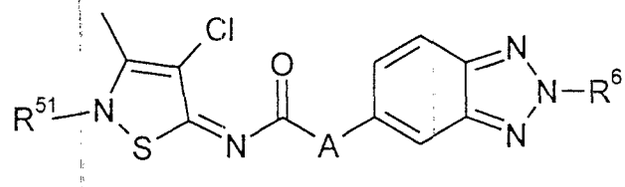


(ID')

TABLE 4

Compound No.	R^{51}	A	R^6
4.1	H	CH_2	$CH_2CH_2CH_3$
4.2	H	CH_2	CH_3
4.3	H	CH_2	*para*-fluorobenzyl
4.4	H	CH_2	CH_2CH_3
4.5	H	CH_2	$(CH_2)_4CH_3$
4.6	H	CH_2	2-chloro-4-trifluoromethylphenyl
4.7	H	CH_2	$CH(CH_3)CH_2CH_3$
4.8	H	CH_2	CH_2CH_3
4.9	H	CH_2	$CH_2C(CH_3)_3$
4.10	CH_2CH_3	CH_2	$CH_2CH_2CH_3$
4.11	$CH_2OCH_2CH_3$	CH_2	$CH_2CH_2CH_3$
4.12	H	CH_2	4-trifluoromethylphenyl
4.13	H	$CH(CH_2CH_2CH(CH_3)2)$	$CH_2CH_2CH(CH_3)_2$
4.14	H	CH_2	$CH_2CF_2OCH_3$
4.15	H	CH_2	$CH_2CH_2CH(CH_3)_2$
4.16	H	CH_2	$CH_2CH(CH_3)_2$

Table 5 provides compounds of the formula (1E')



(IE')

TABLE 5

Compound No.	R^{51}	A	R^6
5.1	CH_2CH_3	H	$CH_2CH_2CH_3$
5.2	$CH_2OCH_2CH_3$	H	$CH_2CH_2CH_3$

The following abbreviations are used throughout this description:

m.p. = melting point
ppm = parts per million
s = singlet
br = broad
d = doublet
dd = doublet of doublets
t = triplet
q = quartet
m = multiplet

Table 6 shows selected NMR data, all with $CDCl_3$, as the solvent (unless otherwise stated; if a mixture of solvents is present, this is indicated as, for example ($CDCl_3$ / *d6*-DMSO)), (no attempt is made to list all characterising data in all cases) for compounds of tables 1 - 5

TABLE 6

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
1.1	1.0 (t, 3H); 2.15 (m, 2H);2.35 (s, 3H); 4.0 (s, 2H); 4.7(t, 2H); 7.35 (dd, 1H); 7.85 (d, 1H); 7.95 (d, 1H); 8.15 (br, 1H)
1.2	2.35 (s, 3H); 4.0 (s, 2H); 4.5 (s, 3H); 7.35 (dd, 1H); 7.8 (d, 1H); 7.9 (d, 1H); 8.05 (br, 1H)
1.3	(*d6*-DMSO): 2.35 (s, 3H); 4.05 (s, 2H); 5.8 (s, 2H) 7.0 (m, 2H); 7.4 (m, 3H); 7.8 (m, 2H): 10.9 (br, 1H)

TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
1.4	2.4 (s, 3H); 4.0 (s, 2H); 5.3 (q, 2H); 7.4 (dd, 1H) 7.85 (d, 1H); 7.95 (d, 1H); 8.15 (br, 1H)
1.5	0.9 (t, 3H); 1.35 (m, 4H); 2.15 (m, 2H); 2.4 (s, 3H): 4.05 (s, 2H); 4.7 (t, 2H); 7.35 (dd, 1H); 7.85 (d, 2H); 7.9 (d, 2H); 8.15 (br, 1H)
1.6	2.4 (s, 3H); 4.05 (s, 2H); 7.45 (dd, 1H); 7.75 (dd, 1H); 7.95 (m, 3H); 8.05 (m, 1H); 8.2 (br, 1H)
1.7	0.85 (t, 3H); 1.7 (d, 3H); 2.0-2.2 (m, 2H); 2.35 (s, 3H); 4.0(s, 2H); 4.9 (m, 1H); 7.3 (dd, 1H); 7.85 (d, 1H); 7.9 (d, 1H); 8.15 (br, 1H)
1.8	1.75 (t, 3H); 2.35 (s, 3H); 4.0 (s, 2H); 4.8(q, 2H); 7.35 (dd, 1H); 7.8 (br, 1H); 7.9 (d, 1H); 8.1 (br, 1H)
1.9	1.05 (s, 9H); 2.4(s, 3H); 4.05 (s, 2H); 4.55 (s, 2H); 7.35 (dd, 1H); 7.85 (br, 1H); 7.95(d, 1H); 8.15 (br, 1H)
1.10	0.95 (t, 3H); 1.2 (t, 3H); 2.13 (m, 2H); 2.5 (s, 3H) 3.65 (br, 2H); 3.8 (br, 2H); 4.65 (t, 2H); 7.15 (br, 1H); 7.5 (br, 1H); 7.78 (dd, 1H)
1.11	0.95 (t, 3H); 1.2 (t, 3H); 2.1 (m, 2H); 2.5 (s, 3H); 3.6 (q, 2H) 3.7 (br, 2H); 4.7 (t, 2H); 5.2 (br, 2H); 7.15 (br, 1H); 7.55 (br, 1H); 7.8 (d, 1H)
1.12	2.4 (s, 3H); 4.1 (s, 2H); 7.5 (m, 1H); 7.8-7.9 (m, 4H); 8.5(br, 2H); 10.35 (s, 1H)
1.13	0.88 (dd, 6H); 1.0 (d, 6H); 1.62 (m, 4H); 2.0 (m, 2H); 2.32 (m 2H); 2.36 (s, 3H); 3.77 (dd, 1H); 4.77 (dd, 2H); 7.37 (dd, 1H); 7.83 (s, 1H); 7.9 (d, 1H); 8.06 (s, 1H)
1.14	2.39 (s, 3H); 3.61 (s, 3H); 4.03 (s, 2H); 5.19 (t, 2H) 7.40 (dd, 1H); 7.88 (s, 1H); 7.97 (d, 1H); 8.16 (s, 1H)

TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
1.15	1.0 (d, 6H); 2.03 (q, 2H); 2.17 (s, 3H); 2.37 (m, 1H); 4.0 (s, 2H); 4.77 (dd, 2H); 7.34 (dd, 1H); 7.83 (s, 1H); 7.92 (d, 1H); 8.16 (s, 1H)
1.16	1.0 (d, 6H); 2.37 (s, 3H); 2.54 (m, 1H); 4.03 (s, 2H); 4.56 (d, 2H); 7.36 (dd, 1H); 7.84 (s, 1H); 7.94 (d, 1H)
2.1	
2.2	2.35 (s, 3H); 4.1 (s, 2H); 4.23 (s, 3H); 7.3(d, 1H); 7.55 (d, 1H): 8.1 (d, 1H); 8.3 (br, 1H)
2.3	
2.4	2.4 (s, 3H); 4.1 (s, 2H); 5.25 (q, 1H); 7.6 (m, 2H); 8.1 (br, 1H); 8.25 (br, 1H)
2.5	
2.6	
2.7	
2.8	
2.9	
2.10	
2.11	
2.12	
2.13	
2.14	
2.15	
2.16	
2.17	2.40(s, 3H); 3.03 (s, 3H); 4.09 (s, 2H); 7.66 (dd, 2H); 8.10 (d, 1H); 8.2 (br, 1H); 8.34 (d, 1H)
3.1	

TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
3.2	2.35 (s, 3H); 4.1 (s, 2H); 4.3 (s, 3H); 7.55 (m, 2H); 8.0 (d, 1H); 8.3(br, 1H)
3.3	
3.4	2.4 (s, 3H); 4.05 (s, 2H); 7.4 (dd, 1H); 7.6 (d, 1H); 8.15 (d, 1H); 8.3 (br, 1H)
3.5	
3.6	
3.7	
3.8	
3.9	
3.10	
3.11	
3.12	
3.13	
3.14	
3.15	
3.16	
3.17	2.40 (s, 3H); 3.03 (s, 3H); 4.10 (s, 2H); 7.52 (dd, 2H); 8.19 (d, 1H); 8.2 (br, 1 H); 8.3 (d, 1H)
4.1	1.0 (t, 3H); 1.25 (t, 3H); 2.15 (m, 2H); 2.85 (q, 2H); 3.95 (s, 2H); 4.7 (t, 2H); 7.35 (m, 1H) 7.85 (br, 1H); 7.95 (d, 1H); 7.95 (br, 1H); 8.2 (d, 1H); 8.35 (d, 1H)
4.2	
4.3	
4.4	

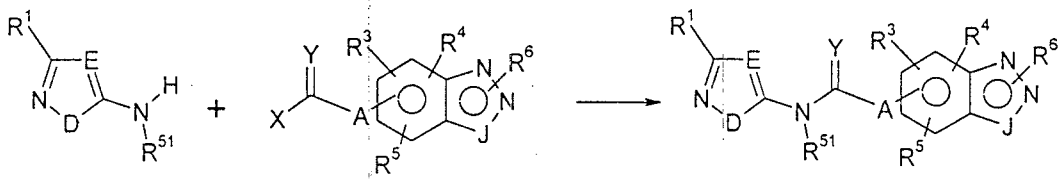
TABLE 6 (Continued)

Compound No.	1H NMR δ ppm ($CDCl_3$ unless stated)
4.5	
4.6	
4.7	
4.8	
4.9	
4.10	
4.11	
4.12	
4.13	
4.14	
4.15	
4.16	
5.1	0.95 (t, 3H); 1.4 (t, 3H); 2.12 (m, 2H); 2.5 (s, 3H); 3.9 (q, 2H); 4.2 (s, 2H), 4.65 (t, 2H); 7.42 (dd, 1H); 7.8 (br, 1H); 7.81 (br, 1H)
5.2	0.95 (t, 3H); 1.15 (t, 3H); 2.1 (m, 2H); 2.55 (s, 3H); 3.5 (q, 2H); 4.2 (s, 2H); 4.7 (t, 2H); 5.2 (s, 2H); 7.4 (dd, 1H); 7.8 (m, 2H)

The compounds of the invention may be made in a variety of ways. For example, as shown in Scheme 1, compounds (I) wherein Y is O and A is alkylene, alkenylene, alkylenoxy, alkylenamino or alkylenethio may be prepared by reacting amine (II) with an appropriate carboxylic ester (III) (X = alkoxy or aryloxy) or with a carboxylic acid (III, X = OH) in the presence of a known coupling agent such as 1,3-dicyclohexylcarbodiimide or 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide. Alternatively the carboxylic acid may first be converted to an acid chloride, anhydride or chloroformate suitable for reaction with an amine to form an amide; such procedures are well known to those skilled in the art and are

described, for example in J. March, Advanced Organic Chemistry, Third Edition, John Wiley and Sons, New York, 1985, pps 370-376 and references therein.

Scheme 1



(II) (III) (I)

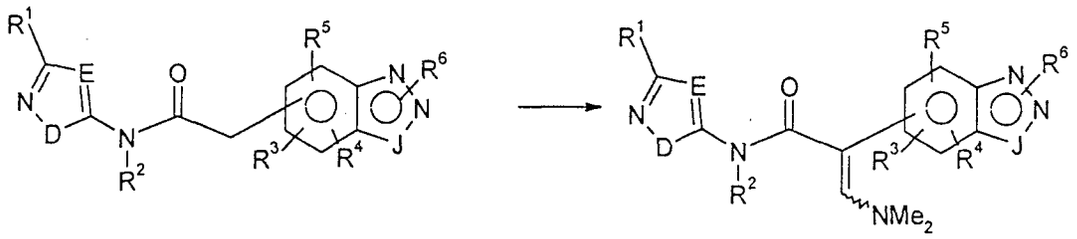
Amines (II) are known compounds, or may be prepared from commercially available starting materials by methods described in the literature (see, for example, C. Oliver Kappe, Robert Flammang, and Curt Wentrup, Heterocycles, Vol. 37, No. 3, 1615, (1994), A. Adams and R. Slack, J. Chem. Soc., 3061, (1959) and Ronald E Hackler, Kenneth W. Burow, Jr., Sylvester V. Kaster and David I. Wickiser, J. Heterocyclic Chem, 26, 1575, (1989), Ronald E Hackler, Glen P Jourdan, Peter L Johnson, Brian R Thoreen and Jack G Samaritoni, PCT Int. Appl., WO9304580 A1, and references therein).

The syntheses of substituted benzotriazoles and indazoles is described in the chemical literature (see, for example Alan R. Katritsky and Charles W. Rees, Comprehensive Heterocyclic Chemistry, Pergamon Press, 1984; Christoph Ruchardt and Volker Hassmann, Liebis Ann. Chem., 1980, 908; Jean-Jacques Vandenbossche and Alain Lagrange, Eur. Pat. Appl., EP904769; F. Halley and X. Sava, Synth. Commun. 1997, 27 (7), 1199; Donald R. James, Don R. Baker, Steven D. Mielich, William J. Michaely, Steven Fitzjohn, Christopher G. Knudsen, Christopher Mathews and John M. Gerdes, PCT Int. Appl., WO9318008 A1, Donald Richard James and Raymond Anthony Felix, PCT Int. Appl., WO9425446 A1) and similar methods may be used to prepare Compounds (III) starting from appropriately substituted anilines, as detailed in the experimental section. Alternatively, halobenzotriazoles and haloindazoles (especially where the halogen is bromo or iodo), which may be prepared by the above methods, may be converted into Compounds (III) via procedures involving transition-metal catalysed transformations analogous to those described by Nitya G. Kundu

et al., Tetrahedron, 53 (39), 13397, (1997), Takao Sakamoto et al. Heterocycles, 36 (11), 2509 (1993), Motoi Kawatsura and John F. Hartwig, JACS, 1999, 121, 1473, and others.

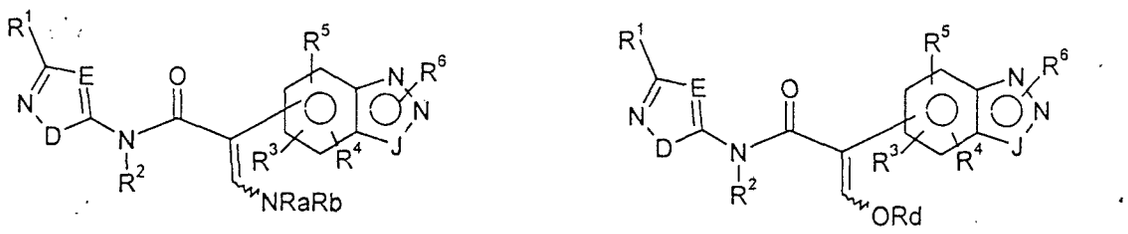
A compound of formula (I), wherein Y is sulphur, may be prepared by reacting a compound of formula (I), wherein Y is oxygen, with a suitable thionating agent such as 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Lawesson's reagent), 2,4-bis(methylthio)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy reagent methyl), 2,4-bis(*para*-tolyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide (Davy reagent *p*-tolyl) or phosphorus pentasulfide in a suitable solvent such as toluene or fluorobenzene.

Compounds of formula (IV) may be made from (V) by treatment with N,N-dimethylformamide dialkyl acetal in a suitable solvent such as toluene or N,N-dimethylformamide. Frequently this reaction produces a mixture of E and Z isomers which are sometimes separable by standard techniques such as flash column chromatography and recrystallisation. This invention covers isolated isomers together with mixtures of isomers.



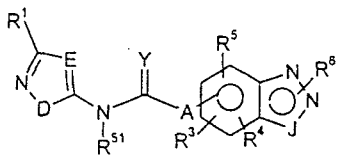
(V) (IV)

Compounds (IV) may be treated subsequently with amines (HNRaRb) to give Compounds (VI); compounds (V) may be treated in an analogous manner with trialkylorthoformates ($HC(ORd)_3$) to afford Compounds (VII):

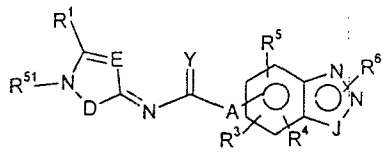


(VI) (VII)

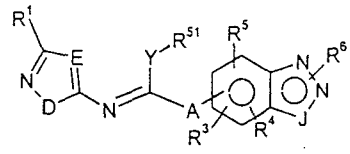
Compounds (I), wherein R^{51} is hydrogen, may be treated with an optionally substituted alkylating agent (such as an alkyl halide, chloromethylether, dialkyl sulfate or trialkyloxonium salt) optionally in the presence of a base to give additional compounds (I) wherein R^{51} is optionally substituted alkyl which form a further part of this invention. When Y is O, this reaction usually produces a mixture of isomeric products (I) and (VIII). In contrast, when Y is S, (IX) is the predominant product



(I)



(VIII)



(IX)

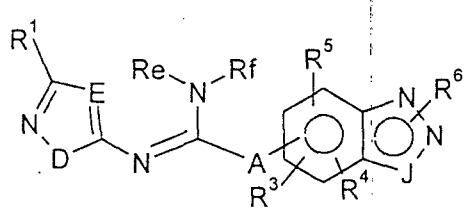
Compounds of formula (VIII) are novel, and as such form a further aspect of the invention. Certain of these compounds also possess insecticidal and fungicidal activity

Those skilled in the art will recognise that analogous reactions involving sulfenylation, sulfonylation and acylation are possible when Y is O.

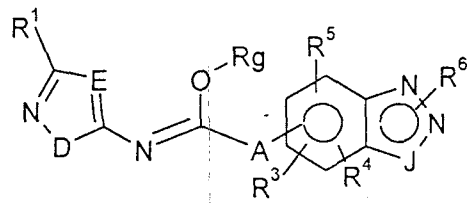
Compounds (I) where R^{51} is alkoxymethyl or acyloxymethyl, may also be prepared from Compound (I) where R^{51} is hydrogen by sequential reaction with formaldehyde and an alkylating or acylating agent.

Additional compounds (I) may be prepared from (I) where R^{51} is hydrogen by reaction with hydroxymethylbenzotriazole or benzotriazoles and aldehydes according to the method of A. R. Katritzky et al., J. Org. Chem., (1993), 58, 2086.

Compounds (IX), Y = S may be reacted with alcohols, amines, O-alkylhydroxyl-amines and hydrazines, optionally in the presence of a mercuric salt (such as mercuric chloride), according to known procedures to give compounds (X) and (XI) respectively:



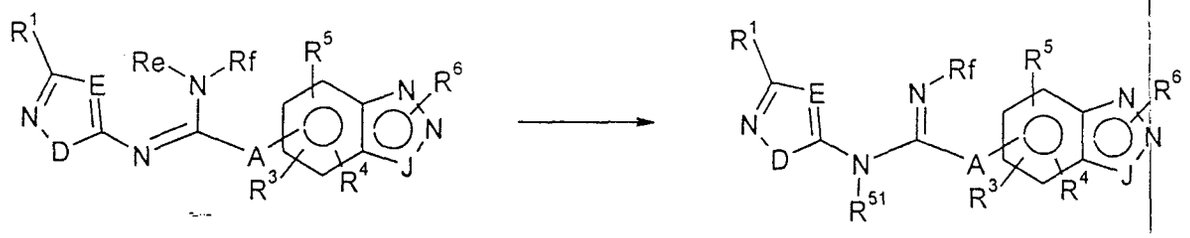
(X)



(XI)

where Re is H, optionally substituted alkyl, alkenyl or alkynyl, Rf is substituted alkyl, alkenyl alkynyl, amino, substituted amino or alkoxy and Rg is optionally substituted alkyl, alkenyl or alkynyl.

Compounds (X) where Re is hydrogen may be treated with an optionally substituted alkylating agent (such as an alkyl halide, chloromethylether, dialkyl sulfate or trialkyloxonium salt) optionally in the presence of a base to give further Compounds (I)



(X)

Heteroaryl N-Oxides can be produced by methods known to the skilled person.

The compounds of formula (I) can be used to combat and control infestations of insect pests such as Lepidoptera, Diptera, Hemiptera, Thysanoptera, Orthoptera, Dictyoptera, Coleoptera, Siphonaptera, Hymenoptera and Isoptera and also other invertebrate pests, for example, acarine, nematode and mollusc pests. Insects, acarines, nematodes and molluscs are hereinafter collectively referred to as pests. The pests which may be combated and controlled by the use of the invention compounds include those pests associated with agriculture (which term includes the growing of crops for food and fibre products), horticulture and animal husbandry, companion animals, forestry and the storage of products of vegetable origin (such as fruit, grain and timber); those pests associated with the damage of man-made structures and the transmission of diseases of man and animals; and also nuisance pests (such as flies).

Examples of pest species which may be controlled by the compounds of formula (I) include: *Myzus persicae* (aphid), *Aphis gossypii* (aphid), *Aphis fabae* (aphid), *Lygus* spp. (capsids), *Dysdercus* spp. (capsids), *Nilaparvata lugens* (planthopper), *Nephotettixc incticeps* (leafhopper), *Nezara* spp. (stinkbugs), *Euschistus* spp. (stinkbugs), *Leptocorisa* spp. (stinkbugs), *Frankliniella occidentalis* (thrip), Thrips spp. (thrips), *Leptinotarsa*

decemlineata (Colorado potato beetle), *Anthonomus grandis* (boll weevil), *Aonidiella* spp. (scale insects), *Trialeurodes* spp. (white flies), *Bemisia tabaci* (white fly), *Ostrinia nubilalis* (European corn borer), *Spodoptera littoralis* (cotton leafworm), *Heliothis virescens* (tobacco budworm), *Helicoverpa armigera* (cotton bollworm), *Helicoverpa zea* (cotton bollworm), *Sylepta derogata* (cotton leaf roller), *Pieris brassicae* (white butterfly), *Plutella xylostella* (diamond back moth), *Agrotis* spp. (cutworms), *Chilo suppressalis* (rice stem borer), *Locusta migratoria* (locust), *Chortiocetes terminifera* (locust), *Diabrotica* spp. (rootworms), *Panonychus ulmi* (European red mite), *Panonychus citri* (citrus red mite), *Tetranychus urticae* (two-spotted spider mite), *Tetranychus cinnabarinus* (carmine spider mite), *Phyllocoptruta oleivora* (citrus rust mite), *Polyphagotarsonemus latus* (broad mite), *Brevipalpus* spp. (flat mites), *Boophilus microplus* (cattle tick), *Dermacentor variabilis* (American dog tick), *Ctenocephalides felis* (cat flea), *Liriomyza* spp. (leafminer), *Musca domestica* (housefly), *Aedes aegypti* (mosquito), *Anopheles* spp. (mosquitoes), *Culex* spp. (mosquitoes), *Lucillia* spp. (blowflies), *Blattella germanica* (cockroach), *Periplaneta americana* (cockroach), *Blatta orientalis* (cockroach), termites of the Mastotermitidae (for example *Mastotermes* spp.), the Kalotermitidae (for example *Neotermes* spp.), the Rhinotermitidae (for example *Coptotermes formosanus*, *Reticulitermes flavipes*, *R. speratu*, *R. virginicus*, *R. hesperus*, and *R. santonensis*) and the Termitidae (for example *Globitermes sulphureus*), *Solenopsis geminata* (fire ant), *Monomorium pharaonis* (pharaoh's ant), *Damalinia* spp. and *Linognathus* spp. (biting and sucking lice), *Meloidogyne* spp. (root knot nematodes), *Globodera* spp. and *Heterodera* spp. (cyst nematodes), *Pratylenchus* spp. (lesion nematodes), *Rhodopholus* spp. (banana burrowing nematodes), *Tylenchulus* spp.(citrus nematodes), *Haemonchus contortus* (barber pole worm), *Caenorhabditis elegans* (vinegar eelworm), *Trichostrongylus* spp. (gastro intestinal nematodes) and *Deroceras reticulatum* (slug).

The compounds of formula (I) are also active fungicides and may be used to control one or more of the following pathogens: *Pyricularia oryzae* (*Magnaporthe grisea*) on rice and wheat and other *Pyricularia* spp. on other hosts; *Puccinia recondita*, *Puccinia striiformis* and other rusts on wheat, *Puccinia hordei*, *Puccinia striiformis* and other rusts on barley, and rusts on other hosts (for example turf, rye, coffee, pears, apples, peanuts, sugar beet,

vegetables and ornamental plants); *Erysiphe cichoracearum* on cucurbits (for example melon); *Erysiphe graminis* (powdery mildew) on barley, wheat, rye and turf and other powdery mildews on various hosts, such as *Sphaerotheca macularis* on hops, *Sphaerotheca fusca* (*Sphaerotheca fuliginea*) on cucurbits (for example cucumber), *Leveillula taurica* on tomatoes, aubergine and green pepper, *Podosphaera leucotricha* on apples and *Uncinula necator* on vines; *Cochliobolus* spp., *Helminthosporium* spp., *Drechslera* spp. (*Pyrenophora* spp.), *Rhynchosporium* spp., *Mycosphaerella graminicola* (*Septoria tritici)* and *Phaeosphaeria nodorum* (*Stagonospora nodorum* or *Septoria nodorum*), *Pseudocercosporella herpotrichoides* and *Gaeumannomyces graminis* on cereals (for example wheat, barley, rye), turf and other hosts; *Cercospora arachidicola* and *Cercosporidium personatum* on peanuts and other *Cercospora* spp. on other hosts, for example sugar beet, bananas, soya beans and rice; *Botrytis cinerea* (grey mould) on tomatoes, strawberries, vegetables, vines and other hosts and other *Botrytis* spp. on other hosts; *Alternaria* spp. on vegetables (for example carrots), oil-seed rape, apples, tomatoes, potatoes, cereals (for example wheat) and other hosts; *Venturia* spp. (including *Venturia inaequalis* (scab)) on apples, pears, stone fruit, tree nuts and other hosts; *Cladosporium* spp. on a range of hosts including cereals (for example wheat) and tomatoes; *Monilinia* spp. on stone fruit, tree nuts and other hosts; *Didymella* spp. on tomatoes, turf, wheat, cucurbits and other hosts; *Phoma* spp. on oil-seed rape, turf, rice, potatoes, wheat and other hosts; *Aspergillus* spp. and *Aureobasidium* spp. on wheat, lumber and other hosts; *Ascochyta* spp. on peas, wheat, barley and other hosts; *Stemphylium* spp. (*Pleospora* spp.) on apples, pears, onions and other hosts; summer diseases (for example bitter rot (*Glomerella cingulata*), black rot or frogeye leaf spot (*Botryosphaeria obtusa*), Brooks fruit spot (*Mycosphaerella pomi*), Cedar apple rust (*Gymnosporangium juniperi-virginianae*), sooty blotch (*Gloeodes pomigena*), flyspeck (*Schizothyrium pomi*) and white rot (*Botryosphaeria dothidea*)) on apples and pears; *Plasmopara viticola* on vines; other downy mildews, such as *Bremia lactucae* on lettuce, *Peronospora* spp. on soybeans, tobacco, onions and other hosts, *Pseudoperonospora humuli* on hops and *Pseudoperonospora cubensis* on cucurbits; *Pythium* spp. (including *Pythium ultimum*) on turf and other hosts; *Phytophthora infestans* on potatoes and tomatoes and other *Phytophthora* spp. on vegetables, strawberries, avocado, pepper, ornamentals, tobacco,

cocoa and other hosts; *Thanatephorus cucumeris* on rice and turf and other *Rhizoctonia* spp. on various hosts such as wheat and barley, peanuts, vegetables, cotton and turf; *Sclerotinia* spp. on turf, peanuts, potatoes, oil-seed rape and other hosts; *Sclerotium* spp. on turf, peanuts and other hosts; *Gibberella fujikuroi* on rice; *Colletotrichum* spp. on a range of hosts including turf, coffee and vegetables; *Laetisaria fuciformis* on turf; *Mycosphaerella* spp. on bananas, peanuts, citrus, pecans, papaya and other hosts; *Diaporthe* spp. on citrus, soybean, melon, pears, lupin and other hosts; *Elsinoe* spp. on citrus, vines, olives, pecans, roses and other hosts; *Verticillium* spp. on a range of hosts including hops, potatoes and tomatoes; *Pyrenopeziza* spp. on oil-seed rape and other hosts; *Oncobasidium theobromae* on cocoa causing vascular streak dieback; *Fusarium* spp., *Typhula* spp., *Microdochium nivale*, *Ustilago* spp., *Urocystis* spp., *Tilletia* spp. and *Claviceps purpurea* on a variety of hosts but particularly wheat, barley, turf and maize; *Ramularia* spp. on sugar beet, barley and other hosts; post-harvest diseases particularly of fruit (for example *Penicillium digitatum*, *Penicillium italicum* and *Trichoderma viride* on oranges, *Colletotrichum musae* and *Gloeosporium musarum* on bananas and *Botrytis cinerea* on grapes); other pathogens on vines, notably *Eutypa lata*, *Guignardia bidwellii*, *Phellinus igniarus*, *Phomopsis viticola*, *Pseudopeziza tracheiphila* and *Stereum hirsutum*; other pathogens on trees (for example *Lophodermium seditiosum*) or lumber, notably *Cephaloascus fragrans*, *Ceratocystis* spp., *Ophiostoma piceae*, *Penicillium* spp., *Trichoderma pseudokoningii*, *Trichoderma viride*, *Trichoderma harzianum*, *Aspergillus niger*, *Leptographium lindbergi* and *Aureobasidium pullulans*; and fungal vectors of viral diseases (for example *Polymyxa graminis* on cereals as the vector of barley yellow mosaic virus (BYMV) and *Polymyxa betae* on sugar beet as the vector of rhizomania).

A compound of formula (I) may move acropetally, basipetally or locally in plant tissue to be active against one or more fungi. Moreover, a compound of formula (I) may be volatile enough to be active in the vapour phase against one or more fungi on the plant.

The invention therefore provides a method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a pest, a locus of pest, or to a plant

susceptible to attack by a pest, and a method of combating and controlling fungi which comprises applying a fungicidally effective amount of a compound of formula (I), or a composition containing a compound of formula (I), to a plant, to a seed of a plant, to the locus of the plant or seed, to soil or to any other growth medium (for example a nutrient solution). The compounds of formula (I) are preferably used against insects, acarines, nematodes or fungi.

The term "plant" as used herein includes seedlings, bushes and trees. Furthermore, the fungicidal method of the invention includes protectant, curative, systemic, eradicant and antisporulant treatments.

As fungicides, the compounds of formula (I) are preferably used for agricultural, horticultural and turfgrass purposes in the form of a composition.

In order to apply a compound of formula (I) as an insecticide, acaricide, nematicide or molluscicide to a pest, a locus of pest, or to a plant susceptible to attack by a pest, or, as a fungicide to a plant, to a seed of a plant, to the locus of the plant or seed, to soil or to any other growth medium, a compound of formula (I) is usually formulated into a composition which includes, in addition to the compound of formula (I), a suitable inert diluent or carrier and, optionally, a surface active agent (SFA). SFAs are chemicals which are able to modify the properties of an interface (for example, liquid/solid, liquid/air or liquid/liquid interfaces) by lowering the interfacial tension and thereby leading to changes in other properties (for example dispersion, emulsification and wetting). It is preferred that all compositions (both solid and liquid formulations) comprise, by weight, 0.0001 to 95%, more preferably 1 to 85%, for example 5 to 60%, of a compound of formula (I). The composition is generally used for the control of pests or fungi such that a compound of formula (I) is applied at a rate of from 0.1g to10kg per hectare, preferably from 1g to 6kg per hectare, more preferably from 1g to 1kg per hectare.

When used in a seed dressing, a compound of formula (I) is used at a rate of 0.0001g to 10g (for example 0.001g or 0.05g), preferably 0.005g to 10g, more preferably 0.005g to 4g, per kilogram of seed.

In another aspect the present invention provides an insecticidal, acaricidal, nematicidal, molluscicidal or fungicidal composition comprising an insecticidally,

acaricidally, nematicidally, molluscicidally or fungicidally effective amount of a compound of formula (I) and a suitable carrier or diluent therefor. The composition is preferably an insecticidal, acaricidal, nematicidal or fungicidal composition.

In a still further aspect the invention provides a method of combating and controlling pests or fungi at a locus which comprises treating the pests or fungi or the locus of the pests or fungi with an insecticidally, acaricidally, nematicidally, molluscicidally or fungicidally effective amount of a composition comprising a compound of formula (I). The compounds of formula (I) are preferably used against insects, acarines, nematodes or fungi.

The compositions can be chosen from a number of formulation types, including dustable powders (DP), soluble powders (SP), water soluble granules (SG), water dispersible granules (WG), wettable powders (WP), granules (GR) (slow or fast release), soluble concentrates (SL), oil miscible liquids (OL), ultra low volume liquids (UL), emulsifiable concentrates (EC), dispersible concentrates (DC), emulsions (both oil in water (EW) and water in oil (EO)), micro-emulsions (ME), suspension concentrates (SC), aerosols, fogging/smoke formulations, capsule suspensions (CS) and seed treatment formulations. The formulation type chosen in any instance will depend upon the particular purpose envisaged and the physical, chemical and biological properties of the compound of formula (I).

Dustable powders (DP) may be prepared by mixing a compound of formula (I) with one or more solid diluents (for example natural clays, kaolin, pyrophyllite, bentonite, alumina, montmorillonite, kieselguhr, chalk, diatomaceous earths, calcium phosphates, calcium and magnesium carbonates, sulphur, lime, flours, talc and other organic and inorganic solid carriers) and mechanically grinding the mixture to a fine powder. Soluble powders (SP) may be prepared by mixing a compound of formula (I) with one or more water-soluble inorganic salts (such as sodium bicarbonate, sodium carbonate or magnesium sulphate) or one or more water-soluble organic solids (such as a polysaccharide) and, optionally, one or more wetting agents, one or more dispersing agents or a mixture of said agents to improve water dispersibility/solubility. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water soluble granules (SG).

Wettable powders (WP) may be prepared by mixing a compound of formula (I) with one or more solid diluents or carriers, one or more wetting agents and, preferably, one or more dispersing agents and, optionally, one or more suspending agents to facilitate the dispersion in liquids. The mixture is then ground to a fine powder. Similar compositions may also be granulated to form water dispersible granules (WG).

Granules (GR) may be formed either by granulating a mixture of a compound of formula (I) and one or more powdered solid diluents or carriers, or from pre-formed blank granules by absorbing a compound of formula (I) (or a solution thereof, in a suitable agent) in a porous granular material (such as pumice, attapulgite clays, fuller's earth, kieselguhr, diatomaceous earths or ground corn cobs) or by adsorbing a compound of formula (I) (or a solution thereof, in a suitable agent) on to a hard core material (such as sands, silicates, mineral carbonates, sulphates or phosphates) and drying if necessary. Agents which are commonly used to aid absorption or adsorption include solvents (such as aliphatic and aromatic petroleum solvents, alcohols, ethers, ketones and esters) and sticking agents (such as polyvinyl acetates, polyvinyl alcohols, dextrins, sugars and vegetable oils). One or more other additives may also be included in granules (for example an emulsifying agent, wetting agent or dispersing agent).

Dispersible Concentrates (DC) may be prepared by dissolving a compound of formula (I) in water or an organic solvent, such as a ketone, alcohol or glycol ether. These solutions may contain a surface active agent (for example to improve water dilution or prevent crystallisation in a spray tank).

Emulsifiable concentrates (EC) or oil-in-water emulsions (EW) may be prepared by dissolving a compound of formula (I) in an organic solvent (optionally containing one or more wetting agents, one or more emulsifying agents or a mixture of said agents). Suitable organic solvents for use in ECs include aromatic hydrocarbons (such as alkylbenzenes or alkylnaphthalenes, exemplified by SOLVESSO 100, SOLVESSO 150 and SOLVESSO 200; SOLVESSO is a Registered Trade Mark), ketones (such as cyclohexanone or methylcyclohexanone) and alcohols (such as benzyl alcohol, furfuryl alcohol or butanol), N-alkylpyrrolidones (such as N-methylpyrrolidone or N-octylpyrrolidone), dimethyl amides of fatty acids (such as C_8-C_{10} fatty acid dimethylamide) and chlorinated hydrocarbons. An

EC product may spontaneously emulsify on addition to water, to produce an emulsion with sufficient stability to allow spray application through appropriate equipment. Preparation of an EW involves obtaining a compound of formula (I) either as a liquid (if it is not a liquid at room temperature, it may be melted at a reasonable temperature, typically below 70°C) or in solution (by dissolving it in an appropriate solvent) and then emulsifiying the resultant liquid or solution into water containing one or more SFAs, under high shear, to produce an emulsion. Suitable solvents for use in EWs include vegetable oils, chlorinated hydrocarbons (such as chlorobenzenes), aromatic solvents (such as alkylbenzenes or alkylnaphthalenes) and other appropriate organic solvents which have a low solubility in water.

Microemulsions (ME) may be prepared by mixing water with a blend of one or more solvents with one or more SFAs, to produce spontaneously a thermodynamically stable isotropic liquid formulation. A compound of formula (I) is present initially in either the water or the solvent/SFA blend. Suitable solvents for use in MEs include those hereinbefore described for use in in ECs or in EWs. An ME may be either an oil-in-water or a water-in-oil system (which system is present may be determined by conductivity measurements) and may be suitable for mixing water-soluble and oil-soluble pesticides in the same formulation. An ME is suitable for dilution into water, either remaining as a microemulsion or forming a conventional oil-in-water emulsion.

Suspension concentrates (SC) may comprise aqueous or non-aqueous suspensions of finely divided insoluble solid particles of a compound of formula (I). SCs may be prepared by ball or bead milling the solid compound of formula (I) in a suitable medium, optionally with one or more dispersing agents, to produce a fine particle suspension of the compound. One or more wetting agents may be included in the composition and a suspending agent may be included to reduce the rate at which the particles settle. Alternatively, a compound of formula (I) may be dry milled and added to water, containing agents hereinbefore described, to produce the desired end product.

Aerosol formulations comprise a compound of formula (I) and a suitable propellant (for example *n*-butane). A compound of formula (I) may also be dissolved or dispersed in a suitable medium (for example water or a water miscible liquid, such as *n*-propanol) to provide compositions for use in non-pressurised, hand-actuated spray pumps.

A compound of formula (I) may be mixed in the dry state with a pyrotechnic mixture to form a composition suitable for generating, in an enclosed space, a smoke containing the compound.

Capsule suspensions (CS) may be prepared in a manner similar to the preparation of EW formulations but with an additional polymerisation stage such that an aqueous dispersion of oil droplets is obtained, in which each oil droplet is encapsulated by a polymeric shell and contains a compound of formula (I) and, optionally, a carrier or diluent therefor. The polymeric shell may be produced by either an interfacial polycondensation reaction or by a coacervation procedure. The compositions may provide for controlled release of the compound of formula (I) and they may be used for seed treatment. A compound of formula (I) may also be formulated in a biodegradable polymeric matrix to provide a slow, controlled release of the compound.

A composition may include one or more additives to improve the biological performance of the composition (for example by improving wetting, retention or distribution on surfaces; resistance to rain on treated surfaces; or uptake or mobility of a compound of formula (I)). Such additives include surface active agents, spray additives based on oils, for example certain mineral oils or natural plant oils (such as soy bean and rape seed oil), and blends of these with other bio-enhancing adjuvants (ingredients which may aid or modify the action of a compound of formula (I)).

A compound of formula (I) may also be formulated for use as a seed treatment, for example as a powder composition, including a powder for dry seed treatment (DS), a water soluble powder (SS) or a water dispersible powder for slurry treatment (WS), or as a liquid composition, including a flowable concentrate (FS), a solution (LS) or a capsule suspension (CS). The preparations of DS, SS, WS, FS and LS compositions are very similar to those of, respectively, DP, SP, WP, SC and DC compositions described above. Compositions for treating seed may include an agent for assisting the adhesion of the composition to the seed (for example a mineral oil or a film-forming barrier).

Wetting agents, dispersing agents and emulsifying agents may be surface SFAs of the cationic, anionic, amphoteric or non-ionic type.

Suitable SFAs of the cationic type include quaternary ammonium compounds (for example cetyltrimethyl ammonium bromide), imidazolines and amine salts.

Suitable anionic SFAs include alkali metals salts of fatty acids, salts of aliphatic monoesters of sulphuric acid (for example sodium lauryl sulphate), salts of sulphonated aromatic compounds (for example sodium dodecylbenzenesulphonate, calcium dodecylbenzenesulphonate, butylnaphthalene sulphonate and mixtures of sodium di-*iso*propyl- and tri-*iso*propyl-naphthalene sulphonates), ether sulphates, alcohol ether sulphates (for example sodium laureth-3-sulphate), ether carboxylates (for example sodium laureth-3-carboxylate), phosphate esters (products from the reaction between one or more fatty alcohols and phosphoric acid (predominately mono-esters) or phosphorus pentoxide (predominately di-esters), for example the reaction between lauryl alcohol and tetraphosphoric acid; additionally these products may be ethoxylated), sulphosuccinamates, paraffin or olefine sulphonates, taurates and lignosulphonates.

Suitable SFAs of the amphoteric type include betaines, propionates and glycinates.

Suitable SFAs of the non-ionic type include condensation products of alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures thereof, with fatty alcohols (such as oleyl alcohol or cetyl alcohol) or with alkylphenols (such as octylphenol, nonylphenol or octylcresol); partial esters derived from long chain fatty acids or hexitol anhydrides; condensation products of said partial esters with ethylene oxide; block polymers (comprising ethylene oxide and propylene oxide); alkanolamides; simple esters (for example fatty acid polyethylene glycol esters); amine oxides (for example lauryl dimethyl amine oxide); and lecithins.

Suitable suspending agents include hydrophilic colloids (such as polysaccharides, polyvinylpyrrolidone or sodium carboxymethylcellulose) and swelling clays (such as bentonite or attapulgite).

A compound of formula (I) may be applied by any of the known means of applying pesticidal or fungicidal compounds. For example, it may be applied, formulated or unformulated, to the pests or to a locus of the pests (such as a habitat of the pests, or a growing plant liable to infestation by the pests) or to any part of the plant, including the foliage, stems, branches or roots, to the seed before it is planted or to other media in which

plants are growing or are to be planted (such as soil surrounding the roots, the soil generally, paddy water or hydroponic culture systems), directly or it may be sprayed on, dusted on, applied by dipping, applied as a cream or paste formulation, applied as a vapour or applied through distribution or incorporation of a composition (such as a granular composition or a composition packed in a water-soluble bag) in soil or an aqueous environment.

A compound of formula (I) may also be injected into plants or sprayed onto vegetation using electrodynamic spraying techniques or other low volume methods, or applied by land or aerial irrigation systems.

Compositions for use as aqueous preparations (aqueous solutions or dispersions) are generally supplied in the form of a concentrate containing a high proportion of the active ingredient, the concentrate being added to water before use. These concentrates, which may include DCs, SCs, ECs, EWs, MEs SGs, SPs, WPs, WGs and CSs, are often required to withstand storage for prolonged periods and, after such storage, to be capable of addition to water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Such aqueous preparations may contain varying amounts of a compound of formula (I) (for example 0.0001 to 10%, by weight) depending upon the purpose for which they are to be used.

A compound of formula (I) may be used in mixtures with fertilisers (for example nitrogen-, potassium- or phosphorus-containing fertilisers). Suitable formulation types include granules of fertiliser. The mixtures suitably contain up to 25% by weight of the compound of formula (I).

The invention therefore also provides a fertiliser composition comprising a fertiliser and a compound of formula (I).

The compositions of this invention may contain other compounds having biological activity, for example micronutrients or compounds having similar or complementary fungicidal activity or which possess plant growth regulating, herbicidal, insecticidal, nematicidal or acaricidal activity.

By including another fungicide, the resulting composition may have a broader spectrum of activity or a greater level of intrinsic activity than the compound of formula (I)

alone. Further the other fungicide may have a synergistic effect on the fungicidal activity of the compound of formula (I).

The compound of formula (I) may be the sole active ingredient of the composition or it may be admixed with one or more additional active ingredients such as a pesticide, fungicide, synergist, herbicide or plant growth regulator where appropriate. An additional active ingredient may: provide a composition having a broader spectrum of activity or increased persistence at a locus; synergise the activity or complement the activity (for example by increasing the speed of effect or overcoming repellency) of the compound of formula (I); or help to overcome or prevent the development of resistance to individual components. The particular additional active ingredient will depend upon the intended utility of the composition. Examples of suitable pesticides include the following:

a) Pyrethroids, such as permethrin, cypermethrin, fenvalerate, esfenvalerate, deltamethrin, cyhalothrin (in particular lambda-cyhalothrin), bifenthrin, fenpropathrin, cyfluthrin, tefluthrin, fish safe pyrethroids (for example ethofenprox), natural pyrethrin, tetramethrin, s-bioallethrin, fenfluthrin, prallethrin or 5-benzyl-3-furylmethyl-(E)-(1R,3S)-2,2-dimethyl-3-(2-oxothiolan-3-ylidenemethyl)cyclopropane carboxylate;

b) Organophosphates, such as, profenofos, sulprofos, acephate, methyl parathion, azinphos-methyl, demeton-s-methyl, heptenophos, thiometon, fenamiphos, monocrotophos, profenofos, triazophos, methamidophos, dimethoate, phosphamidon, malathion, chlorpyrifos, phosalone, terbufos, fensulfothion, fonofos, phorate, phoxim, pirimiphos-methyl, pirimiphos-ethyl, fenitrothion, fosthiazate or diazinon;

c) Carbamates (including aryl carbamates), such as pirimicarb, triazamate, cloethocarb, carbofuran, furathiocarb, ethiofencarb, aldicarb, thiofurox, carbosulfan, bendiocarb, fenobucarb, propoxur, methomyl or oxamyl;

d) Benzoyl ureas, such as diflubenzuron, triflumuron, hexaflumuron, flufenoxuron or chlorfluazuron;

e) Organic tin compounds, such as cyhexatin, fenbutatin oxide or azocyclotin;

f) Pyrazoles, such as tebufenpyrad and fenpyroximate;

g) Macrolides, such as avermectins or milbemycins, for example abamectin, emamectin benzoate, ivermectin, milbemycin, spinosad or azadirachtin;

h) Hormones or pheromones;

i) Organochlorine compounds such as endosulfan, benzene hexachloride, DDT, chlordane or dieldrin;

j) Amidines, such as chlordimeform or amitraz;

k) Fumigant agents, such as chloropicrin, dichloropropane, methyl bromide or metam;

l) Chloronicotinyl compounds such as imidacloprid, thiacloprid, acetamiprid, nitenpyram or thiamethoxam;

m) Diacylhydrazines, such as tebufenozide, chromafenozide or methoxyfenozide;

n) Diphenyl ethers, such as diofenolan or pyriproxifen;

o) Indoxacarb;

p) Chlorfenapyr; or

q) Pymetrozine.

In addition to the major chemical classes of pesticide listed above, other pesticides having particular targets may be employed in the composition, if appropriate for the intended utility of the composition. For instance, selective insecticides for particular crops, for example stemborer specific insecticides (such as cartap) or hopper specific insecticides (such as buprofezin) for use in rice may be employed. Alternatively insecticides or acaricides specific for particular insect species/stages may also be included in the compositions (for example acaricidal ovo-larvicides, such as clofentezine, flubenzimine, hexythiazox or tetradifon; acaricidal motilicides, such as dicofol or propargite; acaricides, such as bromopropylate or chlorobenzilate; or growth regulators, such as hydramethylnon, cyromazine, methoprene, chlorfluazuron or diflubenzuron).

Examples of fungicidal compounds which may be included in the composition of the invention are (*E*)-*N*-methyl-2-[2-(2,5-dimethylphenoxymethyl)phenyl]-2-methoxyiminoacetamide (SSF-129), 4-bromo-2-cyano-*N*,*N*-dimethyl-6-trifluoromethylbenzimidazole-1-sulphonamide, α-[*N*-(3-chloro-2,6-xylyl)-2-methoxyacetamido]-γ-butyrolactone, 4-chloro-2-cyano-*N*,*N*-dimethyl-5-*p*-tolylimidazole-1-sulfonamide (IKF-916, cyamidazosulfamid), 3-5-dichloro-*N*-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-4-methylbenzamide (RH-7281, zoxamide), *N*-allyl-4,5,-dimethyl-2-trimethylsilylthiophene-3-carboxamide (MON65500), *N*-(1-cyano-1,2-dimethylpropyl)-2-

(2,4-dichlorophenoxy)propionamide (AC382042), *N*-(2-methoxy-5-pyridyl)-cyclopropane carboxamide, acibenzolar (CGA245704), alanycarb, aldimorph, anilazine, azaconazole, azoxystrobin, benalaxyl, benomyl, biloxazol, bitertanol, blasticidin S, bromuconazole, bupirimate, captafol, captan, carbendazim, carbendazim chlorhydrate, carboxin, carpropamid, carvone, CGA41396, CGA41397, chinomethionate, chlorothalonil, chlorozolinate, clozylacon, copper containing compounds such as copper oxychloride, copper oxyquinolate, copper sulphate, copper tallate and Bordeaux mixture, cymoxanil, cyproconazole, cyprodinil, debacarb, di-2-pyridyl disulphide 1,1'-dioxide, dichlofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, difenzoquat, diflumetorim, *O*,*O*-di-*iso*-propyl-*S*-benzyl thiophosphate, dimefluazole, dimetconazole, dimethomorph, dimethirimol, diniconazole, dinocap, dithianon, dodecyl dimethyl ammonium chloride, dodemorph, dodine, doguadine, edifenphos, epoxiconazole, ethirimol, ethyl(*Z*)-*N*-benzyl-*N*([methyl(methyl-thioethylideneaminooxycarbonyl)amino]thio)-β-alaninate, etridiazole, famoxadone, fenamidone (RPA407213), fenarimol, fenbuconazole, fenfuram, fenhexamid (KBR2738), fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, fluoroimide, fluquinconazole, flusilazole, flutolanil, flutriafol, folpet, fuberidazole, furalaxyl, furametpyr, guazatine, hexaconazole, hydroxyisoxazole, hymexazole, imazalil, imibenconazole, iminoctadine, iminoctadine triacetate, ipconazole, iprobenfos, iprodione, iprovalicarb (SZX0722), isopropanyl butyl carbamate, isoprothiolane, kasugamycin, kresoxim-methyl, LY186054, LY211795, LY248908, mancozeb, maneb, mefenoxam, mepanipyrim, mepronil, metalaxyl, metconazole, metiram, metiram-zinc, metominostrobin, myclobutanil, neoasozin, nickel dimethyldithio-carbamate, nitrothal-*iso*propyl, nuarimol, ofurace, organomercury compounds, oxadixyl, oxasulfuron, oxolinic acid, oxpoconazole, oxycarboxin, pefurazoate, penconazole, pencycuron, phenazin oxide, phosetyl-Al, phosphorus acids, phthalide, picoxystrobin (ZA1963), polyoxin D, polyram, probenazole, prochloraz, procymidone, propamocarb, propiconazole, propineb, propionic acid, pyrazophos, pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, pyrrolnitrin, quaternary ammonium compounds, quinomethionate, quinoxyfen, quintozene, sipconazole (F-155), sodium pentachlorophenate, spiroxamine, streptomycin, sulphur, tebuconazole, tecloftalam, tecnazene, tetraconazole, thiabendazole, thifluzamid,

2-(thiocyanomethylthio)benzothiazole, thiophanate-methyl, thiram, timibenconazole, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, tricyclazole, tridemorph, trifloxystrobin (CGA279202), triforine, triflumizole, triticonazole, validamycin A, vapam, vinclozolin, zineb and ziram.

The compounds of formula (I) may be mixed with soil, peat or other rooting media for the protection of plants against seed-borne, soil-borne or foliar fungal diseases.

Examples of suitable synergists for use in the compositions include piperonyl butoxide, sesamex, safroxan and dodecyl imidazole.

Suitable herbicides and plant-growth regulators for inclusion in the compositions will depend upon the intended target and the effect required.

An example of a rice selective herbicide which may be included is propanil. An example of a plant growth regulator for use in cotton is PIX™.

Some mixtures may comprise active ingredients which have significantly different physical, chemical or biological properties such that they do not easily lend themselves to the same conventional formulation type. In these circumstances other formulation types may be prepared. For example, where one active ingredient is a water insoluble solid and the other a water insoluble liquid, it may nevertheless be possible to disperse each active ingredient in the same continuous aqueous phase by dispersing the solid active ingredient as a suspension (using a preparation analogous to that of an SC) but dispersing the liquid active ingredient as an emulsion (using a preparation analogous to that of an EW). The resultant composition is a suspoemulsion (SE) formulation.

The invention is illustrated by the following examples.

Example 1

Preparation of Compound 1.1, N-(4-chloro-3-methylisothiazol-5-yl)-(2-propyl-benzotriazol-5-yl)acetamide

Step 1

Preparation of methyl 4-aminophenylacetate

4-Aminophenylacetic acid (100g) was suspended in methanol (1000ml) and gaseous hydrogen chloride was passed through until the mixture was saturated. The mixture was heated at 50°C for 2 hours and was then allowed to cool to room temperature. The solvent

was evaporated *in vacuo*, the residue taken up aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl 4-aminophenylacetate as a pale brown liquid.

^{1}H NMR ($CDCl_3$) δ ppm: 3.5 (s, 2H); 3.7 (s, 3H); 6.65 (m, 2H); 7.05 (m, 2H).

Step 2

Preparation of methyl 4-acetamido-3-nitrophenylacetate

Methyl 4-aminophenylacetate (110g, 0.667mol) was added dropwise to acetic anhydride (600ml), maintaining the temperature of the reaction mixture below 30°C by external cooling. Once the addition was complete the mixture was cooled to below 10°C and concentrated nitric acid (85 ml) was added dropwise. Once the addition of the acid was complete, the mixture was allowed to warm to room temperature and poured onto a mixture of ice and water. The precipitated solid was collected by filtration and dried to give methyl 4-acetamido-3-nitrophenylacetate (120g) as a pale yellow solid.

^{1}H NMR ($CDCl_3$) δ ppm: 2.3 (s, 3H); 3.65 (s, 2H); 3.7 (s, 3H); 7.55 (dd, 1H); 8.1 (d, 1H); 8.7 (d, 1H); 10.3 (b, 1H).

Step 3

Preparation of methyl 4-acetamido-3-aminophenylacetate

Methyl 4-acetamido-3-nitrophenylacetate (40g, 0.159mol)) was dissolved in methanol (400ml) and hydrogenated at 5bar over a 5% palladium on carbon catalyst. The catalyst was removed by filtration and the filtrate evaporated *in vacuo* to give methyl 4-acetamido-3-aminophenylacetate.

Step 4

Preparation of methyl (benzotriazol-5-yl)acetate

Methyl 4-acetamido-3-aminophenylacetate (77g, 0.373mol) was taken up in a mixture of acetic acid (210ml) and water (210ml) and cooled to below 5°C. A solution of sodium nitrite (38.63g, 0.559mol) in water (200ml) was added dropwise, and once the

addition was complete the mixture was stirred for 4hours, warming slowly to room temperature. The mixture was diluted with ethyl acetate and the insoluble material removed by filtration. The filtrate was washed with brine, dried over anhydrous magnesium sulfate, filtered and the solvent evaporated *in vacuo*, to give a viscous residue (51g). The residue was dissolved in a solution of methanol (400ml) previously saturated with hydrogen chloride and the mixture stirred for 2hours. The solvent was removed *in vacuo*, the residue taken up in water, neutralised with saturated aqueous sodium bicarbonate solution and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford methyl (benzotriazol-5-yl)acetate (35g) as a reddish liquid which crystallised on standing.

^{1}H NMR ($CDCl_3$) δ ppm: 3.7 (s, 3H); 3.8 (s, 2H); 7.35 (d, 1H); 7.8 (b, 2H); 13.6 (b, 1H).

Step 5

Preparation of methyl (2-propylbenzotriazol-5-yl)acetate

A solution of methyl (benzotriazol-5-yl)acetate (10g, 0.0523mol) in N,N-dimethylformamide was added dropwise to a chilled (ice-bath) suspension of sodium hydride (60% dispersion in oil, 2.3g, 0.0575mol) in N,N-dimethylformamide. When the addition was complete, the ice-bath was removed and the mixture stirred for 1hour. N-Propyl iodide (9.78g, 0.0575mol) was added dropwise, and once the addition was complete the mixture was stirred at room temperature for 3hours. The reaction mixture was poured onto ice/water, and extracted with ethyl acetate. The organic extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by column chromatography to afford methyl (2-propylbenzotriazol-5-yl)acetate (4.8g).

^{1}H NMR ($CDCl_3$) δ ppm: 0.9 (t, 3H); 2.1 (m, 2H); 3.7 (s, 3H); 3.8 (s, 2H); 4.65 (t, 2H); 7.3 (dd, 1H); 7.7 (d, 1H); 7.8 (d, 1H).

This step also generates methyl (1-propylbenzotriazol-6-yl)acetate and methyl (1-propylbenzotriazol-5-yl)acetate which may be isolated and converted to Compounds (2.1) and (3.1) respectively by procedures similar to those detailed below.

Step 6

Preparation of (2-propylbenzotriazol-5-yl)acetic acid

The acetate prepared in Step 6 above (4.8g, 0.0206mol) was dissolved in methanol (60ml) and potassium hydroxide flakes (1.27g, 0.0226mol) added. The mixture was refluxed for 2hours, then cooled and the solvent evaporated *in vacuo*. The residual solid was dissolved in water and extracted with diethyl ether. The aqueous solution was acidified to pH 1 by addition of dilute aqueous hydrochloric acid and extracted with ethyl acetate. The ethyl acetate extract was washed with brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo* to afford (2-propylbenzotriazol-5-yl)acetic acid (3.6g) as a colourless solid.

Step 7

Preparation of N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)-acetamide

The acid prepared in Step 7 (0.438g, 0.002mol) was dissolved in dichloromethane (5ml) and one drop of N,N-dimethyl formamide was added. Oxalyl chloride (0.307g, 0.0022mol) was added dropwise, and the mixture stirred at room temperature for 2hours. The solvent was removed *in vacuo*, the residue taken up in xylene and added to a mixture of 5-amino-4-chloro-3-methylisothiazole (0.446g, 0.003mol) in xylene and heated at reflux for 2hours. The mixture was cooled to room temperature and the solvent evaporated *in vacuo*. The residue was taken up in ethyl acetate, washed sequentially with saturated aqueous sodium bicarbonate solution and brine, dried over anhydrous magnesium sulfate, filtered and the filtrate evaporated *in vacuo*. The residue was further purified by flash column chromatography, eluting with 2:1 hexane : ethyl acetate, to give N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)-acetamide (0.34g) as a sandy-coloured solid.

^{1}H NMR ($CDCl_3$) δ ppm: 1.0 (t, 3H); 2.15 (m, 2H); 2.35 (s, 3H); 4.0 (s, 2H); 4.7 (t, 2H); 7.35 (dd, 1H); 7.85 (d, 1H); 7.95 (d, 1H); 8.15 (br, 1H).

Example 2.

Preparation of Compound 1.11, N-(4-chloro-3-methylisothiazol-5-yl)-N-(ethoxymethyl)-(2-propylbenzotriazol-5-yl)acetamide and Compound 5.2, N-[2-ethoxyoxymethyl-4-chloro-3-methylisothiazolin-5-ylidene]-(2-propylbenzo-triazol-5-yl) acetamide

Lithium bis(trimethylsilyl)amide (1.0 M solution in tetrahydrofuran, 3.3 ml, 0.0033 mol) was added dropwise to a solution of N-(4-chloro-3-methylisothiazol-5-yl)-(2-propylbenzotriazol-5-yl)acetamide (Compound 1.1) (0.699 g, 0.002 mol) in tetrahydrofuran (10 ml) and once the addition was complete the mixture was stirred at room temperature for 30 minutes. Chloromethylethyl ether (0.620 g, 0.0066 mol) was added and the mixture stirred at room temperature for 2 hours. The mixture was poured into water, neutralised, and extracted with ethyl acetate. The organic extract was dried over anhydrous magnesium sulfate, filtered, and the filtrate evaporated *in vacuo*. The residue was further purified by flash column chromatography, eluting initially with 2:1 hexane : ethyl acetate and then with ethyl acetate to give N-(4-chloro-3-methylisothiazol-5-yl)-N-(ethoxymethyl)-(2-propylbenzotriazol-5-yl)acetamide (Compound 1.11) (0.135 g) as an orange gum and N-[2-ethoxyoxymethyl-4-chloro-3-methylisothiazolin-5-ylidene]-(2-propylbenzotriazol-5-yl) acetamide (Compound 5.2) (0.128 g) as a colourless solid, m.p. 108-109 °C

Compound 1.11

^{1}H NMR ($CDCl_3$) δ ppm: 0.95 (t, 3H); 1.2 (t, 3H); 2.1 (m, 2H); 2.5 (s, 3H); 3.6 (q, 2H), 3.7 (br, 2H); 4.7 (t, 2H); 5.1 (br, 2H); 7.15 (br, 1H); 7.55 (br, 1H); 7.8 (d, 1H)

Compound 5.2

^{1}H NMR ($CDCl_3$) δ ppm: 0.95 (t, 3H); 1.15 (t, 3H); 2.1 (m, 2H); 2.55 (s, 3H); 3.5 (q, 2H); 4.2 (s, 2H); 4.7 (t, 2H), 5.2 (s, 2H); 7.4 (dd, 1H); 7.8 (m, 2H)

EXAMPLE 3

This Example illustrates the pesticidal/insecticidal properties of compounds of formula (I). The activities of samples of individual compounds and mixtures of compounds of formula (I) were determined using a variety of pests., The pests were treated with a liquid

composition containing 500 parts per million (ppm) by weight of a compound . Each composition was made by dissolving the compound in an acetone and ethanol (50:50 by volume) mixture and diluting the solution with water containing 0.05% by volume of a wetting agent, SYNPERONIC NP8, until the liquid composition contained the required concentration of the compound.

Samples used were as follows:

Sample No.	Component A	Component B	Ratio A : B
1	Compound 1.1		
2	Compound 1.2		
3	Compound 2.2	Compound 3.2	1 : 3
4	Compound 1.3		
5	Compound 2.3	Compound 3.3	1 : 1
6	Compound 2.4	Compound 3.4	8 : 92
7	Compound 2.4	Compound 3.4	1 : 2
8	Compound 1.4		
9	Compound 1.5		
10	Compound 2.5	Compound 3.5	1 : 1
11	Compound 1.6		
12	Compound 2.6	Compound 3.6	1 : 1
13	Compound 1.7		
14	Compound 2.7	Compound 3.7	1 : 1
15	Compound 1.8		
16	Compound 2.8	Compound 3.8	1 : 1
17	Compound 1.9		
18	Compound 2.9	Compound 3.9	3 : 2
19	Compound 1.10		
20	Compound 1.11		
21	Compound 1.12		
22	Compound 3.12		

23	Compound 2.12	Compound 3.12	1 : 1
24	Compound 2.1	Compound 3.1	1 : 1
25	Compound 2.12	Compound 3.12	9 : 1
26	Compound 2.17		
27	Compound 3.17		
28	Compound 1.13		
29	Compound 1.14		
30	Compound 1.15		
31	Compound 1.16		
32	Compound 4.1		
33	Compound 5.1		
34	Compound 5.2		

The test procedure adopted with regard to each pest, was essentially the same and comprised supporting a number of the pests on a medium which was usually a substrate, a host plant or a foodstuff on which the pests feed, and treating either or both the medium and the pests with a composition. Pest mortality was assessed usually between two and five days after treatment.

The results of the tests against peach aphid (*Myzus persicae*) are presented below. In this test Chinese cabbage leaves were infested with aphids, the infested leaves were sprayed with the test composition, and the mortality assessed after three days. The results indicate a grading of mortality (score) designated as 9, 5 or 0 wherein 9 indicates 80-100% mortality, 5 indicates 40-79% mortality and 0 indicates less than 40% mortality.

Sample Nos. 2, 13, 15, 19, 20, 30, 31 and 32 each gave a mortality score of 9 whilst Sample Nos. 8, 9, 11, 17, 29 and 34 gave a score of 5

In addition, in a similar test against two-spotted spider mites (*Tetranychus urticae*) Sample Nos. 1, 8, 11, 12, 13, 17, 18, 19, 20 and 30 each gave a mortality score of 9 whilst Sample No. 9 gave a score of 5.

EXAMPLE 4

This Example illustrates the fungicidal properties of compounds of formula (I). The compounds were tested against a variety of foliar fungal diseases of plants. The technique employed was as follows.

Plants were grown in John Innes Potting Compost (No.1 or 2) in 4cm diameter, 3.5cm depth minipots. The test samples were individually formulated as a solution either in acetone or acetone/ethanol (1:1 by volume) which was diluted in deionised water to a concentration of 100ppm (that is, 1mg of compound in a final volume of 10ml) immediately before use. When foliar sprays were applied to monocotyledonous crops, TWEEN 20 (0.1% by volume) was added. TWEEN is a registered trade mark.

Individual compounds of formula (I), or mixtures of compounds of formula (1), were applied as a foliar (Folr) application (where the chemical solution was applied to the foliage of the test plants by spraying the plant to maximum droplet retention.)

These tests were carried out against *Uncinula necator* (UNCINE), on vines; *Phytophthora infestans lycopersici* (PHYTIN) on tomatoes; *Puccinia recondita* (PUCCRT), on wheat; and *Pyricularia oryzae* (PYRIOR) on rice. Each treatment was applied to two or more replicate plants for *Phytophthora infestans lycopersici* and *Uncinula necator*. For tests on *Puccinia recondita* and *Pyricularia oryzae* two replicate pots each containing 6 to10 plants were used for each treatment. The plants were inoculated one day before (Erad) or one day after (Prot) chemical application. The *Phytophthora infestans lycopersici, Puccinia recondita* and *Pyricularia oryzae* plants were inoculated with a calibrated fungal spore suspension. The *Uncinula necator* plants were inoculated using a 'blowing' inoculation technique.

After chemical application and inoculation, the plants were incubated under high humidity conditions and then put into an appropriate environment to allow infection to proceed, until the disease was ready for assessment. The time period between chemical application and assessment varied from five to fourteen days according to the disease and

environment. However, each individual disease was assessed after the same time period for all samples.

Assessments were performed on each of two leaves on each of the replicate plants for *Phytophthora infestans lycopersici*. Assessments were performed on a single leaf of each of the replicate plants for *Uncinula necator*. For *Puccinia recondita and Pyricularia recondita* assessments were carried out collectively on the plants in each replicate pot.

The disease level present (that is, the percentage leaf area covered by actively sporulating disease) was assessed visually. For each treatment, the assessed values for all its replicates were meaned to provide mean disease values. Untreated control plants were assessed in the same manner. The data were then processed by the method, described hereinafter, to provide PRCO (Percentage Reduction from Control) values.

An example of a typical calculation is as follows:

Mean disease level for treatment A = 25%

Mean disease level on untreated controls = 85%

$$PRCO = 100 - \left\{ \frac{\text{Mean disease level for treatment A}}{\{\text{Mean disease level on untreated controls}\}} \right\} \times 100$$

$$= 100 - \left(\frac{25}{85} \times 100\right) = 70.6$$

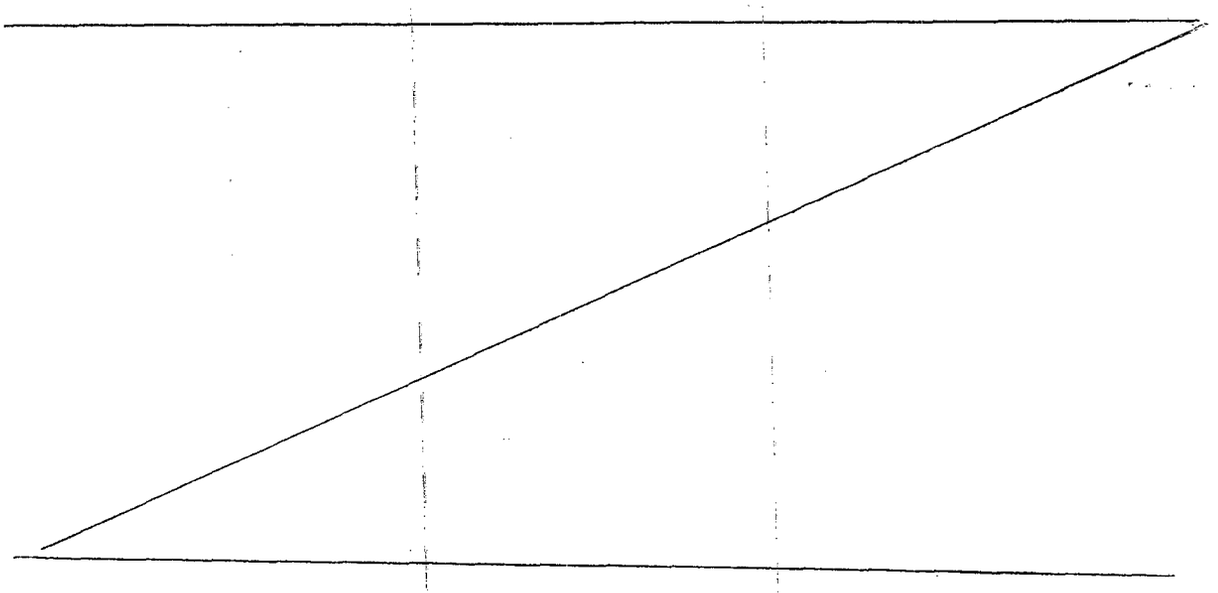
The PRCO is then rounded to the nearest whole number; therefore, in this particular example, the PRCO result is 71.

It is possible for negative PRCO values to be obtained.

PRCO results are shown below in Table 7.

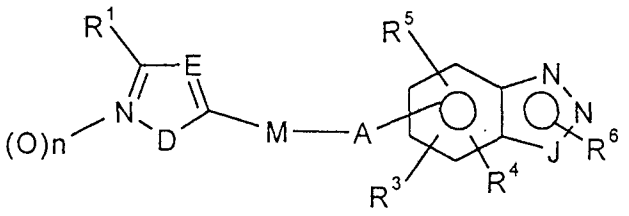
TABLE 7

Sample No.	PHYTIN Prot	PUCCRT Prot	PYRIOR Prot	UNCINE Erad
1	100	100	100	
2			87	
3			40	
4			92	
6	75	16	6	11
7			96	
8			100	
9	100	99	100	
11			100	
12			98	
19	81	87		
30	100	100		100
31	100	100		100
33	30	36		
34	81		93	100



Claims

1. A compound of formula (I):



(I)

wherein n is 0 or 1; A is optionally substituted C_{1-6} alkylene, optionally substituted C_{2-6} alkenylene, optionally substituted C_{2-6} alkynylene, optionally substituted C_{1-6} alkylenoxy, optionally substituted oxy(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenethio, optionally substituted thio(C_{1-6})alkylene, optionally substituted C_{1-6} alkylenamino, optionally substituted amino(C_{1-6})alkylene, optionally substituted [C_{1-6} alkyleneoxy(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenethio(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfinyl(C_{1-6})alkylene], optionally substituted [C_{1-6} alkylenesulfonyl(C_{1-6})alkylene] or optionally substituted [C_{1-6} alkyleneamino(C_{1-6})alkylene];

D is S, NR^{10} CR^8=CR^9, CR^8=N, CR^8=N(O), N=CR^9 or N(O)=CR^9;

R^{10} is C_{1-6} alkyl;

E is N, N-oxide or CR^{12};

M is OC(=Y), N(R^{51})C(=Y), N=C(OR^{52}), N=C(SR^{53}) or N=C($NR^{54}R^{55}$) where O or N is the atom of attachment to the ring containing E and D;

Y is O, S or NR^{13};

J is N or CR^{14};

R^1 is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{3-7} cycloalkyl, cyano, nitro or SF_5;

R^{51} is hydrogen, optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, optionally substituted phenoxycarbonyl, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted C_{1-6} arylthio, optionally substituted C_{1-6} arylsulfinyl, optionally substituted C_{1-6} arylsulfonyl or $R^{20}R^{21}NS$;

R^{52} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, , amino, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted phenoxycarbonyl, tri(C_{1-4})alkylsilyl, aryldi(C_{1-4})alkylsilyl, (C_{1-4})alkyldiarylsilyl or triarylsilyl;

R^{53} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl or optionally substituted phenoxycarbonyl);

R^{54} and R^{55} are, independently optionally substituted C_{1-10} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, hydroxy, amino, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, or optionally substituted phenoxycarbonyl;

R^3, R^4 and R^5 are, independently, hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally

substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5;

R^6 is hydrogen, cyano, optionally substituted C_{1-20} alkyl, optionally substituted C_{2-20} alkenyl(C_{1-6})alkyl, optionally substituted C_{2-20} alkynyl(C_{1-6})alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{5-6} cycloalkenyl, formyl, optionally substituted C_{1-20} alkoxycarbonyl, optionally substituted C_{1-20} alkylcarbonyl, aminocarbonyl, optionally substituted C_{1-20} alkylaminocarbonyl, optionally substituted di(C_{1-20})alkylaminocarbonyl, optionally substituted aryloxycarbonyl, optionally substituted arylcarbonyl, optionally substituted arylaminocarbonyl, optionally substituted N-alkyl-N-arylaminocarbonyl, optionally substituted diarylaminocarbonyl, optionally substituted heteroaryloxycarbonyl, optionally substituted heteroarylcarbonyl, optionally substituted heteroarylaminocarbonyl, optionally substituted alkylheteroarylaminocarbonyl, optionally substituted diheteroarylaminocarbonyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted heterocyclyl, optionally substituted C_{1-20} alkylsulfonyl, or optionally substituted arylsulfonyl;

R^8 and R^9 are, independently, hydrogen, halogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl or optionally substituted C_{1-6} alkoxy;

R^{12} is hydrogen, halogen, optionally substituted C_{1-6} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, cyano, nitro, formyl, $R^{32}ON=C(R^{30})$, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl or SF_5; or R^1 and R^{12} together with the atoms to which they are attached may be joined to form a five, six or seven-membered saturated or unsaturated ring carbocylic or heterocyclic ring which may contain one or two hetero atoms selected from O, N or S and which may be optionally substituted by C_{1-6} alkyl, C_{1-6} haloalkyl or halogen;

R^{13} is hydrogen, cyano, nitro, optionally substituted C_{1-6} alkyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted (C_{2-6})alkenyl(C_{1-6})alkyl, optionally substituted (C_{2-6})alkynyl(C_{1-6})alkyl, optionally substituted phenyl, optionally substituted heteroaryl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylamino, optionally substituted di(C_{1-6})alkylamino, optionally substituted C_{1-6} alkylcarbonylamino, optionally substituted C_{1-6} alkoxycarbonylamino, optionally substituted C_{1-6} alkoxy, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted arylthio, optionally substituted arylsulfinyl, optionally substituted arylsulfonyl or C_{1-6} acyloxy;

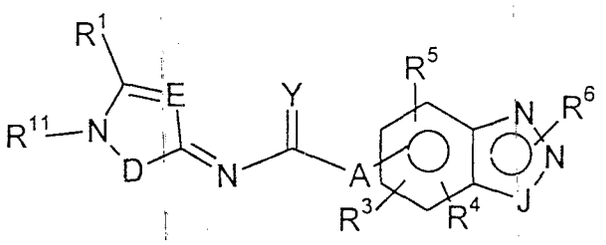
R^{14} is hydrogen, halogen, nitro, cyano, optionally substituted C_{1-8} alkyl, optionally substituted C_{2-6} alkenyl, optionally substituted C_{2-6} alkynyl, optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-6} alkoxycarbonyl, optionally substituted C_{1-6} alkylcarbonyl, optionally substituted C_{1-6} alkylaminocarbonyl, optionally substituted di(C_{1-6})alkylaminocarbonyl, optionally substituted phenyl or optionally substituted heteroaryl;

R^{20} and R^{21} are, independently, optionally substituted C_{1-6} alkyl or R^{20} and R^{21} together with the N atom to which they are attached form a five, six or seven-membered heterocyclic ring which may contain one or two further hetero atoms selected from O, N or S and which may be optionally substituted by one or two C_{1-6} alkyl groups;

R^{30} is hydrogen, optionally substituted phenyl or optionally substituted C_{1-6} alkyl; and

R^{32} is hydrogen, optionally substituted phenyl (C_{1-2})alkyl or optionally substituted C_{1-20} alkyl;

2. A compound of formula (VIII):



(VIII)

wherein A, D, E, Y, J, R^1, R^3, R^4, R^5 and R^6 are as defined in claim 1 and R^{11} is optionally substituted C_{1-10} alkyl, optionally substituted [C_{2-6} alkenyl(C_{1-6})alkyl], optionally substituted [C_{2-6} alkynyl(C_{1-6})alkyl], optionally substituted C_{3-7} cycloalkyl, optionally substituted C_{1-10} alkylcarbonyl, optionally substituted C_{1-10} alkoxycarbonyl, formyl, optionally substituted C_{1-10} alkylaminocarbonyl, optionally substituted di(C_{1-10})alkylaminocarbonyl, optionally substituted phenoxycarbonyl, optionally substituted C_{1-6} alkylthio, optionally substituted C_{1-6} alkylsulfinyl, optionally substituted C_{1-6} alkylsulfonyl, optionally substituted C_{1-6} arylthio, optionally substituted C_{1-6} arylsulfinyl, optionally substituted C_{1-6} arylsulfonyl or $R^{20}R^{21}NS$.

3 A fungicidal, insecticidal, acaricidal, molluscicidal or nematicidal composition comprising a fungicidally, insecticidally, acaricidally, molluscicidally or nematicidally effective amount of a compound of formula (I) as claimed in claim 1 or a compound of formula (VIII) as claimed in claim 2 and a carrier or diluent therefor.

4 A method of combating and controlling fungi comprising applying to a plant, to a seed of a plant, to the locus of the plant or seed or to the soil a fungicidally effective amount of a compound of formula (I) as claimed in claim 1 or a compound of formula (VIII) as claimed in claim 2.

5 A method of combating and controlling insects, acarines, nematodes or molluscs which comprises applying to a pest, to a locus of a pest, or to a plant susceptible to attack by a pest an insecticidally, acaricidally, nematicidally or molluscicidally effective amount of a compound of formula (I) as claimed in claim 1 or a compound of formula (VIII) as claimed in claim 2.

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TRADUCCION

Oficina de Patentes - Autoridad Ejecutiva del Departamento de Comercio e Industria.

Oficina de Patentes - Cardiff Road, Newport, South Wales NP10 8QQ

El que suscribe, funcionario debidamente autorizado para firmar y expedir certificados en representación del Controlador General, en virtud de Artículo 74(1) y (4) de la Ley de Desregulación y Contrataciones de 1994, certifica por la presente que los documentos adjuntos son copia fiel de la documentación presentada originariamente en relación con la solicitud de patente identificada en el presente certificado.

De acuerdo con el Reglamento de Patentes (Reinscripción de Sociedades) de 1982, si una compañía mencionada en este certificado y los documentos adjuntos ha sido reinscripta de acuerdo a la Ley de Sociedades de 1980 con el mismo nombre que aquél con el cual estaba inscripta inmediatamente antes de la reinscripción, excepto la sustitución o inclusión en la última parte del nombre de las palabras "public limited company" o su equivalente en galés, las referencias al nombre de la sociedad que figuren en este certificado y cualesquiera documentos adjuntos se considerarán como referidas al nombre con el cual ha sido reinscripta.

De acuerdo con la norma, las palabras "public limited company" pueden ser sustituidas por p.l.c., plc, P.L.C. o PLC.

Con la reinscripción de acuerdo a la Ley de Sociedades no se constituye una nueva entidad legal, sino que simplemente se somete a la sociedad a determinadas reglas legales societarias adicionales.

Firmado, ilegible. Fecha: 14 de marzo del 2000

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(Sello en relieve sobre oblea y cinta)

En la hoja siguiente dice:

Formulario de Patente 1/77

OFICINA DE PATENTES Oficina de Patentes - Cardiff Road, Newport, Gwent NP9 1RH

Solicitud de Patente

Recibido en mano el 28 de enero del 2000

31 enero 00 E509118-1 D02093 P01/7700 0.00-0002039.6

1. Su referencia: PPD 50466/ GB/ P

2. Solicitud de patente número: **0002039.6**

3. Nombre completo, domicilio y código postal del o los solicitantes:

ZENECA Limited, 15 Stanhope Gate, LONDON WIY 6LN, REINO UNIDO

Número ADP de patentes: 6254007002

Si el solicitante es una corporación, indicar el país/estado : REINO UNIDO

4. Título de la Invención : **COMPUESTOS QUIMICOS**

5. Nombre del agente (si corresponde) :

John Richard Waterman

Domicilio de servicio en el Reino Unido al cual se debe enviar la correspondencia:

Intellectual Property Dept., ZENECA Agrochemicals, Jealott's Hill Research Station, PO Box 3538, Bracknell Berkshire RG42 6YA, Mereside, REINO UNIDO

Número de ADP de patentes: 06791537001

9. Indique la cantidad de hojas de todos los siguientes adjuntos que ingresa con este formulario. No cuente copias de un mismo documento.

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275

Hojas de continuación de este formulario :

Memoria descriptiva: 50

Reivindicaciones: 5

11. Solicito/solicitamos el otorgamiento de una patente sobre la base de esta solicitud. Firmado. Fecha: 28/1/00

12. Nombre y número telefónico del representante en el Reino Unido:

VIJAYA KUMARI MALLIPEDDI - 01344 414365

DAWN LISA ROYAL - 01344 414079

Otros items en blanco.

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UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

No. **D613061**

Date **20 March, 2000**

This document bears
the signature / seal of **A Cressey**

Acting in the capacity of **Official Of The Patent Office Newport**

Signed by: **B. Amarteifio**

FOREIGN AND COMMONWEALTH OFFICE
LONDON

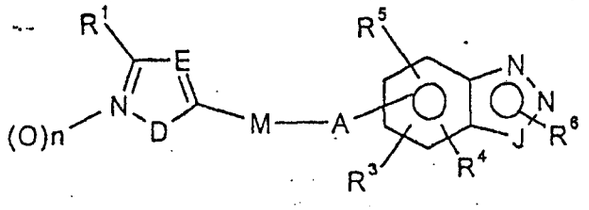
For Her Majesty's Principal Secretary of State
For Foreign and Commonwealth Affairs

COMPUESTOS QUÍMICOS

La presente invención se relaciona con derivados azina y azol, con procesos para prepararlos, con composiciones fungicidas, insecticidas, acaricidas, molusquicidas y nematicidas que los comprenden, con métodos para usarlos para combatir enfermedades provocadas por hongos (especialmente enfermedades provocadas por hongos en las plantas) y con métodos para usarlos para combatir y controlar plagas de insectos, ácaros, moluscos y nematodos.

En WO95/31448, WO97/18198, WO98/02424 y WO98/05670 se describen derivados azina y azol.

La presente invención provee un compuesto de fórmula (I):



(I)

en donde n es 0 o 1; A es C_{1-6} alquileno opcionalmente sustituido, C_{2-6} alquenileno opcionalmente sustituido, C_{2-6} alquinileno opcionalmente sustituido, C_{1-6} alquilenoxi opcionalmente sustituido, oxi (C_{1-6}) alquileno opcionalmente sustituido, C_{1-6} alquilentio opcionalmente sustituido, tio (C_{1-6}) alquileno opcionalmente sustituido, C_{1-6} alquilenamino opcionalmente sustituido, amino (C_{1-6}) alquileno opcionalmente sustituido, [C_{1-6}alquilenoxi (C_{1-6}) alquileno] opcionalmente sustituido, [C_{1-6} alquilentio (C_{1-6}) alquileno] opcionalmente sustituido, [C_{1-6} alquilensulfinil (C_{1-6}) alquileno] opcionalmente sustituido, [C_{1-6} alquilensulfonil (C_{1-6}) alquileno] opcionalmente sustituido o [C_{1-6}alquilenamino (C_{1-6}) alquileno] opcionalmente sustituido;

D es S, NR^{10}, $CR^8=CR^9$, $CR^8=N$, $CR^8=N(O)$, $N=CR^9$ o $N(O)=CR^9$;

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R^{10} es C_{1-6} alquilo;

E es N,N-óxido o CR^{12};

M es $OC(=Y)$, $N(R^{51})C(=Y)$, $N=C(OR^{52})$, $N=C(SR^{53})$ o $N=C(NR^{54}R^{55})$ donde O o N es el átomo de unión al anillo que contiene E y D;

Y es O, S o NR^{13};

J es N o CR^{14};

R^1 es hidrógeno, halógeno, C_{1-6} alquilo opcionalmente sustituido, C_{2-6} alquenilo opcionalmente sustituido, C_{2-6} alquinilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, ciano, nitro o SF_5;

R^{51} es hidrógeno, C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinilo (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, fenoxicarbonilo opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, C_{1-6} ariltio opcionalmente sustituido, C_{1-6} arilsulfinilo opcionalmente sustituido, C_{1-6} arilsulfonilo opcionalmente sustituido o $R^{20}R^{21}NS$;

R^{52} es C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, 1-10 alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(1-10)alquilaminocarbonilo

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opcionalmente sustituido, amino, C_{1-6} alquilamino opcionalmente sustituido, di (C_{1-6}) alquilamino opcionalmente sustituido, fenoxicarbonilo opcionalmente sustituido, tri(C_{1-4})alquilsililo, arildi (C_{1-4})alquilsililo, (C_{1-4})alquildiarilsililo o triarilsililo;

R^{53} es C_{1-10} alquilo opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquil] opcionalmente sustituido, [C_{2-6} alquinil-(C_{1-6})alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido o fenoxicarbonilo opcionalmente sustituido);

R^{54} y R^{55} son, independientemente C_{1-10} alquilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, [C_{2-6} alquenil (C_{1-6}) alquilo] opcionalmente sustituido, [C_{2-6} alquinil (C_{1-6}) alquilo] opcionalmente sustituido, C_{3-7} cicloalquilo opcionalmente sustituido, C_{1-10} alquilcarbonilo opcionalmente sustituido, C_{1-10} alcoxicarbonilo opcionalmente sustituido, formilo, C_{1-10} alquilaminocarbonilo opcionalmente sustituido, di(C_{1-10})alquilaminocarbonilo opcionalmente sustituido, hidroxi, amino, C_{1-6} alquilamino opcionalmente sustituido, di (C_{1-6}) alquilamino opcionalmente sustituido, o fenoxicarbonilo opcionalmente sustituido;

R^3, R^4 y R^5 son, independientemente, hidrógeno, halógeno, C_{1-6}alquilo opcionalmente sustituido, C_{1-6} alcoxi opcionalmente sustituido, C_{1-6} alquiltio opcionalmente sustituido, C_{1-6} alquilsulfinilo opcionalmente sustituido, C_{1-6} alquilsulfonilo opcionalmente sustituido, ciano, nitro, C_{1-6} alquilcarbonilo opcionalmente sustituido, C_{1-6} alcoxicarbonilo opcionalmente sustituido o SF_5;

R^6 es hidrógeno, ciano, C_{1-20} alquilo opcionalmente sustituido, C_{2-20}

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UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND

No. **D613062**

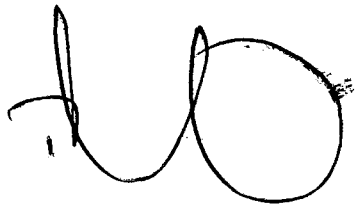
Date **20 March, 2000**

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Acting in the capacity of **Official Of The Patent Office Newport**



Signed by: **B. Amarteifio**



For Her Majesty's Principal Secretary of State
For Foreign and Commonwealth Affairs

CONSULADO GENERAL DE COLOMBIA
LONDRES

AUTENTICACION N° 428-03

EL CONSUL DE COLOMBIA DE FE DE
QUE B. AMARIELLO
EJERCIA EN LA FECHA LAS FUNCIONES
DE Oficial Ministerio Relaciones Exteriores
Y QUE SU FIRMA Y SELLOS SON LOS
QUE ACOSTUMBRA EN SUS ACTOS
OFICIALES 21 MAR 2000
LONDRES
DERECHOS: US$ 25=

CONSULADO GENERAL DE COLOMBIA
LONDRES

ANA GEORGINA CHARRY
Primer Consul

SELLO IMPUESTO
DE TIMBRE