



Industria y Comercio

SUPERINTENDENCIA

Delegatura de propiedad Industrial

División de Nuevas Creaciones

PCT
SOLICITUD

PATENTE DE INVENCION

21 EXPEDIENTE No. 04-2821.

54 TÍTULO 6-(2,6-DIFLUORO-FENIL)-TRIAZOLOQUINOLINOS.

51 CLASIFICACIÓN INTERNACIONAL C07D487/04

71 SOLICITANTE BASE AKTIENGESELLSCHAFT.

DOMICILIO Ludwigshafen, República Federal de Alemania

74 APODERADO Emilio Fajardo

22 BOGOTÁ, D. C., 16-01-04.



Industria y Comercio
SUPERINTENDENCIA



04 002821 00

PETITORIO

SUPERINDUSTRIA Y COMERCIO
Radicación : 0402821 00000000
Fecha (MM): 2004-01-16 17:19:20
Trámite : 011 PCT-PROTEC 379 FASE NAC 411 MARC/NAC
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

FORMULARIO UNICO DE SOLICITUD DE PATENTE PCT ENTRADA EN FASE NACIONAL

1 SOLICITUD DE: ☒ Patente de Invención. ☐ Patente de Modelo de Utilidad.		
☐ Capítulo I. ☒ Capítulo II.		
2 SOLICITANTE (71)	Nombre: BASF AKTIENGESSELLSCHAFT sociedad constituida y existente bajo las leyes de República Federal de Alemania. Dirección: 67056 Ludwigshafen República Federal de Alemania Domicilio: .Ludwigshafen, República Federal de Alemania.	IDENTIFICACION C.C. ☐ NIT ☐ C.E. ☐ Otro ☐ Cual _____ Número: _____
3 REPRESENTANTE O APODERADO	Nombre: EMILIO FERRERO Dirección: Carrera 4ª. No. 72-35 Teléfono: 347 38 11 Fax:: 217 92 11 E-mail: <u>clientes@camva.com.</u> Domicilio: Bogotá, Colombia.	IDENTIFICACION C.C. ☒ NIT ☐ C.E. ☐ Otro ☐ Cual _____ Número: <u>438.019</u> T.P. <u>31.929</u>
4 INVENTOR (ES) (72)	1. Jordi TORMO I BLASCO Mühlweg 47, 67117 Limburgerhof, República Federal de Alemania 2. Hubert SAUTER Neckarpromenade 20, 68167 Mannheim, República Federal de Alemania 3. Bernd MÜLLER Jean-Ganss-Strasse 21, 67227 Frankenthal, República Federal de Alemania 4. Markus GEWEHR Goethestrasse 21, 56288 Kastellaun, República Federal de Alemania 5. Wasillios GRAMMENOS Samuel-Hahnemann-Weg 9, 67071 Ludwigshafen, República Federal de Alemania 6. Thomas GROTE Im Hoehnhausen 18, 67157 Wachenheim, República Federal de Alemania 9. Ingo ROSE C 2, 19, 68159 Mannheim, República Federal de Alemania 10. Peter SCHÄFER Römerstrasse 1, 67308 Ottersheim, República Federal de Alemania 11. Frank SCHIEWECK Lindenweg 4, 67258 Hessheim República Federal de Alemania 12. Eberhard AMMERMAN Von-Gargern-Strasse 2, 64646 Heppenheim, República Federal de Alemania 13. Siegfried STRATHMANN Donnersbergstrasse 9, 67117 Limburgerhof, República Federal de Alemania 14. Gisela LORENZ Erlenweg 13, 67434 Hambach, República Federal de Alemania	

	7. Andreas, GYPSE B 4.4, 68159 Mannheim, República Federal de Alemania 8. Joachim, RHEINHEIMER Merziger Strasse 24, 67063 Ludwigshafen, República Federal de Alemania	15. Reinhard, STIERL Ginsterstrasse 17, 67112 Mutterstadt, República Federal de Alemania
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PCT (88)

 Solicitud Internacional No.: PCT/EP02/07575
 Publicación Internacional No.: WO 03/008415 A1

Fecha: Julio 8 de 2002
 Fecha: Enero 30 de 2003

6

Título (54) 6-(2,6-DIFLORURO-FENIL)-TRIAZOLOPIRIMIDINOS

7

Clasificación Internacional (51) : C07D 487/04

8 Prioridad SI ☒ NO ☐	(33) País de Origen <u>EP</u>	(32) Fecha <u>Julio 18 de 2002</u>	(31) Número de Solicitud <u>01117404.2</u>
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9

Comprobante de pago No.: 04-691 **Fecha:** Enero 6 de 2004

10

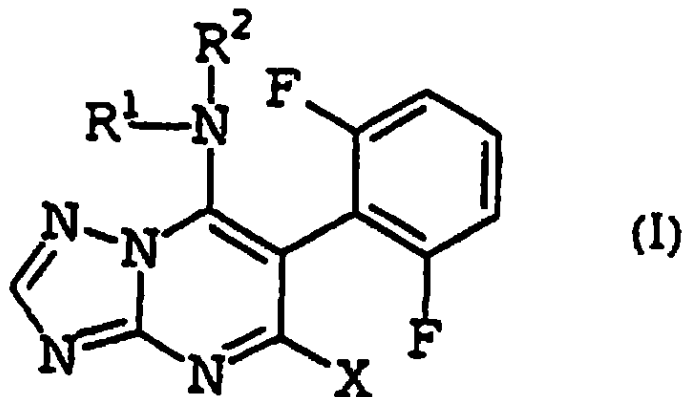
Anexos:

- ☒ Comprobante de pago de la tasa de presentación de la solicitud por \$ 422.000.00.
- ☐ Comprobante de pago por reivindicación de prioridad.
- ☒ Documento que acredita la existencia y representación legal cuando el solicitante sea persona jurídica.
- ☒ Poderes, si fuere el caso.
- ☐ Documento de cesión del inventor al solicitante o a su causante.
- ☐ Declaraciones.
- ☒ Copia de la solicitud internacional. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Traducción de la solicitud internacional al castellano. (Resumen, descripción, reivindicaciones, dibujos)
- ☒ Copia del examen preliminar efectuado por la IPEA.
- ☒ Traducción del examen preliminar efectuado por la IPEA.
- ☐ De ser el caso, copia del contrato de accaso.
- ☐ De ser el caso, documento que acredita la licencia o autorización de uso de conocimientos tradicionales de las comunidades indígenas.
- ☐ De ser el caso, certificado de depósito del material biológico.
- ☒ Arte final 12x12
- ☐ De ser el caso, información sobre otras solicitudes de patente o títulos obtenidos en el extranjero por el mismo titular o su causante, relacionadas parcial o totalmente con la invención de esta solicitud.
- ☐ Otros

13 *

11

FIGURA CARACTERISTICA:



(I)

12

Solicito la concesión de la patente,

NOMBRE: EMILIO FERRERO

FIRMA: 

C.C. 438.019 de Usaquén T.P. 31.929

MRE/lms

BOGOTÁ, COLOMBIA

REPRESENTACION Y PODER

Yo (nosotros), abajo firmado (s)
BASF Aktiengesellschaft

domiciliado(s) en Ludwigshafen, República
Federal de Alemania

por el presente nombramos a GERMAN CAVELIER, tpa. 832; GONZALO PERDOMO, tpa. 831; ERNESTO CAVELIER, tpa. 11519; y EMILIO FERRERO, tpa. 31829; domiciliados en la Carrera 4ª N° 72-35, Bogotá, Colombia, en obediencia a lo dispuesto en el párrafo 1º del Artículo 543 del Código de Comercio, al primero como principal y los demás como suplentes, en su orden, como nuestros representantes en todos los asuntos de propiedad industrial con facultad para recibir notificaciones y nombrar apoderados judiciales o extrajudiciales. El primer representante suplente reemplazará al principal en caso de ausencia o impedimento temporal o definitivo de aquél. La misma regla se aplicará cuando el segundo representante suplente haya de reemplazar al primero, o el tercero al segundo. En tales casos, el representante principal, o el primero, o segundo suplente, en su caso, o ambos, declararán su intención de no ejercer la representación mediante declaración autenticada por Notario Público en Colombia, o por Notario u otro Funcionario Público, o Cónsul de Colombia, en el extranjero; y si se tratare de impedimento, con el certificado respectivo. Si alguno de los nombrados faltare definitivamente, el siguiente tomará su lugar. Cuando cesare la ausencia o impedimento del representante principal, o de su primero o segundo suplente, en su caso, podrán ejercer la representación, en su orden, uno u otros según el caso, asumiéndola por el solo hecho de ejercerla, cesando en ese momento el ejercicio de la representación por el primero, segundo o tercer suplente en su caso. Además, y bajo las mismas reglas, conferimos poder a los abogados arriba nombrados, para obtener la protección de mi (nuestra) propiedad industrial y contra la competencia desleal, a cuyo efecto autorizo (amos) a los dichos apoderados para que me (nos) representen ante cualesquiera entidades o personas, ejerzan o no jurisdicción, especialmente ante las del orden administrativo, contencioso-administrativo y judicial, en todo lo concerniente a los siguientes asuntos: a) Obtención de patentes de invención, modelos y dibujos industriales; el registro de marcas de fábrica, colectivas, defensivas y de servicios; el depósito de nombres comerciales y enseñas; su renovación, traspaso, cambio de nombre o domicilio, cancelación voluntaria; y el registro de licencias de uso de estos derechos; b) Las acciones de oposición, cancelación, nulidad, medidas cautelares, concesión de licencias y en general los juicios civiles, penales, administrativos o contencioso-administrativos relacionados con estos derechos; acciones y juicios que promovamos o se nos promuevan. Y para que en todos los asuntos arriba determinados, puedan sustituir este mandato, transigir, desistír, cancelar, recibir, renunciar, y ratificar los actos hechos por agentes oficiales.

Dado y firmado hoy 17 de marzo de 1989
en D-6700 Ludwigshafen

BASF Aktiengesellschaft

Firma
ppa. Welzel

Ich (wir) unten Unterzeichnender (de)
BASF Aktiengesellschaft

wohnhaft in Ludwigshafen, Republica Federal
de Alemania

verleihen durch dieses Schreiben an GERMAN CAVELIER, tpa. 832; GONZALO PERDOMO, tpa. 831; ERNESTO CAVELIER, tpa. 11519; und EMILIO FERRERO, tpa. 31829; wohnhaft in der Carrera 4ª N° 72-35, Bogotá, Kolumbien, um die Verfügung des Absatzes 1 im Artikel 543 des Handelsgesetzbuch zu beachten, der erste als Hauptvertreter und die übrigen als Stellvertreter, beziehungsweise, als unsere Vertreter in allen was sich auf das industrielle Eigentum bezieht, berechtigt Meldungen zu empfangen und gerichtliche und aussergerichtliche Bevollmächtigte zu ernennen. Der erste Stellvertreter wird den Hauptvertreter ersetzen wegen zeitweiligen oder definitiven Abwesenheit oder Hindernisses des ersten. Dieselbe Regel wird angewandt werden wenn der zweite Stellvertreter den ersten ersetzen muss, oder der dritte den zweiten. In solchen Fälle der Hauptvertreter, oder der erste oder der zweite Stellvertreter, beziehungsweise, oder beide, werden ihre Absicht aussprechen um nicht die Vertretung auszuüben mittelst Aussage notariell beglaubigt in Kolumbien, oder vor Notar oder vor einem anderen öffentlichen Beamten, oder Kolumbianischen Konsul im Auslande; und wenn es ein Hindernis sei, mittels der betreffenden Beglaubigung. Wenn einer der Genannten immerfort abwesend wäre, der Folgende wird ihn ersetzen. Im Falle dass die Abwesenheit oder das Hindernis des Hauptvertreters, oder diejenigen seines ersten, zweiten oder dritten Vertreters, beziehungsweise, beendet, einer oder anderen, ordnungsgemäss werden die Vertretung ausüben und sie zu sich nehmen nur auf Grund sie auszuüben, mit Aufhören zur Zeit der Ausübung der Vertretung durch den ersten, den zweiten oder den dritten Stellvertreter beziehungsweise. Ausserdem, und unter dieselben Regeln, wir verleihen den genannten Rechtsanwälte die Vollmacht, und um den Schutz meines (unseres) industriellen Eigentum zu erhalten, und gegen den unfaulsten Wettbewerb; zu dessen Zweck ich (wir) die vorgenannten Bevollmächtigten ernenne (nenne) um alle vor beliebigen Institutionen oder Personen, die demselben Zweck dienen oder nicht, vor allem vor dem Verwaltungs-, Verwaltungs-, streitigem Verwaltungs-, und juristischen Charakter, in allen was sich auf folgende Angelegenheiten bezieht, zu vertreten: a) Erlangung von Marken, Modellen und Zeichnungen; Registrierung von Waren, Handel, Defensiv- und Service-Marken; Aufrechterhaltung von Handelsnamen und Zeichen; Erneuerung und Übertragung, Namen und Wohnortänderung, freiwillige Annullierung und die Beglaubigung von Vertragsklauseln; b) Die Oppositionsklagen, Annullierung, Ungültigkeit, Vorrichtungsmaßnahmen, Lizenzen und im allgemeinen die Zivil-, Straf-, Verwaltungs- oder streitigen Verwaltungsprozesse, die mit diesen Rechten verbunden sind, Aktionen und Verhandlungen, die wir vorantreiben oder die man uns vorantreibt und; c) damit sie in allen oben bestimmten Angelegenheiten dieses Mandat ersetzen, regeln, davon Abstand nehmen, annullieren, empfangen, verzichten, Meldungen annehmen und gerichtliche und aussergerichtliche Bevollmächtigte ernennen, und die Handlungen der halbamtlichen Vertreter bestätigen.

Unterzeichnet heute am 17. März 1989
in D-6700 Ludwigshafen

Unterschrift
ppa. Richters



U.R.Nr. 1407/89

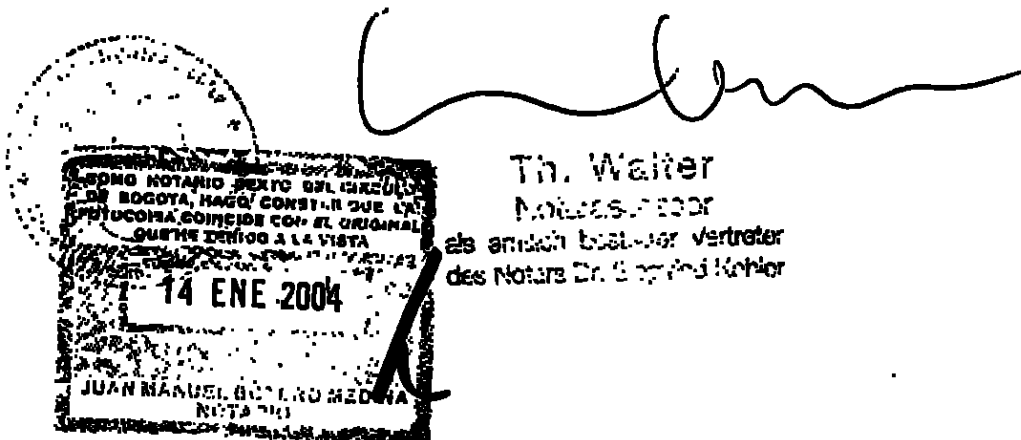
Ich beglaube hiermit die Echtheit der vorst.
eigenhändig vor mir vollzogenen Unterschriften der für
die Firma BASF Aktiengesellschaft Ludwigshafen am Rhein
handelnden Herren:

1. Dr. Günther W e l z e l , Chemiker in
Ludwigshafen am Rhein,
2. Dr. Peter R i c h t e r s , Chemiker in
Ludwigshafen am Rhein.

Die Herren Dr. Welzel und Dr. Richters sind mir persönlich
bekannt.

Aufgrund heutiger Einsichtnahme in das Handelsregister
beim Amtsgericht Ludwigshafen am Rhein HR B 3000 be-
scheinige ich, daß die Herren Dr. Welzel und Dr. Richters
als Prokuristen gemeinschaftlich zur Vertretung und
Zeichnung der Firma BASF Aktiengesellschaft mit dem
Sitz in Ludwigshafen am Rhein berechtigt sind.

Ludwigshafen am Rhein, den 17. März 1989



Die Echtheit vorstehender Unterschrift des Notarassessors

Thomas Walter

als amtlich bestellter Vertreter des Notars Justizrat Dr. Kohler
in Ludwigshafen am Rhein und die Echtheit des begedruckten
Dienststempels werden hiermit bestätigt. Zugleich wird bescheinigt,
daß der Vorgenannte zur Vornahme der Amtshandlung befugt war.

Frankenthal (Pfalz), den einundzwanzigsten März neunzehnhundert-
neunundachtzig

LUZ ARMADA DE HERRER
INSTRUMENTA E INTER
2002
Boletín No. 569 Michuila

Präsident des Landgerichts
Franz Serfas
(Franz Serfas)



Kostenvermerk: Gebühr 20.-- DM



El suscrito Cónsul General de Colombia en Frankfurt
am Main, República Federal de Alemania, vistos los
documentos presentados por los interesados,

C E R T I F I C A:

Que el señor Thomas Walter-----
quien como Notario en Ludwigshafen am Rhein-----
autenticó la(s) firma(s) del(os) signatario(s) del
Poder precedente, ejercía las funciones indicadas y
su firma corresponde a la registrada ante el Tribunal Re-
gional de Frankenthal (Pfalz)-----
que la compañía BASF Aktiengesellschaft-----
es una sociedad constituida de acuerdo con las leyes
de la República Federal de Alemania y cumple su objeto
conforme a las mismas; que el(los) señor(es) Dr. Gunther
WELZEL y el Dr. Peter RICHTERS-----
quien(es) en sus carácter(es) de apoderados-----
----- y cuya(s) firma(s) fué
(fueron) autenticada(s) ante el Notario Thomas Walter-----
----- es(son) su(s) representante(s) legal(es) en este país.

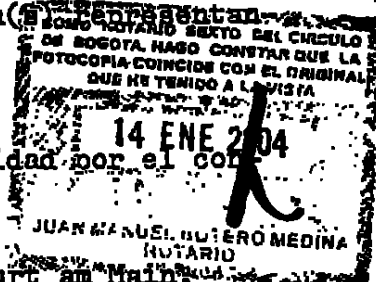
El Cónsul General no asume responsabilidad por el con-
tenido del documento.
Esta Certificación se expide en Frankfurt am Main,
el seis de Abril de mil novecientos ochenta y nueve.

Frankfurt a. M 06 APR 1989

M-0077

PAGADO IMPUESTO DE TIMBRE

Por 4 U.S. \$ de Ley E. S. N. N.



SECRETARIA GENERAL

MINISTERIO DE RELACIONES EXTERIORES
LEGALIZACIONES
No. 85064
12 ABR. 1994
MEXICO
Martha Nino
cuya firma aparece al pie del presente documento, expedida en esta fecha
de conformidad con lo anterior.

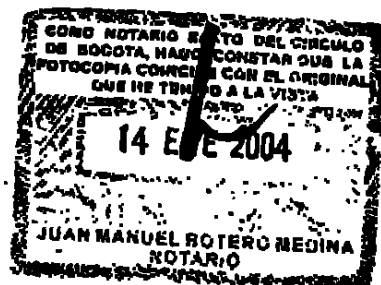
Manuel Enríquez Acuña
MANUEL ENRIQUEZ ACUÑA
Secretario General

COMO NOTARIO SEXTO DEL CIRCULO
DE NOTARIA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA
14 ENE 2004
JUAN MANUEL BOTERO MEDINA
NOTARIO



6

COMO NOTARIO SEKTO DEL CIRCUITO
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON EL ORIGINAL
QUE HE TENIDO A LA VISTA
14 ENE 2004
JUAN MANUEL B. GONZALEZ
NOTARIO



Die konsularische Legalisierung ist notwendig.

NOTA PARA EL SEÑOR CONSUL COLOMBIANO: Según los artículos 65 del C. de P. C. y 480 del C. Co., si el poderdante es una sociedad, el señor Cónsul debe certificar que tuvo a la vista las pruebas su existencia, que ejerce su objeto social, que quien confiere el poder es su representante y puede otorgar poder, seguidamente autenticar la firma de éste.

TRADUCCION OFICIAL NO. 2056

de un documento escrito en Alemán, el cual para su identificación se sella con el sello de la traductora, lo mismo que la presente.-

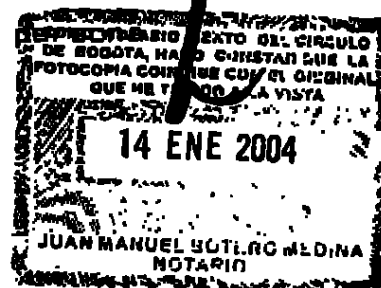
(A continuación del poder conferido a GERMAN CAVELIER, GONZALO PERDOMO, ERNESTO CAVELIER y EMILIO FERRERO, domiciliados en la Cra. 4 No. 72-35, Bogotá, el 17 de marzo de 1989, por la sociedad BASF Aktiengesellschaft, domiciliada en Ludwigshafen, RFA:)

Protocolo notarial No. 1407/89

Certifico la autenticidad de las firmas anteriores puestas ante mí, por los señores:

1. Dr. Gunther W e l z e l , químico, domiciliado en Ludwigshafen am Rhein,
2. Dr. Peter R i c h t e r s , químico, domiciliado en Ludwigshafen am Rhein.

A los doctores Welzel y Richters los conozco en



LUZ ANRAGA DE HERBES
TRADUCCION OFICIAL
Resolución No. 599 Mijusticia

a

Certifico, por haber tenido a la vista el registro de comercio HR B 3000, del juzgado de Ludwigshafen, que los doctores Wlzel y Richters, en su calidad de apoderados, están facultados para representar conjuntamente y firmar por la sociedad BASF Aktiengesellschaft, con sede en Ludwigshafen.

Ludwigshafen am Rhein, 17 de marzo de 1989

(sello redondo:)

Dr. Siegfried Kohler

Fdo.: firma ilegible

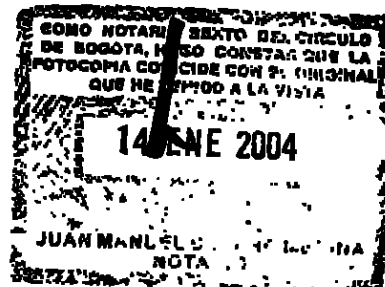
Notario de Ludwigshafen

Th. Walter

Asesor del notario como representante oficialmente designado del notario Dr. Siegfried Kohler

Se certifica la autenticidad de la firma anterior del asesor del notario, consejero de justicia Dr. Kohler, domiciliado en Ludwigshafen am Rhein, y la del sello oficial que la acompaña. Al mismo tiempo se certifica que el mencionado notario estaba facultado para realizar ese acto oficial.

Frankenthal (Pfalz), veintiuno de marzo de mil novecientos ochenta y nueve



LUZ ARRIAGA DE HENRIK
TRADUCCION Y INTERPRETACION
Resolución No. 599 Ministerio

El Presidente del Tribunal Regional

Fdn.: firma ilegible (sello redondo:)

(Franz Serfas)

El Presidente del Tribunal Regional
de Frankenthal (Pfalz)

Nota: Derrechos 20,-- DM

EN ESPAÑOL: La legalización de las firmas anteriores por el
Consulado de General de Colombia en Frankfurt, bajo el No.
0077 (Certificación consular) del 6 de abril de 1989 y del
Ministerio de Relaciones Exteriores de Colombia bajo el No.
85061 del 24 de abril de 1989.

Pagado impuesto de timbre US\$ 6,00

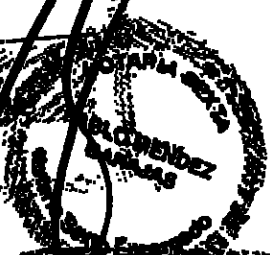
ES TRADUCCION FIEL Y COMPLETA, de la cual se deja copia en
los archivos de estas oficinas para su confrontación.

Bogotá, 26 de abril de 1989

LUZ ARRIAGA DE HERBEN
TRADUCTORA E INTERPRETE OFICIAL

Luz Arriaga de Herben
Resolución No. 599 Minjusticia

COPIA DEL ORIGINAL DE SANTAFE DE
BOGOTA, H-
MAIS, PUEBLO, ETC.
Luz Arriaga de Herben
AUTENTICACION
05 AGO. 1999
SANTAFE DE BOGOTA



COPIA DEL ORIGINAL DE SANTAFE DE BOGOTA, H-
MAIS, PUEBLO, ETC.
AUTENTICACION
14 ENE 2004
JUAN MANUEL SI...
NOTA

MINISTERIO DE RELACIONES EXTERIORES
LEGALIZACIONES
 Bogotá 28 MAR 1985 No. 89045
HACE CONSTAR
 Que el señor LUZ DE HEREDIA
 cuya firma aparece al pie del presente
 documento, desempeña en esa fecha
 las funciones allí indicadas.

**COMO NOTARIO SEXTO DEL CIRCULO
 DE BOGOTA, HAGO CONSTAR QUE LA
 FOTOCOPIA COINCIDE CON EL ORIGINAL
 QUE HE TENIDO A LA VISTA**
14 ENE 2004
JUAN MANUEL BOTERO MEDINA
NOTARIO

Generales
División Consular
Encargado

881051599954

B C C 13
SUCURSAL CORPORATIVA



DECLARACION Y PAGO DEL

IMPUESTO D

TIMBR
NACIONAL

16 013 01 000045 1

RECIBO DE 15780000

16 013 01 000045 1

DATOS GENERALES
CONCEPTO

1 Administración de Impuestos de:		Código	2 Teléfono
BOGOTA		0,3	2120100
3 Documento de Identificación (marque X)		4 Apellidos y Nombres o Razón Social de las partes (máximo 60 caracteres).	
C.C. o T.I. ☐ C ☐ NIT. ☐ A ☒ Y No. 860041367 D.V. ☐ 3		CAVELIER ABOGADOS	
5 Documento de Identificación (marque X)		6 Apellidos y Nombres o Razón Social de las partes (máximo 60 caracteres).	
C.C. o T.I. ☐ C ☒ NIT. ☐ A ☐ Y No. 19'301.629 D.V. ☐		FORERO ROCHA JAIME	
7 Dirección (de la persona o entidad identificada en la casilla 4)		Municipio	Departamento
Cra. 4a. No. 72-35		BOGOTA	CUNDINAMARCA
8 Relación al tipo(s) de documento(s), indicando número, fecha, valor y naturaleza de la transacción		9 Número de documento	
TIMBRE TRADUCCION OFICIAL No. 2056 DE ABRIL 26 DE 1989		1	
PAGO DERECHOS TRADUCCION DE UN PODER			
COLO 0361-52-218-8			

REVISADO
SECCION DE NEGOCIOS GENERALES
DE ASUNTOS CONSULARES
DE RELACIONES EXTERIORES

FIRMA	Responsable del pago
	Nombre C.C. No. 19301629

1 VALOR DEL IMPUESTO A PAGAR	750
2 Sanciones	0
3 Impuesto de mora	0
4 TOTAL A PAGAR (suma de 1 + 2 + 3)	750
5 Estado	☒ X
6 Cédula	☐
7 No.	0
8 Código	1

DEM-31-V-88

CONTRIBUYENTE

1 037 ***750.00

CON PAGO

COMO NOTARIO SEATO DEL CIRCULO
DE BOGOTA, HAGO CONSTAR QUE LA
FOTOCOPIA COINCIDE CON LA ORIGINAL
QUE HE TENIDO A LA VISTA
14 ENE 2004
JUAN MANUEL BOTERO MEDINA
NOTARIO

CAVELIER

ABOGADOS

EDIFICIO SISKI

CARRERA 49, No. 72-35

BOGOTA 8, COLOMBIA

CORREO ELECTRONICO MUNDIAL CAVE

TELEFONO (57) (1) 2120100

CABLE: CAVELEYES

Señor Jefe de la
DIVISION DE NUEVAS CREACIONES
Superintendencia de Industria y Comercio
E. S. D.

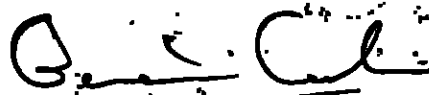
Poderdante: BASF AKTIENGESELLSCHAFT

Poder conferido el: 17-03-89

Yo, GERMAN CAVELIER, obrando en mi calidad de apoderado principal del poderdante arriba mencionado, manifiesto a Usted que sustituyo el poder conferido en el doctor EMILIO FERRERO, Abogado con Tarjeta Profesional No. 31.929, con todas las facultades que me fueron conferidas.

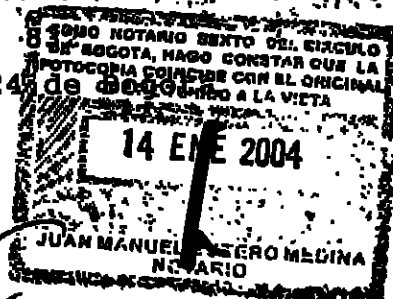
Hago la anterior sustitución conforme al artículo 66 del Código de Procedimiento Civil ya que los otros sustitutos faltan en este momento.

Señor Jefe,


GERMAN CAVELIER.

T.P.A. No. 8

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Acepto:



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2e-780-2

(Art. 1.º del Decreto 2282 de 1989).

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(Art. 1º, del Decreto 2/82 de 1969)

(Art. 1º, del Decreto 2/82 de 1969)

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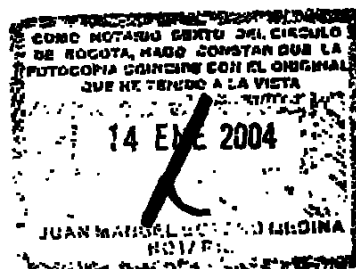
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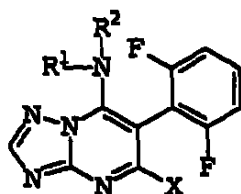
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(54) Title: 6-(2,6-DIFLUOROPHENYL)-TRIAZOLOPYRIMIDINES AS FUNGICIDES



(1)

(57) Abstract: 6-(2,6-Difluoro-phenyl)-triazolopyrimidines of formula (I), in which R¹ and R² independently denote hydrogen or Alkyl, Alkyl, Alkenyl, Alkynyl, or alkadienyl, cycloalkyl, phenyl, naphthyl, or 5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulphur or oxygen atom. Or 5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulphur or oxygen atom where R¹ and R² radicals may be unsubstituted or substituted as defined in the description, or R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulphur or oxygen atom, which may be substituted; X is halogen, cyano, alkoxy, haloalkoxy or alkenyloxy; Processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

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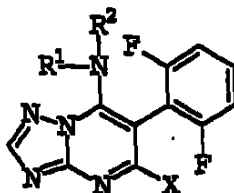
6-(2,6-DIFLUOROPHENYL) TRIAZOLOPYRIMIDINES AS FUNGICIDES

Description

5

The invention relates to 6-(2,6-difluoro-phenyl)-triazolopyrimidines of formula I

10



I

in which

15

R¹ and R² independently denote hydrogen or

C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, or C₄-C₁₀-alka-
dienyl, C₃-C₁₀-cycloalkyl, phenyl, naphthyl, or

20

5- or 6-membered heterocyclyl, containing one to four
nitrogen atoms or one to three nitrogen atoms and one sulfur
or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen
atoms or one to three nitrogen atoms and one sulfur or oxygen
atom, or

25

where R¹ and R² radicals may be unsubstituted or may carry one
to three groups R^a,

30

R^a is cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₃-C₆-cycloalkyl,
C₁-C₆-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-
C₁-C₆-alkylamino, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy,
C₂-C₆-alkynyl, C₃-C₆-alkynyloxy and C₁-C₄-alkylenedioxy;
or

35

R¹ and R² together with the interjacent nitrogen atom represent a
5- or 6-membered heterocyclic ring, containing one to four
nitrogen atoms or one to three nitrogen atoms and one sulfur
or oxygen atom, which may be substituted by one to three R^a
radicals;

40

X is halogen, cyano, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₆-al-
kenyloxy.

45 Moreover, the invention relates to processes for their prepara-
tion, compositions containing them and to their use for combating
phytopathogenic fungi.

CONFIRMATION COPY

6-Phenyl-7-amino-triazolopyrimidines are generally known from US 4,567,262 and US 5,593,996.

Triazolopyrimidines with a trifluorophenyl group in 6-position are disclosed in WO-A 98/46607 and EP-A 945 453.

From WO-A 98/46608 some 6-(2,6-difluoro-phenyl)-triazolopyrimidines are known, which are substituted in the 7-position by fluorinated alkylamines.

10

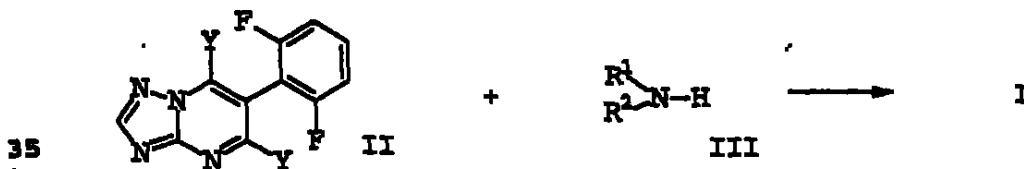
The compounds disclosed in the documents discussed above are said to be active against various phytopathogenic fungi.

It is an object of the present invention to provide compounds having improved fungicidal activity.

We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their preparation, compositions comprising them and methods for controlling phytopathogenic fungi using the compounds I.

The compounds of the formula I differ from the compounds known from WO-A 98/46608 in the combination of the 2,6-difluoro-phenyl group with an halogen free amino group in the 7-position of the triazolopyrimidine system.

The present invention further provides a process for the preparation of compounds of formula I as defined above which comprises treating a 5,7-dihalo compound of formula II in which X is halogen with an amine of formula III.



The reaction between the 5,7-dihalo compound II and the amine of formula III can be carried out under conditions known from WO-A 98/46608.

40

Compounds of formula II are known from EP-A 550 113; they can be prepared by known methods [cf. EP-A 550 113 or EP-A 770 615].

The reaction is preferably carried out in the presence of a solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons

15

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such as dichloromethane and aromatic hydrocarbons, for example toluene.

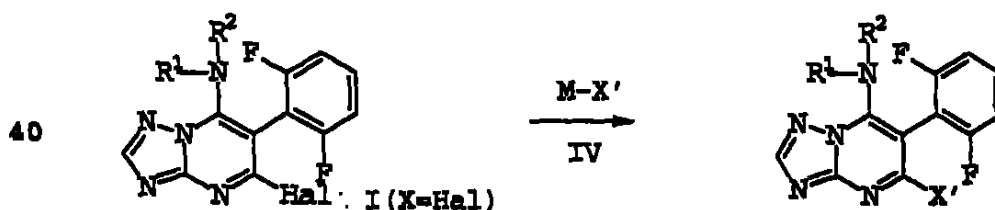
The reaction is suitably carried out at a temperature in the range from 0°C to 70°C, the preferred reaction temperature being from 10°C to 35°C.

It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula III may serve as a base.

The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile components under reduced pressure and at moderately elevated temperatures. If the end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

Compounds of formula II are known in the art and can be obtained by synthesis routes disclosed in EP-A 550 113, EP-A 770 615 and WO-A 98/46608.

Compounds of formula I in which X denotes cyano, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₆-alkenyloxy can be prepared by reacting compounds I in which X is halogen, preferably chloro, with compounds of formula IV, which are, dependent from the value of X' to be introduced to yield formula I compounds, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, respectively, preferably in the presence of a solvent. The cation M in formula IV has minor influence; for practical and economical reasons usually ammonium-, tetraalkylammonium- or alkalimetal- and earth metal salts are preferred.



The reaction is suitably carried out at a temperature in the range from 0 to 120°C, the preferred reaction temperature being from 10 to 40°C [cf. J. Heterocycl. Chem., Vol. 12, p. 861-863 (1975)].

Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

5

If individual compounds I are not obtainable by the routes described above, they can be prepared by derivatization of other compounds I.

10 In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:

- halogen: fluorine, chlorine, bromine and iodine;

15

- C₁-C₁₀-alkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 10, especially 1 to 6 carbon atoms, for example C₁-C₄-alkyl as mentioned above or pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-di-methylpropyl, 1-ethylpropyl, 20 hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methyl- 25 propyl and 1-ethyl-2-methylpropyl;

- C₂-C₁₀-alkenyl: unsaturated, straight-chain or branched ~~hydrocarbon radicals having 2 to 10, especially 2 to 6 carbon~~ atoms and a double bond in any position, for example ethenyl, 30 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl and 2-methyl-2-propenyl;

C₂-C₁₀-alkynyl: straight-chain or branched hydrocarbon radicals 35 having 2 to 10, especially 2 to 4 carbon atoms and a triple bond in any position, for example ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne and 1-methyl-2-propynyl;

haloalkyl moieties of C₁-C₆-haloalkoxy: straight-chain or branched 40 alkyl groups having 1 to 6, preferably 1 to 4 carbon atoms (as mentioned above), where the hydrogen atoms in these groups may be partially or fully replaced by halogen atoms as mentioned above, for example C₁-C₂-haloalkoxy, such as chloromethoxy, bromomethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoro- 45 methoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 1-chloroethoxy, 1-bromoethoxy, 1-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 2,2,2-tri-

5

fluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy and pentafluoroethoxy;

- 5 C₃-C₁₀-cycloalkyl: mono- or bicyclic cycloalkyl groups having 3 to 10 carbon atoms; monocyclic groups preferably have 3 to 8, especially 3 to 6 ring members, bicyclic groups preferably have 8 to 10 ring members.
- 10 A 5- or 6-membered heterocyclyl group, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, preferably one oxygen atom.

- 5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom:
- 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 20 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 25 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl;

-
- 6-membered heteroaryl, containing one to four nitrogen atoms:
- 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

- 35 With respect to their intended use, preference is given to triazolopyrimidines of the formula I having the following substituents, where the preference is valid in each case on its own or in combination:

- 40 A preferred cycloalkyl moiety is cyclopentyl being optionally substituted by one or more nitro, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy groups.

- A preferred heteroaryl moiety is pyridyl, pyrimidyl, pyrazolyl or 45 thienyl.

Preference is given to compounds of formula I in which any alkyl part of the groups R^1 or R^2 , which may be straight chained or branched, contains 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R^1 or R^2 contains 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R^1 or R^2 contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any bicycloalkyl part of the substituents R^1 or R^2 contains from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl group may be linear or branched.

Compounds of formula I are preferred in which R^1 is not hydrogen.

Moreover, compounds of formula I are preferred in which R^1 represents a straight-chained or branched C_1 - C_{10} -alkyl, in particular a branched C_3 - C_{10} -alkyl group, a C_3 - C_8 -cycloalkyl, a C_5 - C_9 -bicycloalkyl, a C_3 - C_8 -cycloalkyl- C_1 - C_6 -alkyl, C_1 - C_{10} -alkoxy- C_1 - C_6 -alkyl, or a phenyl group being optionally substituted by one to three C_1 - C_{10} -alkyl or C_1 - C_{10} -alkoxy groups.

Particular preference is given to compounds I in which R^2 represents a hydrogen atom or a C_1 - C_{10} -alkyl group, in particular a hydrogen atom.

25

Moreover, particular preference is given to compounds I in which R^2 is methyl or ethyl.

If R^1 denotes an optionally substituted C_3 - C_8 -cycloalkyl group, preferably a cyclopentyl or cyclohexyl group, R^2 preferably represents a hydrogen atom or C_1 - C_6 -alkyl group.

Moreover, particular preference is given to compounds I in which R^1 and R^2 together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C_3 - C_7 -heterocyclic ring, in particular a pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydropyridine or azepane ring which is optionally substituted by one or more C_1 - C_{10} -alkyl groups.

40

Besides, particular preference is given to compounds I in which X is chloro or bromo, especially chloro.

Moreover, preference is given to compounds I in which X is cyano or methoxy.

45

Furthermore, particular preference is given to compounds I in which X is ethoxy, n-propoxy, iso-propoxy, allyloxy, or 3-methylallyloxy.

- 5 Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.
- 10 With respect to their use, particular preference is given to the compounds I compiled in the tables below. The groups mentioned in the tables for a substituent are furthermore for their part, independently of the combination in which they are mentioned, a particularly preferred embodiment of the respective substituents.

15

Table 1

Compounds of the formula I, in which X is chloro and R¹ and R² correspond to one row in Table A

20 Table 2

Compounds of the formula I, in which X is bromo and R¹ and R² correspond to one row in Table A

Table 3

25 Compounds of the formula I, in which X is cyano and R¹ and R² correspond to one row in Table A

Table 4

Compounds of the formula I, in which X is methoxy and R¹ and R² correspond to one row in Table A

30

Table 5

Compounds of the formula I, in which X is ethoxy and R¹ and R² correspond to one row in Table A

35

Table 6

Compounds of the formula I, in which X is n-propoxy and R¹ and R² correspond to one row in Table A

40 Table 7

Compounds of the formula I, in which X is iso-propoxy and R¹ and R² correspond to one row in Table A

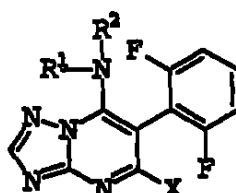
Table 8

45 Compounds of the formula I, in which X is allyloxy and R¹ and R² correspond to one row in Table A

Table 9

Compounds of the formula I, in which X is 3-methylallyloxy and R¹ and R² correspond to one row in Table A

5 Table A



I

10

No.	R ¹	R ²
A-1	H	H
15 A-2	CH ₂ CH ₃	H
A-3	CH ₂ CH ₃	CH ₃
A-4	CH ₂ CH ₃	CH ₂ CH ₃
A-5	CH ₂ CH ₂ CH ₃	H
20 A-6	CH ₂ CH ₂ CH ₃	CH ₃
A-7	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-8	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-9	CH(CH ₃) ₂	H
25 A-10	CH(CH ₃) ₂	CH ₃
A-11	CH(CH ₃) ₂	CH ₂ CH ₃
A-12	(±) CH(CH ₃)-CH ₂ CH ₃	H
A-13	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-14	(±) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
30 A-15	(S) CH(CH ₃)-CH ₂ CH ₃	H
A-16	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-17	(S) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-18	(R) CH(CH ₃)-CH ₂ CH ₃	H
35 A-19	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₃
A-20	(R) CH(CH ₃)-CH ₂ CH ₃	CH ₂ CH ₃
A-21	(±) CH(CH ₃)-CH(CH ₃) ₂	H
A-22	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
40 A-23	(±) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
A-24	(S) CH(CH ₃)-CH(CH ₃) ₂	H
A-25	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-26	(S) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃
45 A-27	(R) CH(CH ₃)-CH(CH ₃) ₂	H
A-28	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₃
A-29	(R) CH(CH ₃)-CH(CH ₃) ₂	CH ₂ CH ₃

No.	R ¹	R ²
A-30	(±) CH(CH ₃)-C(CH ₃) ₃	H
A-31	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₃
5 A-32	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-33	(S) CH(CH ₃)-C(CH ₃) ₃	H
A-34	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-35	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
10 A-36	(R) CH(CH ₃)-C(CH ₃) ₃	H
A-37	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-38	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-39	CH ₂ C(CH ₃)=CH ₂	H
A-40	CH ₂ C(CH ₃)=CH ₂	CH ₃
15 A-41	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃
A-42	cyclopentyl	H
A-43	cyclopentyl	CH ₃
A-44	cyclopentyl	CH ₂ CH ₃
20 A-45	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	

The compounds I are suitable as fungicides. They have outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Deuteromycetes, 25 Phycomycetes and Basidiomycetes. Some of them act systemically, and they can be employed in crop protection as foliar- and soil-acting fungicides.

They are especially important for controlling a large number of 30 fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

35

Specifically, they are suitable for controlling the following plant diseases:

- *Alternaria* species, *Podospheera* species, *Sclerotinia* species, *Phylospora* canker on vegetables and fruit,
- 40 • *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamentals and grapevines,
- *Corynespora cassicola* on cucumbers,
- *Colletotrichum* species on fruit and vegetables,
- *Diplocarpon rosae* on roses,
- 45 • *Elsinoe fawcetti* and *Diaporthe citri* on citrus fruit,
- *Sphaerotheca* species on cucurbits, strawberries and roses,
- *Cercospora* species on peanuts, sugar beets and aubergines,

10

- *Erysiphe cichoracearum* on cucurbits,
 - *Leveillula taurica* on paprika, tomatoes and aubergines,
 - *Mycosphaerella* species on apples and japanese apricot,
 - *Phyllactinia kakicola*, *Gloesporium kaki* on japanese apricot,
 - 5 • *Gymnosporangium yamadai*, *Leptothyrium pomi*, *Podosphaera leucotricha* and *Gloeodes pomigena* on apples,
 - *Cladosporium carpophilum* on pears and japanese apricot,
 - *Phomopsis* species on pears,
 - *Phytophthora* species on citrus fruit, potatoes, onions, especially *Phytophthora infestans* on potatoes and tomatoes,
 - 10 • *Blumeria graminis* (powdery mildew) on cereals,
 - *Fusarium*- and *Verticillium* species on various plants,
 - *Glomerella cingulata* on tee,
 - *Drechslera*- and *Bipolaris* species on cereals and rice,
 - 15 • *Mycosphaerella* species on bananas and peanuts,
 - *Plasmopara viticola* on grapevines,
 - *Peronospora* species on onions, spinach and chrysanthemum,
 - *Phaeoisariopsis vitis* and *Sphaceloma ampelina* on grapefruits,
 - *Pseudocercospora harpotrichoides* on wheat and barley,
 - 20 • *Pseudoperonospora* species on hop and cucumbers,
 - *Puccinia* species and *Typhula* species on cereals and turf,
 - *Pyricularia oryzae* on rice,
 - *Rhizoctonia* species on cotton, rice and turf,
 - *Stagonospora nodorum* and *Septoria tritici* on wheat,
 - 25 • *Uncinula necator* on grapevines,
 - *Ustilago* species on cereals and sugar cane, and
 - *Venturia* species (scab) on apples and pears.
-

Moreover, the compounds I are suitable for controlling harmful
30 fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and in the protection of stored products.

The compounds I are applied by treating the fungi, or the plants,
35 seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.

40 In general, the fungicidal compositions comprise from 0.1 to 95, preferably 0.5 to 90, % by weight of active ingredient.

When used in crop protection, the rates of application are from
0.01 to 2.0 kg of active ingredient per ha, depending on the na-
45 ture of the effect desired.

In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

5 When used in the protection of materials or stored products, the rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are, for example, from 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of
10 active ingredient per cubic meter of material treated.

The compounds I can be converted into the customary formulations, e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; in
15 any case, it should guarantee a fine and uniform distribution of the compound according to the invention.

The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible
20 to use other organic solvents as auxiliary solvents if water is used as the diluent. Auxiliaries which are suitable are essentially: solvents such as aromatics (e.g. xylene), chlorinated aromatics (e.g. chlorobenzenes); paraffins (e.g. mineral oil
25 fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, clays, talc, chalk) and ground synthetic minerals (e.g. highly-disperse silica, silicates); emulsifiers such as non-ionic and
30 anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and
35 ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl-naphthalenesulfonic acid, alkylaryl-sulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives with
40 formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol or formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated iso-octylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers,
45 alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol

12

polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly
5 sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene,
10 lane, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

15

Powders, materials for scattering and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

20 Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths, such as silicas, silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bone, loess, clay, dolomite, diatomaceous
25 earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

30

In general, the formulations comprise of from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

35

The following are exemplary formulations:

- I. 5 parts by weight of a compound according to the invention are mixed intimately with 95 parts by weight of finely divided
40 kaolin. This gives a dust which comprises 5% by weight of the active ingredient.
- II. 30 parts by weight of a compound according to the invention are mixed intimately with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil
45 which had been sprayed onto the surface of this silica gel. This gives a formulation of the active ingredient with good

adhesion properties (comprises 23% by weight of active ingredient).

- 5 III. 10 parts by weight of a compound according to the invention are dissolved in a mixture composed of 90 parts by weight of xylene, 6 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 2 parts by weight of calcium dodecylbenzenesulfonate and 2 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 9% by weight of active ingredient).
- 10
- 15 IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 16% by weight of active ingredient).
- 20
- 25 V. 80 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl-naphthalene- α -sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill (comprises 80% by weight of active ingredient).
-
- 30 VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, which gives a solution which is suitable for use in the form of microdrops (comprises 90% by weight of active ingredient).
- 35 VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil. Pouring the solution into 100,000 parts by weight of water and finely distributing it therein gives an aqueous dispersion which comprises 0.02% by weight of the active ingredient.
- 40
- 45 VIII. 20 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutyl-naphthalene- α -sulfonate, 17 parts by weight of the so-

dium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill. Finely distributing the mixture in 20,000 parts by weight of water gives a spray mixture which comprises 0.1% by weight of the active ingredient.

The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, e.g. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading, or granules, by means of spraying, atomizing, dusting, scattering or pouring. The use forms depend entirely on the intended purposes; in any case, this is intended to guarantee the finest possible distribution of the active ingredients according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances as such or dissolved in an oil or solvent, can be homogenized in water by means of wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active ingredient concentrations in the ready-to-use products can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even the active ingredient without additives.

Various types of oils, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate also only immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

In the use form as fungicides, the compositions according to the invention can also be present together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or the compositions comprising them in the use form as fungicides

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with other fungicides frequently results in a broader fungicidal spectrum of action.

The following list of fungicides, together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:

- 10 sulfur, dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc (N,N'-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;
- 15 nitro derivatives, such as dinitro(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl 5-nitro-isophthalate;
- 20 heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine, O,O-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4-triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbonyl)-2-benzimidazolecarbamate,
- 25 2-methoxycarbonylaminobenzimidazole, 2-(2-furyl)benzimidazole, 2-(4-thiazolyl)benzimidazole, N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide; N-trichloromethylthiophthalimide, 5-Chloro-2-cyano-4-p-tolyl-imidazole-1-sulfonic acid dimethylamide, N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfo-diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole, 2-thiocyanatomethylthiobenzothiazole,
- 30 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone, pyridine-2-thiol 1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2-Chloro-N-(4'-chloro-biphenyl-2-yl)-nicotinamide, 2,4,5-trimethylfuran-3-carboxanilide, N-cyclohexyl-2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-
- 40 N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine-2,2,2-trichloroethyl acetal, piperazine-1,4-diylbis-1-(2,2,2-trichloro-
- 45

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- ethyl)formamide, 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane; 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethyl-morpholine, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-piperidine, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol, (2RS,3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-triazole, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidinemethanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine, bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene, 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene,
- strobilurines such as azoxystrobin, kresoxim methyl, methyl-E-methoxyimino-[α -(2-phenoxyphenyl)]-acetamide, methyl E-methoxyimino-[α -(2,5-dimethylphenoxy)-o-tolyl]acetamide, picoxystrobin, pyraclostrobin, trifloxystrobin, anilinopyrimidines such as N-(4,6-dimethylpyrimidin-2-yl)aniline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]aniline, N-[4-methyl-6-cyclopropylpyrimidin-2-yl]aniline, phenylpyrroles such as 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile,
-
- cinnamamides such as 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, 3-(4-fluorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine,
- and a variety of fungicides such as dodecylguanidine acetate, 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutaramide, hexachlorobenzene, methyl N-(2,6-dimethylphenyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-amino-butyrolactone, DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine, 3-[3,5-dichlorophenyl(5-methyl-5-methoxymethyl)-1,3-oxazolidine-2,4-dione, 3-(3,5-dichlorophenyl)-1-isopropylcarbamoylhydantoin, N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]acetamide, 3,5-Dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxo-propyl)-4-methyl-benzamide, 1-(3-Bromo-6-methoxy-2-methyl-phenyl)-1-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 1-[2-(2,4-dichloro-phenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro-

α -(1H-1,2,4-triazolyl-1-methyl)benzhydryl alcohol, N-(3-chloro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluoromethyl-3-chloro-2-aminopyridine, 1-((bis(4-fluorophenyl)methylsilyl)methyl)-1H-1,2,4-triazole.

5

Synthesis Examples

With due modification of the starting compounds, the protocol shown in the synthesis example below was used for obtaining further compounds I. The resulting compounds I, together with physical data, are listed in the Table I which follows.

10

Example 1 Preparation of 5,7-dihydroxy-6-(2,6-difluorophenyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine

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A mixture of 3-amino-1,2,4-triazole (14 g), diethyl (2,6-difluorophenyl)-malonate (0,17 mol, cf. EP-A 10 02 788) and tributylamine (50 ml) was heated at about 180°C for six hours. The reaction mixture was cooled to about 70°C. 200 ml of 10 % aqueous sodium hydroxide solution were added and the reaction mixture were stirred for 30 minutes. The phases were separated, the aqueous phase was extracted with diethyl ether. The aqueous phase is acidified. The precipitate was filtered off and dried to yield 40 g of the title compound.

20

Example 2 Preparation of 5,7-dichloro-6-(2,6-difluorophenyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine

25

A mixture of 5,7-dihydroxy-6-(2,6-difluorophenyl)-[1,2,4]-triazolo-[1,5-a]pyrimidine (30 g, obtained from Ex. 1) and phosphorous oxychloride (50 ml) was refluxed for about eight hours. Phosphorous oxychloride was partly distilled off. The residue was poured into a mixture of dichloromethane and water. The organic layer was separated, dried and filtered. The filtrate was concentrated in vacuo to yield 28 g of the title compound of mp. 121°C.

35

Example 3 Preparation of 5-chloro-6-(2,6-difluorophenyl)-7-isopropylamino-[1,2,4]-triazolo[1,5-a]pyrimidine [I-3]

A mixture of isopropylamine (1,5 mmol), triethylamine (1,5 mmol) and dichloromethane (10 ml) was added to a mixture of 5,7-dichloro-6-(2,6-difluorophenyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine (1,5 mmol, obtained from Ex. 2) and dichloromethane (20 ml) under stirring. The reaction mixture was stirred for about 16 hours at about 20 to 25°C and subsequently washed with dilute hydrochloric acid (5%). The organic layer was separated, dried and filtered. The filtrate was evaporated under reduced pressure and the resi-

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due was chromatographed to yield 0,43 g of the title compound of mp. 169°C.

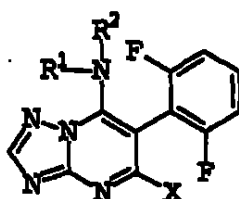
Example 4 Preparation of 5-cyano-6-(2,6-difluorophenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-18]

A mixture of 5-chloro-6-(2,6-difluorophenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5-a]pyrimidine (0,1 mol; I-4) and tetraethylammonium cyanide (0,25 mol) in 750 ml Dimethylformamide (DMF) (750 ml) was stirred for 16 hours at about 20 to 25°C. To this mixture water was added and methyl tert.butyl ether (MTBE), the organic phase was separated, washed with water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 6,95 g of the title compound of mp. 212°C.

Example 5 Preparation of 5-methoxy-6-(2,6-difluorophenyl)-7-(diethylamino)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-19]

To a solution of 5-chloro-6-(2,6-difluorophenyl)-7-(diethylamino)-[1,2,4]-triazolo[1,5-a]pyrimidine (65 mmol; I-6) in 400 ml dry methanol was added a 30% solution of sodium methanolate (71,5 mmol) at about 20 to 25°C. This mixture was further stirred for 16 hours. Methanol was evaporated and the residue was dissolved with dichloromethane. The organic phase was washed with water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 16,3 g of the title compound of mp. 153°C.

Table I



I

No.	R ¹	R ²	X	phys. data (m.p. [°C])
I-1	H	H	Cl	250
I-2	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	Cl	96
I-3	CH(CH ₃) ₂	H	Cl	169
I-4	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		Cl	196
I-5	cyclopentyl	H	Cl	165
I-6	CH ₂ CH ₃	CH ₂ CH ₃	Cl	159

No.	R ¹	R ²	X	phys. data (m.p. [°C])
I-6	CH ₂ CH ₃	CH ₂ CH ₃	Cl	159
I-7	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	Cl	125
I-8	CH(CH ₃) ₂	CH ₃	Cl	168
I-9	(±) CH(CH ₃)-CH ₂ CH ₃	H	Cl	184
I-10	(S) CH(CH ₃)-CH ₂ CH ₃	H	Cl	176
I-11	(R) CH(CH ₃)-CH ₂ CH ₃	H	Cl	176
I-12	(±) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	157
I-13	(S) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	149
I-14	(R) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	149
I-15	(±) CH(CH ₃)-C(CH ₃) ₃	H	Cl	160
I-16	(S) CH(CH ₃)-C(CH ₃) ₃	H	Cl	175
I-17	(R) CH(CH ₃)-C(CH ₃) ₃	H	Cl	175
I-18	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		CN	212
I-19	CH ₂ CH ₃	CH ₂ CH ₃	OCH ₃	153

20 Examples of the action against harmful fungi

The fungicidal action of the compounds of the formula I was demonstrated by the following experiments:

- 25 The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone, 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersant action based on ethoxylated alkyl-phenols) and 10% by weight of Wettol® EM (nonionic emulsifier based on ethoxylated castor oil) and diluted with water to the desired concentration.

Biological activity trial - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

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- Young seedlings of tomato plants of the variety "Große Fleischtomate St. Pierre" were grown in pots to the 2 to 4 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. The next day, the treated plants were inoculated with an aqueous suspension of *Alternaria solani* containing 0,2 x 10⁶ spores per ml. Then the trial plants were immediately transferred to a humid chamber. After 6 days at 20 to 23°C and a relative humidity

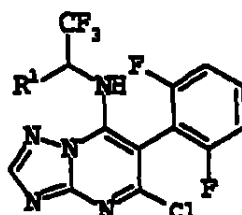
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close to 100 %, the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of 5 compounds I-2 to I-9, I-11, I-12, I-14, I-15 and I-17 showed an infection of not more than 1%, whereas the untreated plants were infected to 90%.

Active compounds A and B known from WO-A 98/46608 were used as 10 comparison compounds:

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No.	known from	R ¹
A	WO-A 98/46608, No. 5	hydrogen
B	WO-A 98/46608, No. 7	methyl

Comparison trial - Control of gray mould (*Botrytis cinerea*) on fruit slices of green pepper

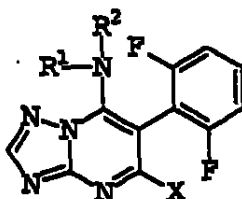
25 Fruit slices of green pepper were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. After 2 hours the sprayed- 30 on layer had dried, the disks were inoculated with a spore suspension of *Botrytis cinerea* containing $1,7 \times 10^6$ spores per ml in 2 wt. % aqueous biomalt solution. The infected fruit slices were then incubated in chambers with high humidity for four days at 18-20°C. The fruit slice area under fungal attack was then assessed 35 visually in percent.

In this test, the plants which had been treated with 500 ppm of compounds I-2, I-8 and I-14, resp., showed an infection of not more than 3%, whereas the the plants treated with 500 ppm of comparison compounds A and B, resp., were infected to 100 and 20%, 40 and the untreated plants were infected to 100%.

45

Claims:

1. 6-(2,6-Difluoro-phenyl)-triazolopyrimidines of formula I



I

in which

R¹ and R² independently denote hydrogen or

C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, or C₄-C₁₀-alkadienyl,

C₃-C₁₀-cycloalkyl, phenyl, naphthyl, or

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom,

where R¹ and R² radicals may be unsubstituted or may carry one to three groups R^a,

R^a is cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy, C₂-C₆-alkynyl, C₃-C₆-alkynyloxy and C₁-C₄-alkylenedioxy; or

R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

X is halogen, cyano, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₆-alkenyloxy.

22

2. Compounds of formula I according to claim 1, in which

R¹ is straight chained or branched C₁-C₆-alkyl,
C₂-C₆-alkenyl, or C₃-C₆-cycloalkyl, and

5

R² is hydrogen or C₁-C₆-alkyl, or

R¹ and R² together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C₁-C₆-alkyl groups.

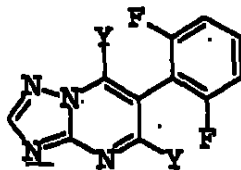
10

3. Compounds according to claims 1 or 2 in which R² is hydrogen.

15 4. Compounds according to claims 1 to 3 in which X is halogen.

5. A process for the preparation of compounds of formula I as defined in claim 4 which comprises reacting 5,7-dihalogen-6-(2,6-difluoro-phenyl)-triazolopyrimidines of formula II

20



II

25 in which Y is halogen with an amine of formula III



III

30 in which R¹ and R² are defined as for formula I to produce compounds of formula I.

35 6. A composition suitable for controlling phytopathogenic fungi, comprising a solid or liquid carrier and a compound of the formula I as claimed in claim 1.

40 7. A method for controlling phytopathogenic fungi, which comprises treating the fungi or the materials, plants, the soil or the seed to be protected against fungal attack with an effective amount of a compound of the formula I as claimed in claim 1.

45

INTERNATIONAL SEARCH REPORT

In International Application No
PCT/EP 02/07575

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D487/04 A01N43/90 //(C07D487/04,249:00,239:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 834 513 A (AMERICAN CYANAMID CO.) 8 April 1998 (1998-04-08) claims 1-13	1-7
Y	US 5 994 360 A (W. PFRENGLE) 30 November 1999 (1999-11-30) column 2, line 3 -column 2, line 34; claims 1-14	1-7
Y	US 5 965 561 A (K. J. PEES ET AL.) 12 October 1999 (1999-10-12) column 2, line 1 -column 2, line 25; claims 1-18	1-7
Y	US 6 117 865 A (K.-J. PEES) 12 September 2000 (2000-09-12) claims 1-9	1-7
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

19 September 2002

Date of mailing of the international search report

26/09/2002

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Authorized officer

Herz, C

INTERNATIONAL SEARCH REPORT

In International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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International Application No

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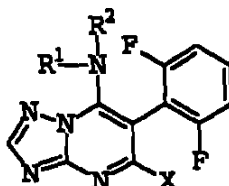
6-(2,6-Difluoro-phenyl)-triazolopyrimidines

Description

5

The invention relates to 6-(2,6-difluoro-phenyl)-triazolopyrimidines of formula I

10



I

in which

15

R^1 and R^2 independently denote hydrogen or

C_1 - C_{10} -alkyl, C_2 - C_{10} -alkenyl, C_2 - C_{10} -alkynyl, or C_4 - C_{10} -alkadienyl, C_3 - C_{10} -cycloalkyl, phenyl, naphthyl, or

20

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

25

where R^1 and R^2 radicals may be unsubstituted or may carry one to three groups R^a ,

30

R^a is cyano, nitro, hydroxyl, C_1 - C_6 -alkyl, C_3 - C_6 -cycloalkyl, C_1 - C_6 -alkoxy, C_1 - C_6 -alkylthio, C_1 - C_6 -alkylamino, di- C_1 - C_6 -alkylamino, C_2 - C_6 -alkenyl, C_2 - C_6 -alkenyloxy, C_2 - C_6 -alkynyl, C_3 - C_6 -alkynyloxy and C_1 - C_4 -alkylenedioxy; or

35

R^1 and R^2 together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

40

X is halogen, cyano, C_1 - C_6 -alkoxy, C_1 - C_6 -haloalkoxy or C_3 - C_8 -alkenyloxy.

45 Moreover, the invention relates to processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

6-Phenyl-7-amino-triazolopyrimidines are generally known from US 4,567,262 and US 5,593,996.

Triazolopyrimidines with a trifluorophenyl group in 6-position are disclosed in WO-A 98/46607 and EP-A 945 453.

From WO-A 98/46608 some 6-(2,6-difluoro-phenyl)-triazolopyrimidines are known, which are substituted in the 7-position by fluorinated alkylamines.

10

The compounds disclosed in the documents discussed above are said to be active against various phytopathogenic fungi.

It is an object of the present invention to provide compounds having improved fungicidal activity.

We have found that this object is achieved by the compounds defined at the outset. Furthermore, we have found processes for their preparation, compositions comprising them and methods for controlling phytopathogenic fungi using the compounds I.

The compounds of the formula I differ from the compounds known from WO-A 98/46608 in the combination of the 2,6-difluoro-phenyl group with an halogen free amino group in the 7-position of the triazolopyrimidine system.

The present invention further provides a process for the preparation of compounds of formula I as defined above which comprises treating a 5,7-dihalo compound of formula II in which X is halogen with an amine of formula III.



The reaction between the 5,7-dihalo compound II and the amine of formula III can be carried out under conditions known from WO-A 98/46608.

40

Compounds of formula II are known from EP-A 550 113; they can be prepared by known methods [cf. EP-A 550 113 or EP-A 770 615].

The reaction is preferably carried out in the presence of a solvent. Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons

45

such as dichloromethane and aromatic hydrocarbons, for example toluene.

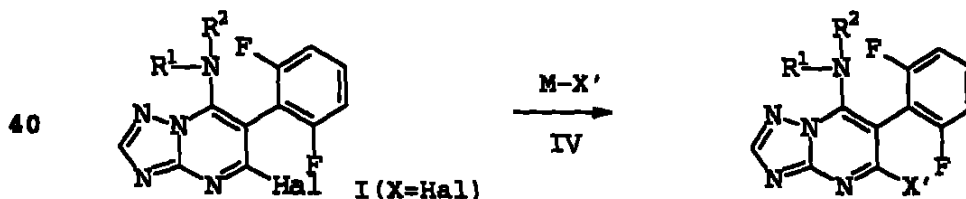
The reaction is suitably carried out at a temperature in the range from 0°C to 70°C, the preferred reaction temperature being from 10°C to 35°C.

It is also preferred that the reaction is carried out in the presence of a base. Suitable bases include tertiary amines, such as triethylamine, and inorganic bases, such as potassium carbonate or sodium carbonate. Alternatively, an excess of the compound of formula III may serve as a base.

The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile components under reduced pressure and at moderately elevated temperatures. If the end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

Compounds of formula II are known in the art and can be obtained by synthesis routes disclosed in EP-A 550 113, EP-A 770 615 and WO-A 98/46608.

Compounds of formula I in which X denotes cyano, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy can be prepared by reacting compounds I in which X is halogen, preferably chloro, with compounds of formula IV, which are, dependent from the value of X' to be introduced to yield formula I compounds, an anorganic cyano salt, an alkoxylate, haloalkoxylate or an alkenyloxylate, respectively, preferably in the presence of a solvent. The cation M in formula IV has minor influence; for practical and economical reasons usually ammonium-, tetraalkylammonium- or alkalimetal- and earth metal salts are preferred.



The reaction is suitably carried out at a temperature in the range from 0 to 120°C, the preferred reaction temperature being from 10 to 40°C [cf. J. Heterocycl. Chem., Vol. 12, p. 861-863 (1975)].

4

Suitable solvents include ethers, such as dioxane, diethyl ether and, especially, tetrahydrofuran, halogenated hydrocarbons such as dichloromethane and aromatic hydrocarbons, for example toluene.

5

If individual compounds I are not obtainable by the routes described above, they can be prepared by derivatization of other compounds I.

10 In the symbol definitions given in the formulae above, collective terms were used which generally represent the following substituents:

- halogen: fluorine, chlorine, bromine and iodine;

15

- C₁-C₁₀-alkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 10, especially 1 to 6 carbon atoms, for example C₁-C₄-alkyl as mentioned above or pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl,

20 hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methyl-
25 propyl and 1-ethyl-2-methylpropyl;

- C₂-C₁₀-alkenyl: unsaturated, straight-chain or branched hydrocarbon radicals having 2 to 10, especially 2 to 6 carbon atoms and a double bond in any position, for example ethenyl,

30 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl and 2-methyl-2-propenyl;

C₂-C₁₀-alkynyl: straight-chain or branched hydrocarbon radicals
35 having 2 to 10, especially 2 to 4 carbon atoms and a triple bond in any position, for example ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne and 1-methyl-2-propynyl;

haloalkyl moieties of C₁-C₆-haloalkoxy: straight-chain or branched
40 alkyl groups having 1 to 6, preferably 1 to 4 carbon atoms (as mentioned above), where the hydrogen atoms in these groups may be partially or fully replaced by halogen atoms as mentioned above, for example C₁-C₂-haloalkoxy, such as chloromethoxy, bromomethoxy, dichloromethoxy, trichloromethoxy, fluoromethoxy, difluoromethoxy, trifluoromethoxy, chlorofluoromethoxy, dichlorofluoromethoxy, chlorodifluoromethoxy, 1-chloroethoxy, 1-bromoethoxy, 1-fluoroethoxy, 2-fluoroethoxy, 2,2-difluoroethoxy, 2,2,2-tri-
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fluoroethoxy, 2-chloro-2-fluoroethoxy, 2-chloro-2,2-difluoroethoxy, 2,2-dichloro-2-fluoroethoxy, 2,2,2-trichloroethoxy and pentafluoroethoxy;

5 C₃-C₁₀-cycloalkyl: mono- or bicyclic cycloalkyl groups having 3 to 10 carbon atoms; monocyclic groups preferably have 3 to 8, especially 3 to 6 ring members, bicyclic groups preferably have 8 to 10 ring members.

10 A 5- or 6-membered heterocyclyl group, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, preferably one oxygen atom.

5-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom:

15 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 20 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 25 1,2,4-thiadiazol-5-yl, 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl;

6-membered heteroaryl, containing one to four nitrogen atoms:

6-membered heteroaryl groups which, in addition to carbon atoms, 30 may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl.

35 With respect to their intended use, preference is given to triazolopyrimidines of the formula I having the following substituents, where the preference is valid in each case on its own or in combination:

40 A preferred cycloalkyl moiety is cyclopentyl being optionally substituted by one or more nitro, cyano, C₁-C₆-alkyl, C₁-C₆-alkoxy groups.

A preferred heteroaryl moiety is pyridyl, pyrimidyl, pyrazolyl or 45 thienyl.

37

6

Preference is given to compounds of formula I in which any alkyl part of the groups R^1 or R^2 , which may be straight chained or branched, contains 1 to 9 carbon atoms, more preferably 2 to 6 carbon atoms, any alkenyl or alkynyl part of the substituents R^1 or R^2 contains 2 to 9 carbon atoms, more preferably 3 to 6 carbon atoms, any cycloalkyl part of the substituents R^1 or R^2 contains from 3 to 10 carbon atoms, preferably from 3 to 8 carbon atoms, more preferably from 3 to 6 carbon atoms, and any bicycloalkyl part of the substituents R^1 or R^2 contains from 7 to 9 carbon atoms. Any alkyl, alkenyl or alkynyl group may be linear or branched.

Compounds of formula I are preferred in which R^1 is not hydrogen.

- 15 Moreover, compounds of formula I are preferred in which R^1 represents a straight-chained or branched C_1 - C_{10} -alkyl, in particular a branched C_3 - C_{10} -alkyl group, a C_3 - C_8 -cycloalkyl, a C_5 - C_9 -bicycloalkyl, a C_3 - C_8 -cycloalkyl- C_1 - C_6 -alkyl, C_1 - C_{10} -alkoxy- C_1 - C_6 -alkyl, or a phenyl group being optionally substituted by one to three
- 20 C_1 - C_{10} -alkyl or C_1 - C_{10} -alkoxy groups.

Particular preference is given to compounds I in which R^2 represents a hydrogen atom or a C_1 - C_{10} -alkyl group, in particular a hydrogen atom.

25

Moreover, particular preference is given to compounds I in which R^2 is methyl or ethyl.

- If R^1 denotes an optionally substituted C_3 - C_8 -cycloalkyl group,
- 30 preferably a cyclopentyl or cyclohexyl group, R^2 preferably represents a hydrogen atom or C_1 - C_6 -alkyl group.

- Moreover, particular preference is given to compounds I in which R^1 and R^2 together with the interjacent nitrogen atom form an optionally substituted heterocyclic ring, preferably an optionally substituted C_3 - C_7 -heterocyclic ring, in particular a pyrrolidine, piperidine, tetrahydropyridine, in particular 1,2,3,6-tetrahydropyridine or azepane ring which is optionally substituted by one or more C_1 - C_{10} -alkyl groups.

40

Besides, particular preference is given to compounds I in which X is chloro or bromo, especially chloro.

- Moreover, preference is given to compounds I in which X is cyano
- 45 or methoxy.

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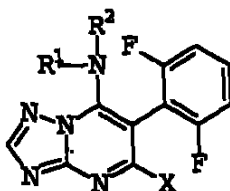
Furthermore, particular preference is given to compounds I in which X is ethoxy, n-propoxy, iso-propoxy, allyloxy, or 3-methylallyloxy.

- 5 Included in the scope of the present invention are (R) and (S) isomers of compounds of general formula I having a chiral center and the racemates thereof, and salts, N-oxides and acid addition compounds.
- 10 With respect to their use, particular preference is given to the compounds I compiled in the tables below. The groups mentioned in the tables for a substituent are furthermore for their part, independently of the combination in which they are mentioned, a particularly preferred embodiment of the respective substituents.
- 15
- Table 1
Compounds of the formula I, in which X is chloro and R¹ and R² correspond to one row in Table A
- 20 Table 2
Compounds of the formula I, in which X is bromo and R¹ and R² correspond to one row in Table A
- Table 3
25 Compounds of the formula I, in which X is cyano and R¹ and R² correspond to one row in Table A
- Table 4
Compounds of the formula I, in which X is methoxy and R¹ and R²
30 correspond to one row in Table A
- Table 5
Compounds of the formula I, in which X is ethoxy and R¹ and R² correspond to one row in Table A
- 35
- Table 6
Compounds of the formula I, in which X is n-propoxy and R¹ and R² correspond to one row in Table A
- 40 Table 7
Compounds of the formula I, in which X is iso-propoxy and R¹ and R² correspond to one row in Table A
- Table 8
45 Compounds of the formula I, in which X is allyloxy and R¹ and R² correspond to one row in Table A

Table 9

Compounds of the formula I, in which X is 3-methylallyloxy and R¹ and R² correspond to one row in Table A

5 Table A



I

10

No.	R ¹	R ²
A-1	H	H
15 A-2	CH ₂ CH ₃	H
A-3	CH ₂ CH ₃	CH ₃
A-4	CH ₂ CH ₃	CH ₂ CH ₃
A-5	CH ₂ CH ₂ CH ₃	H
20 A-6	CH ₂ CH ₂ CH ₃	CH ₃
A-7	CH ₂ CH ₂ CH ₃	CH ₂ CH ₃
A-8	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃
A-9	CH(CH ₃) ₂	H
A-10	CH(CH ₃) ₂	CH ₃
25 A-11	CH(CH ₃) ₂	CH ₂ CH ₃
A-12	(±) CH(CH ₃) - CH ₂ CH ₃	H
A-13	(±) CH(CH ₃) - CH ₂ CH ₃	CH ₃
A-14	(±) CH(CH ₃) - CH ₂ CH ₃	CH ₂ CH ₃
30 A-15	(S) CH(CH ₃) - CH ₂ CH ₃	H
A-16	(S) CH(CH ₃) - CH ₂ CH ₃	CH ₃
A-17	(S) CH(CH ₃) - CH ₂ CH ₃	CH ₂ CH ₃
A-18	(R) CH(CH ₃) - CH ₂ CH ₃	H
35 A-19	(R) CH(CH ₃) - CH ₂ CH ₃	CH ₃
A-20	(R) CH(CH ₃) - CH ₂ CH ₃	CH ₂ CH ₃
A-21	(±) CH(CH ₃) - CH(CH ₃) ₂	H
A-22	(±) CH(CH ₃) - CH(CH ₃) ₂	CH ₃
40 A-23	(±) CH(CH ₃) - CH(CH ₃) ₂	CH ₂ CH ₃
A-24	(S) CH(CH ₃) - CH(CH ₃) ₂	H
A-25	(S) CH(CH ₃) - CH(CH ₃) ₂	CH ₃
A-26	(S) CH(CH ₃) - CH(CH ₃) ₂	CH ₂ CH ₃
A-27	(R) CH(CH ₃) - CH(CH ₃) ₂	H
45 A-28	(R) CH(CH ₃) - CH(CH ₃) ₂	CH ₃
A-29	(R) CH(CH ₃) - CH(CH ₃) ₂	CH ₂ CH ₃

36

No.	R ¹	R ²
A-30	(±) CH(CH ₃)-C(CH ₃) ₃	H
A-31	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₃
5 A-32	(±) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-33	(S) CH(CH ₃)-C(CH ₃) ₃	H
A-34	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-35	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
10 A-36	(R) CH(CH ₃)-C(CH ₃) ₃	H
A-37	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-38	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-39	CH ₂ C(CH ₃)=CH ₂	H
A-40	CH ₂ C(CH ₃)=CH ₂	CH ₃
15 A-41	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃
A-42	cyclopentyl	H
A-43	cyclopentyl	CH ₃
A-44	cyclopentyl	CH ₂ CH ₃
20 A-45	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	

The compounds I are suitable as fungicides. They have outstanding activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the Ascomycetes, Deuteromycetes, 25 Phycomycetes and Basidiomycetes. Some of them act systemically, and they can be employed in crop protection as foliar- and soil-acting fungicides.

They are especially important for controlling a large number of 30 fungi on a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar cane, grapevines, fruit species, ornamentals and vegetables such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

35

Specifically, they are suitable for controlling the following plant diseases:

- *Alternaria* species, *Podosphaera* species, *Sclerotinia* species, *Physalospora* canker on vegetables and fruit,
- 40 • *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamentals and grapevines,
- *Corynespora cassiicola* on cucumbers,
- *Colletotrichum* species on fruit and vegetables,
- *Diplocarpon rosae* on roses,
- 45 • *Elsinoe fawcetti* and *Diaporthe citri* on citrus fruit,
- *Sphaerotheca* species on cucurbits, strawberries and roses,
- *Cercospora* species on peanuts, sugar beets and aubergines,

10

- *Erysiphe cichoracearum* on cucurbits,
- *Leveillula taurica* on paprika, tomatoes and aubergines,
- *Mycosphaerella* species on apples and japanese apricot,
- *Phyllactinia kakicola*, *Gloesporium kaki* on japanese apricot,
- 5 • *Gymnosporangium yamadae*, *Leptothyrium pomi*, *Podosphaera leucotricha* and *Gloeodes pomigena* on apples,
- *Cladosporium carpophilum* on pears and japanese apricot,
- *Phomopsis* species on pears,
- *Phytophthora* species on citrus fruit, potatoes, onions, especially *Phytophthora infestans* on potatoes and tomatoes,
- 10 • *Blumeria graminis* (powdery mildew) on cereals,
- *Fusarium*- and *Verticillium* species on various plants,
- *Glomerella cingulata* on tee,
- *Drechslera*- and *Bipolaris* species on cereals and rice,
- 15 • *Mycosphaerella* species on bananas and peanuts,
- *Plasmopara viticola* on grapevines,
- *Personospora* species on onions, spinach and chrysanthemum,
- *Phaeoisariopsis vitis* and *Sphaceloma ampelina* on grapefruits,
- *Pseudocercospora herpotrichoides* on wheat and barley,
- 20 • *Pseudoperonospora* species on hop and cucumbers,
- *Puccinia* species and *Typhula* species on cereals and turf,
- *Pyricularia oryzae* on rice,
- *Rhizoctonia* species on cotton, rice and turf,
- *Stagonospora nodorum* and *Septoria tritici* on wheat,
- 25 • *Uncinula necator* on grapevines,
- *Ustilago* species on cereals and sugar cane, and
- *Venturia* species (scab) on apples and pears.

Moreover, the compounds I are suitable for controlling harmful
 30 fungi such as *Paecilomyces variotii* in the protection of materials (e.g. wood, paper, paint dispersions, fibers and tissues) and in the protection of stored products.

The compounds I are applied by treating the fungi, or the plants,
 35 seeds, materials or the soil to be protected against fungal infection, with a fungicidally active amount of the active ingredients. Application can be effected both before and after infection of the materials, plants or seeds by the fungi.

40 In general, the fungicidal compositions comprise from 0.1 to 95, preferably 0.5 to 90, % by weight of active ingredient.

When used in crop protection, the rates of application are from
 0.01 to 2.0 kg of active ingredient per ha, depending on the na-
 45 ture of the effect desired.

In the treatment of seed, amounts of active ingredient of from 0.001 to 0.1 g, preferably 0.01 to 0.05 g, are generally required per kilogram of seed.

5 When used in the protection of materials or stored products, the rate of application of active ingredient depends on the nature of the field of application and on the effect desired. Rates of application conventionally used in the protection of materials are, for example, from 0.001 g to 2 kg, preferably 0.005 g to 10 1 kg, of active ingredient per cubic meter of material treated.

The compounds I can be converted into the customary formulations, e.g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular purpose; in 15 any case, it should guarantee a fine and uniform distribution of the compound according to the invention.

The formulations are prepared in a known manner, e.g. by extending the active ingredient with solvents and/or carriers, if desired using emulsifiers and dispersants, it also being possible 20 to use other organic solvents as auxiliary solvents if water is used as the diluent. Auxiliaries which are suitable are essentially: solvents such as aromatics (e.g. xylene), chlorinated aromatics (e.g. chlorobenzenes), paraffins (e.g. mineral oil 25 fractions), alcohols (e.g. methanol, butanol), ketones (e.g. cyclohexanone), amines (e.g. ethanolamine, dimethylformamide) and water; carriers such as ground natural minerals (e.g. kaolins, clays, talc, chalk) and ground synthetic minerals (e.g. highly-disperse silica, silicates); emulsifiers such as non-ionic and 30 anionic emulsifiers (e.g. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignin-sulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and 35 ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutyl-naphthalenesulfonic acid, alkylaryl-sulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and their alkali metal and alkaline earth metal salts, salts of sulfated fatty alcohol glycol ether, condensates of sulfonated naphthalene and naphthalene derivatives 40 with formaldehyde, condensates of naphthalene or of naphthalene-sulfonic acid with phenol or formaldehyde, polyoxyethylene octyl-phenyl ether, ethoxylated iso-octylphenol, octylphenol, nonyl-phenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol 45 ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl

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alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e.g. benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly polar solvents, e.g. dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for scattering and dusts can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, e.g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers. Examples of solid carriers are mineral earths, such as silicas, silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, e.g. ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise of from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active ingredient. The active ingredients are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are exemplary formulations:

- I. 5 parts by weight of a compound according to the invention are mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dust which comprises 5% by weight of the active ingredient.
- II. 30 parts by weight of a compound according to the invention are mixed intimately with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel.

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This gives a formulation of the active ingredient with good adhesion properties (comprises 23% by weight of active ingredient).

- 5 III. 10 parts by weight of a compound according to the invention are dissolved in a mixture composed of 90 parts by weight of xylene, 6 parts by weight of the adduct of 8 to 10 mol of ethylene oxide and 1 mol of oleic acid N-monoethanolamide, 2 parts by weight of calcium dodecylbenzenesulfonate and 2 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 9% by weight of active ingredient).
- 10
- IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 5 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil (comprises 16% by weight of active ingredient).
- 15
- 20
- V. 80 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diisobutylphenol- α -sulfonate, 10 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill (comprises 80% by weight of active ingredient).
- 25
- 30 VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, which gives a solution which is suitable for use in the form of microdrops (comprises 90% by weight of active ingredient).
- 35
- VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture composed of 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the adduct of 7 mol of ethylene oxide and 1 mol of isooctylphenol and 10 parts by weight of the adduct of 40 mol of ethylene oxide and 1 mol of castor oil. Pouring the solution into 100,000 parts by weight of water and finely distributing it therein gives an aqueous dispersion which comprises 0.02% by weight of the active ingredient.
- 40
- 45
- VIII. 20 parts by weight of a compound according to the invention are mixed thoroughly with 3 parts by weight of sodium diiso-

butyl naphthalene- α -sulfonate, 17 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and the mixture is ground in a hammer mill. Finely distributing the mixture in 20,000 parts by weight of water gives a spray mixture which comprises 0.1% by weight of the active ingredient.

The active ingredients can be used as such, in the form of their formulations or the use forms prepared therefrom, e.g. in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading, or granules, by means of spraying, atomizing, dusting, scattering or pouring. The use forms depend entirely on the intended purposes; in any case, this is intended to guarantee the finest possible distribution of the active ingredients according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances as such or dissolved in an oil or solvent, can be homogenized in water by means of wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active ingredient concentrations in the ready-to-use products can be varied within substantial ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active ingredients may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active ingredient, or even the active ingredient without additives.

Various types of oils, herbicides, fungicides, other pesticides, or bactericides may be added to the active ingredients, if appropriate also only immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

In the use form as fungicides, the compositions according to the invention can also be present together with other active ingredients, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or

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the compositions comprising them in the use form as fungicides with other fungicides frequently results in a broader fungicidal spectrum of action.

5 The following list of fungicides, together with which the compounds according to the invention can be used, is intended to illustrate the possible combinations, but not to impose any limitation:

- 10 sulfur, dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate, manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc
- 15 (N,N-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;
- 20 nitro derivatives, such as dinitro(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl 3,3-dimethylacrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl 5-nitro-isophthalate;
- heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine,
- 25 O,O-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4-triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, 2-methoxycarbonylaminobenzimidazole, 2-(2-furyl)benzimidazole,
- 30 2-(4-thiazolyl)benzimidazole, N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide, N-trichloromethylthiophthalimide, 5-Chloro-2-cyano-4-p-tolyl-imidazole-1-sulfonic acid dimethylamide, N-dichlorofluoromethylthio-N',N'-di-
- 35 methyl-N-phenylsulfo-diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole, 2-thiocyanatomethylthiobenzothiazole, 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone, pyridine-2-thiol 1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine 4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2-Chloro-N-(4'-chloro-biphenyl-2-yl)-nicotinamide, 2,4,5-trimethylfuran-3-carboxanilide,
- 40 N-cyclohexyl-2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine-2,2,2-trichloro-

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- roethyl acetal, piperazine-1,4-diylbis-1-(2,2,2-trichloroethyl)formamide, 1-(3,4-dichloroanilino)-1-formylamino-2,2,2-trichloroethane; 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethyl-morpholine, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-piperidine, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolyl-urea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol, (2RS,3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)-oxiran-2-ylmethyl]-1H-1,2,4-triazole, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidinemethanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine, bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene, 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene,
- strobilurines such as azoxystrobin, kresoxim methyl, methyl-E-methoxyimino-[α -(2-phenoxyphenyl)]-acetamide, methyl E-methoxyimino-[α -(2,5-dimethylphenoxy)-o-tolyl]acetamide, picoxystrobin, pyraclostrobin, trifloxystrobin,
- anilinopyrimidines such as N-(4,6-dimethylpyrimidin-2-yl)aniline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]-aniline, N-[4-methyl-6-cyclopropylpyrimidin-2-yl]aniline,
- phenylpyrroles such as 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile,
- cinnamamides such as 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine, 3-(4-fluorophenyl)-3-(3,4-dimethoxy-phenyl)acryloylmorpholine,
- and a variety of fungicides such as dodecylguanidine acetate, 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutaramide, hexachlorobenzene, methyl N-(2,6-dimethylphenyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-amino-butylolactone, DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine, 3-[3,5-dichlorophenyl(5-methyl-5-methoxymethyl)-1,3-oxazolidine-2,4-dione, 3-(3,5-dichlorophenyl)-1-isopropylcarbamoylhydantoin, N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]acetamide,
- 3,5-Dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxo-propyl)-4-methyl-benzamide, 1-(3-Bromo-6-methoxy-2-methyl-phenyl)-1-(2,3,4-trimethoxy-6-methyl-phenyl)-methanone, 1-[2-(2,4-di-

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chloro-phenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro-
α-(1H-1,2,4-triazolyl-1-methyl)benzhydryl alcohol, N-(3-chlo-
ro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluorome-
thyl-3-chloro-2-aminopyridine, 1-((bis(4-fluorophenyl)methyl-
silyl)methyl)-1H-1,2,4-triazole.

Synthesis Examples

With due modification of the starting compounds, the protocol
shown in the synthesis example below was used for obtaining fur-
ther compounds I. The resulting compounds I, together with
physical data, are listed in the Table I which follows.

Example 1 Preparation of 5,7-dihydroxy-6-(2,6-difluorophe- nyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine

A mixture of 3-amino-1,2,4-triazole (14 g), diethyl (2,6-difluo-
rophenyl)-malonate (0,17 mol, cf. EP-A 10 02 788) and tributyl-
amine (50 ml) was heated at about 180°C for six hours. The reac-
tion mixture was cooled to about 70°C. 200 ml of 10 % aqueous so-
dium hydroxide solution were added and the reaction mixture were
stirred for 30 minutes. The phases were separated, the aqueous
phase was extracted with diethyl ether. The aqueous phase is aci-
dified. The precipitate was filtered off and dried to yield 40 g
of the title compound.

Example 2 Preparation of 5,7-dichloro-6-(2,6-difluorophe- nyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine

A mixture of 5,7-dihydroxy-6-(2,6-difluorophenyl)-[1,2,4]-tri-
azolo-[1,5-a]pyrimidine (30 g, obtained from Ex. 1) and phospho-
rous oxychloride (50 ml) was refluxed for about eight hours.
Phosphorous oxychloride was partly distilled off. The residue was
poured into a mixture of dichloromethane and water. The organic
layer was separated, dried and filtered. The filtrate was concen-
trated in vacuo to yield 28 g of the title compound of mp. 121°C.

Example 3 Preparation of 5-chloro-6-(2,6-difluorophenyl)-7-iso- propylamino-[1,2,4]-triazolo[1,5-a]pyrimidine [I-3]

A mixture of isopropylamine (1,5 mmol), triethylamine (1,5 mmol)
and dichloromethane (10 ml) was added to a mixture of 5,7-di-
chloro-6-(2,6-difluorophenyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine
(1,5 mmol, obtained from Ex. 2) and dichloromethane (20 ml) under
stirring. The reaction mixture was stirred for about 16 hours at
about 20 to 25°C and subsequently washed with dilute hydrochloric

acid (5%). The organic layer was separated, dried and filtered. The filtrate was evaporated under reduced pressure and the residue was chromatographed to yield 0,43 g of the title compound of mp. 169°C.

5

Example 4 Preparation of 5-cyano-6-(2,6-difluorophenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-18]

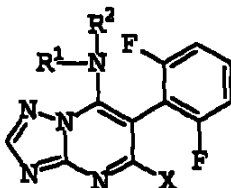
10 A mixture of 5-chloro-6-(2,6-difluorophenyl)-7-(4-methylpiperidin-1-yl)-[1,2,4]-triazolo-[1,5-a]-pyrimidine (0,1 mol; I-4) and tetraethylammonium cyanide (0,25 mol) in 750 ml Dimethylformamide (DMF) (750 ml) was stirred for 16 hours at about 20 to 25°C. To this mixture water was added and methyl tert.butyl ether (MTBE),
15 the organic phase was separated, washed with water, dried and filtered. The filtrate was evaporated and the residue was chromatographed to yield 6,95 g of the title compound of mp. 212°C.

Example 5 Preparation of 5-methoxy-6-(2,6-difluorophenyl)-7-(diethylamino)-[1,2,4]-triazolo[1,5-a]pyrimidine [I-19]
20

To a solution of 5-chloro-6-(2,6-difluorophenyl)-7-(diethylamino)-[1,2,4]-triazolo-[1,5-a]-pyrimidine (65 mmol; I-6) in
25 400 ml dry methanol was added a 30% solution of sodium methanolate (71,5 mmol) at about 20 to 25°C. This mixture was further stirred for 16 hours. Methanol was evaporated and the residue was dissolved with dichloromethane. The organic phase was washed with water, dried and filtered. The filtrate was evaporated and the
30 residue was chromatographed to yield 16,3 g of the title compound of mp. 153°C.

Table I

35



I

40

No.	R ¹	R ²	X	phys. data (m.p. [°C])
I-1	H	H	Cl	250
I-2	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	Cl	96
45 I-3	CH(CH ₃) ₂	H	Cl	169
I-4	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		Cl	196
I-5	cyclopentyl	H	Cl	165

46

19

No.	R ¹	R ²	X	phys. data (m.p. [°C])
I-6	CH ₂ CH ₃	CH ₂ CH ₃	Cl	159
I-7	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	Cl	125
I-8	CH(CH ₃) ₂	.CH ₃	Cl	168
I-9	(±) CH(CH ₃)-CH ₂ CH ₃	H	Cl	184
I-10	(S) CH(CH ₃)-CH ₂ CH ₃	H	Cl	176
I-11	(R) CH(CH ₃)-CH ₂ CH ₃	H	Cl	176
I-12	(±) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	157
I-13	(S) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	149
I-14	(R) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	149
I-15	(±) CH(CH ₃)-C(CH ₃) ₃	H	Cl	160
I-16	(S) CH(CH ₃)-C(CH ₃) ₃	H	Cl	175
I-17	(R) CH(CH ₃)-C(CH ₃) ₃	H	Cl	175
I-18	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		CN	212
I-19	CH ₂ CH ₃	CH ₂ CH ₃	OCH ₃	153

20 Examples of the action against harmful fungi

The fungicidal action of the compounds of the formula I was demonstrated by the following experiments:

25 The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone, 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersant action based on ethoxylated alkyl-phenols) and 10% by weight of Wettol® EM (nonionic emulsifier based on ethoxylated castor oil) and diluted with water to the desired concentration.

Biological activity trial - Fungicidal control of early blight on tomatoes (*Alternaria solani*)

35

Young seedlings of tomato plants of the variety "Große Fleisch-
tomate St. Pierre" were grown in pots to the 2 to 4 leaf stage.
These plants were sprayed to run-off with an aqueous suspension,
containing the concentration of active ingredient mentioned in
40 the table below, prepared from a stock solution containing 10 %
of the active ingredient, 85 % cyclohexanone and 5 % emulsifier.
The next day, the treated plants were inoculated with an aqueous
suspension of *Alternaria solani* containing 0,2 x 10⁶ spores per
ml. Then the trial plants were immediately transferred to a hu-
45 mid chamber. After 6 days at 20 to 23°C and a relative humidity

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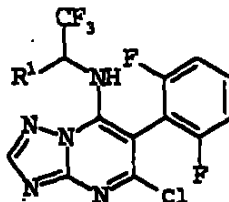
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close to 100 %, the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the plants which had been treated with 250 ppm of 5 compounds I-2 to I-9, I-11, I-12, I-14, I-15 and I-17 showed an infection of not more than 1%, whereas the untreated plants were infected to 90%.

Active compounds A and B known from WO-A 98/46608 were used as 10 comparison compounds:

15



20

No.	known from	R ¹
A	WO-A 98/46608, No. 5	hydrogen
B	WO-A 98/46608, No. 7	methyl

Comparison trial - Control of gray mould (*Botrytis cinerea*) on fruit slices of green pepper

25 Fruit slices of green pepper were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below, prepared from a stock solution containing 10 % of the active ingredient, 85 % cyclohexanone and 5 % emulsifier. After 2 hours the sprayed-
30 on layer had dried, the disks were inoculated with a spore suspension of *Botrytis cinerea* containing $1,7 \times 10^6$ spores per ml in 2 wt. % aqueous biomalt solution. The infected fruit slices were then incubated in chambers with high humidity for four days at 18-20°C. The fruit slice area under fungal attack was then assessed
35 visually in percent.

In this test, the plants which had been treated with 500 ppm of compounds I-2, I-8 and I-14, resp., showed an infection of not more than 3%, whereas the the plants treated with 500 ppm of comparison compounds A and B, resp., were infected to 100 and 20%,
40 and the untreated plants were infected to 100%.

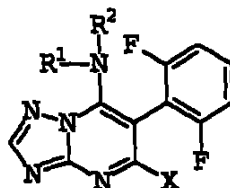
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Claims:

1. 6-(2,6-Difluoro-phenyl)-triazolopyrimidines of formula I

5



I

10

in which

R¹ and R² independently denote hydrogen or

15

C₁-C₁₀-alkyl, C₂-C₁₀-alkenyl, C₂-C₁₀-alkynyl, or C₄-C₁₀-alkadienyl,

C₃-C₁₀-cycloalkyl, phenyl, naphthyl, or

20

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

25

where R¹ and R² radicals may be unsubstituted or may carry one to three groups R^a,

30

R^a is cyano, nitro, hydroxyl, C₁-C₆-alkyl, C₁-C₆-haloalkyl, C₃-C₆-cycloalkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino, di-C₁-C₆-alkylamino, C₂-C₆-alkenyl, C₂-C₆-alkenyloxy, C₂-C₆-alkynyl, C₃-C₆-alkynyloxy and C₁-C₄-alkylenedioxy; or

35

R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted by one to three R^a radicals;

40

X is halogen, cyano, C₁-C₆-alkoxy, C₁-C₆-haloalkoxy or C₃-C₈-alkenyloxy.

45

22

2. Compounds of formula I according to claim 1, in which

R¹ is straight chained or branched C₁-C₆-alkyl,
C₂-C₆-alkenyl, or C₃-C₆-cycloalkyl, and

5

R² is hydrogen or C₁-C₆-alkyl, or

10

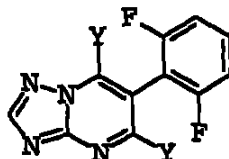
R¹ and R² together with the interjacent nitrogen atom represent a heterocyclic ring with 5 or 6 carbon atoms being optionally substituted with one or two C₁-C₆-alkyl groups.

3. Compounds according to claims 1 or 2 in which R² is hydrogen.

15 4. Compounds according to claims 1 to 3 in which X is halogen.

5. A process for the preparation of compounds of formula I as defined in claim 4 which comprises reacting 5,7-dihalogen-6-(2,6-difluoro-phenyl)-triazolopyrimidines of formula II

20



II

25 in which Y is halogen with an amine of formula III



III

30 in which R¹ and R² are defined as for formula I to produce compounds of formula I.

6. A composition suitable for controlling phytopathogenic fungi, comprising a solid or liquid carrier and a compound of the formula I as claimed in claim 1.

35

7. A method for controlling phytopathogenic fungi, which comprises treating the fungi or the materials, plants, the soil or the seed to be protected against fungal attack with an effective amount of a compound of the formula I as claimed in claim 1.

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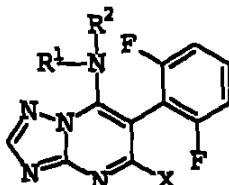
6-(2,6-Difluoro-phenyl)-triazolopyrimidines

Abstract

5

6-(2,6-Difluoro-phenyl)-triazolopyrimidines of formula I

10



I

in which

15 R¹ and R² independently denote hydrogen or

alkyl, alkenyl, alkynyl, or alkadienyl, cycloalkyl, phenyl, naphthyl, or

20

5- or 6-membered heterocyclyl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, or

5- or 6-membered heteroaryl, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom,

25

where R¹ and R² radicals may be unsubstituted or substituted as defined in the description, or

30

R¹ and R² together with the interjacent nitrogen atom represent a 5- or 6-membered heterocyclic ring, containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom, which may be substituted;

X is halogen, cyano, alkoxy, haloalkoxy or alkenyloxy;

35

processes for their preparation, compositions containing them and to their use for combating phytopathogenic fungi.

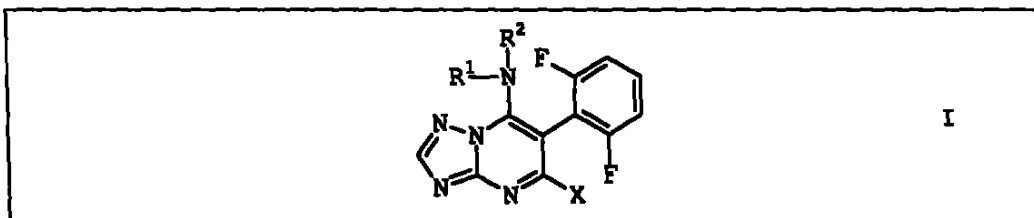
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6-(2,6-Difluoro-fenil)-triazolopirimidinas

Descripción

La invención se refiere a 6-(2,6-difluoro-fenil)-triazolopirimidinas de la fórmula I



en la que

R^1 y R^2 significan, independientemente, hidrógeno o

alquilo- C_1-C_{10} , alquenilo- C_2-C_{10} , alquinilo- C_2-C_{10} , o alcadienilo- C_4-C_{10} ,
cicloalquilo- C_3-C_{10} , fenilo, naftilo, o

heterociclilo de 5 ó 6 miembros, que contiene de uno a cuatro átomos de
nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de
oxígeno, o

heteroarilo de 5 ó 6 miembros, que contiene de uno a cuatro átomos de
nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de
oxígeno, o

en donde los radicales R^1 y R^2 pueden estar sustituidos o no sustituidos y
llevar de uno a tres groups R^a ,

R^a es ciano, nitro, hidroxilo, alquilo- C_1-C_8 , cicloalquilo- C_3-C_8 , alcoxi- C_1-C_8 ,
alquiltio- C_1-C_8 , alquilamino- C_1-C_8 , di-alquilamino- C_1-C_8 , alquenilo- C_2-C_8 ,
alqueniloxi- C_2-C_8 , alquinilo- C_2-C_8 , alquiniloxi- C_3-C_8 y alquilenodioxo- C_1-C_4 ; o

R^1 y R^2 representan junto con el átomo de nitrógeno interyacente un anillo heterocíclico de 5 ó 6 miembros, que contiene de uno a cuatro átomos de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de oxígeno, que puede estar sustituido por uno a tres radicales R^n ;

X es halógeno, ciano, alcoxi- C_1-C_8 , haloalcoxi- C_1-C_8 o alquenilo- C_3-C_8 .

Además, la invención se refiere a un procedimiento para su preparación, a composiciones que las contienen y a su uso para combatir hongos fitopatógenos. 6-Fenil-7-amino-triazolopirimidinas son generalmente conocidas de las memorias US 4,567,262 y US 5,593,996.

Triazolopirimidinas con un grupo trifluorofenilo en la posición 6 se divulgan en la WO-A 98/46607 y EP-A 945 453.

De la WO-A 98/46608 se conocen algunas 6-(2,6-difluoro-fenil)-triazolopirimidinas, que están sustituidas en la posición 7 por alquilaminas fluoradas.

Los compuestos divulgados en los documentos arriba indicados se describen como activos contra varios hongos fitopatógenos.

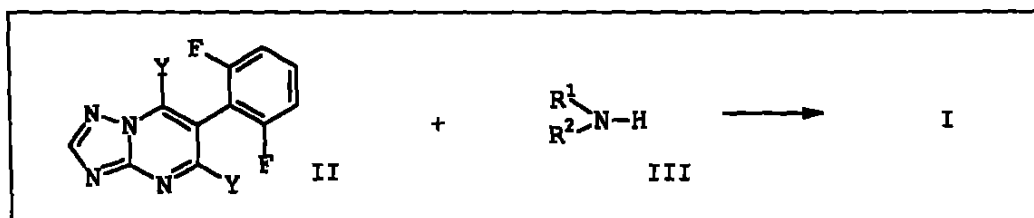
El objeto de la presente invención es proveer compuestos con actividad fungicida mejorada.

Se ha encontrado, que este objeto se alcanza con los compuestos definidos al comienzo. Además, se han encontrado procedimientos para su obtención, composiciones que los comprenden y métodos para controlar hongos nocivos usando los compuestos I.

Los compuestos de la fórmula I se distinguen de los compuestos conocidos de la memoria WO-A 98/46608 en la combinación del grupo 2,6-difluoro-fenilo con un

grupo amino exento de halógeno en la posición 7 del sistema de triazolopirimidina.

Además, la presente invención provee un procedimiento para la preparación de los compuestos de la fórmula I arriba definidos, que comprende tratar un compuesto de 5,7-dihalógeno de la fórmula II, en la que X es halógeno, con una amina de la fórmula III.



La reacción entre el compuesto de 5,7-dihalógeno II y la amina de la fórmula III puede ser efectuada bajo las condiciones conocidas de la WO-A 98/46608.

Los compuestos de la fórmula II se conocen de la EP-A 550 113; pueden ser preparados mediante métodos conocidos [ver EP-A 550 113 o EP-A 770 815].

La reacción se efectúa, preferentemente, en presencia de un disolvente. Disolventes apropiados incluyen los éteres, tales como dioxano, éter dietílico y, especialmente, tetrahidrofurano, hidrocarburos halogenados, tal como diclorometano, y hidrocarburos aromáticos, por ejemplo, tolueno.

La reacción se efectúa, ventajosamente, a una temperatura de 0°C a 70°C, asendiendo la temperatura de reacción preferida a 10°C hasta 35°C.

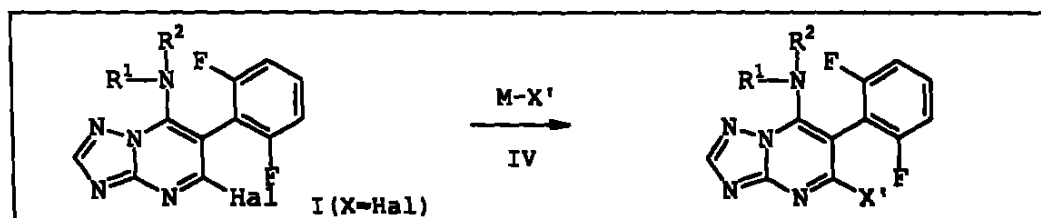
Preferentemente, se efectúa la reacción en presencia de una base. Bases adecuadas incluyen las aminas terciarias, tal como trietilamina y bases inorgánicas, tales como carbonato de potasio o carbonato de sodio. Alternativamente, se puede usar un exceso del compuesto de la fórmula III como base.

Las mezclas de reacción se elaboran ulteriormente de manera acostumbrada, por ejemplo, mezclando con agua, separando las fases y purificando los productos

crudos, de ser necesario, por cromatografía. Algunos de los productos finales se obtienen en forma de aceites viscosos incoloros o ligeramente parduzcos, que son purificados o librados de los componentes volátiles bajo presión reducida y temperatura ligeramente elevada. Si los productos finales se obtienen como sólidos, se puede purificarlos también por recristalización o digestión.

Los compuestos de la fórmula II son conocidos en la técnica y pueden ser obtenidos por métodos de síntesis descritos en las memorias EP-A 550 113, EP-A 770 615 y WO-A 98/46608.

Los compuestos de la fórmula I, en la que X significa ciano, alcoxi-C₁-C₈, haloalcoxi-C₁-C₈ o alquenioksi-C₂-C₈, pueden ser preparados, haciendo reaccionar compuestos I, donde X es halógeno, preferentemente, cloro, con compuestos de la fórmula IV, que, dependiendo del valor de X' a ser introducido para proporcionar compuestos de la fórmula I, es una sal inorgánica de ciano, un alcoxilato, haloalcoxilato o un alquenioksilato, respectivamente, preferentemente, en presencia de un disolvente. El catión M en la fórmula IV tiene menor influencia; por razones prácticas y económicas, se suelen preferir las sales amónicas, tetraalquilamónicas o de metal alcalino o alcalinotérreo.



La reacción se efectúa, ventajosamente, a una temperatura de 0 a 120°C, preferentemente, de 10 a 40°C [ver J. Heterocycl. Chem., Vol. 12, p. 861-863 (1975)].

Disolventes apropiados incluyen los éteres, tales como dioxano, éter dietílico y, especialmente, tetrahidrofurano, hidrocarburos halogenados, tal como

diclorometano y hidrocarburos aromáticos, por ejemplo, tolueno.

Si algunos compuestos individuales no pueden ser obtenidos mediante los métodos arriba descritos, entonces se puede prepararlos por derivatización de otros compuestos.

En las definiciones de los símbolos arriba indicados, se usan términos colectivos que representan, generalmente, los sustituyentes siguientes:

- halógeno: flúor, cloro, bromo e yodo;

alquilo- C_1-C_{10} : radicales hidrocarburo saturados, de cadena recta o ramificados, con 1 a 10, especialmente, 1 a 6 átomos de carbono, por ejemplo, alquilo- C_1-C_4 como los arriba mencionados, o pentilo, 1-metilbutilo, 2-metilbutilo, 3-metilbutilo, 2,2-dimetilpropilo, 1-etilpropilo, hexilo, 1,1-dimetilpropilo, 1,2-dimetilpropilo, 1-metilpentilo, 2-metilpentilo, 3-metilpentilo, 4-metilpentilo, 1,1-dimetilbutilo, 1,2-dimetilbutilo, 1,3-dimetilbutilo, 2,2-dimetilbutilo, 2,3-dimetilbutilo, 3,3-dimetilbutilo, 1-etilbutilo, 2-etilbutilo, 1,1,2-trimetilpropilo, 1,2,2-trimetilpropilo, 1-etil-1-metilpropilo y 1-etil-2-metilpropilo;

alqueno- C_2-C_{10} : radicales hidrocarburo no saturados, de cadena recta o ramificados, con 2 a 10, especialmente, 2 a 6 átomos de carbono y un doble enlace en cualquier posición, por ejemplo, etenilo, 1-propenilo, 2-propenilo, 1-metiletlenilo, 1-butenilo, 2-butenilo, 3-butenilo, 1-metil-1-propenilo, 2-metil-1-propenilo, 1-metil-2-propenilo y 2-metil-2-propenilo;

alquino- C_2-C_{10} : radicales hidrocarburo de cadena recta o ramificados, con 2 a 10, especialmente, 2 a 4 átomos de carbono y un triple enlace en cualquier posición, por ejemplo, etinilo, 1-propinilo, 2-propinilo, 1-butinilo, 2-butinilo, 3-butinilo y 1-metil-2-propinilo;

radicales halógenoalquilo de halógenoalcoxi- C_1-C_6 : grupos alquilo lineales o ramificados con 1 a 6, preferentemente, 1 a 4 átomos de carbono (como los arriba definidos), pudiendo los átomos de hidrógeno en estos grupos estar parcial o completamente reemplazados por átomos de halógeno como los arriba mencionados, por ejemplo, haloalcoxi- C_1-C_2 , como p.ej. clorometoxi, bromometoxi, diclorometoxi, triclorometoxi, fluorometoxi, difluorometoxi, trifluorometoxi, clorofluorometoxi, diclorofluorometoxi, clorodifluorometoxi, 1-cloroetoxi, 1-bromoetoxi, 1-fluoroetoxi, 2-fluoroetoxi, 2,2-difluoroetoxi, 2,2,2-trifluoroetoxi, 2-cloro-2-fluoroetoxi, 2-cloro-2,2-difluoroetoxi, 2,2-dicloro-2-fluoroetoxi, 2,2,2-tricloroetoxi y pentafluoroetoxi;

cicloalquilo- C_3-C_{10} : grupos cicloalquilo mono o bicíclicos, con 3 a 10 átomos de carbono; grupos monocíclicos con, preferentemente, 3 a 8, especialmente, 3 a 6 miembros de anillo, grupos bicíclicos con, preferentemente, 8 to 10 miembros de anillo.

Un grupo heterociclilo de 5 ó 6 miembros, que contiene de uno a cuatro átomos de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de oxígeno, preferentemente, un átomo de oxígeno.

Un heterociclo de cinco miembros, que contiene de uno a cuatro átomos de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de oxígeno: grupos heteroarilo de 5 miembros, que además de átomos de carbono pueden contener de uno a cuatro átomos de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de oxígeno como miembros de anillo, por ejemplo, 2-furilo, 3-furilo, 2-tienilo, 3-tienilo, 2-pirrolilo, 3-pirrolilo, 3-isoxazolilo, 4-isoxazolilo, 5-isoxazolilo, 3-isotiazolilo, 4-isotiazolilo, 5-isotiazolilo, 3-pirazolilo, 4-pirazolilo, 5-pirazolilo, 2-oxazolilo, 4-oxazolilo, 5-oxazolilo, 2-tiazolilo, 4-tiazolilo, 5-tiazolilo, 2-imidazolilo, 4-imidazolilo, 1,2,4-oxadiazol-3-ilo, 1,2,4-oxadiazol-5-ilo, 1,2,4-tiadiazol-3-ilo, 1,2,4-tiadiazol-5-ilo, 1,2,4-triazol-3-ilo, 1,3,4-oxadiazol-2-ilo, 1,3,4-tiadiazol-2-ilo y 1,3,4-triazol-2-ilo;

un heterociclo de 6 miembros, que contiene de uno a cuatro átomos de nitrógeno: grupos heteroarilo de 6 miembros, que además de átomos de carbono, pueden contener de uno a tres o de uno a cuatro átomos de nitrógeno como miembros de anillo, por ejemplo, 2-piridinilo, 3-piridinilo, 4-piridinilo, 3-piridacnilo, 4-piridacnilo, 2-pirimidinilo, 4-pirimidinilo, 5-pirimidinilo, 2-piracnilo, 1,3,5-triacin-2-ilo y 1,2,4-triacin-3-ilo.

Con respecto al uso a que están destinadas, se prefieren aquellas triazolopirimidinas de la fórmula I con los siguientes sustituyentes, valiendo las preferencias en cada caso para los sustituyentes individuales o las combinaciones:

Un radical cicloalquilo preferido es ciclopentilo opcionalmente sustituido con uno o más grupos nitro, ciano, alquilo-C₁-C₆, alcoxi-C₁-C₆.

Un radical heteroarilo preferidos es: piridilo, pirimidilo, pirazolilo o tienilo.

Son preferidos los compuestos de la fórmula I, en los que cualquier parte de alquilo de los grupos R¹ o R², que pueden ser lineales o ramificados, contiene 1 hasta 9 átomos de carbono, preferentemente, 2 a 6 átomos de carbono, cualquier parte de alquenilo o alquinilo de los sustituyentes R¹ o R² contiene 2 hasta 9 átomos de carbono, preferentemente, 2 a 9 átomos de carbono, más preferentemente, 3 a 6 átomos de carbono, cualquier parte de cicloalquilo de los sustituyentes R¹ o R² contiene de 3 a 10 átomos de carbono, preferentemente, de 3 a 6 átomos de carbono, y en los que cualquier parte de cicloalquilo de los sustituyentes R¹ o R² contiene de 3 a 10 átomos de carbono, preferentemente, de 3 to 8 átomos de carbono, más preferentemente, 3 a 6 átomos de carbono, y cualquier parte de bicicloalquilo de los sustituyentes R¹ o R² contiene de 7 a 9 átomos de carbono. Cualquier grupo alquilo, alquenilo o alquinilo puede ser lineal o ramificado.

Son preferidos los compuestos de la fórmula I, en la que R¹ no es hidrógeno.

Además, son preferidos los compuestos de la fórmula I, en los que R¹ representa alquilo-C₁-C₁₀ lineal o ramificado, especialmente, un grupo alquilo-C₃-C₁₀ ramificado, un grupo cicloalquilo-C₃-C₈, un bicicloalquilo-C₆-C₉, un cicloalquil-C₃-C₈-alquilo-C₁-C₈, alcoxi-C₁-C₁₀-alquilo-C₁-C₈ o un grupo fenilo opcionalmente sustituido por uno a tres átomos de halógeno o grupos alquilo-C₁-C₁₀ o alcoxi-C₁-C₁₀.

Son especialmente preferidos los compuestos I en los que R² representa un átomo de hidrógeno o un grupo alquilo-C₁-C₁₀, especialmente, un átomo de hidrógeno.

Además, son especialmente preferidos los compuestos I, en los que R² es metilo o etilo.

Si R¹ significa un grupo cicloalquilo-C₃-C₈ opcionalmente sustituido, preferentemente, un grupo ciclopentilo o ciclohexilo, R² representa, preferentemente, un átomo de hidrógeno o un grupo alquilo-C₁-C₈.

Además, son especialmente preferidos los compuestos I, en los que R¹ y R² forman junto con el átomo de nitrógeno interyacente un anillo heterocíclico opcionalmente sustituido, preferentemente, un anillo heterociclilo con 3 a 7 átomos de carbono opcionalmente sustituido, especialmente una pirrolidina, piperidina, tetrahidropiridina, especialmente, 1,2,3,6-tetrahidropiridina o un anillo azepano opcionalmente sustituido por uno o más grupos alquilo-C₁-C₁₀.

Adicionalmente, son especialmente preferidos los compuestos I, en los que X es cloro o bromo, especialmente cloro.

Además, son preferidos los compuestos I, en los que X es ciano o metoxi.

Adicionalmente, son especialmente preferidos los compuestos I, en los que X es etoxi, n-propoxi, iso-propoxi, aliloxi, o 3-metilaliloxi.

En el ámbito de la presente invención están incluidos los isómeros (R) y (S) de compuestos de la fórmula general I, que poseen un centro de quiralidad y los racematos de los mismos y las sales, N-óxidos y compuestos de adición ácidos.

Con respecto a su uso son especialmente preferidos los compuestos I relacionados en las siguientes tablas. Los grupos mencionados en las tablas para un sustituyente son, además, para su parte, independientemente de la combinación en que son mencionados, una modalidad preferida de los respectivos sustituyentes.

Tabla 1

Compuestos de la fórmula I, en la que X es cloro y R¹ y R² corresponden a una línea en la Tabla A

Tabla 2

Compuestos de la fórmula I, en la que X es bromo y R¹ y R² corresponden a una línea en la Tabla A

Tabla 3

Compuestos de la fórmula I, en la que X es ciano y R¹ y R² corresponden a una línea en la Tabla A

Tabla 4

Compuestos de la fórmula I, en la que X es metoxi y R¹ y R² corresponden a una línea en la Tabla A

Tabla 5

Compuestos de la fórmula I, en la que X es etoxi y R¹ y R² corresponden a una línea en la Tabla A

Tabla 6

Compuestos de la fórmula I, en la que X es n-propoxi y R¹ y R² corresponden a una línea en la Tabla A

Tabla 7

Compuestos de la fórmula I, en la que X es iso-propoxi y R¹ y R² corresponden a una línea en la Tabla A

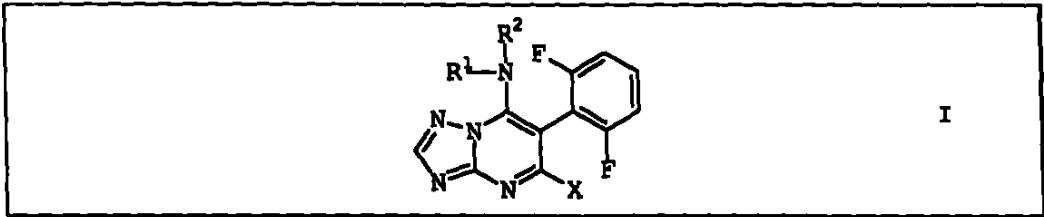
Tabla 8

Compuestos de la fórmula I, en la que X es aliloxi y R¹ y R² corresponden a una línea en la Tabla A

Tabla 9

Compuestos de la fórmula I, en la que X es 3-metilaliloxi y R¹ y R² corresponden a una línea en la Tabla A

Tabla A



No.	R ¹	R ²
A-1	H	H
A-2	CH ₂ CH ₃	H
A-3	CH ₂ CH ₃	CH ₃
A-4	CH ₂ CH ₃	CH ₂ CH ₃
A-5	CH ₂ CH ₂ CH ₃	H
A-6	CH ₂ CH ₂ CH ₃	CH ₃

A-7	$\text{CH}_2\text{CH}_2\text{CH}_3$	CH_2CH_3
A-8	$\text{CH}_2\text{CH}_2\text{CH}_3$	$\text{CH}_2\text{CH}_2\text{CH}_3$
A-9	$\text{CH}(\text{CH}_3)_2$	H
A-10	$\text{CH}(\text{CH}_3)_2$	CH_3
A-11	$\text{CH}(\text{CH}_3)_2$	CH_2CH_3
A-12	$(\pm) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	H
A-13	$(\pm) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	CH_3
A-14	$(\pm) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	CH_2CH_3
A-15	$(S) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	H
A-16	$(S) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	CH_3
A-17	$(S) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	CH_2CH_3
A-18	$(R) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	H
A-19	$(R) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	CH_3
A-20	$(R) \text{CH}(\text{CH}_3)\text{-CH}_2\text{CH}_3$	CH_2CH_3
A-21	$(\pm) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	H
A-22	$(\pm) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	CH_3
A-23	$(\pm) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	CH_2CH_3
A-24	$(S) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	H
A-25	$(S) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	CH_3
A-26	$(S) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	CH_2CH_3
A-27	$(R) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	H
A-28	$(R) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	CH_3
A-29	$(R) \text{CH}(\text{CH}_3)\text{-CH}(\text{CH}_3)_2$	CH_2CH_3
A-30	$(\pm) \text{CH}(\text{CH}_3)\text{-C}(\text{CH}_3)_3$	H
A-31	$(\pm) \text{CH}(\text{CH}_3)\text{-C}(\text{CH}_3)_3$	CH_3
A-32	$(\pm) \text{CH}(\text{CH}_3)\text{-C}(\text{CH}_3)_3$	CH_2CH_3

A-33	(S) CH(CH ₃)-C(CH ₃) ₃	H
A-34	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-35	(S) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-36	(R) CH(CH ₃)-C(CH ₃) ₃	H
A-37	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₃
A-38	(R) CH(CH ₃)-C(CH ₃) ₃	CH ₂ CH ₃
A-39	CH ₂ C(CH ₃)=CH ₂	H
A-40	CH ₂ C(CH ₃)=CH ₂	CH ₃
A-41	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃
A-42	ciclopentilo	H
A-43	ciclopentilo	CH ₃
A-44	ciclopentilo	CH ₂ CH ₃
A-45	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	

Los compuestos I son apropiados como fungicidas. Se destacan por presentar una excelente actividad contra un amplio espectro de hongos fitopatógenos, especialmente, de la clase de los *ascomicetos*, *deuteromicetos*, *ficoomicetos* y *basidiomicetos*. Algunos actúan sistémicamente y pueden ser usados en la fitosanidad como fungicidas foliares y del suelo.

Son especialmente importantes para controlar un amplio número de hongos en una variedad de plantas de cultivo, tales como trigo cebada, centeno, avena, arroz, maíz, pasto, plátanos, algodón, soya, café, caña de azúcar, vid, especies de frutas, plantas de adorno y legumbres, como p.ej. pepinos, frijoles, tomates, papas y cucurbitáceas y en las semillas de estas plantas.

Son especialmente apropiados para controlar las siguientes enfermedades de las plantas:

1. _____

- especies de *Alternaria*, especies de *Podosphaera*, especies de *Sclerotinia*, *Physalospora* canker en legumbres y frutas,
- *Botrytis cinerea* (oidio) en fresas, legumbres, plantas de adorno y vid,
- *Corynespora cassicola* en pepinos,
- especies de *Colletotrichum* en frutas y legumbres,
- *Diplocarpon rosae* en rosas,
- *Elsinoe fawcetti* y *Diaporthe citri* en frutas cítricas,
- especies de *Sphaerotheca* en cucurbitáceas, fresas y rosas,
- especies de *Cercospora* en maní, remolachas de azúcar y berenjenas,
- *Erysiphe cichoracearum* en cucurbitáceas,
- *Leveillula taurica* en pimientos, tomates y berenjenas,
- especies de *Mycosphaerella* en manzanas y albaricoques japonesas,
- *Phyllactinia kakicola*, *Gloesporium kaki* en albaricoques japonesas,
- *Gymnosporangium yamadae*, *Leptothyrium pomi*, *Podosphaera leucotricha* y *Gloeodes pomigena* en manzanas,
- *Cladosporium carpophilum* en peras y albaricoques japonesas,
- especies de *Phomopsis* en peras,
- especies de *Phytophthora* en frutas cítricas, papas, cebollas, especialmente, *Phytophthora infestans* en papas y tomates,
- *Blumeria graminis* (mildíu pulverulento) en cereales,
- especies de *Fusarium* y *Verticillium* en varias plantas,
- *Glomerella cingulata* en té,
- especies de *Drechslera* y *Bipolaris* en cereales y arroz,
- especies de *Mycosphaerella* en plátanos y maní,
- *Plasmopara viticola* en vid,
- especies de *Peronospora* en cebollas, espinaca y crisantemos,
- *Phaeoisariopsis vitis* y *Sphaceloma ampelina* en toronjas,
- *Pseudocercospora herpotrichoides* en trigo y cebada,
- especies de *Pseudoperonospora* en lúpulo y pepinos,
- especies de *Puccinia* y de *Typhula* en cereales y césped,
- *Pyricularia oryzae* en arroz,
- especies de *Rhizoctonia* en algodón, arroz y césped,

- *Stagonospora nodorum* y *Septoria tritici* en trigo,
- *Uncinula necator* en vid,
- especies de *Ustilago* especies en cereales y caña de azúcar, y
- especies de *Venturia* (roña) en manzanas y peras.

Además, los compuestos I son apropiados para controlar hongos nocivos, como p.ej. *Paecilomyces variotii* en la protección de materiales (p.ej. madera, dispersiones de pinturas, fibras y telas) y en la protección de productos almacenados.

Los compuestos I se aplican, tratando los hongos o las plantas, semillas, materiales o el suelo a proteger frente a una infección fungosa con una cantidad activa fungicida de los ingredientes activos. La aplicación puede efectuarse antes o después de la infección de los materiales, plantas o semillas por los hongos.

Generalmente, las composiciones fungicidas contienen de entre 0.1 y 95, preferentemente, 0.5 y 90% en peso de ingrediente activo.

Cuando se usan en la protección de plantas, las cantidades de aplicación varían de 0.01 a 2.0 kg de ingrediente activo por ha, dependiendo del tipo de efecto deseado.

En el tratamiento de las semillas, las cantidades de ingrediente activo varían, generalmente, de 0.001 a 0.1 g, preferentemente, de 0.01 a 0.05 g, por kilogramo de semilla.

En la protección de materiales o de productos almacenados, la cantidad de aplicación de ingrediente activo depende de la naturaleza de la aplicación y del efecto deseado. Las cantidades de aplicación generalmente usados para la protección de materiales varían, por ejemplo, de 0.001 g a 2 kg, preferentemente, de 0.005 g a 1 kg, de ingrediente activo por metro cúbico del material tratado.

Los compuestos I pueden ser transformados en las formulaciones acostumbradas, tales como soluciones, emulsiones, suspensiones, polvos, pastas y granulados. El uso depende del fin respectivo, pero en todo caso debe estar asegurada una dispersión fina y uniforme del compuesto según la invención.

Las formulaciones se preparan de manera conocida, por ejemplo, diluyendo el ingrediente activo con disolventes y/o soportes, en caso de desearlo, usando emulsionantes y dispersantes. También se pueden usar otros disolventes orgánicos como disolventes auxiliares, si se usa agua como diluyente. Auxiliares apropiados son, substancialmente: disolventes, tales como aromáticos (por ejemplo, xileno), aromáticos clorados (p.ej. clorobencenos), parafinas (por ejemplo, fracciones de aceite mineral), alcoholes (por ejemplo, metanol, butanol), cetonas (por ejemplo, ciclohexanona), aminas (p.ej. etanolamina, dimetilformamida) y agua; soportes, como p.ej. minerales molidos naturales (tales como caolinas, arcillas, talco, tiza) y minerales sintéticos molidos (tales como sílice altamente disperso, silicatos); emulsionantes, como p.ej. emulsionantes no iónicos y aniónicos (tales como éteres de alcoholes grasos de polioxietileno, sulfonatos de alquilo y sulfonatos de arilo) y dispersantes, como p.ej. lejías residuales lignino-sulfíticas y metilcelulosa.

Tensoactivos apropiados son las sales de metal alcalino, alcalinotérreo y de amonio del ácido ligninosulfónico, ácido naftalinsulfónico, ácido fenolsulfónico, ácido dibutilnaftalinsulfónico, sulfonatos de alquilarilo, sulfatos de alquilo, sulfonato de alquilo, sulfatos de alcohol graso, ácidos grasos y glicoléteres de alcohol graso sulfatados, además, condensados de naftalina sulfonada y derivados de naftalina con formaldehído, condensados de naftalina o de ácido naftalinsulfónico con fenol y formaldehído, éter octilfenílico de polioxietileno, isooctilfenol etoxilado, octilfenol, nonilfenol, alquilfenil poliglicol éteres, tributilfenil-poliglicol éter, tristearilfenil-poliglicol éter, poliéter alcoholes de alquilarilo, condensados de alcohol y de alcohol graso/óxido de etileno, aceite de ricino etoxilado, éteres alquílicos de polioxietileno, polioxipropileno etoxilado, alcohol laurílico de poliglicoléter acetal, ésteres de sorbitol, lejías residuales lignino-sulfíticas y metilcelulosa.

Sustancias apropiadas para la preparación de soluciones, emulsiones, pastas o dispersiones de aceite directamente pulverizables son: fracciones de aceite mineral de punto de ebullición mediano hasta elevado, como p.ej. keroseno o aceite diesel, además, aceites de alquitrán de carbón, y aceites de origen vegetal o animal, hidrocarburos alifáticos, cíclicos y aromáticos, por ejemplo, tolueno, xileno, parafina, tetrahidronaftalina, naftalinas alquiladas y sus derivados, metanol, etanol, propanol, butanol, ciclohexanol, ciclohexanona, isoforona, disolventes fuertemente polares, por ejemplo, sulfóxido de dimetilo, N-metilpirrolidona y agua.

Polvos, agentes de pulverización y rociado pueden ser preparados mezclando o moliendo conjuntamente las sustancias activas con un soporte sólido.

Los granulados, p.ej. granulados recubiertos, impregnados o homogéneos, se pueden preparar uniendo el ingrediente activo con un soporte sólido. Ejemplos de cargas sólidas son: tierras minerales, tales como silicagel, ácidos silícicos, geles silícicos, silicatos, talco, caolín, caliza, cal, bol, loess, arcilla, dolomita, tierra de diatomeas, sulfato de calcio y sulfato de magnesio, óxido de magnesio, plásticos molidos, así como abonos, tales como sulfato de amonio, fosfato de amonio, nitrato de amonio, ureas y productos vegetales, tales como harina de cereales, polvos de corteza, de madera y de cáscaras de nueces, polvos de celulosa u otros soportes sólidos.

Generalmente, las formulaciones comprenden de 0.01 a 95% en peso, preferentemente, de 0.1 a 90% en peso del ingrediente activo. Los ingredientes activos se usan en una pureza de 90% a 100%, preferentemente, de 95% a 100% (según espectro de NMR).

Ejemplos de formulaciones son:

- I. 5 partes en peso de un compuesto según la invención se mezclan íntimamente con 95 partes en peso de caolín finamente particulado. De esta forma se obtiene un agente de espolvoreo que contiene 5% en peso del

ingrediente activo.

- II. 30 partes en peso de un compuesto según la invención se mezclan íntimamente con una mezcla de 92 partes en peso de silicagel pulverulento y 8 partes en peso de aceite de parafina, que se ha pulverizado sobre la superficie del silicagel. De esta forma se obtiene una preparación del ingrediente activo con buena adherencia (contenido en ingrediente activo 23% en peso).
- III. 10 partes en peso de un compuesto según la invención se disuelven en una mezcla, que se compone de 90 partes en peso de xileno, 8 partes en peso del producto de adición de 8 a 10 moles de óxido de etileno a 1 mol de N-monoetanolamina de ácido oleico, 2 partes en peso de la sal cálcica del ácido dodecibencenosulfónico y 2 partes en peso del producto de adición de 40 moles de óxido de etileno a 1 mol de aceite de ricino (contenido en ingrediente activo 9% en peso).
- IV. 20 partes en peso de un compuesto según la invención se disuelven en una mezcla, que se compone de 60 partes en peso de ciclohexanona, 30 partes en peso de isobutanol, 5 partes en peso del producto de adición de 7 moles de óxido de etileno a 1 mol de isooctilfenol y 5 partes en peso del producto de adición de 40 moles de óxido de etileno a 1 mol de aceite de ricino (contenido en ingrediente activo 16% en peso).
- V. 80 partes en peso de un compuesto según la invención se mezclan bien con 3 partes en peso de la sal sódica del ácido diisobutilnaftalin-alfa-sulfónico, 10 partes en peso de la sal sódica de un ácido ligninosulfónico de una lejía residual sulfúrica y 7 partes en peso de silicagel pulverulento y se muelen en un molino de martillos (contenido en ingrediente activo 80% en peso).
- VI. Se mezclan 90 partes en peso de un compuesto según la invención con 10 partes en peso de N-metil-a-pirrolidona y se obtiene una solución apropiada

para ser aplicada en forma de gotas minúsculas (contenido en ingrediente activo 90% en peso).

- VII. 20 partes en peso de un compuesto según la invención se disuelven en una mezcla, que se compone de 40 partes en peso de ciclohexanona, 30 partes en peso de isobutanol, 20 partes en peso del producto de adición de 7 moles de óxido de etileno a 1 mol de isooctilfenol y 10 partes en peso del producto de adición de 40 moles de óxido de etileno a 1 mol de aceite de ricino. Vertiendo la solución en 100 000 partes en peso de agua y distribuyéndola finamente se obtiene una dispersión acuosa, que contiene 0,02% en peso del ingrediente activos.
- VIII. 20 partes en peso de un compuesto según la invención se mezclan bien con 3 partes en peso de la sal sódica del ácido diisobutilnaftalín- α -sulfónico, 17 partes en peso de la sal sódica de una lejía residual sulfítica y 60 partes en peso de silicagel pulverulento y se muelen en un molino de martillos. Distribuyendo la mezcla finamente en 20000 partes en peso de agua, se obtiene un caldo de pulverización, que contiene 0,1% en peso del ingrediente activo.

Los ingredientes activos pueden ser usados como tales, en forma de sus formulaciones o las formas de aplicación preparadas a partir de las mismas, por ejemplo, como soluciones, polvos, suspensiones o dispersiones, emulsiones, dispersiones de aceite directamente pulverizables, pastas, polvos pulverizables, agente de rociado o de regado. Las formas de aplicación dependen enteramente del fin de aplicación, pero en todo caso hay que asegurar una distribución lo más fina posible de los ingredientes activos según la invención.

Las formas de aplicación acuosas pueden ser preparadas a partir de concentrados de emulsión, pastas o polvos humectables (polverizables, dispersiones de aceite) adicionando agua. Para preparar emulsiones, pastas o dispersiones de aceite se pueden homogeneizar las sustancias como tales o disueltas en un aceite

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o disolvente en agua con la ayuda de un humectante, agente adherente, dispersante o emulsionante. Alternativamente, se pueden preparar concentrados compuestos de la sustancia activa, humectante, adherente, dispersante o emulsionante, en caso dado, disolvente o aceite, y tales concentrados son apropiados para ser diluidos con agua.

Las concentraciones en ingrediente activo en los productos listos para el uso pueden variar ampliamente. En general, varían de 0.0001 a 10%, preferentemente, de 0.01 a 1%.

Los ingredientes activos también pueden ser usados con éxito en el procedimiento de volumen ultrabajo (ULV), pudiéndose aplicar formulaciones con más del 95% en peso de ingrediente activo, o aún el ingrediente activo sin aditivos.

Se pueden adicionar varios tipos de aceite, humectantes, adyuvantes, herbicidas, fungicidas, u otros pesticidas o bactericidas a los ingredientes activos, en caso dado, recién antes de la aplicación (mezcla de tanque). Estos agentes pueden ser mezclados con los agentes según la invención en una relación ponderal de 1:10 hasta 10:1.

Cuando se usan como fungicidas, las composiciones de la invención pueden estar presentes también junto con otros ingredientes activos, por ejemplo, con herbicidas, insecticidas, reguladores del crecimiento, fungicidas u otros fertilizantes. Cuando se mezclan los compuestos o las composiciones según la invención como fungicidas con otros fungicidas, entonces se alcanza, frecuentemente, ampliar el espectro de acción.

La siguiente lista de fungicidas con los que se pueden mezclar los compuestos según la invención sirve para ilustrar las combinaciones posibles, pero no debe entenderse como limitativa:

azufre, ditiocarbamatos y sus derivados, tales como hierro(III) dimetilditiocarbamato, dimetilditiocarbamato de cinc, etilenobisditiocarbamato de cinc, etilenobisditiocarbamato de manganeso, metilenodiaminobisditiocarbamato de manganeso-cinc, disulfuro de tetrametiltiuram, complejo amoniacal de cinc (N,N'-etilenobisditiocarbamato), complejo amoniacal de (N,N'-propilenobisditiocarbamato) de cinc, (N,N'-propilenobisditiocarbamato), disulfuro de N,N'-polipropilenobis(tiocarbamoilo);

derivados nitrogenados, tales como crotonato de dinitro(1-metilheptil)fenilo, 2-sec-butil-4,6-dinitrofenil- 3,3-dimetilacrilato, 2-sec-butil-4,6-dinitrofenilisopropil-carbonato, diisopropil 5-nitro-isoftalato;

sustancias heterocíclicas, tales como acetato de 2-heptadecil-2-imidazolina, 2,4-dicloro-6-(o-cloroanilino)-s-triacina, O,O-dietil ftalimidofosfonotioato, 5-amino-1-[bis(dimetilamino)fosfinil]-3-fenil-1,2,4-triazol, 2,3-diciano-1,4-ditioantraquinona, 2-tio-1,3-ditiolo[4,5-b]quinoxalina, 1-(butilcarbamoil)-2-benzimidazolcarbamato de metilo, 2-metoxycarbonilaminobenzimidazol, 2-(2-furil)benzimidazol, 2-(4-tiazolil)benzimidazol, N-(1,1,2,2-tetracloroetil)tetrahidroftalimida, N-triclorometiltiotetrahidroftalimida, N-triclorometiltioftalimida, dimetilamida de ácido 5-cloro-2-ciano-4-p-tolil-imidazol-1-sulfónico, N-diclorofluorometiltio-N',N'-dimetil-N-fenilsulfo-diamida, 5-etoxi-3-tri-clorometil-1,2,3-tiadiazol, 2-tiocianatometiltiobenzotiazol, 1,4-dicloro-2,5-dimetoxibenceno, 4-(2-clorofenilhidrazono)-3-metil-5-isoxazolona, 1-óxido de piridin-2-tiol, 8-hidroxiquinolina o sus sales de cobre, 2,3-dihidro-5-carboxanilido-6-metil-1,4-oxatiina, 4,4-dióxido de 2,3-dihidro-5-carboxanilido-6-metil-1,4-oxatiina, 2-metil-5,6-dihidro-4H-piran-3-carboxanilida, 2-metilfuran-3-carboxanilida, 2,5-dimetilfuran-3-carboxanilida, 2-cloro-N-(4'-cloro-bifenil-2-il)-nicotinamida, 2,4,5-trimetilfuran-3-carboxanilida, N-ciclohexil- 2,5-dimetilfuran-3-carboxamida, N-ciclohexil-N-metoxi-2,5-dimetilfuran-3-carboxamida, 2-metilbenzanilida, 2-iodobenzanilida, N-formil-N-morfolin-2,2,2-tricloroetil acetal, piperacin-1,4-diilbis-1-(2,2,2-tricloroetil)formamida, 1-(3,4-dicloroanilino)-1-formilamino-2,2,2-tricloroetano; 2,6-dimetil-N-tridecilmorfolina o sus sales, 2,6-dimetil-N-ciclododecilmorfolina o sus sales, N-[3-(p-terc-butilfenil)-2-metilpropil]-cis-2,6-dimetil- morfolina, N-[3-(p-terc-butilfenil)-2-metilpropil]-piperidina, 8-terc.-butil-1,4-

dioxaspiro[4.5]decan-2-ilmetil(etil)(propil)amina, (RS)-2-[2-(1-clorociclopropil)-3-(2-clorofenil)-2-hidroxipropil]-2,4-dihidro-1,2,4-triazol-3-iona, 1-[2-(2,4-diclorofenil)-4-etil-1,3-dioxolan-2-il-etil]-1H-1,2,4-triazol, 1-[2-(2,4-diclorofenil)-4-n-propil-1,3-dioxolan-2-il-etil]-1H-1,2,4-triazol, N-(n-propil)-N-(2,4,6-triclorofenoxietil)-N'-imidazolil-urea, 1-(4-clorofenoxi)-3,3-dimetil-1-(1H-1,2,4-triazol-1-il)-2-butanona, 1-(4-clorofenoxi)-3,3-dimetil-1-(1H-1,2,4-triazol-1-il)-2-butanol, (2RS,3RS)-1-[3-(2-clorofenil)-2-(4-fluorofenil)-oxiran-2-ilmetil]-1H-1,2,4-triazol, α -(4-clorofenil)- α -(1-ciclopropiletil)-1H-1,2,4-triazol-1-etanol, α -(2-clorofenil)- α -(4-clorofenil)-5-pirimidinmetanol, 5-butil-2-dimetilamino-4-hidroxi-6-metilpirimidina, bis(p-clorofenil)-3-piridinmetanol, 1,2-bis(3-etoxicarbonil-2-tioureido)benceno, 1,2-bis(3-metoxicarbonil-2-tioureido)benceno, estrobilurines tales como azoxistrobina, kresoxim metilo, metil-E-metoxiimino-[α -(2-fenoxifenil)]-acetamida, metil E-metoxiimino-[α -(2,5-dimetilfenoxi)-o-tolil]acetamida, picoxistrobina, piraclostrobina, trifloxistrobina, anilino pirimidinas tales como N-(4,6-dimetilpirimidin-2-il)anilina, N-[4-metil-6-(1-propinil)pirimidin-2-il]-anilina, N-[4-metil-6-ciclopropilpirimidin-2-il]anilina, fenilpirroles tales como 4-(2,2-difluoro-1,3-benzodioxol-4-il)pirrol-3-carbonitrilo, cinamamidas tales como 3-(4-clorofenil)-3-(3,4-dimetoxi-fenil)acrilolmorfolina, 3-(4-fluorofenil)-3-(3,4-dimetoxi-fenil)acrilolmorfolina, y una variedad de fungicidas, tales como acetato de dodecilguanidina, 3-[3-(3,5-dimetil-2-oxiciclohexil)-2-hidroxietil]glutarimida, hexaclorobenceno, metil-N-(2,6-dimetilfenil)-N-(2-furoil)-DL-alaninato, éster metílico de DL-N-(2,6-dimetilfenil)-N-(2'-metoxiacetil)-alanina, N-(2,6-dimetilfenil)-N-cloroacetil-D,L-2-amino-butirolactona, éster metílico de DL-N-(2,6-dimetilfenil)-N-(fenilacetil)alanina, 5-metil-5-vinil-3-(3,5-diclorofenil)-2,4-dioxo-1,3-oxazolidina, 3-[3,5-diclorofenil(5-metil-5-metoximetil)-1,3-oxazolidin-2,4-diona, 3-(3,5-diclorofenil)-1-isopropilcarbamoilhidantoina, N-(3,5-diclorofenil)-1,2-dimetilciclopropane-1,2-dicarboximida, 2-ciano-[N-(etilaminocarbonil)-2-metoximino]acetamida, 3,5-dicloro-N-(3-cloro-1-etil-1-metil-2-oxo-propil)-4-metilbenzamida, 1-(3-bromo-6-metoxi-2-metil-fenil)-1-(2,3,4-trimetoxi-6-metil-fenil)-metanona, 1-[2-(2,4-dicloro-fenil)pentil]-1H-1,2,4-triazol, alcohol 2,4-difluoro- α -(1H-1,2,4-triazolil-1-metil)benzohidrílico, N-(3-cloro-2,6-dinitro-4-trifluorometilfenil)-

5-trifluorometil-3-cloro-2-aminopiridina, 1-((bis(4-fluorofenil)metilsilil)metil)-1H-1,2,4-triazol.

Ejemplos de síntesis

Variando en forma correspondiente los compuestos de partida, los protocolos prepresentados en los ejemplos de síntesis siguientes fueron usados para obtener otros compuestos I. Los resultantes compuestos I, junto con los datos físicos están relacionados en la siguiente Tabla I.

Ejemplo 1 Preparación de 5,7-dihidroxi-6-(2,6-difluorofenil)-[1,2,4]-triazolo[1,5-a]-pirimidina

Se calentó una mezcla de 3-amino-1,2,4-triazol (14 g), (2,6-difluorofenil)-malonato de dietilo (0,17 mol, ver EP-A 10 02 788) y tributilamina (50 ml) a unos 160°C durante seis horas. Se enfrió la mezcla de reacción a unos 70°C. Se adicionaron 200 ml de solución acuosa al 10 % de hidróxido sódico y se agitó la mezcla de reacción durante 30 minutos. Se separaron las fases, se extrajo la fase acuosa con éter dietílico. Se aciduló la fase acuosa y se filtró el precipitado y se secó, dando 40 g del compuesto indicado en el título.

Ejemplo 2 Preparación de 5,7-dicloro-6-(2,6-difluorofenil)-[1,2,4]-triazolo[1,5-a]-pirimidina

Se calentó una mezcla de 5,7-dihidroxi-6-(2,6-difluorofenil)-[1,2,4]-triazolo-[1,5-a]pirimidina (30 g, obtenida del Ej. 1) y oxiclورو fosforoso (50 ml) durante aprox, ocho horas a reflujo. El oxiclورو fosforoso se destiló parcialmente. El residuo se vertió en una mezcla de diclorometano y agua. Se separó la capa orgánica, se secó y se filtró. El filtrado se concentró en vacío, dando 28 g del compuesto indicado en el título del p.f. 121°C.

Ejemplo 3 Preparación de 5-cloro-6-(2,6-difluorofenil)-7-isopropilamino-[1,2,4]-triazolo[1,5-a]pirimidina [I-3]

Una mezcla de isopropilamina (1,5 mmoles), trietilamina (1,5 mmoles) y diclorometano (10 ml) se adicionó a una mezcla de 5,7-dicloro-6-(2,6-difluorofenil)-[1,2,4]-triazolo[1,5-a]-pirimidina (1,5 mmoles, obtenida del Ej. 2) y diclorometano (20 ml) bajo agitación. Se agitó la mezcla de reacción durante aprox. 16 horas a unos 20 to 25°C y luego se lavó con ácido clorhídrico diluido (al 5%). La capa orgánica se separó, se secó y se filtró. El filtrado se evaporó bajo presión reducida y el residuo se purificó cromatográficamente, dando 0,43 g del compuesto indicado en el título del p.f. 189°C.

Ejemplo 4 Preparación de 5-ciano-6-(2,6-difluorofenil)-7-(4-metilpiperidin-1-il)-[1,2,4]-triazolo[1,5-a]pirimidina [I-18]

Una mezcla de 5-cloro-6-(2,6-difluorofenil)-7-(4-metilpiperidin-1-il)-[1,2,4]-triazolo[1,5-a]-pirimidina (0,1 mol; I-4) y cianuro de tetraetilamonio (0,25 mol) en 750 ml dimetilformamida (DMF) (750 ml) se agitó durante 16 horas a aprox. 20 a 25°C. A esta mezcla se adicionó agua y éter metil terc.-butílico (MTBE), se separó la fase orgánica, se lavó con agua, se secó y se filtró. El filtrado se evaporó y el residuo se purificó por cromatografía, dando 6,95 g del compuesto indicado en el título del p.f. 212°C.

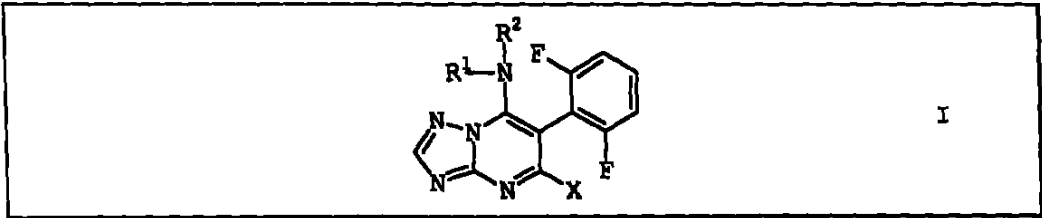
Ejemplo 5 Preparación de 5-metoxi-6-(2,6-difluorofenil)-7-(dietilamino)-[1,2,4]-triazolo[1,5-a]pirimidina [I-19]

A una solución de 5-cloro-6-(2,6-difluorofenil)-7-(dietil-amino)-[1,2,4]-triazolo[1,5-a]-pirimidina (65 mmoles; I-6) en 400 ml de metanol seco se adicionó una solución al 30% de metanolato de sodio (71,5 mmoles) a aprox. 20 a 25°C. Esta mezcla se agitó ulteriormente durante 16 horas. Se evaporó el metanol y se disolvió el residuo en diclorometano. La fase orgánica se lavó con agua, se secó y se filtró. El filtrado

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se evaporó y el residuo se purificó por cromatografía, dando 16,3 g del compuesto indicado en el título del p.f. 153°C.

Tabla I



No.	R ¹	R ²	X	Datos físicos (p.f..[°C])
I-1	H	H	Cl	250
I-2	CH ₂ C(CH ₃)=CH ₂	CH ₂ CH ₃	Cl	96
I-3	CH(CH ₃) ₂	H	Cl	169
I-4	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		Cl	198
I-5	ciclopentilo	H	Cl	165
I-6	CH ₂ CH ₃	CH ₂ CH ₃	Cl	159
I-7	CH ₂ CH ₂ CH ₃	CH ₂ CH ₂ CH ₃	Cl	125
I-8	CH(CH ₃) ₂	CH ₃	Cl	168
I-9	(±) CH(CH ₃)-CH ₂ CH ₃	H	Cl	184
I-10	(S) CH(CH ₃)-CH ₂ CH ₃	H	Cl	176
I-11	(R) CH(CH ₃)-CH ₂ CH ₃	H	Cl	176
I-12	(±) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	157
I-13	(S) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	149
I-14	(R) CH(CH ₃)-CH(CH ₃) ₂	H	Cl	149
I-15	(±) CH(CH ₃)-C(CH ₃) ₃	H	Cl	160

I-16	(S) CH(CH ₃)-C(CH ₃) ₃	H	Cl	175
I-17	(R) CH(CH ₃)-C(CH ₃) ₃	H	Cl	175
I-18	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -		CN	212
I-19	CH ₂ CH ₃	CH ₂ CH ₃	OCH ₃	153

Ejemplos de la acción contra hongos nocivos

La acción fungicida de los compuestos de la fórmula I puede ser demostrada en los siguientes experimentos:

Los ingredientes activos, separada o conjuntamente, fueron formulados como emulsión al 10% en una mezcla de 70% en peso de ciclohexanona, 20% en peso de Nekanil® LN (Lutensol® AP6, agente humectante de acción emulsionante y dispersante a base de alquifhenoles etoxilados) y 10% en peso de Wettol EM (emulsionante no iónico a base de aceite de ricino etoxilado) y diluidos con agua a la concentración deseada.

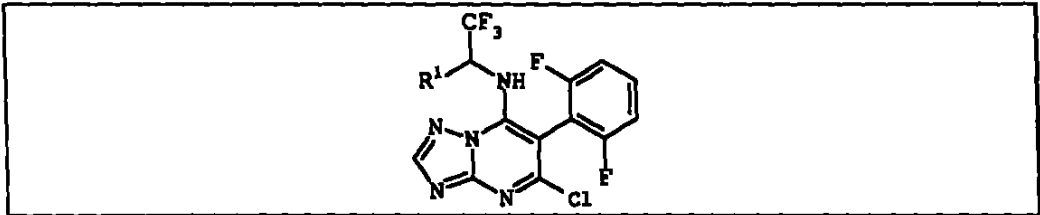
Ensayo de actividad biológica - Control fungicida de la marchitez temprana de tomates (*Alternaria solani*)

Plántulas jóvenes de tomate de la variedad: "Große Fleischtomate St. Pierre" se cultivaron en macetas hasta alcanzar el estadio de 2 a 4 hojas. Estas plantas se pulverizaron hasta chorrear con una suspensión acuosa, que contenía la concentración en ingrediente activo indicada en la tabla de abajo, preparada de una solución madre de 10% en peso del ingrediente activo en una mezcla de 85% de ciclohexanona y 5% en peso de emulsionante. El día siguiente, se inocularon las plantas con una suspensión acuosa de *Alternaria solani*, que contenía 0,2 x 10⁸ esporas por ml. A continuación, se colocaron las plantas de ensayo inmediatamente en una cámara húmeda. Después de 6 días a 20 hasta 23°C y una humedad relativa de cerca del 100%, se evaluó visualmente la extensión del ataque del

hongo en las hojas como % de área de hoja muerta.

En este ensayo, las plantas que se habían tratado con 250 ppm respectivamente de los compuestos I-2 hasta I-9, I-11, I-12, I-14, I-15 y I-17 y I-20, presentaban una infección de, como máximo, 1%, mientras que las plantas no tratadas estaban infectadas en un 90%.

Los compuestos activos A y B conocidos de la WO-A 98/48608 se usaron como compuestos comparativos:



No.	conocidos de	R ¹
A	WO-A 98/48608, No. 5	hidrógeno
B	WO-A 98/48608, No. 7	metilo

Ensayo comparativo - Control de la podredumbre (*Botrytis cinerea*) en rodajas de pimiento verde

Se pulverizaron rodajas de pimiento verde hasta chorrear con una suspensión acuosa, que contenía la concentración en ingrediente activo o la mezcla mencionada en la Tabla de abajo, preparada de una solución madre conteniendo 10% del ingrediente activo, 85 % de ciclohexanona y 5 % de emulsionante. Después de dos horas, la capa pulverizada estaba seca y se inocularon las rodajas con una suspensión de esporas de *Botrytis cinerea*, que contenía 1,7 x 10⁸ esporas por ml en solución acuosa al 2% en peso de biomalta. Las rodajas de pimiento se incubaron en cámaras con alta humedad durante cuatro días a 18-20°C. Se evaluó

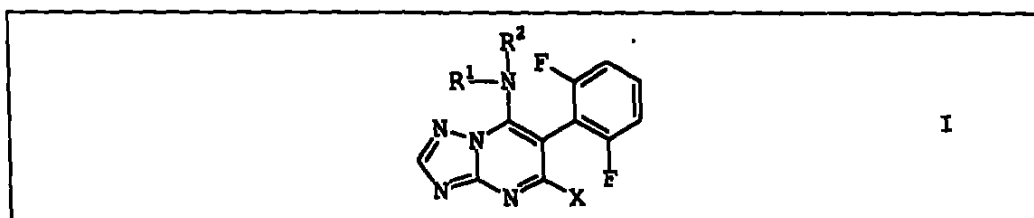
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visualmente el área infectada de las rodajas de fruta en por cien.

En este ensayo, las plantas tratadas con 500 ppm de los compuestos I-2, I-8 y I-14, resp., presentaban una infección de, como máximo, 3%, mientras que las plantas tratadas con 500 ppm de los compuestos comparativos A y B, resp., estaban infectadas en un 100 y 20%, y las plantas no tratadas estaban infectadas en un 100%.

Reivindicaciones:

1. 6-(2,6-Difluoro-fenil)-triazolopirimidinas de la fórmula I



en donde

R^1 y R^2 significan, independientemente, hidrógeno o

alquilo- C_1-C_{10} , alquenilo- C_2-C_{10} , alquinilo- C_2-C_{10} , o alcadienilo- C_4-C_{10} ,
cicloalquilo- C_3-C_{10} , fenilo, naftilo, o

heterociclilo de 5 ó 6 miembros, que contiene de uno a cuatro átomos
de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre
o de oxígeno, o

heteroarilo de 5 ó 6 miembros, que contiene de uno a cuatro átomos de
nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o
de oxígeno, o

en donde los radicales R^1 y R^2 pueden estar sustituidos o no sustituidos
y llevar de uno a tres groups R^a ,

R^a es ciano, nitro, hidroxilo, alquilo- C_1-C_6 , cicloalquilo- C_3-C_6 , alcoxi-
 C_1-C_6 , alquiltio- C_1-C_6 , alquilamino- C_1-C_6 , di-alquilamino- C_1-C_6 ,
alquenilo- C_2-C_6 , alqueniloxi- C_2-C_6 , alquinilo- C_2-C_6 , alquinitoxi- C_3-
 C_6 y alquilenodioxo- C_1-C_4 ; o

R^1 y R^2 representan junto con el átomo de nitrógeno Interyacente un anillo
heterocíclico de 5 ó 6 miembros, que contiene de uno a cuatro átomos
de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre

o de oxígeno, que puede estar sustituido por uno a tres radicales R^a ;

X es halógeno, ciano, alcoxi- C_1-C_6 , haloalcoxi- C_1-C_6 o alquenilo- C_3-C_6 .

2. Compuestos de la fórmula I según la reivindicación 1, en donde

R^1 es alquilo- C_1-C_6 lineal o ramificado, alquenilo- C_2-C_6 o cicloalquilo- C_3-C_6 , y

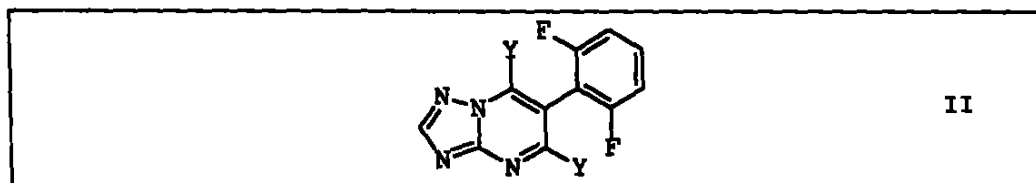
R^2 es hidrógeno o alquilo- C_1-C_6 , o

R^1 y R^2 representan junto con el átomo de nitrógeno interyacente un anillo heterocíclico con 5 ó 6 miembros, opcionalmente sustituido por uno o dos grupos alquilo- C_1-C_6 .

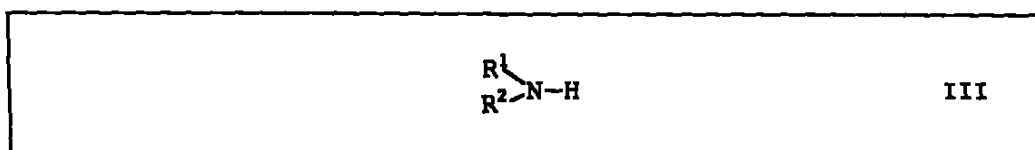
3. Compuestos según las reivindicaciones 1 ó 2, en donde R^2 es hidrógeno.

4. Compuestos según las reivindicaciones 1 a 3, en donde X es halógeno.

5. Procedimiento para la preparación de compuestos de la fórmula I tal y como se definen en la reivindicación 4, que comprende la reacción de 5,7-dihalógeno-6-(2,6-difluoro-fenil)-triazolopirimidinas de la fórmula II



en la que Y es halógeno, con una amina de la fórmula III



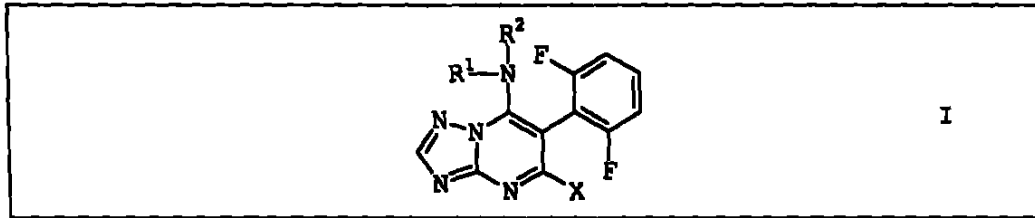
en la que R^1 y R^2 tienen las definiciones indicadas para la fórmula I, dando compuestos de la fórmula I.

6. Una composición apropiada para controlar hongos fitopatógenos, que comprende un soporte sólido o líquido y un compuesto de la fórmula I según la reivindicación 1.
7. Un método para controlar hongos fitopatógenos, que comprende el tratamiento de los hongos o de materiales, plantas, el suelo o las semillas a proteger frente a la infección por los hongos nocivos, con una cantidad efectiva de un compuesto de la fórmula I según la reivindicación 1.

6-(2,6-Difluoro-fenil)-triazolopirimidinas

Resumen

6-(2,6-Difluoro-fenil)-triazolopirimidinas de la fórmula I



en la que

R^1 y R^2 significan, independientemente, hidrógeno o

alquilo, alquenilo, alquinilo o alcadienilo, cicloalquilo, fenilo, naftilo, o heterociclilo de 5 ó 6 miembros, que contiene de uno a cuatro átomos de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de oxígeno, o

heteroarilo de 5 ó 6 miembros, que contiene de uno a cuatro átomos de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de oxígeno, o

en donde los radicales R^1 y R^2 pueden estar no sustituidos o suatituidos en la forma definida en la memoria descriptiva,

R^1 y R^2 representan junto com el átomo de nitrógeno interyacente un anillo heterocíclico de 5 ó 6 miembros, que contiene de uno a cuatro átomos de nitrógeno o de uno a tres átomos de nitrógeno y un átomo de azufre o de oxígeno, que puede estar sustituido;

X es halógeno, ciano, alcoxi, haloalcoxi o alqueniloxi.

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procedimientos para su preparación, composiciones que las contienen y su uso para combatir hongos fitopatógenos

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

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Applicant's or agent's file reference 0000052657		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEAA/16)	
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International Patent Classification (IPC) or both national classification and IPC C07D487/04			
Applicant BASF AKTIENGESELLSCHAFT et al.			
1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of 4 sheets, including this cover sheet. ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 807 of the Administrative Instructions under the PCT). These annexes consist of a total of sheets.			
3. This report contains indications relating to the following items: I ☒ Basis of the opinion II ☐ Priority III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV ☐ Lack of unity of invention V ☒ Reasoned statement under Rule 66.2(a)(II) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI ☐ Certain documents cited VII ☐ Certain defects in the international application VIII ☐ Certain observations on the international application			
Date of submission of the demand 18.10.2002		Date of completion of this report 06.10.2003	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2369 - 0 Tx: 523656 epmu d Fax: +49 89 2369 - 4465		Authorized Officer Herz, C Telephone No. +49 89 2369-8275 	

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP02/07575**

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I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*)

Description, Pages

1-20 as originally filed

Claims, Numbers

1-7 as originally filed

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

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**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP02/07575**

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims	1-7
	No: Claims	
Inventive step (IS)	Yes: Claims	1-7
	No: Claims	
Industrial applicability (IA)	Yes: Claims	1-7
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP02/07575

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1. Due to the specific substitution pattern of the phenyl ring at position 6 of the triazolopyrimidine core the compounds claimed are considered to be novel vis-à-vis the state of the art as represented by the documents cited in the International Search Report (ISER) (Art. 33 (2) PCT).
2. With regard to the results of comparative tests submitted with Applicant's letter dated 25/07/03 against compounds disclosed in the closest prior art, EP-A-0 834 513 (D1) and US-A-5 965 561 (D3), which are closely related in structure to those presently claimed, a surprising improvement has been demonstrated being indicative of an inventive solution of the technical problem of providing compounds exhibiting a significantly improved antifungal activity (Art. 33 (3) PCT).

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TRATADO DE COOPERACIÓN DE PATENTES

PCT

INFORME INTERNACIONAL DE EXAMEN PRELIMINAR

Artículo 36 y Norma 70 del PCT

Referencia del archivo del solicitante o representante: 0000052657		Para trámite adicional: véase notificación del informe internacional de examen preliminar (de PCT/PEA/416)
Solicitud internacional No.: PCT/EP02/07575	Fecha de presentación internacional: 08.07.2002	Fecha de prioridad: 18.07.2001
Clasificación internacional de patentes (IPC) o clasificación nacional e IPC: C07D487/04		
Solicitante: BASF AKTIENGESELLSCHAFT et al.		

1. Este Informe Internacional de examen preliminar ha sido elaborado por esta Autoridad Internacional de Examen Preliminar y se le da traslado de él al Solicitante de conformidad con el Artículo 36.
2. El presente INFORME consta en total de 4 folios, incluida esta carátula. ☐ El presente informe también se acompaña de ANEXOS, es decir, folios de la descripción, reivindicaciones o ilustraciones que han sido modificadas y que constituyen la base del presente informe, o folios que contienen rectificaciones realizadas ante esta Autoridad (véase la Norma 70.1.6 y la Sección 607 de las Instrucciones Administrativas bajo el PCT). Los mencionados anexos constan de folios
3. El presente informe contiene indicaciones relativas a los siguientes asuntos: I. ☒ Base del informe II. ☐ Prioridad III. ☐ Falta establecer opinión con respecto a novedad, nivel inventivo y aplicabilidad industrial. IV. ☐ Falta de unidad de invención V. ☒ Declaración razonada conforme a lo previsto en el Artículo 35(2) en lo atinente a novedad, nivel inventivo o aplicabilidad industrial; citas y explicaciones en respaldo de la mencionada declaración VI. ☐ Ciertos documentos citados VII. ☐ Ciertos defectos de la solicitud internacional VIII. ☐ Ciertas observaciones sobre la solicitud internacional

Fecha de presentación de la demanda 18.10.2002	Fecha de terminación de este informe 08.10.2003
Nombre y dirección de la autoridad examinadora primaria internacional: Oficina Europea de Patentes D-80298 Munich Tel: +49 89 2399 – 0 Tx: 523656 epmu d Fax: +49 89 2399 – 4465	Funcionario autorizado: HERZ, C Teléfono No. +49 89 2399 – 8275

I. Base del Informe

1. Con respecto a los elementos de la solicitud internacional: *(Los folios sustitutivos que le han sido entregados a la Oficina receptora en respuesta a una invitación extendida según lo previsto en el Artículo 14 se refieren a este Informe "tal como se presentó originalmente" y no se anexan al presente informe porque no contienen modificaciones (Normas 70.16 y 70.17)).*

Descripción, páginas

1-20 tal como fueron presentadas

Reivindicaciones, No.:

1-7 tal como fueron presentadas

2. Con respecto al idioma, todos los elementos marcados arriba estaban disponibles o se le presentaron a esta Autoridad en el idioma en el cual se presentó la solicitud internacional, a menos que se indique lo contrario en este artículo.

Estos elementos se pusieron a disposición de esta Autoridad en el siguiente idioma

_____ el cual es:

- ☐ El idioma de una traducción presentada para propósitos de búsqueda internacional (según la norma 23.1(b)).
- ☐ El idioma de publicación de la solicitud internacional
- ☐ El idioma de la traducción presentada para propósitos del examen preliminar (según las Normas 55.2 o 55.3).

3. Con respecto a cualquier secuencia de nucleótidos o aminoácidos revelada en la solicitud internacional, el examen internacional preliminar se llevó a cabo con base en los listados de secuencias.

- ☐ Contenidos en la solicitud internacional en forma escrita X
- ☐ Presentados juntos con la solicitud internacional en forma de archivo electrónico X
- ☐ Presentados más adelante a esta Autoridad en forma escrita
- ☐ Presentados más adelante en forma de archivo electrónico
- ☐ Se ha adjuntado la declaración de que el listado de secuencia presentado más adelante por escrito no va más allá de la revelación contenida en la solicitud internacional tal como ha sido presentada

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☐ Se ha adjuntado la declaración de que la información registrada en forma de archivo electrónico es idéntica a los listados escritos de secuencias.

4. Las modificaciones han dado lugar a la cancelación de:

- ☐ La descripción, páginas
- ☐ Las reivindicaciones, Nos.
- ☐ Las ilustraciones, folios / figuras

5. ☐ Este Informe ha sido establecido como si (algunas de) las modificaciones no se hubiesen realizado, ya que se ha considerado que van más allá de la revelación tal como ha sido presentada, según lo previsto en la Casilla Complementaria (Norma 70.2(c)).

(Cualquier folio sustitutivo que contenga una modificación de esta naturaleza deberá ir referenciado en el numeral 1 y anexo al presente informe.)

6. Observaciones adicionales, si es necesario:

V. Declaración razonada conforme al Artículo 35(2) en lo que respecta a la novedad, el nivel inventivo o la aplicabilidad industrial; citas y explicaciones en respaldo de dicha declaración

1. Declaración

Novedad (N)	SÍ	Reivindicaciones	1-7
	NO:	Reivindicaciones	
Nivel inventivo (NI)	SÍ	Reivindicaciones	1-7
	NO:	Reivindicaciones	
Aplicabilidad Industrial	SÍ	Reivindicaciones	1-7
	NO:	Reivindicaciones	

7. Citas y explicaciones:

Véase página separada.

1. Debido al patrón específico de sustitución del anillo fenilo en la posición 6 del núcleo triazolopirimidina, se considera que los compuestos reivindicados son novedosos frente al arte previo representado por los documentos citados en el Reporte de Búsqueda Internacional (RBI) (Art. 33 (2) del PCT).
2. Respecto a los resultados de las pruebas comparativas presentadas con la carta del solicitante fechada 25/07/03 contra los compuestos divulgados en el arte previo más cercano, EP-A-0 834 513 (D1) y US-A-5 965 561 (D3), los cuales están cercanamente relacionados en estructura con aquellos reivindicados en la presente solicitud, se ha demostrado un sorprendente mejoramiento indicativo de la solución inventiva del problema técnico de proporcionar compuestos que exhiben una actividad antifúngica significativamente mejorada (Art. 33(3) del PCT).

FORMATO DE DIGITALIZACION
RELACION DE ANEXOS



Royal
Technologies S.A.
Sede: Calle 100 No. 100-100, San José, Costa Rica

Expediente No		No de Folio
04002821		91
Item	No de unidades	
1	CD	
2	DVD	
3	REVISTA	
4	LIBRO	
5	PERIODICO	
6	DISQUETES	
7	SOBRE DE MANILA	
8	SOBRE BLANCO TAMAÑO CARTA	
9	SOBRE BLANCO TAMAÑO OFICIO	
10	OTROS:	

Observaciones:

Arte final 112 figuras

290

SUPERINDUSTRIA Y COMERCIO
 Radicación : 04000021 000000000
 Fecha (MM): 2004-01-16 17:19:28
 Trámite : 011 PCR-PACIENTE 3/9 FASE MACI 411 PRESENTAC
 Dependencia: 2020 DIVISION DE NUEVAS CREACIONES

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	10497411	06/01/2004	67,154,000.00

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01	SOLICITUDES	
		1	TRAMITES DE SOL. DE PATENTE DE IN
			422,000.00
		TOTAL :	\$ 422,000.00

RESPONSABLE : 

Co 00361-841-020-7

REQUISITOS NECESARIOS PARA PRESEN TRAMITE

Indicacion : 04002021 00000000
Fecha (MM): 2004-01-16 17:19:20
Tramite : 011 PCI-PATENTE 379 FASE NDL 421 Presentar.
Dependencia: 2000 DIVISION DE MARCA ORIGIN.

	USUARIO	RADICADOR
PATENTE DE INVENCION	()	()
MODELO DE UTILIDAD	()	()
- Indicación de que se solicita la concesión de una patente.	()	()
- Datos de identificación del solicitante o de la persona que se presenta la solicitud.	()	()
- Descripción de la invención.	()	()
- Dibujos de ser estos pertinentes.	()	()
- Comprobante de Pago de las tasas establecidas.	()	()

COMPLETA () INCOMPLETA ()

DISEÑO INDUSTRIAL ()

- Indicación de que se solicita el registro de Diseño Industrial	()	()
- Datos de identificación del solicitante o de la persona que presenta la solicitud.	()	()
- Representación gráfica y fotográfica del Diseño Industrial o muestra del Material que incorpora el diseño.	()	()
- Comprobante de pago de las tasas establecidas	()	()

COMPLETA () INCOMPLETA ()

ESQUEMA DE TRAZADO ()

- Indicación de que solicita el registro de un Esquema de trazado.	()	()
- Datos de identificación del solicitante o de la persona que presenta La solicitud.	()	()
- Representación gráfica del esquema de trazado	()	()
- Comprobante de pago de las tasas establecidas.	()	()

COMPLETA () INCOMPLETA ()

Firma Responsable:

Fecha:



92
94

2020
Bogotá, D.C.,

Doctor:
EMILIO FERRERO
Apoderado
BASF AKTIENGESELLSCHAFT.

Oficio N° 04221

ASUNTO:	Radicación N°	04-2821
	Solicitud Internacional	PCT/EP02/07575
	Fecha Inicio fase nacional	18/02/2005
	Trámite	011
	Evento	379
	Actuación	430
	Folios	001

Como resultado del examen de forma, realizado con fundamento en el artículo 38 de la Decisión 486 de la Comisión de la Comunidad Andina, artículo 27 del Tratado de Cooperación en Materia de Patentes (PCT), regla 51 bis del Reglamento y Circular Única de la Superintendencia de Industria y Comercio, se le comunica que:

□ La solicitud no contiene la copia del documento en que consta la cesión del derecho a la patente del inventor al solicitante o a su causante. (Art. 26-k) Decisión 486).

En cumplimiento de lo dispuesto por el artículo 39 de la Decisión 486, se le requiere para que dentro del término de dos meses siguientes a la fecha de notificación del presente oficio, complete los requisitos anteriormente enunciados. En caso de no dar cumplimiento al presente requerimiento, la solicitud se considerará abandonada y perderá su prelación.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.


ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

El anterior requerimiento fue notificado por fijación en lista de fecha 29 de Feb. 2004.

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