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Influence of processing on the content of sugars in green Arabica coffee beans

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Abstract Quantitative analyses of low molecular sugars in green coffees (*Coffea arabica* L. var. Acaia) that were processed in parallel either by the traditional wet or the traditional dry method, revealed a close correlation between the kind of post-harvest treatment and the contents of fructose and glucose. While in *washed* coffee beans (wet processing) only low amounts of these both hexoses were present, those in *unwashed* coffees (dry processing) were significantly higher. Model-processing experiments in the laboratory confirmed these findings. Moreover, a comparison with the untreated controls revealed that the low levels of both sugars are the consequence of a decrease in the case of wet processing, whereas they remained unchanged or even increased in the case of dry processing. Further minor sugars are also affected by post-harvest treatment. The amounts of galactose, arabinose and mannose show a similar arrangement as those for glucose and fructose, although their overall concentration is about 100-fold lower. Sucrose, the major low molecular sugar in green coffee beans, is not significantly affected by coffee processing. The influence of an active seed metabolism on the observed alterations of the sugars concentrations is discussed.

Keywords *Coffea arabica* · Glucose · Fructose · Sucrose · Green coffee · Post-harvest treatment · Coffee processing

Introduction

The world coffee market distinguishes between “washed” and “unwashed” Arabicas (*Coffea arabica* L.) depending on the processing method applied to convert the freshly harvested coffee cherries into green coffee. It is well accepted that green coffees resulting from the wet method—the so-called washed Arabicas—yield roasted beans and coffee

beverages, respectively, that are characteristically different from those produced with the dry method (i.e. unwashed Arabicas) [1, 2]. There is no doubt, that these flavour differences in part have to be attributed to differences in the thoroughness applied during either method of post-harvest treatment and the fact that only fully ripe coffee cherries are used for wet processing, whereas fruits of all stages of ripeness are utilized for dry processing [3, 4]. However, according to our previous results [5] these aspects appear to play a minor role in this context, as the typical differences in cup quality between washed and unwashed Arabicas also occurred when identical and thoroughly sorted starting material was used for either method of coffee processing. In a recent study [6] we have demonstrated for the first time that during post-harvest treatment, various metabolic processes occur inside the coffee seeds which significantly alter the chemical composition of the green beans. This metabolism becomes evident by the conversion of glutamic acid into γ -aminobutyric acid mediated by an enzymatic α -decarboxylation. The reaction is related to a physiological drought stress situation and is specific to the mode of processing applied [6].

Suchlike alterations in the pool of free amino acids—components which are considered as essential precursors of flavour and colour of the coffee brew [7]—may be suitable to explain some of the sensorial differences between washed and unwashed Arabicas. However, it seems most unlikely that changes in the spectra of amino acids are the only metabolic response of the viable coffee seed to the imposed post-harvest treatment. There are some early reports on the loss of sugars in the coffee beans during the fermentation step of wet processing [8]. Just recently, we presented evidence for an active germination-related metabolism in the seeds; this metabolism is induced during the post-harvest processing of the coffee fruits and beans, respectively [9, 10]. During seed germination soluble carbohydrates are among the first components which are affected by a resumption of an active metabolism. Next to the free amino acids, the soluble carbohydrates are considered as most prominent precursors of numerous volatile and non-volatile components of roast coffee flavour and

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colour [11–13]. Earlier analyses of the concentrations of the soluble sugars in commercial green Arabica samples revealed significant variations; e.g. the values for sucrose ranging from 5 to 8.5%, and those for glucose from less than 0.01–0.45% [11, 14]. Two previous works dealing with the influence of the mode of post-harvest treatment on the sugar content of the green coffee beans rendered results contradictory to each other [15, 16]. Consequently, it is still quite unclear, if all these variations are already inherent to the seeds, or whether they are also a consequence of the post-harvest treatment. We therefore analyzed changes in the contents of low molecular carbohydrates in Arabica coffee beans submitted to the dry and wet way of processing.

Material and methods

Commercial samples

A variety of green Arabica coffees was kindly provided by the Tchibo Röstfrisch GmbH.

Batch processing

The field experiments were carried out in June and July 2002. In Brazil, fruits of *C. arabica* var. Acaiá were processed at the facilities of Ipanema Agricola, Alfenas, Minas Gerais, Brazil. For the experiments, only fully ripe and sound coffee fruits were used. This was ensured by thorough manual sorting of single batches of freshly harvested coffee cherries. The experiments were undertaken in parallel (wet, dry and semi-dry processing) and in three repetitions (semi-dry process only in two repetitions).

Wet processing

The coffee fruits were mechanically pulped using a Pinhalense drum pulper, and submitted to 22 h of underwater tank fermentation. Subsequently, the washed parchment coffee beans were dried on a separate plot of the sun terrace of the Ipanema factory Conquista. After 6 days, the final water content of 12% (wet basis) was achieved.

Dry processing

The coffee cherries from the same batch used for the wet processing (see earlier) were dried as whole fruits on a separate plot of the sun terrace. The final water content of 12% was achieved after 16 days of drying.

Semi-dry processing

Like for the wet processing, the coffee fruits were mechanically pulped using a Pinhalense drum pulper. However, for the production of semi-washed Arabica, the tank fermenta-

tion was omitted and the wet and mucilaginous parchment coffee beans were immediately dried on a separate plot of the sun terrace. After 6 days, the final water content of 12% (wet basis) was achieved.

Shipping of the experimental coffee samples

Within 4 weeks after field processing, the dry coffee samples were sent to Germany, where the parchment coffees were manually husked. The samples were subsequently frozen in liquid nitrogen and the samples were then stored at -70°C prior to the analysis.

Model processing in the laboratory

The fresh fruits of *C. arabica* were harvested on coffee plantations in Tanzania and Mexico, respectively, and directly transferred to Germany by cargo express flights. To prevent the fruits from perishing during transport, some plastic bags with ordinary ice cubes were added. The cultivars used were *C. arabica* var. KP 345 (Tanzania) and *Caturra* (Mexico). Thorough manual sorting ensured that only fully ripe and sound coffee cherries were used. The time span between harvest and model processing was less than 36 h. The germination rate was in all cases over 95% and thus not affected by shipment.

Wet model processing

The fruits were manually pulped. The mucilaginous parchment beans were then transferred into 5-l Erlenmeyer-flasks and an excess of fresh water was added. The coffee was fermented at RT for 36 h. The water was exchanged three times. The resulting parchment coffee was dried in a laboratory oven at $35\text{--}40^{\circ}\text{C}$ until the final water content of 12% (wet basis) was achieved. The beans were manually hulled and stored at -70°C prior to analysis.

Dry model processing

Mature coffee cherries were dried in an oven at $35\text{--}40^{\circ}\text{C}$ until a water content of 12% (wet basis) was achieved. The beans were manually husked and stored at -70°C prior to analysis.

Extraction and determination of low molecular sugars

To exclude variability due to individual variations, 60 sound and faultless beans were weighed and pooled as one sample, frozen with liquid nitrogen and ground to a fine powder using a Retsch MM 200 ball mill. The powder was then lyophilized and 50 mg aliquots were transferred to a centrifuge tube and mixed with 5 ml of hot ethanol ($80\% \text{ v/v}$, 80°C) plus $100 \mu\text{l}$ aqueous melezitose-solution (7 mmol/l ,

as internal standard). The mixture was extracted in an ultra sonic bath (80 °C, 10 min) and centrifuged (4000 rpm, 5 min). The pellet was washed twice at room temperature with ethanol (60% v/v). The supernatants were combined and evaporated to dryness. The remaining solutes were then resolved in 10 ml water (ELGA Maxima, >18 MΩ cm) using ultra-sonication (10 min, RT). In order to bind the phenolic substances, a small quantity of polyvinylpolypyrrolidone (PVPP) was added prior to ultra-sonication. After adjusting the total volume to 50 ml, an aliquot was centrifuged in order to remove the PVPP (4000 rpm, 5 min) and the supernatant was further purified on a Sep-Pak C18-cartridge (Waters). The clear eluate was then directly transferred to the HPAEC-PAD for the determination of the minor low molecular sugars, or was diluted four times for the determination of sucrose, respectively.

For separation and determination of the sugars a DIONEX® BIO-LC HPAEC-PAD with a DIONEX® PA20 column was used. Separation was performed by applying following concentration changes of NaOH (step and linear gradients): 17→12.5 mmol/l in 9.5 min; 12.5→28 mmol/l as step; 28 mmol/l for 8 min; 28→108 mmol/l as step; 108 mmol/l for 11.5 min). Flow was 0.5 ml/min. The column temperature was 30 °C. Detection was carried out using a DIONEX®-ED50 electrochemical detector with gold electrode. For calculation, the Chromeleon software (version 6.4) was used.

Results and discussion

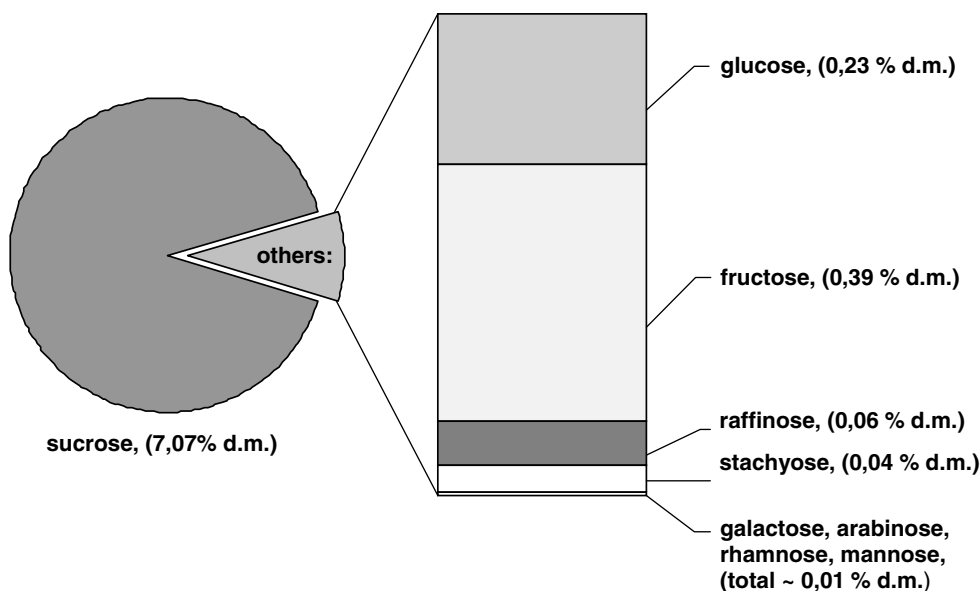
The amounts of the different low molecular carbohydrates present in green coffee differ strongly. A typical pattern is exemplified in Fig. 1, where the corresponding contents

and distribution of the sugars present in an unwashed Arabica from Brazil are mentioned. Sucrose, which in general corresponds to about 7–8% DM, accounts for more than 90% of total low molecular carbohydrates. Compared to sucrose, the monosaccharides fructose and glucose occur in levels that are about 20 times lower. The contents of the oligosaccharides stachyose and raffinose are approximately 100 times lower than the sucrose content. Finally, the monosaccharides galactose, arabinose, rhamnose, and mannose are detectable only in very low amounts.

The comparison of the different low molecular sugars in experimentally processed green coffees from Brazil revealed that some sugars (e.g. sucrose, stachyose, raffinose, and rhamnose) are not significantly affected by the way of processing applied (Fig. 2). In contrast, the contents of the two hexoses fructose and glucose appeared to be strongly influenced by post-harvest treatment. While unwashed Arabicas (green coffees prepared through dry processing) exhibited relatively high contents of fructose and glucose, the washed Arabicas (processed in parallel by the wet method) contained explicitly lower amounts of these sugars. Semi-washed green coffees, i.e. green coffees prepared in the semi-dry process, a technique that is considered to produce qualities lying intermediately between washed and unwashed coffees [2], contained also intermediate concentrations of glucose and fructose. The same pattern of differences was also observed for arabinose and mannose. Indeed, the concentrations of these two sugars are about 100-fold lower than those of glucose and fructose, respectively. However, their amounts in dry-processed coffees are significantly higher than in wet-processed ones. As already shown for glucose and fructose, also in the case of arabinose and mannose, the related amounts in semi-washed coffees lie in between wet- and dry-processed coffees.

Fig. 1 Survey on the low molecular sugars in a green coffee. The circle represents the overall content of the low molecular sugars, totalling 7.79% DM

Coffea arabica, var. Acaià, dry process, Brazil



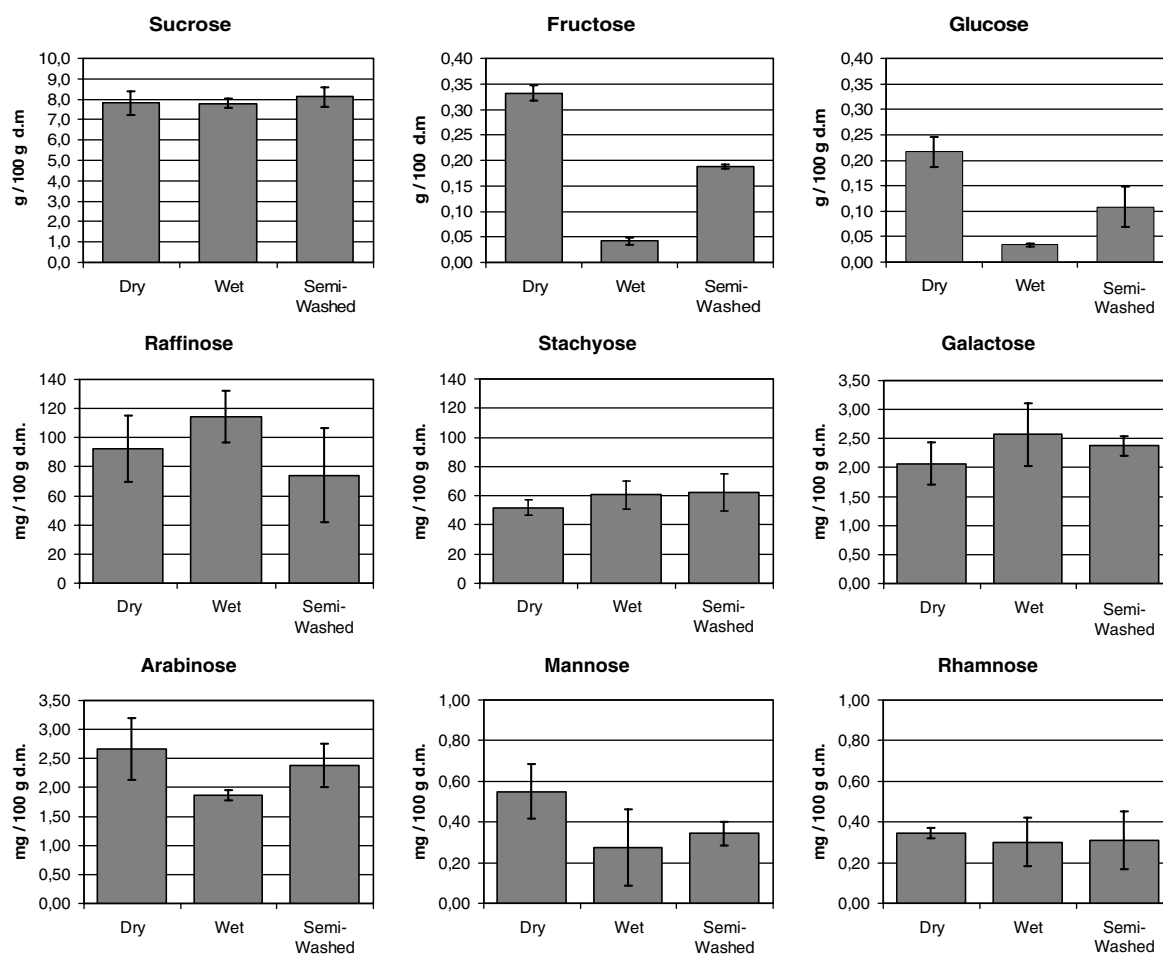
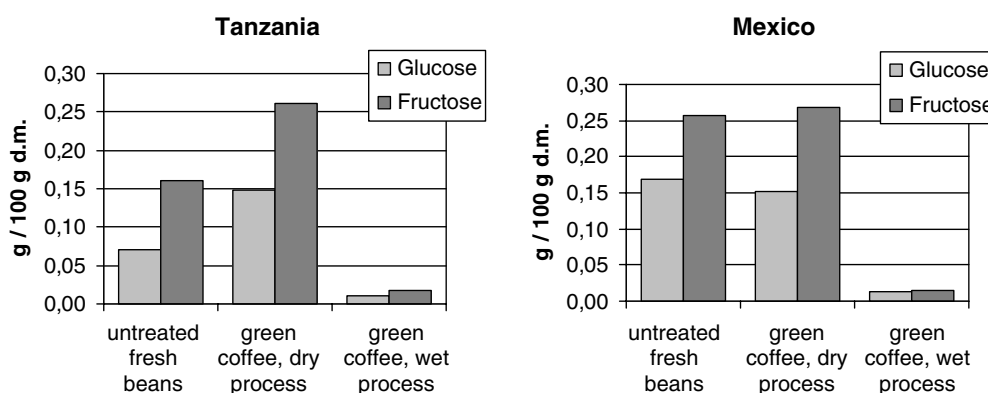


Fig. 2 Concentration of low molecular sugars in differentially processed green coffees. Due to the different magnitudes in contents, concentrations are presented in different scales

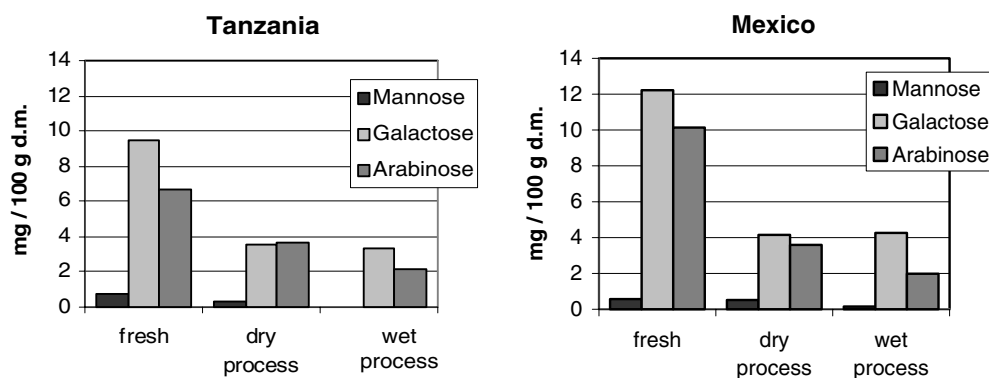
Fig. 3 Glucose and fructose concentration in fresh and differentially processed green coffees



These data so far do not allow any deduction whether the differences were a consequence of a concentration decrease in wet-processed coffee or of a rise in dry-process coffee seeds; even both possibilities could apply. Thus, a comparison with the fresh and untreated coffee sample material was required. Consequently, we prepared corresponding model processings. In two independent experiments with fresh Arabica coffee from Mexico and from Tanzania, this matter was investigated (Fig. 3).

The results from the model-processing experiments concerning the correlation between the contents of fructose, glucose, arabinose, and mannose and post-harvest treatment were fully confirmed. Moreover, it turned out again that sucrose and the other low molecular sugars were not affected by the mode of processing (data not shown). The comparison of the sugar concentrations in the model-processed green coffee beans with those in the starting material (i.e. the fresh and untreated beans) revealed that

Fig. 4 Mannose, galactose, and arabinose concentration in fresh and differentially processed green coffees



the glucose and fructose concentrations in the dry-process beans are as high as those in the untreated control, or even higher. Obviously, there is no net consumption. In contrast, the original high contents of glucose and fructose decrease during wet processing. The terminal content accounts just for 10–20% of the amount originally present in fresh seeds. Also the contents of arabinose, galactose and mannose decline during the course of post-harvest treatment (Fig. 4). Whereas the contents of mannose and arabinose decrease much stronger during wet processing than during dry processing, the galactose content declines in both treatments to the same degree, resulting in a similar galactose concentration in wet- and dry-processed beans. Again, it should be noted that the overall concentration of arabinose, galactose and mannose are about 100-fold lower than the corresponding concentration of glucose and fructose, respectively.

A decrease in sugars could principally be the consequence of a passive leaching of the low molecular substances into the environment, like it was already proposed earlier by Wootton (1973) [8]. However, while the leaching of low molecular substances upon imbibition and rehydration of dry seeds is quite a common phenomenon [17], this is rather unlikely for a still fully hydrated seed as it is represented by a coffee bean, which has just been submitted to post-harvest treatment.

Taking into account that in the recent time the coffee seed's capability for metabolic response during post-harvest treatment was repeatedly demonstrated [6, 9] it seems more likely that the decrease of the fructose and glucose contents originates from an active metabolism taking place in the coffee seeds. During the fermentation step of wet processing the oxygen concentration in the tank declines rapidly due to microbial action [18]. It is well known that under anoxic conditions, plant tissues are able to switch from respiration to alcoholic or lactic fermentation [19–21]. In contrast to the wet process, dry-processed coffee remains in a well-aerated environment throughout the treatment, in which a respiratory metabolism can be maintained until the reduction of the water content leads to a virtual shut-down of metabolic activity. As compared to respiration, fermentation processes consume exceedingly more molecules of hexoses for the generation of the same number of ATP-molecules. We therefore conclude that the decrease in glucose and fructose in wet-processed coffee beans is a consequence of a fermentation-enhanced glu-

cose turnover due to anaerobic fermentation in the coffee endosperm.

In coffee beans, also the minor sugars galactose and mannose are of special interest, because these sugars were expected to be produced when the storage carbohydrate, a galactomannan, is degraded [13]. However, mannose and galactose are present only in traces [13]. Moreover, in this study we show that the low concentrations of this two sugars even decrease during the course of processing. In plant metabolism, glucose takes part in dynamic interconversions with other sugars. In the case of mannose, a conversion into other sugars is a highly necessary step, as increased mannose levels are toxic to the cells [22, 23].

With respect to the major sugars, both, the results of the field experiments in Brazil and those of the model-processing experiments in our laboratory are in contradiction to the findings of Guyot et al. [15] referring to processing experiments with Robusta coffee. The opposite way around, these authors correlated the dry-processing method with a lower content of fructose, and wet treatment with higher fructose content. Moreover, they claimed to have found a correlation between the content of sucrose and the mode of treatment. However, already Bucheli et al. [16] disagreed with those results, after not being able to detect any influence of the post-harvest treatment on the sucrose contents, neither for Arabica nor for Robusta coffee. About the reasons for the contradictory results of Guyot et al. [15] it can only be speculated since the method used for the sugar quantification was not explicitly described. With regard to sucrose, Mazzafera et al. [24] demonstrated that maturation and presence of pathogens are important factors of influence for the sugar content in green coffee beans. Furthermore, it was demonstrated just lately, that the conditions during growth and development of the fruit, like altitude and slope exposure, have a strong impact on the sucrose contents of the beans [25]. Altogether, it appears that the sucrose concentration—in contrast to that of glucose and fructose—is determined rather by pre-harvest than by post-harvest factors.

In a previous work, we demonstrated that the mode of processing used for the production of a certain lot of commercial green coffee is causatively linked with the metabolism of the two amino acids γ -aminobutyric acid and glutamic acid in these samples [6]. We therefore suggested using the ratio of the contents of these two amino acids as a tool to

Table 1 Concentration of the major sugars in commercial green coffee samples

Species/process	Sample/province	Sugar content (% DM)		
		Sucrose	Fructose	Glucose
Arabica/dry	Ethiopia 1	8.255	0.165	0.044
	Brasil 1	9.252	0.140	0.043
	Brazil 2	8.703	0.154	0.042
	Ethiopia 2	6.301	0.008	0.005
	Brazil 3	7.605	0.015	0.006
	Mexico	9.643	0.052	0.032
	Honduras	6.923	0.050	0.028
Arabica/wet	Kenya	9.308	0.058	0.028
	Peru	8.209	0.050	0.022
	Salvador	9.890	0.047	0.021
	Cameroon	5.870	0.036	0.013
	Guatemala	8.514	0.085	0.045
	Columbia 1	8.763	0.059	0.042
	Columbia 2	8.069	0.009	0.005
	Colombia 3	7.155	0.195	0.005
	Indonesia	4.846	0.183	0.057
Robusta/dry	Ivory Coast	3.267	0.182	0.027
	Uganda	4.554	0.108	0.030
	Vietnam	3.149	0.157	0.096

chemically identify whether the coffee was produced with the dry or the wet method. In this paper we showed that also the contents of the two hexoses glucose and fructose are related to the mode of processing applied. Consequently they might serve also as a suitable tool for the chemical identification of the processing method.

In order to verify this assumption, we analysed an assortment of commercial green coffees of different proveniences (15 Arabica coffees and four Robusta coffees). For all samples, the information on the type of processing method applied was available. In Table 1, the levels of the major sugars are presented. The data confirmed the high variability of the sucrose levels in green Arabica coffees. Again, the sucrose contents appeared to be independent from both, provenience and type of processing. Remarkably, an analogous situation was found for glucose, too. The fructose values however, were found to expose the strong tendency of being relatively high in unwashed Arabicas (dry process) and—with the single exception of a sample from Colombia—relatively low in washed Arabicas (wet process). Also the Robusta coffees revealed relatively high levels of fructose, just as the unwashed Arabicas. However, since exclusively unwashed Robusta coffee was part of the assortment a relation to the way of processing must remain speculative. These data show that—due to the high variations in the sugar contents—the glucose and fructose concentrations indeed might indicate the history of post-harvest treatment. However, this feature alone does not represent a reliable tool for the exact differentiation of the processing method.

The data mentioned in this work underline that the mode of processing significantly influences the chemical composition of green coffees. Apart from the amino acids,

also the soluble carbohydrates are strongly affected by the metabolic processes occurring during the course of wet or dry processing, respectively. It is most likely that these metabolic alterations are the basis for the well known sensorial differences between wet and dry-processed coffees. However, due to the high complexity of this topic, a solid proof for a direct interrelation is still missing. Nevertheless, the data presented in this work are an important basis for the understanding of this complex topic. Analyses of the flavour profiles of corresponding samples should help to further elucidate the coherences between post-harvest treatment and coffee quality.

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