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Influence of drying on the content of sugars in wet processed green Arabica coffees

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ABSTRACT

When wet processed coffee beans are dried, the resulting decrease in the water potential induces various metabolic responses. This study was aimed at elucidating the impact of these reactions on the composition of sugars, representing potential aroma precursors. Wet processed green coffees were dried under defined conditions, and the relevant sugars were analysed. Special emphasis was put on the influence of the drying regime, i.e. continuous dryings and such interrupted by pauses in order to mimic sun dryings.

The contents of fructose and glucose decreased significantly within the first day of drying. This diminution for the first time proves that the lower contents of glucose and fructose generally present in wet processed coffee beans in comparison to dry processed ones are – at least in part – due to metabolic processes and are not related to the leaching of sugars into the process water in the course of wet processing.

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1. Introduction

The mode of coffee processing, i.e. the wet or the dry method, determines the characteristic flavour and thereby establishes the typical differences in quality of the resulting green coffees (for details see Sivetz & Desrosier, 1979; Wintgens, 2004). In the course of classical dry processing, the harvested fruits, the so-called coffee cherries, are dried for several weeks on drying patios before they are hulled to obtain the coffee beans. In contrast, in wet processing, the fruit flesh of the coffee beans is removed by mechanical depulping followed by a fermentative degradation of the remaining mucilage before the beans are dried. Recently, it was shown that various metabolic activities are present in green coffee beans during the course of processing (Selmar, Bytof, & Knopp, 2002; Selmar, Bytof, Knopp, & Breitenstein, 2006). These metabolic reactions, which are mainly due to germination processes (Bytof et al., 2007) as well as stress metabolism, are responsible for significant changes in the composition of substances present in the coffee beans and thus for their quality (Bytof, Knopp, Schieberle, Teutsch, & Selmar, 2005). It could be shown that quantity and composition of soluble, low molecular weight carbohydrates, amino acids and stress metabolites i.e. γ -amino butyric acid (GABA), respectively, strongly depend on the characteristic conditions of the green coffee processing (Bucheli, Meyer, Pasquier, & Locher, 1996; Bytof et al.,

2005; Knopp, Bytof, & Selmar, 2006). Although various studies on the influence of the overall processing have been carried out, until recently only limited data on the distinctive influence of the drying procedure on wet processed coffees has been available (for review see Bytof et al., 2007; Selmar & Bytof, 2007). At this time, Kramer, Breitenstein, Kleinwächter, and Selmar (submitted for publication) demonstrated that also during drying, in especially its first phase, numerous metabolic reactions take place to a remarkable extent. Due to their role as relevant aroma precursors, soluble carbohydrates represent one of the most important classes of substances (for review see Bradbury, 2001), whose concentrations are markedly effected by the mode of processing (Knopp et al., 2006). Accordingly, we analysed changes in the contents of sugars in order to monitor the putative influence of the drying conditions on these relevant aroma precursors. In the past, it was frequently mentioned that sun drying yields much better green coffee quality than machine drying (Wintgens, 2004). Apart from few studies that were done over 30 years ago (Gibson, 1973; Wootton, Verkade, & Mitchell, 1968), these considerations are based only on traditional knowledge and experience. However, new scientific approaches to elucidate the reasons for the putative quality differences between sun and machine dried green coffees are missing. In the older literature mentioned above, these differences are explained by various effects of visible or UV-light on the drying beans (Wootton et al., 1968). Yet, in this context it has to be conceded that that the opaque, hardly translucent parchment predominantly is impermeable for most light qualities. Thus, there must be another explanation





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for the merits of sun drying. The major difference between sun and machine drying is due to the fact that machine drying is performed continuously whereas sun drying follows a natural day-and-nightrhythm. Consequently, in the present study, this fact was considered by comparing the composition of carbohydrates in coffees which had been dried either continuously or with pauses, mimicking the day-and-night-rhythm.

2. Materials and methods

2.1. Sample processing

Defined green coffee samples were produced under carefully controlled processings at the facilities of CECA S.A./NKG. San Jose. Costa Rica. For these sample processings, only unspoiled and fully mature red coffee fruits of Coffea arabica were used. The coffee fruits were mechanically depulped using a *Bendig* drum pulper, followed by mechanical demucilation. The moist beans were transferred without any addition of water into small plastic barrels (51) for air transport to Germany. Thus, the transport was performed under conditions of a so-called "dry fermentation" (Wootton, 1974): The entire process from the depulping to the arrival of the beans in the laboratory in Braunschweig took about 32–36 h, the ambient temperature was between 15 and 25 °C. Over all, these conditions closely comprised the conditions of a traditional wet processing including a tank or bucket-scale fermentation. Scrutiny revealed that the samples had been correctly fermented; any overfermentation could be excluded due to the lack of typical off-notes (e.g. acetic or fishy smell). Directly after arrival, blank samples of each batch (about 150 beans per lot) were shock frozen in liquid nitrogen. The major part of the samples was dried down to 11% under controlled parameters in the laboratory drying oven at 30 °C. Drying was performed either continuously, or by applying a dayand-night rhythm, i.e. after 14 h of drying, the oven was shut down for 10 h in order to mimic a classical sun drying, traditionally used in coffee producing countries.

As the content of soluble sugars in green coffee seeds is subject to high individual variation (Knopp et al., 2006; Selmar, Bytof, & Knopp, 2008) we decided to analyse few sample specimens comprising of a huge number of beans rather than numerous samples containing only small numbers of individual beans. Accordingly, in appropriate intervals, samples of 150 beans were taken out of the drying ovens and shock frozen. These samples were ground in liquid nitrogen to a fine powder using a Retsch MM 200 ball mill and stored at -80 °C for further analyses. Overall, for each sample four independent analyses had been performed.

2.2. Extraction and determination of low molecular sugars

Extraction and determination of low molecular sugars was performed according to Knopp et al. (2006). The frozen powder was lyophilised, and 50 mg aliquots were transferred to a centrifuge tube and mixed with 5 ml of hot ethanol (80% v/v, 80 °C) plus 100 µl 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 M Ω × 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): $17 \rightarrow 12.5 \text{ mmol/l}$ in 9.5 min; $12.5 \rightarrow 28 \text{ mmol/l}$ as step; 28 mmol/l for 8 min; 28 \rightarrow 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.

3. Results

When the coffee seeds arrived in the laboratory facilities in Braunschweig, they revealed a water content of about 56%. In the course of the dryings it decreased to about 12% – a water content which generally is present in customary green coffees. The entire desiccation process lasted about five days in the case of the continuous drying and about eight days when pauses were introduced to mimic a day-and-night-rhythm.

The amounts of many low molecular carbohydrates present in green coffee are significantly affected by the drying procedure. The most pronounced changes have been detected for fructose and glucose (Figs. 1 and 2). In the freshly processed beans, a fructose content of nearly 110 mg/100 g d.w. was present. Within the first day of drying, fructose concentration decreased down to about 40 mg/100 g d.w. in the case of continuous drying, and to about 30 mg/100 g d.w. in beans dried with pauses (Fig. 1). Later on, the fructose content basically remained constant, although several fluctuations appeared. Due to an overall standard deviation of about 10%, it could not be decided reliably, if such changes - i.e. the small increases after 4-5 days - indeed were related to certain metabolic events and their effect on substance composition, or if they were due to natural deviation. In spite of this fact, it should be noted, that similar alterations occur almost in parallel to corresponding changes in the glucose and galactose content (see below).

The initial glucose content in the fresh beans was about 55 mg/ 100 g d.w. Similar to the corresponding pattern of fructose, the glucose content also decreases within the first day of drying (Fig. 2). In comparison to the alterations of the fructose content, the fluctuations of glucose content in the second half of the drying process were much more pronounced, especially for the coffee beans that had been dried by applying a day-and-night rhythm. In these green coffees the glucose content re-increased from less than 15 mg/ 100 g d.w. to nearly 40 mg/100 g d.w., before it decreased again to about 20 mg/100 g d.w. in the fully dried coffee seeds.

In green coffee the content of galactose is about one magnitude lower than that of glucose and fructose. The fresh, non-dried beans revealed a content of free galactose of approximately 6 mg/100 g d.w. (Fig. 3). As shown for both hexoses, glucose and fructose, significant changes in the galactose contents could also be detected. However, the corresponding changes of galactose content are much less pronounced. In contrast to fructose and glucose, whose contents decreased within the first day of drying, the galactose content diminished rather slowly within the first four days of drying. Apart from some marked alterations in the galactose content during the first phase of drying, the fluctuations in the galactose content in the second half of the drying process occurred nearly simultaneously to those mentioned for glucose and fructose.

Sucrose represents the major sugar present in coffee seeds. The green coffees used for the experimental dryings presented here contained about 6000 mg/100 g d.w., corresponding to more than 60-times the fructose content in the fresh, non-dried seeds and even more than 100-times than that of glucose. In contrast to all other sugars analysed, the sucrose content remained more or less



Fig. 1. Fructose contents in drying coffee seeds. Fully mature red coffee fruits of *C. arabica* were mechanically depulped and dried in laboratory dryers, either continuously, or by applying a drying/pause rhythm of 14/10 h. The content of fructose was estimated by HPAEC; all values correspond to at least four analyses. Average standard deviation is given as vertical bars.



Fig. 2. Glucose contents in drying coffee seeds. Fully mature red coffee fruits of *C. arabica* were mechanically depulped and dried in laboratory dryers, either continuously, or by applying a drying/pause rhythm of 14/10 h. The content of glucose was estimated by HPAEC; all values correspond to at least four analyses. Average standard deviation is given as vertical bars.

constant (Fig. 4). Although the content of sucrose also showed some variability, the extent of these fluctuations is far less than in the case of the hexoses analysed.

4. Discussion

It is well established that wet processed green coffees (i.e. the typical washed Arabicas) reveal much lower glucose and fructose concentrations than dry processed ones, in which the concentrations of these hexoses are nearly the same as those of the corresponding fresh beans (Knopp et al., 2006). Whereas in early literature it was argued that the decrease in glucose and fructose might be due to leaching of these sugars during fermentation (Wootton, 1974), like it is described for seeds of several other plants (Bewley & Black, 1994). Knopp et al. (2006) stated that these

diminutions should be related to the various metabolic events occurring during green coffee processing. However, a related proof was still missing. In this paper we have shown that a strong decline in glucose and fructose contents takes place during the first day of drying. As this decrease occurs in the absence of processing water, any elution can be excluded as its cause. Hence, in principle, sugars might be leached out in the small water film surrounding the moist beans and might be directly metabolised by microorganisms. However, due to the fact that sucrose contents remained constant, this eventuality can be excluded, too. Consequently, metabolic processes must be responsible for the changes observed. Indeed, this argumentation is only valid for those amounts of glucose and fructose which disappeared during the first day of drying. Yet, in this context it has to be taken into consideration that the original glucose and fructose contents in unprocessed, green coffees might



Fig. 3. Galactose contents in drying coffee seeds. Fully mature red coffee fruits of *C. arabica* were mechanically depulped and dried in laboratory dryers, either continuously, or by applying a drying/pause rhythm of 14/10 h. The content of galactose was estimated by HPAEC; all values correspond to at least four analyses. Average standard deviation is given as vertical bars.



Fig. 4. Sucrose contents in drying coffee seeds. Fully mature red coffee fruits of *C. arabica* were mechanically depulped and dried in laboratory dryers, either continuously, or by applying a drying/pause rhythm of 14/10 h. The content of sucrose was estimated by HPAEC; all values correspond to at least four analyses. Average standard deviation is given as vertical bars.

even be markedly higher (e.g. more than 150 mg glucose or 250 mg fructose/100 g d.w.; Knopp et al., 2006) than those determined for the fresh beans utilised for the drying experiments of this study (55 mg glucose or 110 mg fructose/100 g d.w.). It is most likely that the metabolic reactions occurring during the first day of drying had also occurred already - at least in part - during the transport in plastic barrels, which was mimicking a so-called "dry fermentation" step. Consequently, it could be assumed that not all of the glucose and fructose which disappeared within the first day of drying had been metabolised, but also considerable amounts of these hexoses should have been degraded during transport and fermentation. This assumption is underlined by the finding that a putative "anoxia-induced" metabolism occurs during fermentation as well as within the first day of drying (Kramer et al., submitted for publication). A further point confirms this argumentation: in samples where the time required for transportation, and thus for fermentation, was extended by one or two days, the corresponding concentration of glucose and fructose in the arriving beans already decreased further and reached the final contents determined in the standard samples at the end of drying process (data not shown). A corresponding shifting was also observed for the anoxia-induced stress reactions when fermentation was prolonged (Kramer et al., submitted for publication).

The marked consumption of glucose and fructose during anoxia-induced metabolism could be explained by relevant changes in the energy demand of the cells. Under aerobic conditions energy requirements are covered completely by cell respiration. In contrast, under anoxia sugars are catabolised by fermentation, which results only in about 5–6% of the energy yield provided by respiration. Consequently, to provide the basic coverage of energy necessary for sustaining the vigor of cells, under anoxia nearly a 20-fold higher consumption of sugars is required. In this context, it has to be considered that – in contrast to glucose and fructose, representing direct energy sources of living cells – sucrose generally acts as a storage compound which is not catabolised directly due to short term changes in energy requirements. Thus, in contrast to the strong decrease of glucose and fructose, sucrose content remained constant during short term, anoxia-induced increase of sugar catabolism. Only when the time span of an active metabolism is extended, the stored sucrose should also be catabolised to maintain energy supply. These coherences are underlined by the observation of Bucheli, Meyer, Pittet, Vuataz, and Viani (1998), who found a significant increase of glucose content when coffee seeds are stored for several months under moist conditions (85% relative humidity), which should be due to a mobilising hydrolysis of sucrose to yield glucose and fructose.

Like glucose and fructose, galactose is catabolised to a higher extent in fermenting coffee beans. However, due to the fact that this minor sugar first has to be converted to glucose before entering catabolism, the consumption of galactose is retarded in relation to the other hexoses.

The main difference between the sugar contents of continuously dried green coffee beans and those dried with pauses - and thereby mimicking a sun drying - is due to the fact that the observed alterations in the contents of the various sugars are slightly more pronounced. This points out that the metabolic events responsible for these fluctuations in sugar metabolism should also be more distinct. A possible explanation for this effect could be due to a synchronising effect of the applied day-and-night-rhythm. However, despite these differences occurring in the differentially dried beans, the particular concentration in the resulting dried coffee beans - either continuously dried or with pauses - are more or less identical. Consequently, they are not affected by the drying method applied. Thus, the sugar composition cannot be the direct cause for the observed quality differences in differentially dried coffees. However, the fluctuations in glucose and fructose contents confirm the finding of significant alterations in metabolic activity reported by Kramer et al. (submitted for publication) and confirm the involvement of various metabolic reactions during the drving procedure. Future research should be aimed at elucidating, which compounds indeed are relevant for the differences in green coffee quality of differentially dried beans and how their content is influenced by the metabolic reactions occurring during drying.

5. Conclusion

The marked decrease in the contents of fructose and glucose within the first day of drying for the first time prove that the lower contents of glucose and fructose generally present in wet processed coffees in comparison to dry processed ones are - at least in part - due to the metabolic processes occurring in the coffee seeds and are not related, as formerly proposed, to the leaching of sugars into the process water in the course of wet processing. Similar to glucose, galactose is also catabolised during the drving process; however the rate of the corresponding decrease is lower, obviously due to the fact that galactose first has to be converted to glucose before being degraded. In contrast to the hexoses mentioned, the content of sucrose does not change significantly during the drying process. It is assumed that this major sugar represents a long term storage compound, which - unlike the hexoses that cover the short term energy demands - is not catabolised before the reserves are required for seedling development.

The main difference in the sugar contents of continuously dried green coffees and those dried with pauses is due to the fact that the observed alterations are slightly more pronounced. However, the particular concentrations in the final product are more or less identical. Nevertheless, the observed fluctuations demonstrate the occurrence of marked metabolic activity during the drying. Future research should be aimed at elucidating the impact of these processes on the quality of green coffees and its controllability by the drying conditions.

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