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Food Chemistry 90 (2005) 287–291
Food Chemistry
www.elsevier.com/locate/foodchem

The effect of roasting on the presence of bioactive amines in coffees of different qualities

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Received 1 December 2003; accepted 22 March 2004

Abstract

The effect of roasting on the levels of amines in high and low quality coffee was investigated. Arabica green coffee samples previously classified by cup as soft (high quality) and rio (low quality) were roasted at 220 °C. Bean samples were collected every 4 min during roasting. HPLC analysis was carried out for detection and quantification of bioactive amines. Putrescine was the prevailing amine in both samples, followed by spermidine and spermine. Putrescine levels were significantly higher for the rio sample compared to the soft one. Also, both histamine and tryptamine were only present in the rio sample. There was a significant decrease in total amine content during roasting, with degradation of putrescine, spermine, histamine and tyramine taking place mostly during the drying stage. Degradation of spermidine occurred at a slower rate.

Keywords: Putrescine; Histamine; Tyramine; Coffee; Roasting

1. Introduction

Amines are organic bases formed during metabolic processes in all living organisms, thus they are present in most food products. Dietary amines are traditionally classified as (i) polyamines, formed during *de novo* biosynthesis (agmatine, cadaverine, putrescine, spermidine and spermine) and (ii) biogenic amines, formed by non-specific decarboxylation reactions (agmatine, cadaverine, histamine, phenyletilamine, putrescine, serotonin, tyramine, tryptamine). Polyamines such as putrescine, spermidine and spermine have been found in all higher plants and are involved in physiological processes such as fruit growth and development. Some biogenic amines can be naturally present in some plant tissues and can also be formed during processing or storage of food products, due to thermal or enzymatic decarboxylation of free amino acids. The levels of biogenic amines in a specific product will vary depending on several factors including plant variety, growth conditions, degree of ripening and storage conditions (Bardócz, 1995; Cirilo et al., 2003; Glória, 2003). In general, dietary amines at levels normally present in foods are non-toxic, even though they are toxic at high intakes (Bardócz, 1995).

The quality of coffee used for beverage is related to the chemical composition of the roasted beans, which, in turn, is affected by the chemical composition of the green beans and by post-harvesting processing conditions (drying, storage, roasting and grinding). The characteristic flavor and aroma of coffee represent a combination of hundreds of chemical compounds produced by the reactions that occur during roasting. Roasting is comprised of three consecutive stages. The first stage, drying, is characterized by a slow release of water and volatile substances. Bean color changes from green to yellow. Pyrolysis reactions take place during the second stage, resulting in considerable changes in both physical and chemical properties of the beans. Large quantities of CO_2, water and volatile substances are released and the beans turn brown, due to sugar caramelization and Maillard reactions. At this point, a third stage of cooling is required in order to avoid burning the coffee (Dutra, Oliveira, Franca, Ferraz, &

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doi:10.1016/j.foodchem.2004.03.056

Afonso, 2001; Franca, Oliveira, & Vitorino, 2002; Sivetz & Desrosier, 1979).

The criteria commonly used to evaluate the quality of coffee beans include bean size, color, shape, processing method, crop year, flavor or cup quality and presence of defects (Banks, McFadden, & Atkinson, 1999). Among those, flavor (cup quality) and presence of defects (type classification) are the most important criteria employed worldwide in coffee trading.

Brazilian coffees are officially categorized by reference to a flavor scale as presented in Table 1 (Banks et al., 1999; Clarke & Macrae, 1987). This classification, also known as cup quality, is assessed using the brewing method of steeping (Lingle, 1993).

The presence of defects is quite relevant in establishing coffee quality, for they are associated with problems during harvesting and pre-processing operations. In commercial practice, the term defect is not only related to the presence of defective beans (black, sour or brown, immature, insect-damaged, etc.), but also of extraneous matter (twigs, stones, etc.) in a given coffee sample. The New York Coffee and Sugar Exchange devised the ''black bean count basis'', according to which all defects are accounted for in terms of equivalence to black beans. This is known as type classification, as shown in Table 2. One black bean is counted as one defect, and the other types of defects are related to black beans. For example, two sour beans or five insect-damaged beans correspond to one black bean or one defect.

Table 1
Summary description of the coffee cup classification system

Classification	Flavor characteristics
Strictly soft	Low acidity, mellow sweetness, pleasant row of the mouth easiness
Soft	Same characteristics as strictly soft, only less accentuated
Softish	Same characteristics as soft, only less accentuated
Hard	Lacks sweetness and softness
Rioysh	Iodine, medicine like inky flavor from microbe-tainted beans
Rio	Same characteristics as rioysh, only more accentuated

Table 2
Summary description of the coffee type classification system

Type no.	Maximum allowable number of defects per 300 g sample
NY 2	6
NY 3	13
NY 4	30
NY 5	60
NY 6	120
NY 7	240
NY 8	450

Amine contents of several food products can be found in the literature (Bardócz, 1995; Eliassen, Reistad, Esoen, & Ronning, 2002; Mietz & Karmas, 1978; Okamoto, Sugi, Koizumi, Yanagida, & Udaka, 1997; Santos, Souza, Cerqueira, & Glória, 2003; Vinci & Antonelli, 2002). However, only a few studies have discussed the presence of amines in coffee (Amorim, Basso, Crocomo, & Teixeira, 1977; Cirilo et al., 2003). Amorim et al. (1977) investigated the presence of polyamines in coffee, prior to and after roasting at 240 °C for 12 min. Putrescine, spermine and spermidine were detected before roasting. Only putrescine was detected after 10 min of roasting and no amines were detected after 12 min. Cirilo et al. (2003) investigated the presence of both natural and biogenic amines in coffee submitted to two levels of roasting (300 °C for 6 and 12 min, respectively). These authors encountered serotonin, putrescine, spermine and spermidine in green coffee and, even though the total amine content decreased after roasting, agmatine was detected after 12 min roasting. Furthermore, amine levels were quite different from those reported by Amorim et al. (1977).

The chemistry of flavor development during roasting of coffee is not well understood. The flavor and aroma of coffee are highly complex, and difficult to describe, resulting from the combined action of over 800 volatile substances. Thus, in view of the large variety of coffees available, of variations in processing and storage conditions, and also of the fact that the content of amines is known to be related to quality of food products in general, an investigation of the profiles of amines in coffee samples of different qualities, as well as the effects of processing on those compounds is relevant. Therefore, the present study aims to evaluate the effect of roasting on the levels of amines in coffee samples of different qualities.

2. Methodology

Arabica green coffee samples previously classified by cup and type were used in the roasting tests (Table 3). Cup classification is employed for sample identification throughout this paper. The percentage mass of defective and non-defective bean is also presented in Table 3. A lab-scale coffee roaster was employed for roasting at 220 °C. The roaster, working at a rotation speed of 80 rpm, was pre-heated during 10 min and then loaded with 1.5 kg coffee. The roasting time was selected so it would be enough to char the beans, assuring that the optimal degree of roast was achieved. Bean samples were collected every 4 min during roasting. HPLC analysis was carried out for detection and quantification of the following amines: Putrescine, spermidine, spermine,

Table 3
Classification of coffee samples used in this study

Sample	Type	Cup	% Mass of beans in each sample				
			Defective				Non-defective
			Immature	Sour	Bored	Others[a]	
1	NY 3/4	Soft	0.0	0.7	1.8	1.0	96.5
2	NY 7/8	Rio	4.2	8.8	10.7	2.6	73.7

[a] Broken, husks, shells, etc.

agmatine, cadaverine, serotonin, histamine, tyramine, tryptamine and phenylethylamine, according to the methodology described by Cirilo et al. (2003). The obtained data was submitted to analysis of variance and the means were compared by the Duncan test at 5% probability.

3. Results and discussion

Results obtained for total amine levels in green coffee in comparison to the ones available in the literature are presented in Table 4. Values were higher than those found by Amorim et al. (1977) and Cirilo et al. (2003). According to Cirilo et al. (2003), differences in amine content and profile could be associated to variations in coffee variety and cultivation conditions.

Five of the 10 evaluated amines were detected in green coffee: Putrescine, spermidine, spermine, histamine and tryptamine (Fig. 1). Among those, only putrescine, spermidine and spermine were detected in both samples. Putrescine was the prevailing amine in the samples, representing in average approximately 75% of the total amine content. Spermidine and spermine contents were quite similar, each representing approximately 12% of the total amine content. Amorim et al. (1977) obtained average percentages of 64% for putrescine, 23% for spermidine and 12% for spermine, regarding contribution of each amine to total polyamine content. Cirilo et al. (2003) obtained average percentages of 50% for putrescine, 29% for spermidine and 21% for spermine in terms of total polyamine content. However, they also detected a considerable amount of serotonin (1.13 mg/100 g). The presence of putrescine, spermidine and spermine was expected, for these amines

Table 4
Levels of bioactive amines in green coffee

Value	Levels (mg/100 g)		
	This study	Amorim et al. (1977)	Cirilo et al. (2003)
Minimum	8.4	6.0	3.03
Maximum	13.7	8.4	4.44
Mean	11.0	6.6	3.21
CV (%)	22.6	11.6	4

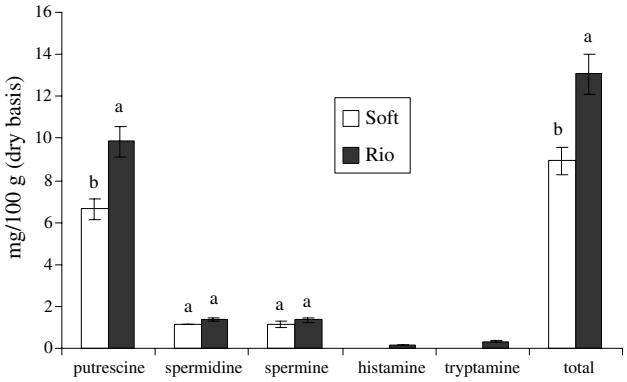

Fig. 1. Amine levels in soft and rio green coffee samples. Mean values with the same letter for a specific amine do not differ significantly by the Duncan test at 5% probability.

are usually present in most plants (Cirilo et al., 2003; Flores, Protácio, & Signs, 1989). Also, putrescine is a precursor of spermidine and spermine. Both spermidine and spermine content did not vary significantly with respect to cup quality. However, putrescine levels were significantly higher for the rio sample compared to the soft one. Also, both histamine and tryptamine were only present in the low quality coffee sample.

The effect of roasting on total amine content can be viewed in Fig. 2. There was a significant decrease in total amine content during roasting. After 4 min, total amine levels decreased by approximately 44%, for both samples. After 8 min, amine levels were approximately 20% and 5% of the original values, for the soft and rio samples, respectively. The weight loss curve (Fig. 3) presents a behavior similar to that reported in the

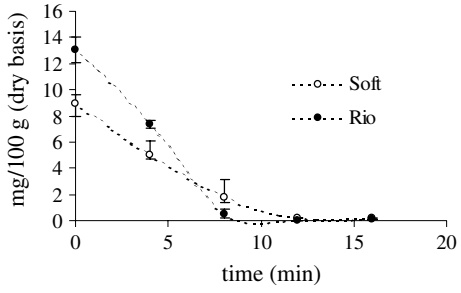

Fig. 2. Effect of roasting on total amine contents in soft and rio coffee samples.

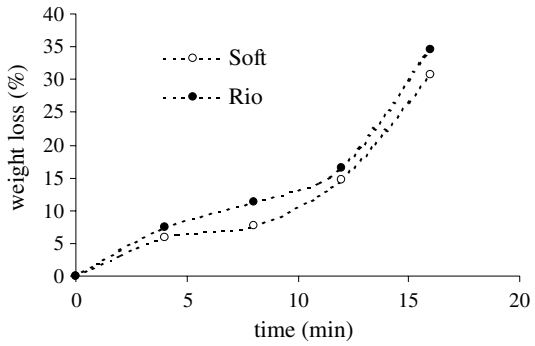

Fig. 3. Weight loss during roasting of soft and rio coffee samples.

literature (Dutra et al., 2001; Sivetz & Desrosier, 1979), occurring at two different rates. The weight loss during the first 10–12 min is due to the slow release of water and volatile components (drying stage). The increase in weight loss rate after that time can be attributed to an intensive release of organic compounds and CO_2 during pyrolysis. The onset of pyrolysis can be associated with the transition between the two slopes. According to the reviewed literature, transition should occur at about 10% weight loss (Sivetz & Desrosier, 1979). A comparison of the results presented in Figs. 2 and 3 indicates that amine degradation takes place mainly during the drying stage. Thus, even after a mild roast, total amine levels should be quite small. This is in agreement with the few results presented in the literature. Amorim et al. (1977) observed a reduction of approximately 97% in polyamines after 9–10 min roasting at 240 °C (9–10% weight loss). These authors did not detect any polyamines after 12 min roasting (15–17% weight loss). Cirilo et al. (2003) reported a reduction of approximately 90% in total amine levels after a light roast (6 min – 300 °C). However, an increase in total amine content was observed for a darker roast (12 min – 300 °C) due to the formation of agmatine and increase in serotonin and spermidine concentrations.

The effect of roasting on the levels of putrescine, spermidine and spermine is shown in Fig. 4. These results show that both putrescine and spermine are completely consumed during the drying stage, regardless of coffee quality. This is in agreement with Amorim et al. (1977), who detected only small amounts of putrescine (0.2 g/100 g) in coffee roasted at 240 °C for 9–10 min and did not detect any polyamines after 12 min roasting. Also, Cirilo et al. (2003) reported total losses of putrescine and spermine after roasting for 6 min at 300 °C. Degradation of spermidine was slower than for both putrescine and spermine (Fig. 4), and approximately 10% of the original contents were still present after 16 min roasting, for the soft sample. Cirilo et al. (2003) observed an 80% reduction of spermidine contents after roasting for 6 min at 300 °C. However, they observed an

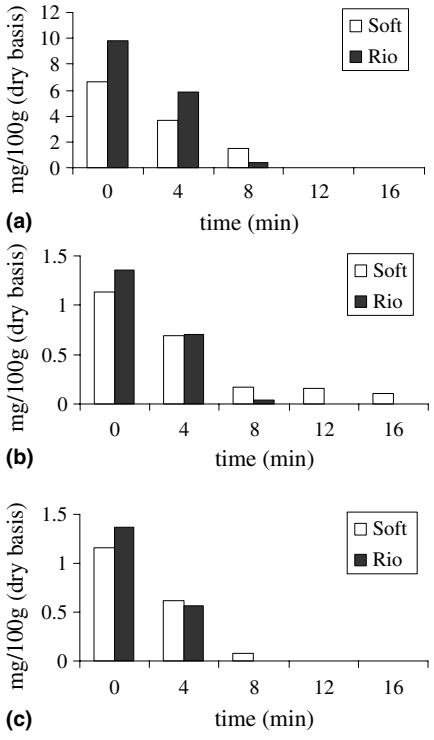

Fig. 4. Effect of roasting on: (a) putrescine; (b) spermidine; (c) spermine contents.

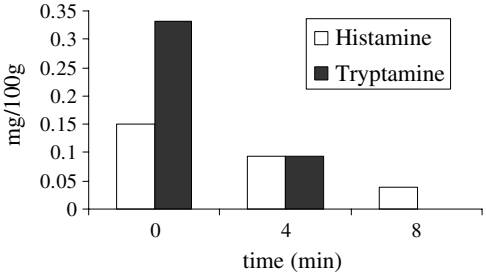

Fig. 5. Effect of roasting on histamine and tryptamine contents in the rio coffee sample.

increase in spermidine contents after increasing roasting time.

Both the histamine and tryptamine present in the rio sample were totally consumed during the drying stage, as shown in Fig. 5. It is noteworthy to mention that traces of cadaverine and tyramine were detected in the rio sample after 16 min roasting. Amorim et al. (1977) detected only small amounts of putrescine (0.2 g/100 g) in coffee roasted at 240 °C for 9–10 min and did not detect any polyamines after 12 min roasting. The results presented here indicate that the presence of histamine, tryptamine, cadaverine and tyramine could be associated with low coffee quality, which is in turn related to the presence of defective beans. In that sense, further studies will be conducted aiming the evaluation of amine

levels for specific types of defects, such as black, sour and immature beans.

4. Conclusions

High quality (soft) and low quality (rio) green coffee were characterized by the presence of three bioactive amines: Putrescine, spermine and spermidine. Putrescine was the prevailing amine, followed by spermidine and spermine. Furthermore, histamine and tryptamine were detected in the low quality coffee sample. There was a significant decrease in total amine content during roasting, with degradation of putrescine, spermine, histamine and tyramine taking place mostly during the drying stage. Degradation of spermidine occurred at a slower rate. Traces of cadaverine and tyramine were detected in the low quality coffee sample after roasting. Results indicate that high levels of putrescine and the presence of histamine and tryptamine in green coffee could be associated with low quality due to the presence of defective beans.

Acknowledgements

The authors acknowledge financial support from CNPq, CAPES (Brazilian Government agencies) and FAPEMIG (Minas Gerais State Government agency) and thank Sindicafé-MG (Minas Gerais State Coffee Industries Union) for providing the coffee samples.

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