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A comparative study of chemical attributes and levels of amines in defective green and roasted coffee beans

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Abstract

Differences in chemical attributes (proximate composition, water activity, sucrose, acidity and pH levels) and amine levels between defective and healthy coffee beans were studied. Before roasting, significant differences ($p < 0.05$) were observed for the ash contents of the coffee samples, with the highest values found for black beans. Moisture content was higher for non-defective beans in comparison to defective beans. Non-defective coffee beans had higher lipids contents than both sour and black beans. There were no significant differences ($p > 0.05$) for protein levels between defective and non-defective beans. After roasting, protein levels remained constant, there was a small decrease in ash contents and a slight increase in oil contents of black and sour beans. Both black and sour beans had higher acidity levels than immature and non-defective beans. Acidity levels decreased after roasting. Water activity levels also decreased with roasting, with slightly higher levels for defective beans in comparison to non-defective ones. Sucrose levels were much higher in non-defective beans, and the lowest values were in black beans, prior to roasting. After roasting, only traces of sucrose were found. Total amine levels were much lower for black beans, in comparison to the other coffee samples. Putrescine was the prevailing amine in all samples. Histamine was only detected in the defective coffee samples. Small amounts of serotonin, cadaverine and tryptamine were found in some of the samples. After roasting to a light degree, only traces of serotonin were detected and no amines were detected after roasting to medium and dark degrees.

Keywords: Coffee; Defective beans; Chemical composition; Amines; Roasting

1. Introduction

Coffee quality is evaluated according to a wide variety of criteria, including bean size, colour, shape, roast potential, processing method, crop year, flavour or cup quality and presence of defective beans (Banks, McFadden, & Atkinson, 1999; Franca, Oliveira, Mendonça, & Silva, 2005). Among these, flavour is the main and most important criterion, which is directly affected by the presence of defective coffee beans.

The presence of defective beans is usually a consequence of problems that occur during harvesting and pre-processing operations. The most important types of defects are black, sour or brown, immature, bored or insect-damaged, and broken beans. Both black and sour defects are associated with bean fermentation and have been reported as quite important in downgrading coffee flavour (Clarke, 1987). Immature beans, those that come from immature fruits, contribute to beverage astringency. Even though defects are known to negatively affect coffee flavour, the number of defects alone cannot be used to accurately predict flavour quality (Smith, 1985). Such defective beans are usually present in the coffee produced in Brazil, due to the strip-picking harvesting and processing practices adopted

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by the coffee producers. They are separated from the non-defective beans prior to selling on external markets, and dumped on the Brazilian internal market. Thus, the majority of the roasting industry in Brazil has been using these defective beans in blends with healthy ones, and, overall, a low grade roasted and ground coffee is consumed in the country. In order to eliminate these defective beans from the internal market, there is a need for more attractive alternative uses for them. In view of that, an assessment of chemical attributes that could allow for differentiation between defective and non-defective beans is of relevance (Oliveira, Franca, Mendonça, & Barros-Júnior, 2006).

Only a few studies have addressed physical and chemical attributes of defective coffee beans, in comparison to non-defective ones (Franca, Oliveira, Mendonça, et al., 2005; Mazzafera, 1999; Oliveira et al., 2006). Mazzafera (1999) evaluated chemical attributes of defective (immature and immature/black) and non-defective green coffee beans. According to this study, non-defective beans were heavier, higher in moisture, and contained higher levels of sucrose, protein and total oil content than either immature-black or black beans. Franca, Oliveira, Mendonça, et al. (2005) evaluated both physical (bean and bulk densities, bean volume and colour) and chemical attributes (caffeine, trigonelline and chlorogenic acids) of defective and non-defective coffee beans, prior to and after roasting. Black beans were the defective types that had the most distinct characteristics. It was also shown that black beans roast to a smaller degree than non-defective beans, under the same conditions of roasting. The study by Oliveira et al. (2006) reported that non-defective coffee beans had a higher lipids content than defective ones. However, no differences were observed in the fatty acid compositions of all samples, crude and roasted. There are no reports in the reviewed literature regarding data on acidity, pH and sucrose levels for black and sour beans. Furthermore, data on the effect of roasting on defective coffee beans attributes are restricted to only one roasting degree.

Amines have been employed as a criterion for quality evaluation and spoilage detection in a wide variety of food products (Santos, 1996). These substances, encountered in most food products, are organic bases, classified as (i) natural, formed during de novo polyamine biosynthesis, or (ii) biogenic, formed by action of decarboxylase-positive microorganisms. Amine levels and distribution will vary considerably among different foodstuffs and also, for a specific food product (Kalač & Krausová, 2005). Factors that affect amine content include product variety, origin, growth and manufacturing conditions. Biogenic amines can be expected in all foods that contain free amino acids from protein, if conditions that enable microbial or biochemical activity are available (Santos, 1996). In non-fermented foods, the presence of biogenic amines above a certain level has been associated with undesirable microbial activity. Thus, the amine level could be indicative of microbial spoilage (Bardócz, 1995; Santos, 1996).

Few studies have discussed the presence of amines in coffee (Amorim, Basso, Crocomo, & Teixeira, 1977; Casal et al., 2004; Cirilo et al., 2003; Oliveira, Franca, Glória, & Borges, 2005). Amorim et al. (1977) investigated the presence of polyamines in coffee, before and after roasting at 240 °C for 12 min. Their experiments were conducted with Arabica coffees harvested in the same year, but having different organoleptic properties (soft vs. rio). They obtained average percentages of 64% for putrescine, 23% for spermidine and 12% for spermine, regarding contribution of each amine to total polyamine content. They found approximately the same amount of putrescine, spermidine and spermine in all samples. Only putrescine was detected after 10 min of roasting (~2 μg of putrescine per g of coffee) and no amines were detected after 12 min. No significant differences were detected in terms of amine contents among the samples, prior to or after roasting. Cirilo et al. (2003) investigated the presence of both natural and biogenic amines in coffees submitted to two levels of roasting (300 °C for 6 and 12 min, respectively). These authors encountered serotonin, putrescine, spermine and spermidine in crude 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 the ones reported by Amorim et al. (1977). Casal et al. (2004) evaluated the levels of biogenic amines (putrescine, cadaverine, serotonin, tyramine, spermidine, and spermine) in robusta and arabica coffees. Putrescine was the most abundant amine in both species, followed by spermidine, spermine, and serotonin. They also detected small amounts of cadaverine and tyramine. Their results indicated that putrescine could be used in the discrimination of the referred species. These authors also mentioned that amines could be used for discrimination between green coffees subjected to different postharvest processes (wet vs. dry). They reported variations in biogenic amine levels after roast, but the statistical significance for species discrimination was reduced. Oliveira et al. (2005) evaluated the effect of roasting on the levels of amines in high (soft) and low (rio) quality coffees. Putrescine levels were significantly higher for the low quality sample. Also, both histamine and tryptamine were only present in the low quality sample. Their results indicate that both amine levels and profiles could be related to coffee quality. There are no literature reports on amine levels for defective coffee beans.

In view of the above, the objective of the present study was to evaluate chemical attributes (proximate composition, pH, acidity, sucrose levels and water activity) and amine levels in defective coffee beans in comparison to non-defective ones, prior to and after light, medium and dark roasting.

2. Methodology

Arabica green (crude) coffee samples (2002/2003 crop) were obtained from Santo Antonio Estate Coffee (Minas Gerais, Brazil). The coffee beans were subjected to selection

in an electronic sorter. The beans rejected by the sorting machine were used in the present study. This mixture of coffee beans consisted of 7% black, 18% immature, 34% sour and 41% non-defective beans in weight. Black, sour, immature and non-defective beans were manually separated from this mixture to constitute the sampling lots. Samples of 100 randomly selected beans were separated from each lot and roasted in a convective oven at 200 °C for 30 min (light roast), 1 h (medium roast) and 2 h (dark roast), in triplicate.

Nitrogen and fat contents of the coffee samples were determined according to standard AOAC procedures (AOAC, 1995). Protein content was estimated as nitrogen × 6.25. Ash content was evaluated gravimetrically, based on the weight of the sample after burning at 580 °C for 17 h (Clarke & Walker, 1975). Moisture content was evaluated based on oven-drying at 105 °C for 16 h (ISO, 1983). Carbohydrate content was estimated by difference. Titratable acidity was evaluated by titration with NaOH, according to AOAC (1995). Water activity was measured at 25 °C (AQUALAB 3TE). A pH meter (Micronal, Brazil) with glass electrode at 25 °C was employed for pH measurements. Sucrose levels were determined based on colorimetric analysis by a phenol-sulphuric acid method with absorbance readings at 490 nm (Dubois, Gilles, Hamilton, Hebers, & Smith, 1956). The amines putrescine, spermidine, spermine, agmatine, cadaverine, serotonin, histamine, tyramine, tryptamine and phenylethylamine were separated by ion-pair reverse phase high performance liquid chromatography (HPLC) and quantified fluorimetrically, after post-column derivatization with *o*-phthalaldehyde (OPA), according to the methodology described by Cirilo et al. (2003) and summarized as follows. Ground coffee samples (1 g – green coffee; 5 g – roasted coffee) were mixed with 5% trichloroacetic acid (7 ml) and submitted to agitation for 5 min in a vortex mixer. The slurry was then centrifuged at 10,000 × *g* (4 °C) and the supernatant collected. The extraction procedure was repeated twice, the supernatants combined and filtered through 0.45 mm membranes, and then injected into the chromatograph. Chromatography was performed using a LC-10AD system connected to a RF-551 spectrofluorimetric detector at 340 and 445 nm of excitation and emission, respectively, and to a CBM-10AD controller (Shimadzu, Kyoto, Japan). A reversed-phase μBondapak C18 column, 300 × 3.9 mm i.d., 10 mm, was employed with a μBondapak C18 guard-pak insert (Waters, Milford, MA). The mobile phases were: A, a solution of 0.2 M sodium acetate and 15 mM 1-octanesulfonic acid sodium salt, adjusted to pH 4.9 with acetic acid, and B, acetonitrile. The flow rate was set at 0.6 ml/min and the gradient was: 13 min at 11% B, 19 min at 29% B, 24 min at 11% B, and 55 min at 11% B. A detailed description of the post-column derivatization methodology can be found in the article by Cirilo et al. (2003).

Analyses were performed in triplicate. The obtained data were submitted to analysis of variance and the means were compared by the Duncan test at 5% probability.

3. Results and discussion

Results for dry matter loss after roasting are shown in Fig. 1. Average values per roasting degree were 13%, 15% and 17%, corresponding to light, medium and dark roasts, respectively. A comparison of weight loss data between defective and non-defective beans showed that, regardless of roasting conditions, defective beans showed lower weight loss values than non-defective ones. These results confirm that defective beans roast to a lesser degree than non-defective ones, under the same processing conditions, as reported in previous studies (Franca, Oliveira, Mendonça, et al., 2005).

The proximate composition of green and roasted coffee beans is presented in Table 1. Carbohydrate values presented in Table 1 will not be discussed in the present study, since total carbohydrate was determined by difference. Moisture levels for green coffee are within the range reported in the literature for good quality coffee: 8.5–13 g/100 g (Clarke, 1985). The highest value was observed for non-defective beans, whereas both black and immature coffees presented the lowest moisture levels. Other studies (Mazzafera, 1999; Oliveira et al., 2006) have also reported lower moisture levels for defective beans in comparison to non-defective ones. After roasting, moisture levels decreased to an average of 1 g/100 g, without significant variation among the samples or between roasting levels.

Protein levels for green coffee were also in the range reported in the literature for healthy coffee beans: 11–16.5 g/100 g (Macrae, 1985). No significant differences were detected between defective and non defective beans. Slightly higher average levels were observed for black beans, in comparison to the other samples. The same behaviour was observed in previous studies using coffee from a different crop (Oliveira et al., 2006). However, high protein levels in black coffee were actually due to higher caffeine and trigonelline levels (Franca, Oliveira, & Mendonça, 2005). Once protein levels were corrected by subtracting both caffeine and trigonelline, no differences were detected between defective and non defective coffee beans. Protein content showed a slight decrease after roasting for

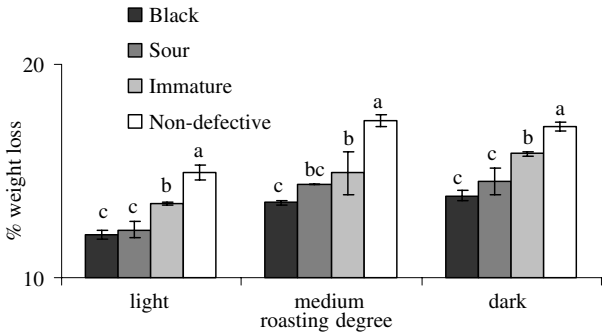

Fig. 1. Dry matter loss during roasting. Values followed by the same letter for a specific roasting degree do not differ significantly by the Duncan test at 5% probability.

Table 1
Proximate composition of coffee beans (g/100 g dry basis green coffee)

	Black	Immature	Sour	Non-defective
Green beans				
Water	$9.4 \pm 0.1^{c,x}$	$9.3 \pm 0.1^{c,x}$	$9.9 \pm 0.1^{b,x}$	$11.5 \pm 0.1^{a,x}$
Protein	$15.6 \pm 1.1^{a,x}$	$14.5 \pm 0.4^{a,x}$	$14.6 \pm 0.5^{a,x}$	$14.1 \pm 0.2^{a,x}$
Lipids	$8.1 \pm 0.0^{b,z}$	$10.2 \pm 0.0^{a,x}$	$8.2 \pm 0.1^{b,z}$	$10.1 \pm 0.5^{a,yz}$
Ash	$6.0 \pm 0.2^{a,x}$	$5.6 \pm 0.2^{b,x}$	$5.5 \pm 0.1^{b,x}$	$4.7 \pm 0.0^{c,x}$
Carbohydrate	70.3	70.0	71.2	72.2
Light roast				
Water	$1.0 \pm 0.3^{a,y}$	$1.0 \pm 0.1^{a,y}$	$1.0 \pm 0.3^{a,y}$	$0.9 \pm 0.1^{a,y}$
Protein	$14.4 \pm 0.2^{a,x}$	$12.9 \pm 1.2^{a,y}$	$13.9 \pm 0.2^{a,y}$	$13.2 \pm 0.5^{a,y}$
Lipids	$10.3 \pm 1.4^{a,y}$	$10.6 \pm 0.0^{a,x}$	$10.0 \pm 1.2^{a,y}$	$9.3 \pm 0.3^{a,z}$
Ash	$5.9 \pm 0.1^{a,xy}$	$5.1 \pm 0.0^{b,y}$	$5.3 \pm 0.1^{c,y}$	$4.6 \pm 0.0^{d,y}$
Carbohydrate	69.4	71.4	70.8	72.9
Medium roast				
Water	$0.8 \pm 0.1^{a,y}$	$0.9 \pm 0.1^{a,y}$	$1.0 \pm 0.1^{a,y}$	$0.9 \pm 0.1^{a,y}$
Protein	$14.5 \pm 0.1^{ab,x}$	$14.0 \pm 0.4^{b,xy}$	$14.6 \pm 0.4^{a,x}$	$13.1 \pm 0.1^{c,y}$
Lipids	$11.4 \pm 0.0^{b,xy}$	$10.9 \pm 0.2^{c,x}$	$11.7 \pm 0.1^{a,x}$	$11.3 \pm 0.1^{b,x}$
Ash	$5.5 \pm 0.1^{a,z}$	$4.8 \pm 0.1^{c,y}$	$5.2 \pm 0.1^{b,y}$	$4.5 \pm 0.1^{d,y}$
Carbohydrate	68.6	70.3	68.5	71.1
Dark roast				
Water	$0.9 \pm 0.1^{a,y}$	$0.8 \pm 0.0^{a,y}$	$1.0 \pm 0.1^{a,y}$	$1.0 \pm 0.1^{a,y}$
Protein	$14.4 \pm 0.1^{b,x}$	$14.7 \pm 0.2^{ab,x}$	$14.8 \pm 0.1^{a,x}$	$13.2 \pm 0.1^{c,y}$
Lipids	$12.3 \pm 0.2^{a,x}$	$10.0 \pm 1.2^{c,x}$	$12.1 \pm 0.2^{ab,x}$	$10.6 \pm 0.0^{bc,xy}$
Ash	$5.8 \pm 0.0^{a,y}$	$4.9 \pm 0.1^{c,y}$	$5.3 \pm 0.1^{b,y}$	$4.4 \pm 0.1^{d,z}$
Carbohydrate	67.5	70.4	67.8	71.8

Average value ± standard deviation. Values followed by the same letter in the same line (a, b) or for a specific substance in the same column (x, y) do not differ significantly using the Duncan test at 5% probability.

non-defective beans, without significant variations between roasting levels. Protein levels did not change significantly during roasting of defective beans. For both medium and dark roasting degrees, defective beans presented higher protein levels than non-defective ones. This could be attributed to defective beans roasting to a lesser degree than non-defective ones, as previously discussed.

Lipid contents of green coffee were closer to the lower limit of the range reported in the literature regarding good quality coffee: 9–16 g/100 g (Folstar, 1985; Speer & Kölling-Speer, 2001). Healthy coffee beans had higher oil contents than both black and sour beans, as reported in previous studies (Mazzafera, 1999; Oliveira et al., 2006). After roasting, lipid contents showed a slight increase for both black and sour beans. Data on lipid contents in the literature are usually a bit higher for roasted coffee in comparison to green coffee, but this occurs only because data for roasted coffee are usually expressed on a roasted basis and do not take into account the overall dry matter content loss during roasting (Folstar, 1985). The slight increase observed in the present study could be due to formation of substances during roasting that are soluble in oil. The mineral content (ash) in green coffee varied from 4.8% to 6.0%, with defective beans having a higher mineral content than non-defective ones. Values obtained for non defective beans are in agreement with those reported in the literature for Brazilian Arabica coffee: 4.1–4.5% (Clarke & Walker, 1975). The higher values observed for defective beans are in agreement with the results obtained in a previous study (Oliveira et al., 2006), using coffee from the same origin and a previous crop. A slight decrease in mineral contents was observed after roasting, but the tendency of higher mineral contents in defective coffee beans was maintained. Such slight decrease could be attributed to the employment of an average weight loss value per type of coffee in dry basis calculations.

Results for chemical attributes of coffee beans are shown in Table 2. Regarding water activity measurements in green coffee, values were lower for defective beans, in comparison

Table 2
Chemical attributes of coffee beans

	Black	Immature	Sour	Non-defective
Crude beans				
Water activity	$0.43 \pm 0.01^{c,x}$	$0.45 \pm 0.00^{b,x}$	$0.44 \pm 0.00^{bc,x}$	$0.48 \pm 0.01^{a,x}$
Acidity (ml NaOH/g coffee)	$192 \pm 3.03^{c,x}$	$279 \pm 5.27^{b,x}$	$313 \pm 8.19^{a,x}$	$277 \pm 2.99^{b,x}$
pH	$6.56 \pm 0.15^{a,w}$	$5.95 \pm 0.13^{b,w}$	$5.94 \pm 0.03^{b,w}$	$5.72 \pm 0.01^{c,w}$
Sucrose (g/100 g)	0.6 ± 0.6^{c}	4.6 ± 0.2^{b}	4.8 ± 0.6^{b}	7.9 ± 0.7^{a}
Light roast				
Water Activity	$0.24 \pm 0.02^{b,y}$	$0.26 \pm 0.04^{ab,y}$	$0.24 \pm 0.03^{b,y}$	$0.32 \pm 0.04^{a,y}$
Acidity (ml NaOH/g coffee)	$112 \pm 9.87^{b,y}$	$152 \pm 4.22^{a,y}$	$167 \pm 10.41^{a,y}$	$165 \pm 5.42^{a,y}$
pH	$5.01 \pm 0.01^{a,z}$	$5.01 \pm 0.00^{a,z}$	$5.01 \pm 0.00^{a,z}$	$5.01 \pm 0.01^{a,z}$
Medium roast				
Water activity	$0.16 \pm 0.01^{a,w}$	$0.17 \pm 0.02^{a,w}$	$0.20 \pm 0.02^{a,w}$	$0.18 \pm 0.04^{a,w}$
Acidity (ml NaOH/g coffee)	$108 \pm 13.51^{a,y}$	$97.4 \pm 5.08^{a,w}$	$99.2 \pm 5.36^{a,w}$	$109 \pm 10.02^{a,w}$
pH	$6.87 \pm 0.01^{a,y}$	$6.28 \pm 0.02^{b,y}$	$6.47 \pm 0.03^{c,y}$	$6.08 \pm 0.04^{d,y}$
Dark roast				
Water activity	$0.15 \pm 0.00^{a,w}$	$0.14 \pm 0.00^{a,w}$	$0.13 \pm 0.01^{a,z}$	$0.14 \pm 0.01^{a,w}$
Acidity (ml NaOH/g coffee)	$92.5 \pm 10.4^{a,y}$	$78.9 \pm 4.73^{a,z}$	$92.6 \pm 4.62^{a,w}$	$85.1 \pm 0.25^{a,z}$
pH	$7.09 \pm 0.02^{a,x}$	$6.66 \pm 0.04^{c,x}$	$6.90 \pm 0.08^{b,x}$	$6.45 \pm 0.03^{d,x}$

Average value ± standard deviation. Values followed by the same letter in the same line (a, b) or for a specific substance in the same column (x, y) do not differ significantly by the Duncan test at 5% probability.

to non-defective ones. The lowest values were observed for black beans. Water activity diminished significantly after roasting, with the encountered values in accordance with literature data (Rahman, 1995). No differences were observed between samples after roasting. Acidity values for green coffee were the highest for sour beans, which could be associated to bean fermentation. Acidity levels were the same for both immature and non-defective beans. The lowest acidity values observed for black beans could be due to loss of acids during soil contact. According to previous studies, acidity should increase as coffee quality decreases (Franca et al., 2005; Mazzafera, 1999). This could be associated to the effect of sour beans, which is usually the most abundant defect in low quality coffee. Acidity values decreased after roasting, without differences among samples. Regarding pH measurements, values were higher for defective beans, in comparison to non-defective ones, prior to and after roasting. The highest pH values were observed for black beans. Sucrose levels were lower for defective beans, in comparison to non-defective ones, with extremely low values for black beans. The same tendency was reported by Mazzafera (1999) comparing immature and immature-black to non-defective coffee beans. Low sucrose levels in immature beans are associated with bean maturation, whereas in the case of black and sour beans, low sucrose levels are due to fermentation. Only traces of sucrose were detected in the light roasted coffee samples, whereas no sucrose was detected for the other roasting degrees. This behaviour is in agreement with data reported by Trugo (1895), who found sucrose degradation values varying from 97% to 100% from light to dark roasts.

Table 3
Amine levels (mg/100 g dry basis green coffee) in green and roasted coffee

Amines	Black	Immature	Sour	Non-defective
Green beans				
Putrescine	0.88 ± 0.16^{c}	5.39 ± 0.28^{b}	4.21 ± 1.09^{b}	7.65 ± 1.56^{a}
Cadaverine	< 0.37	nd	nd	nd
Histamine	0.44 ± 0.08^{c}	0.69 ± 0.00^{b}	1.02 ± 0.18^{a}	nd
Serotonin	0.39^{A}	0.42^{A}	nd	0.52^{A}
Spermidine	0.42^{A}	1.59 ± 0.07^{a}	1.24 ± 0.36^{a}	1.99 ± 0.41^{a}
Spermine	< 0.37	1.89 ± 0.17^{a}	1.74 ± 0.45^{a}	2.26 ± 0.45^{a}
Tryptamine	nd	0.57 ± 0.06	< 0.37	nd
Total	1.61 ± 0.33^{c}	10.4 ± 0.54^{ab}	8.28 ± 1.49^{b}	12.3 ± 2.87^{a}
Light roast				
Serotonin	nd	< 0.37	0.52^{A}	< 0.37

Average value ± standard deviation. Values followed by the same letter in the same line do not differ significantly using the Duncan test at 5% probability. Detection limit: 0.15 mg/100 g d.b.; quantification limit: 0.37 mg/100 g d.b.; nd: non-detected.
[A] Amine detected in only one of three replicates.

Results obtained for amine levels in crude coffee are presented in Table 3. Total amine levels ranged from 1.6 mg/100 g (black beans) to 12.3 mg/100 g (non-defective beans), without significant differences between immature and non-defective beans and slightly lower values for sour ones. Average values were in the same range reported by Casal et al. (2004) and Oliveira et al. (2005), but higher than those found by Cirilo et al. (2003).

Seven of the ten evaluated amines were detected in crude coffee: putrescine, cadaverine, histamine, serotonin, spermidine, spermine and tryptamine (Table 3). A typical chromatogram is shown in Fig. 2. Among the detected amines,

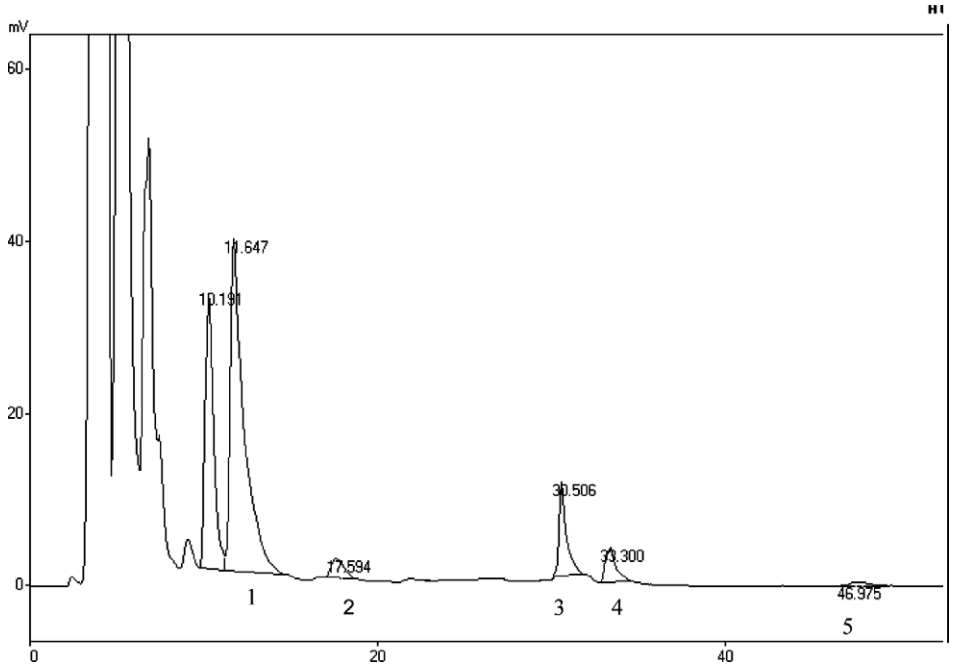

Fig. 2. Chromatogram for analysis of amines in sour green beans. Numbered peaks correspond to: (1) putrescine, (2) histamine, (3) spermidine, (4) spermine, and (5) tryptamine.

only putrescine was detected in all samples above trace levels. Regarding non-defective beans, putrescine was the prevailing amine, being responsible for approximately 60% of the total amine content, followed by spermine and spermidine. This distribution has been reported by other studies (Amorim et al., 1977; Casal et al., 2004; Oliveira et al., 2005) with the exception of the work by Cirilo et al. (2003), which found serotonin as the prevailing amine. The presence of putrescine, spermidine and spermine was expected, since these amines are usually present in most plants (Cirilo et al., 2003; Flores, Protácio, & Signs, 1989). Putrescine is a precursor of spermidine and spermine, which could explain its high levels. Putrescine levels were higher for non-defective beans in comparison to defective ones. However, previous studies (Oliveira et al., 2005) have reported higher putrescine levels for low quality coffee in comparison to high quality coffee. It is noteworthy to mention that the coffee samples employed by Oliveira et al. (2005) did not have the same origin, which is an indication that putrescine levels could be related to coffee quality, growth and processing conditions. Both spermine and spermidine levels were similar between immature, sour and non-defective beans.

Prevalence of putrescine, followed by spermine and spermidine, was observed for all samples but black, for which histamine levels corresponded to approximately 50% of putrescine levels, and both spermine and spermidine were present in much smaller quantities. Histamine was detected, above trace levels, only in the samples that consisted purely of defective coffee beans. This is in agreement with the study by Oliveira et al. (2005), who reported that histamine was detected only in low sensory quality coffee. Both these results are an indication that the detection of histamine in crude coffee could be associated with the presence of defective beans, thus being a possible marker for green coffee quality. Among the defects, histamine levels were the highest for sour beans and the lowest for black beans. It is noteworthy to mention that histamine levels found in coffee do not pose a concern in terms of intoxication. The toxicological levels of amines are not easily established, for they depend on individual characteristics of each amine, as well as on interactions among amines and also with the food substract. Nevertheless, the highest value detected in the present study (sour beans) corresponds to approximately 10% of the suggested limit for histamine toxicity (Halász, Baráth, Simon-Sarkadi, & Holzapfel, 1994; Santos, 1996).

Traces of cadaverine were found in the black beans and tryptamine was found only in the immature at trace levels in the sour beans. Serotonin was detected only in a few samples. After roasting, only traces of serotonin were present in the light roast and no amines were detected in the medium and dark roasts. These results confirm that putrescine, spermine and spermidine should be consumed during the early stages of roasting (Oliveira et al., 2005) and are in agreement with literature data regarding putrescine, spermidine and spermine in roasted coffee. 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. Cirilo et al. (2003) reported that putrescine and spermine were not detected after roasting coffee at 300 °C for 6 (American or light roast) and 12 min (French or dark roast). According to these authors, spermidine levels presented approximately 80% reduction under light roasting conditions, but increased for dark roasting. Casal et al. (2004) reported that all the major biogenic amines were still present after roasting arabica coffee at 160–220 °C during 14 min, but in quite small quantities.

4. Conclusions

A comparative evaluation of chemical attributes and amine levels in defective and non-defective coffee beans was performed for green and roasted coffee. Differences between defective and healthy green coffee were observed for the following parameters: ash, moisture and lipid contents, sucrose levels, acidity and water activity. Putrescine levels were higher for non-defective beans in comparison to defective ones. However, other studies have reported higher putrescine levels for low quality coffee in comparison to high quality coffee, which is an indication that putrescine levels may be related not only to coffee quality, but also to growth and processing conditions. Further studies are needed in order to confirm this hypothesis. Histamine was detected only in the defective coffee samples. After roasting, differences between defective and non-defective coffee beans only remained for ash contents. The results obtained for amine levels indicate that histamine is a potential marker for detection of defective beans in green coffee. However, since amine concentration was drastically reduced by roasting, such compounds do not seem to be appropriate for quality evaluation of roasted coffees.

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