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Correlation between cup quality and chemical attributes of Brazilian coffee

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This work is dedicated to the memory of our dear friend, colleague and mentor, Prof. Luiz Carlos Trugo, after his untimely death on November 20, 2004. His example will keep inspiring all who had the privilege of knowing him.

Abstract

Brazilian arabica coffee is classified for trading according to the quality of the beverage obtained after roasting and brewing. In the present study, Brazilian green and roasted coffee beans were investigated for possible correlations between cup quality and the levels of sucrose, caffeine, trigonelline and chlorogenic acids, determined by HPLC analysis. Trigonelline and 3,4-dicaffeoylquinic acid levels in green and roasted coffee correlated strongly with high quality. To a lesser extent, caffeine levels were also associated with good quality. On the other hand, the amount of defective beans, the levels of caffeoylquinic acids (predominantly 5-caffeoyil-quinic acid), feruloylquinic acids, and their oxidation products were associated with poor cup quality and with the Rio-off-flavor. The fact that similar correlations between cup quality and chemical attributes were observed in green and light roasted samples – the latter used for coffee cup classification – indicates that chemical analysis of green beans may be used as an additional tool for coffee quality evaluation.

Keywords: Coffee quality; Rio-off-flavor; Chlorogenic acids; Trigonelline; Caffeine

1. Introduction

Flavor is the most important criterion for coffee quality evaluation, and also one of the major motivations for consumer preferences (Cantergiani et al., 1999; Clarke, 1987, chap. 2). The assessment of coffee quality by both buyers and sellers in Brazil is based on the brewing method of steeping, which consists on pouring boiling water (~150 mL) directly onto roasted and ground coffee (~10 g; mild roast; fine grind) contained in a small cup and performing sensory (smell, flavor) evaluation after a few minutes (Clarke, 1987, chap. 2; Lingle, 1993). Classification is performed by a trained panel, and the beverage quality denominations, from best to worst, are: Strictly soft, Soft, Barely soft, Hard, Rioysh, Rio and Rio zona (Table 1). This determines the so called cup quality. The lowest quality coffees (Rioysh, Rio and Rio zona) are associated with the Rio off-flavor, usually described as a pungent, medicinal, phenolic or iodine-like flavor associated with a musty, cellarlike odor (Lingle, 1993; Spadone, Takeoka, & Liardon, 1990).

The presence of defects is also relevant in establishing Brazilian coffee quality, since they are associated with

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Table 1
Official classification of Brazilian coffee beverage (Bartholo & Guimarães, 1997)

Classification	Characteristics
Strictly soft	Very smooth flavor; slightly sweet; low acidity
Soft	Smooth flavor; slightly sweet
Barely soft	Smooth flavor, but with slight astringency
Hard	Astringent flavor; rough taste; lacks sweetness
Rioysh	Slight taste of iodoform or phenic acid
Rio	Strong unpleasant taste, reminding iodoform or phenic acid
Rio zona	Intolerable taste and smell

problems during harvesting and pre-processing operations. The term defect is used in reference to the presence of defective (black, sour or brown, immature, immature-black, bored, broken, etc.) beans and also of extraneous matter (husks, twigs, stones, etc.) in a given coffee sample (Clarke, 1987; Franca, Oliveira, Mendonça, & Silva, 2005; Franca, Mendonça, & Oliveira, 2005; Mazzafera, 1999). Black beans are those from over-ripened fruits. Sour beans are from fruits that are fermented on the ground or due to improper processing conditions. Immature beans come from immature fruits, immature-black are beans from immature fruits in which the skin is oxidized, and bored beans are those damaged by insect action. Even though defects are known to negatively affect coffee flavor, the total counting of defects alone cannot be used to accurately predict cup quality (Smith, 1985, (chap. 1)).

The chemistry of flavor development during coffee roasting is highly complex and not completely understood. Even though roasting process appears to be simple in terms of processing conditions, it is quite complex from a chemistry point of view, since hundreds of chemical reactions take place simultaneously. Examples include Maillard and Strecker reactions, degradation of proteins, polysaccharides, trigonelline and chlorogenic acids (De Maria, Trugo, Aquino Neto, Moreira, & Alviano, 1996). Sugars, particularly sucrose as the most abundant, will act as aroma precursors, originating several substances (furans, aldehydes, carboxylic acids, etc.) that will affect both flavor and aroma of the beverage. Trigonelline is a pyridine derivative, known to contribute indirectly to the formation of desirable aromas during roasting (Ky, 2001; Macrae, 1985, (chap. 4)). Caffeine, a xantine derivative, presents a characteristic bitter taste reported to be important to coffee flavor (Trugo, 1984). This compound has also been the subject of several investigations in view of its pharmacological effects (Azam, Hadi, Khan, & Hadi, 2003; Barone & Roberts, 1996; Macrae, 1985, Ribeiro-Alves, Trugo, & Donangelo (chap. 4); Ribeiro-Alves et al., 2003). Chlorogenic acids (CGA), a group of phenolic compounds that represent 6–12% of coffee constituents in mass (Farah, De Paulis, Trugo, & Martin, 2005), are known to be responsible for coffee pigmentation, aroma formation, and astringency (De Maria, Trugo, Moreira, & Petracco, 1995; Trugo, 1984). Furthermore, thermal degradation of chlorogenic acids during roasting will result in phenolic substances that contribute to bitterness (Clifford, 1985, chap. 5). The major CGA subgroups in coffee are the caffeoylquinic acids (CQA), feruloylquinic acids (FQA) and dicaffeoylquinic acids (diCQA) (Clifford & Wight, 1976; Trugo & Macrae, 1984). These compounds have received much attention lately due to various pharmacological activities observed in vitro and in animals (Farah et al., 2005).

Even though more than eight hundred volatile and non-volatile compounds have been already identified in coffee, the question of which constituents are the most relevant contributors to low cup quality coffee is controversial and far from being completely answered, especially in regard to the Rio-off-flavor. According to Spadone et al. (1990), 2,4,6-trichloroanisole and 2,4,6-trichlorophenol were identified as two of the components responsible for the Rio-off-flavor. While Amorim, Basso, Crocomo, and Teixeira (1977) have not observed a correlation between cup quality and the levels of polyamines, Oliveira, Franca, Glória, and Borges (2005) found higher levels of amines in lower quality coffee samples, comparing to those of good quality. Mazzafera (1999) and Franca et al. (2005) associated higher acidity with low cup quality, possibly due to the presence of defective coffee beans, specifically the ones that had undergone fermentation. Chagas (1994) observed a positive association between the levels of reducing and non-reducing sugars and cup quality. 2-Methylbutyraldehyde and 3-methylbutyraldehyde were described as two of the volatile compounds characteristic of green defective beans and low cup quality coffee blends (Cunha, 2005).

In view of the above, a more extensive investigation of chemical attributes of Brazilian coffees of different cup qualities is needed. Therefore, the objective of the present study was to investigate the existence of a possible correlation between cup quality and the content of some of the most important compounds in coffee: sucrose, trigonelline, caffeine and chlorogenic acids.

2. Material and methods

2.1. Samples

Arabica coffee samples classified as Soft, Hard, Rioysh, Rio and Rio zona, (Pinhal, São Paulo, Brazil) were provided by the Brazilian Association of Coffee Industry (ABIC). Samples of randomly selected beans were separated from each lot and the defective (black, sour, immature, bored) and non-defective beans were manually separated and weighted in order to determine the mass composition of defective beans for each lot.

Since it is very difficult to distinguish sour from black-immature beans and the latest constitute a minor defect, comparing to the first, black-immature and sour beans were counted as sour beans. Three hundred grams of each coffee sample were roasted at 200 °C, in an electric labscale roaster (CAEL LTDA, Brazil), for 8, 12, 27 and 45 min, resulting in light, medium, dark and very dark roasting degrees, respectively. Roasting degrees were established according to the reference color system used by ABIC. Disks #75; #55; #35 and #25, from the Roast Color Classification System (Agtron-SCAA, 1995), were used as standards for light; medium; dark and very dark roasting degrees. Temperature variation inside the roaster was monitored by a thermometer during the roasting process. Roasted coffee beans were then grounded to pass through a 0.75 mm sieve and the color was determined by reflectance measurements (Color Test II – Neuhaus Neotec, Germany), as an average of three determinations for each sample. A sample of *C. canephora* cv Conillon or Robusta coffee (Espírito Santo, Brazil), known to be of inferior quality (Martin, Pablo, & Gonsalez, 1998), was also roasted for comparison with the arabica samples.

2.1.1. Extraction

For sucrose evaluation, coffee samples were extracted with 80 °C distilled water and clarified with activated charcoal (Trugo, Farah, & Cabral, 1995). Caffeine and trigonelline were also extracted with hot distilled water. The extracts were clarified with Carrez reagents for caffeine analysis, and with lead acetate (60%) for trigonelline analysis (Trugo, 1984). CGA were extracted with aqueous methanol (40%) and clarified with Carrez reagents (Trugo & Macrae, 1984). All extractions were performed in triplicates.

2.1.2. HPLC analysis

Isocratic systems consisting of Shimadzu pump and integrator (Japan) and a 20 μL Rheodyne fixed loop injector (USA) were used for all analyses. Sucrose was determined by a RI detector (Waters, USA), using a Spherisorb NH_2 column (Supelco, USA), and acetonitrile 80% as mobile phase, at 1 mL/min (Trugo et al., 1995). For caffeine and trigonelline analysis, a Knauer UV detector (Germany) was employed at 272 nm for caffeine and at 264 nm for trigonelline. A reverse-phase column (ODS C-18 Merck, Germany) was used with methanol as mobile phase at 40% for caffeine and 5% for trigonelline. Flow rate was 1 mL/min (Trugo, 1984). For CGA analysis, a reverse-phase column (Rexchrom, Regis, USA) and a Shimadzu UV detector at 325 nm were used. The mobile phase was 10 mM trisodium citrate: methanol (65:35 v/v), adjusted to pH 2.5 with HCl, at 1 mL/min. CGA were identified with the use of non-commercial standards, as previously described (Farah et al., 2005). The concentrations of the compounds were calculated using the peak areas of commercial standards (Aldrich Chem., USA) as references. Because the only commercially available CGA standard is 5-CQA, the quantification of the CGA isomers took into account the area of 5-CQA standard and the area and molar extinction coefficients of each CGA (Farah et al., 2005; Ruback, 1969). All reagents employed for HPLC analysis were of HPLC grade and the others were of analytical grade.

2.1.3. Water content

In order to express the results in dry matter (dm) the water content of each sample was determined according to AOAC procedures (AOAC, 2000).

2.1.4. Statistical analysis

The HPLC results were tested for correlations with the Statistica® software, version 6.0, using the least square difference method and considered significant when $p < 0.05$. The correlations with cup quality were obtained using data from all samples and the correlations with "Rio-off-flavor" excluded data from the Hard sample. Because sample is a qualitative variable, we found inappropriate to propose an equation to describe the correlations between the dependent and independent variables.

3. Results and discussion

The arabica coffee samples used in the present study were classified by cup quality as Soft, Hard, Rioysh, Rio and Rio zona. The sample classified as soft presented a soft, sweet note and lacked off-notes. The Hard one presented a distinct astringent note, and the three last types of beverage showed an increasing perception of the Rio-off-flavor.

3.1. Defective beans

Average results for the distribution of defective and non-defective beans in the coffee samples are shown in Fig. 1. The highest quality sample (Soft) consisted of 100% non-defective beans. The percentage of defective beans increased as cup quality decreased. Franca, Mendonça, et al. (2005) also reported higher percentage of defects in Rioysh and Rio samples, when compared to Soft and Hard samples. The percentage of each type of defect (immature, bored and sour) also increased as cup quality decreased. Black beans were only found in the Rio zona sample. The prevailing defect in all samples consisted of sour beans, followed by immature beans. This could be an indication that the percentage of sour and immature beans could present a positive correlation with low cup quality and/or with the Rio-off-flavor. Further studies employing a wide variety of arabica

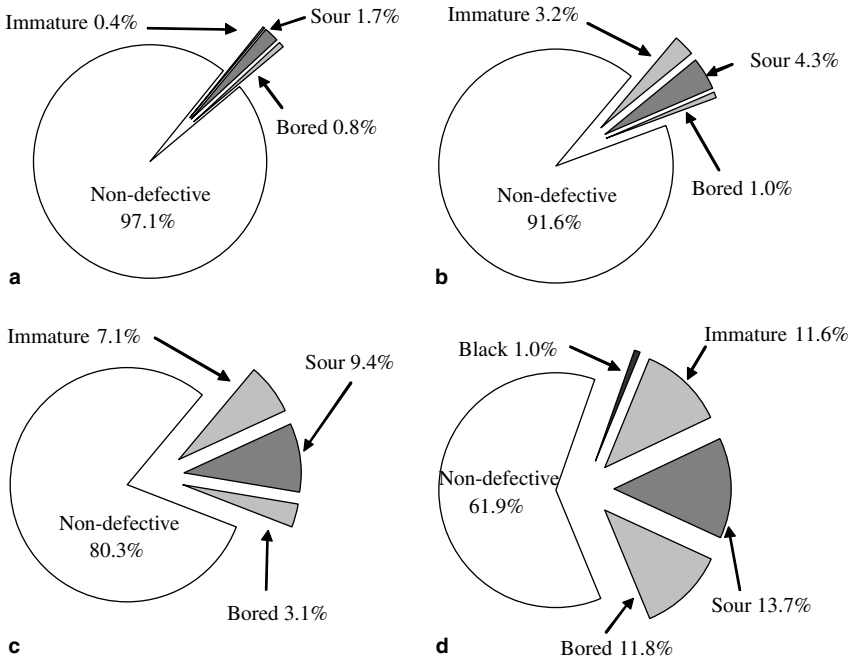

Fig. 1. Distribution of defective beans in Brazilian arabica coffee samples classified by cup quality: (a) Hard; (b) Rioysh; (c) Rio; (d) Rio zona.

coffee samples from different crops and locations are needed in order to verify this possibility.

3.2. Color of the beans and roasting temperature

The color intensity of the green arabica samples increased significantly as their quality decreased (Fig. 2). Such behavior could be attributed to the increasing presence of defective beans as cup quality decreased (Fig. 1) and, indirectly, to the action of the enzyme polyphenol oxidase over phenolic acids (see below). Franca, Oliveira, et al. (2005) showed that both black and sour defective beans presented lower luminosity and color saturation values in comparison to non-defective ones. Even though no significant changes in temperature were recorded inside the roaster for the same time points, there was a small but significant difference in the colorimetric values of arabica samples roasted to the same roasting degrees. This difference did not correspond to the differences in colorimetric values observed in the green samples (Fig. 3).

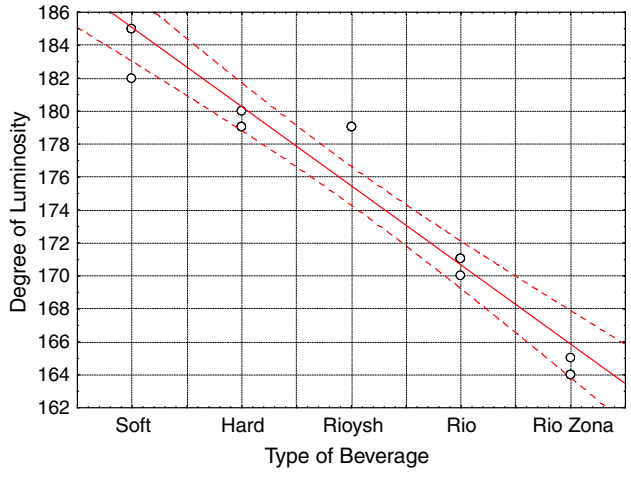

Fig. 2. Correlation between Brazilian arabica green samples classified by cup quality and color, measured by intensity of luminosity. The negative correlation indicates that as the samples worsen, they get darker ($r = -0.96$).

3.3. Trigonelline

Derivatives of trigonelline are known to be important to the coffee aroma (Trugo, 1984). As quality worsened, the levels of trigonelline in the green beans decreased from 1.34 ± 0.05 (dry matter-dm) to 0.96 ± 0.03 g/

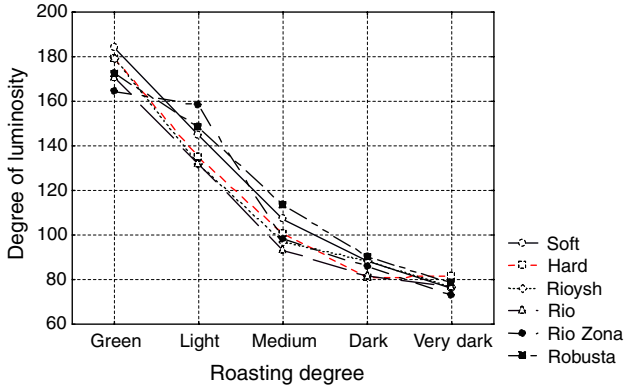

Fig. 3. Colorimetric results obtained for green and roasted Brazilian arabica coffee classified by cup quality and for Robusta coffee beans.

100 g (dm), as shown in Fig. 4, resulting in a strong negative correlation with poor quality ($r = -0.93$) and with the Rio-off-flavor ($r = -0.94$) (Fig. 5). These levels are within the range previously reported for samples from different sources (Ky, 2001; Trugo, 1984). Both higher (Martin et al., 1998; Mazzafera, 1991) and lower (Franca, Mendonça, et al. (2005)) amounts of trigonelline have also been reported for Brazilian coffee samples, which could be attributed to the use of different analytical methods. The roasting process caused a significant decrease in trigonelline content, as expected (Amorim et al., 1975; Franca, Oliveira, et al. (2005); Franca, Mendonça, et al. (2005); Trugo, 1984) (Fig. 4). The average loss of trigonelline from the green beans to the dark roasted beans was 90%. Trigonelline losses of 50–80% after roasting have been previously reported (Franca, Oliveira, et al. (2005); Franca, Mendonça, et al. (2005); Trugo, 1984). These differences may be attributed to distinct roasting conditions, which include differences in colorimetric standards, since trigonelline degradation was reported to be strongly dependent upon the degree of roast (Borges, Mendonça, Franca, & Oliveira, 2004; Casal, Oliveira, & Ferreira, 2000; Trugo, 1984). The negative correlations observed in the green beans were higher for the light roasted beans for both quality and the Rio-off-flavor (Fig. 5). The contents in darker roasting degrees did not show any significant correlations with cup quality. Fig. 4 also presents the content of trigonelline in a Robusta sample, known to be of lower quality than arabica coffee (Martin et al., 1998; Trugo & Macrae, 1984). Trigonelline levels were lower for green Robusta beans in comparison to all arabica beans, but quite similar to the levels found in the worst quality arabica sample, Rio zona.

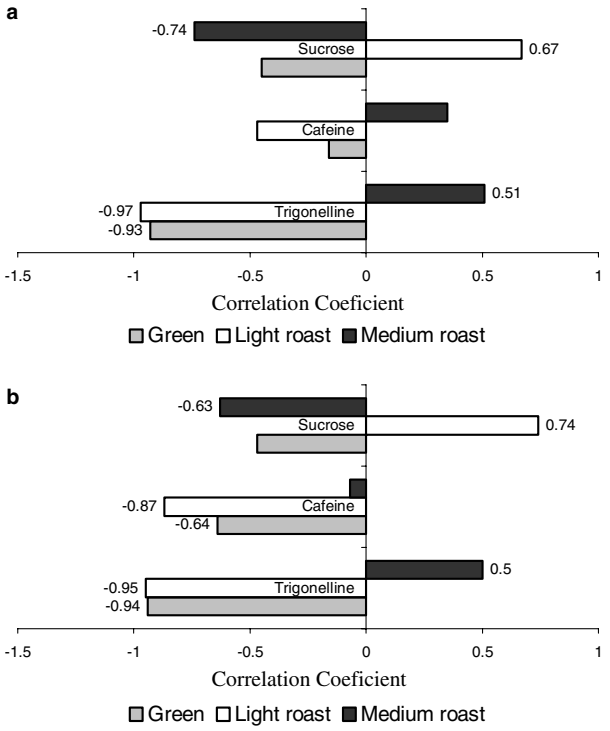

Fig. 5. Correlation coefficients between: (a) cup quality or (b) Rio-off-flavor and the content of sucrose, caffeine, trigonelline. The right side of the *x*-axis indicates: (a) poor cup quality or (b) presence of Rio-off-flavor.

3.4. Sucrose

The highest sucrose level in green beans was found in the Rioysh sample (7.85 ± 0.26 g/100 g, dm) and the lowest level, in the Rio zona sample (4.88 ± 0.10 g/100 g dm). There was a drastic decrease in the sucrose

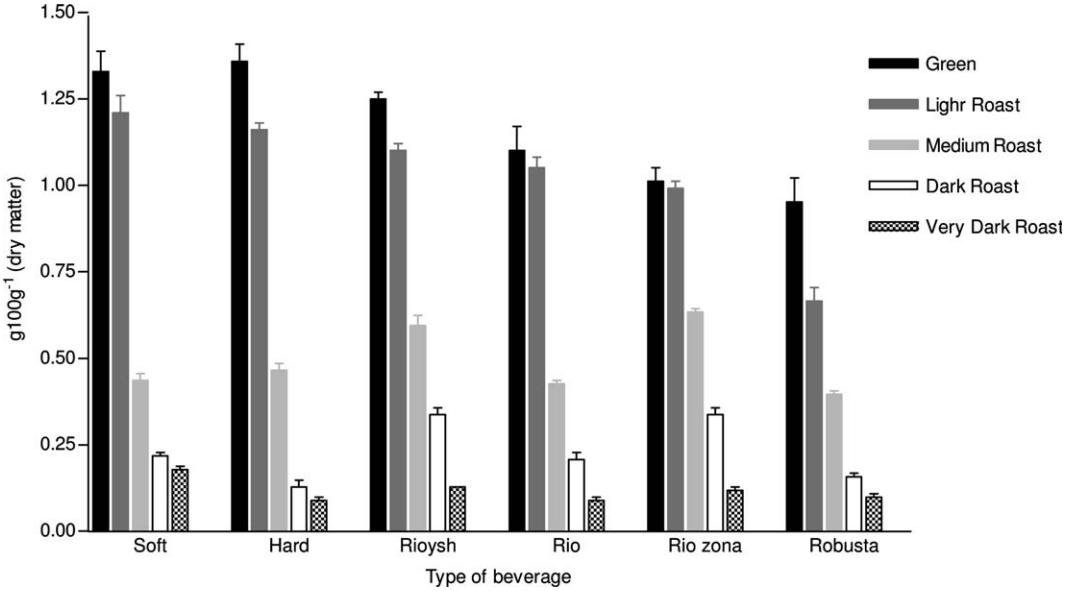

Fig. 4. Trigonelline content in green and roasted Brazilian arabica coffee samples classified by cup quality and in Robusta coffee beans.

content of all samples during the roasting process (average loss of 98% for the dark roasted samples), as a consequence of caramelization and Maillard reactions. Although Mazzafera (1999) had found lower sucrose levels in defective green beans in comparison with non-defective (good quality) green beans, in the present work, the content of sucrose in green and roasted beans correlated neither with quality nor with the Rio-off-flavor (Fig. 5).

3.5. Caffeine

The caffeine content in the green beans showed a small but significant difference. The highest content was observed for the Soft sample (1.23 ± 0.06 g/100 g dm) and the lowest content, for the Hard sample (0.96 ± 0.01 g/100 g dm). As expected, roasting did not affect the content of caffeine other than causing a slight relative increase due to the loss of other components. Caffeine correlated negatively with the Rio-off-flavor only for the light roasted samples ($r = -0.87$, Fig. 5). No other correlations were of significance. Franca, Mendonça, et al. (2005) have also reported higher caffeine content for their highest quality sample (Soft), compared to other arabica samples.

3.6. Chlorogenic acids

Eight CGA were identified. The caffeoylquinic acids accounted for about 83% of the total CGA in green beans. The highest content of total CGA in the green beans were observed for the worst quality sample, Rio zona (7.02 ± 0.17 g/100 g dm), and the lowest content, for the best quality sample, Soft (5.78 ± 0.09 g/100 dm) (Fig. 6). CGA levels decreased gradually during roasting, as previously reported (Farah et al., 2005; Trugo, 1984). The average loss of total CGA from green to dark roasted beans was 93%. One of the descriptions of the Rio-off-flavor is a phenolic note (Spadone et al., 1990). Strong positive correlations were found between the levels of most of CGA monoesters and low cup quality. Fig. 7 shows the correlation coefficients between individual CGA and cup quality (a) or Rio-off-flavor (b). In the green beans, the levels of 5-CQA and 5-FQA correlated strongly with poor cup quality ($r = 0.90$). The levels of 4-CQA, 5-CQA, 4-FQA and 5-FQA correlated strongly with the Rio-off-flavor ($r = 0.93$, 0.94, 0.82 and 0.90, respectively). In contrast, the levels of 3,4-diCQA were negatively correlated with poor cup quality ($r = -0.88$) and with the Rio-off-flavor ($r = -0.83$). To a lesser extent, 3,5-diCQA levels in the green beans also correlated negatively with the Rio-off-flavor ($r = -0.75$). As displayed in Fig. 7, even though not all the dicaffeoylquinic acids have shown high correlations with cup quality and the Rio-off-flavor, in the green samples, the correlation coefficients for all three dicaffeoylquinic acids showed a tendency towards the left side of the x axis, which indicates good quality. Conversely, Ohiokpehai, Brumen, and Clifford (1982) reported that the addition of dicaffeoylquinic acids conferred a disagreeable flavor to coffee beverage, which disappeared on subsequent addition of monocaffeoylquinic acid.

Menezes (1994) have observed an inverse association of the levels of CQA and coffee fruits maturation. We have also observed that immature and immature-black defective beans contain significantly higher levels of all CGA, but mostly CQA and FQA, comparing to healthy and black defective beans (unpublished data). According to Mazzafera (1999) immature and immature-black

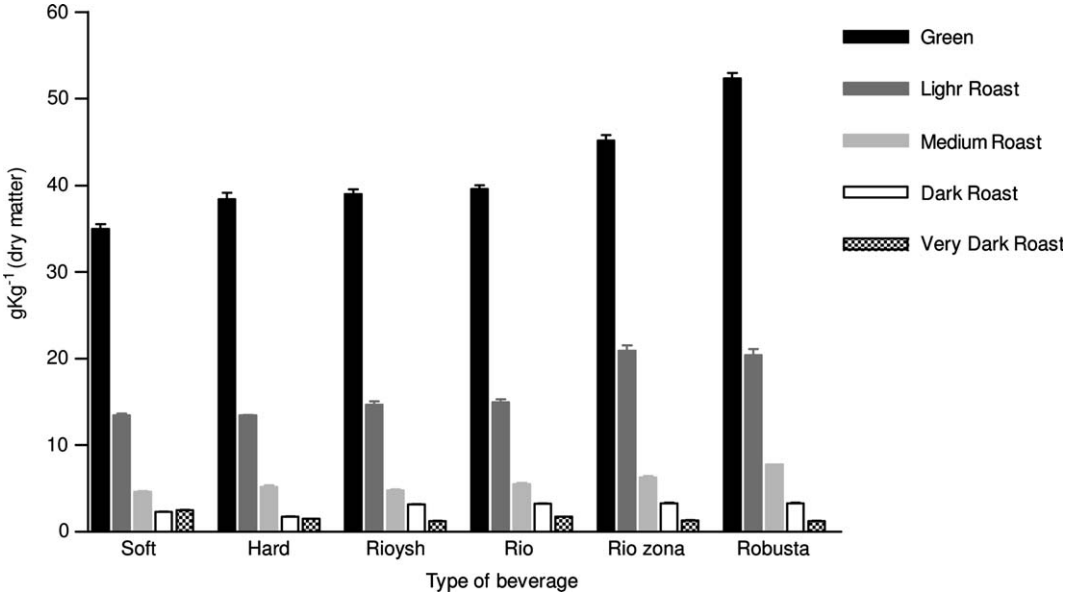

Fig. 6. 5-CQA content in green and roasted Brazilian arabica coffee samples classified by cup quality and in Robusta coffee beans.

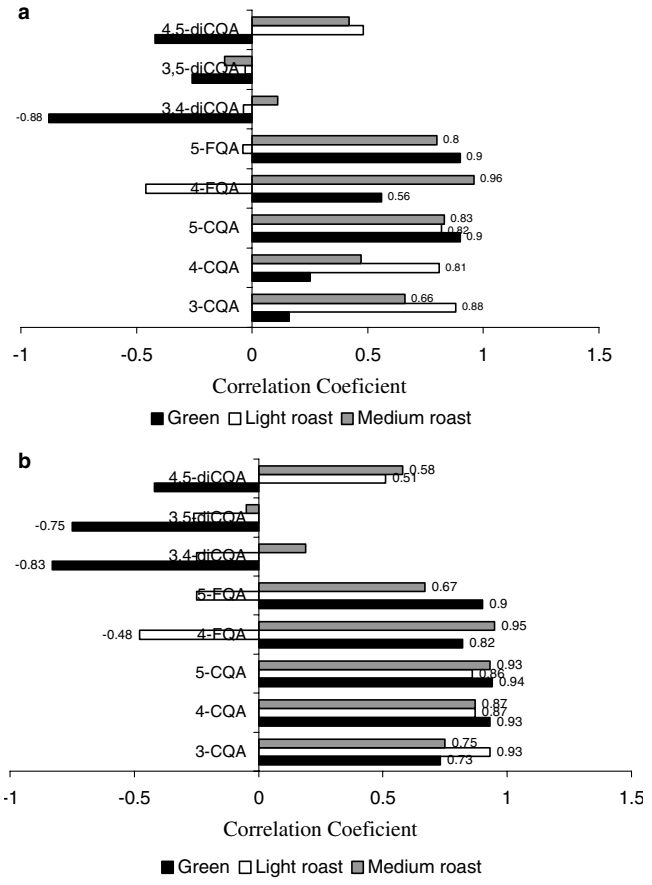

Fig. 7. (a) Correlation coefficients between each of eight chlorogenic acids and (a) cup quality or (b) presence of Rio-off-flavor. The right side of the *x* axis indicates (a) poor cup quality or (b) presence of Rio-off-flavor.

beans are critical defects for coffee quality. The fact that in the present study as cup quality decayed the percentage of immature beans and the levels of 5-CQA increased, reiterates the association of 5-CQA with poor quality.

For the light roasted beans, only 3-CQA, 4-CQA and 5-CQA levels presented positive correlations with both poor cup quality ($r = 0.87$, 0.81, 0.9, respectively) and the Rio-off-flavor ($r = 0.93$, 0.87, 0.86, respectively). For the beans roasted to medium degree, the levels of 5-CQA, 4-FQA and 5-FQA were correlated with poor cup quality ($r = 0.83$; $r = 0.96$; $r = 0.81$, respectively), and the levels of 3-CQA, 4-CQA, 5-CQA, 4-FQA, and 5-FQA were positively correlated with the Rio-off-flavor ($r = 0.75$, 0.85, 0.93, 0.95, respectively). Correlations were not significant for darker roasting degrees.

3.7. Chlorogenic acids and color

Similar to that observed for 5-CQA, as sample quality decreased, the color intensity of green arabica beans increased significantly ($r = -0.96$). A high correlation was found between intensity of color and the content of 5-CQA and total CGA ($r = 0.90$, 0.80, respectively). When considering only the samples with Rio-off-flavor, the correlations were even higher for 5-CQA and total CGA ($r = 0.91$, 0.93, respectively). Because 5-CQA accounts for 61.8% of the total CGA, there may be an important contribution of this compound to color intensity, augmented by other CGA. 5-CQA is very likely to be the major substrate for the enzyme polyphenol oxidase in coffee (Mazzafera & Robinson, 2000). Therefore, another possibility is that ortho-quinones, formed by the action of polyphenol oxidase on 5-CQA, cause darkening of the grains. Moreover, Amorim, Cruz, Dias, Mello, and Teixeira (1977) related the action of polyphenol oxidase, triggered by structural changes of bean cell membranes, as a possible cause of the Rio-off-flavor. This hypothesis is in accordance with our results and indicates that oxidation products of 5-CQA may contribute to the Rio-off-flavor.

4. Conclusions

In the present study, trigonelline and 3,4-dicaffeoilquinic acid and, to a lesser extent, caffeine, showed association with good cup quality, for both green and light roasted coffee. In contrast, along with the amount of defective beans, higher levels of caffeoylquinic acids (predominantly 5-CQA), feruloylquinic acids (to a lesser extent), and their oxidation products were associated with poor cup quality and with the Rio-off-flavor. The fact that similar correlations between cup quality and chemical attributes were observed in green and light roasted samples – the latter used for coffee cup classification – indicates that chemical analysis of green beans may be used as an additional tool for evaluating coffee quality.

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