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Role of Roasting Conditions in the Level of Chlorogenic Acid Content in Coffee Beans: Correlation with Coffee Acidity

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Total chlorogenic acids of nine isomers from seven commercial green and roasted coffee beans ranged from 34.43 ± 1.50 to 41.64 ± 3.28 mg/g and from 2.05 ± 0.07 to 7.07 ± 0.16 mg/g, respectively. Methanol/water (7:3) extracts from four commercial green coffee beans roasted at different conditions (230 °C, 12 min; 24 °C, 14 min; 250 °C, 17 min; and 250 °C, 21 min) were also analyzed for chlorogenic acids. The total chlorogenic acid found in green coffee beans ranged from 86.42 ± 2.04 to 61.15 ± 1.40 mg/g. Total chlorogenic acids present were reduced in accordance with the intensity of roasting conditions. When green beans were roasted at 230 °C for 12 min and at 250 °C for 21 min, total chlorogenic acid content was reduced to nearly 50% and to almost trace levels, respectively. The results indicate that roasting conditions play an important role in chlorogenic acid content in roasted coffee beans. A general correlation between total caffeoylquinic acids and pH was observed.

KEYWORDS: Chlorogenic acids; coffee beans; coffee acidity; coffee extracts; roasting conditions

INTRODUCTION

Coffee is one of the most popular beverages in the world. The chemical components of coffee have been studied intensively and continuously since the beginning of last century, in particular from the viewpoint of flavor chemicals. The number of flavor chemicals identified in coffee has reached over 1000 (*1*, *2*). The consumers' preference toward brewed coffee is known to be strongly correlated with its acidity (*3*). Chlorogenic acids are involved in the bitterness of coffee due to their decomposition in phenolic compounds during roasting. Chlorogenic acids mainly include caffeoylquinic acids (CQA), dicaffeoylquinic acids (diCQA), and feruloylquinic acids (FQA). Therefore, the CQA composition in brewed coffee is very important in the evaluation of coffee quality (*4*). Concentrations of CQA in samples prepared from seven commercial brand coffees have been reported previously (*5*). In this paper, the concentration of total CQA ranged from 5.26 to 17.1 mg/g of ground coffee.

Because coffee is one of the world's most popular beverages (*6*), it has received a great deal of attention by many researchers involved in health-related studies (*7*, *8*). Most studies on coffee associated with human health have focused on the negative aspects, such as the toxicity of caffeine (*9*, *10*). Coffee drinking, however, does not always have exclusively nonbeneficial results (*11*). Recent reports indicate that brewed coffee contains large numbers of health-beneficial antioxidants, such as volatile heterocyclic compounds (*12*) and chlorogenic acids (*5*, *13*).

To take advantage of coffee drinking, it is significant to know about the presence of medicinal components, including volatile chemicals and CQA, in coffee. It is well-known that roasting conditions have a major impact on the physical and chemical properties of roasted coffee beans (*14*). There have been many reports on the role of roasting conditions in the formation of various coffee components, including CQA (*15*, *16*), acrylamide (*17*), and volatile compounds (*18*). For example, when Brazilian *Coffea arabica* and *Coffea canephora* coffee cultivars were roasted under different conditions, the concentrations of total CQA ranged from 79.46 mg/g (light roasting) to 2.37 mg/g (heavy roasting) (*19*).

In the present study, coffee beans were roasted under various conditions and then chlorogenic acid content was analyzed to investigate the role of roasting conditions in the chlorogenic acid content in coffee beans.

MATERIALS AND METHODS

Materials and Chemicals. Caffeine, formic acid, potassium hexacyanoferrate(II) trihydrate, and zinc acetate dihydrate were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). 5-Caffeoylquinic acid (5-CQA) was purchased from Cayman Chemical Co. (Ann Arbor, MI). 3- and 4-CQA were prepared from 5-CQA using the isomerization method reported previously (*20*). Other CQA standards were bought from Chengdu Purification Technology Development Co., Ltd. (Sichuan, China) or a gift from TAKATA Koryo Co., Ltd. (Osaka, Japan). Numbering of substituted position on CQA was designated according to the IUPAC system (*21*).

HPLC grade methanol and water were purchased from Fisher Co. (Pittsburgh, PA). All other chemicals and solvents were bought from reliable commercial sources.

Stock solutions of caffeine (2.0 mg/mL) and CQA (2.0 mg/mL) were prepared in methanol to create standard solutions.

Organic green coffee beans and commercially roasted coffee beans (Colombian, Ethiopian, Guatemalan, Mexican, Nicaraguan, Papuan, and

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Table 1. Water Content and Mass Lost in Coffee Beans Roasted under Various Conditions

			Ethiopian		Nicaraguan		Panamanian		Sumatran	
type of roast	roasting time (min)	roasting temp (°C)	water content (%)	mass lost (%)	water content (%)	mass lost (%)	water content (%)	mass lost (%)	water content (%)	mass lost (%)
green			6.86	0	5.15	0	8.46	0	4.77	0
light	12	230	3.81	9.4	2.41	10.5	3.12	8.5	2.86	9.8
medium	14	240	2.64	12.8	2.11	13.3	2.87	12.4	2.08	13.6
city	17	250	1.99	18.8	1.77	18.9	2.65	18.6	1.58	19.1
French	21	250	1.29	21.8	1.53	22.0	2.25	21.8	1.12	22.6

Sumatran) were bought from Napa Valley Coffee Roasting Co. (Napa, CA). Panamanian green beans were purchased from Sweet Maria Coffee Co. (Oakland, CA).

Measurement of Water Content in Coffee Beans. Water content of the coffee beans was measured with an oven-drying method (*22*). Briefly, a sample was dried for 3 h at 105 °C in a flat-bottom metallic flask predried at 98 °C for 1 h. The percent water content was calculated as follows:

$$\text{water content (\%)} = \frac{\text{original sample wt} - \text{final sample wt}}{\text{original sample wt}} \times 100$$

Sample Preparations for Chlorogenic Acids and Caffeine Analysis from Commercial Coffee Green Beans and Commercially Roasted Coffee Beans. Green or roasted Colombian, Ethiopian, Guatemalan, Mexican, Nicaraguan, Papuan, Panamanian, or Sumatran coffee beans (50 g each) were ground with a La Pavoni coffee grinder (Milan, Italy). Green coffee beans were ground with 10 g of crushed dry ice.

Ground green and commercially roasted coffee beans (1 g) were soaked in 50 mL of deionized hot water (85 °C) in a 100 mL Erlenmeyer flask, and the solution was allowed to stand at room temperature for 3 h. After the extract was filtered, the coffee extract was treated with Carrez reagents I and II [I, 250 mM potassium ferrocyanide trihydrate [$K_4Fe(CN)_6 \cdot 3H_2O$] solution; II, 1 M zinc acetate dehydrate [$Zn(CH3COO)_2 \cdot 2H_2O$] solution containing 3% glacial acetic acid (v/v)] according to a previously reported method (*23*) to eliminate polymeric components. The coffee extract (4 mL), along with 0.1 mL each of Carrez reagents I and II and 0.8 mL of methanol, was vortex-mixed in a centrifuge tube and allowed to stand for 10 min. Precipitate was separated by centrifuging at 5000 rpm for 10 min. After the solution was decanted and filtered with an Acrodisc syringe filter with 0.2 μm HT Tuffryn membrane (Pall Corp., Ann Arbor, MI), the sample was stored at 5 °C until used for CQA and caffeine analysis.

Sample Preparations for CQA and Caffeine Analysis from Coffee Beans Roasted under Various Conditions. Green coffee beans (100 g) of Ethiopian, Nicaraguan, Panamanian, and Sumatran origin were roasted with a Gene Café coffee bean roaster (Fresh Beans Inc.) at 230 °C for 12 min (light), at 240 °C for 14 min (medium), at 250 °C for 17 min (city), or at 250 °C for 21 min (French) (the terms for roasting conditions are from descriptions shown on the roaster). Roasted beans (50 g) were ground with a Starbucks Barista coffee grinder (Seattle, WA). Roasting characteristics of these coffee beans are shown in **Table 1**.

Ground coffee beans (1 g) were soaked in a methanol/water (7:3, v/v) solution (50 mL) in a 100 mL Erlenmeyer flask at room temperature for 7 h. The extract was further treated as described above, and the sample was stored at 5 °C until used for CQA and caffeine analysis.

The extraction solvent (methanol/water 7:3) used for these experiments increased recovery of CQA by nearly 40% over the method with hot water simulated brewing of the coffee. For example, the recovery of total CQA from Ethiopian green coffee beans increased from 38.66 ± 3.18 mg/g (hot water) to 69.02 ± 2.36 mg/g (methanol/water). This solvent was used for further experiments because of the high recovery efficiency for CQA.

Analysis of CQA and Caffeine. Quantitative analyses of caffeine and CQA were performed using an Agilent 1100 model HPLC system equipped with a Phenomenex Gemini C-18 5 μ column (250 mm × 4.6 mm i.d.) and a multiple-wavelength detector. Mobile phase A was water (containing 0.1% formic acid) and mobile phase B was acetonitrile (containing 0.1% formic acid). The gradient mode was initially set at an A/B ratio of 95:5 from 0 to 3 min, then linearly increased to 75:25 at 45−50 min and then to 50:50 at 53−57 min. The flow rate was 0.8 mL/min.

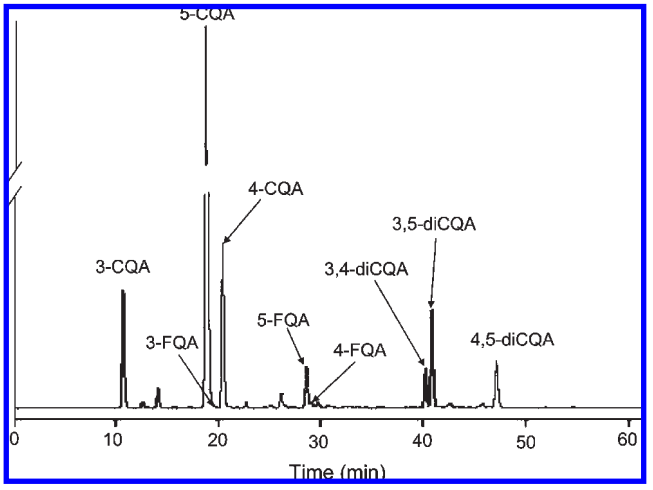

Figure 1. Typical HPLC chromatogram of a methanol extract obtained from Colombian green coffee beans. 3-CQA, 3-caffeoylquinic acid; 5-CQA, 5-caffeoylquinic acid; 3-FQA, 3-feruloylquinic acid; 4-CQA, 4-caffeoylquinic acid; 5-FQA, 5-feruloylquinic acid; 4-FQA, 4-feruloylquinic acid; 3,4-diCQA, 3,4-dicaffeoylquinic acid; 3,5-diCQA, 3,5-dicaffeoylquinic acid; 4,5-diCQA, 4,5- dicaffeoylquinic acid.

The detector was set at 325 nm for CQA and at 276 nm for caffeine; injection volume was 10 μL. Concentrations of CQA and caffeine were calculated using the regression equation of their concentration and peak area.

Identification of caffeine and CQA in brewed coffee was confirmed by a Hewlett-Packard 1100 liquid chromatograph interfaced to an Applied Biosystems API 2000 MS/MS via electrospray ionization (ESI) source operating in the positive ion mode at 400 °C.

The pH of each brewed coffee sample was measured with a Corning pH-meter 430 (Corning, NY).

RESULTS AND DISCUSSION

Figure 1 shows a typical HPLC of a methanol extract obtained from Colombian green coffee beans. A previous paper indicated that 4-CQA and 3-FQA were not satisfactorily separated by HPLC (*20*), but they were resolved satisfactorily in the present study as shown in **Figure 1**.

Figure 2 shows the total CQA—shown in **Figure 1**—found in commercial green and roasted beans. There were no significant differences in the content of total CQA among the commercial coffee beans analyzed in the present study. In decreasing order, total CQA concentration in commercial green coffee beans was Colombian (41.64 ± 3.28 mg/g) > Mexican > Guatemalan > Papuan > Ethiopian > Nicaraguan > Sumatran (34.43 ± 1.50 mg/g).

Tables 2 and **3** show the individual CQA and caffeine contents along with pH in commercial green coffee beans and roasted beans, respectively. 3-FQA was not listed because only trace amounts were detected in all coffee beans. The decreasing order of pH of

samples from commercial green coffee beans was Sumatran (5.85) > Papuan > Colombian, Nicaraguan > Mexican > Guatemalan > Ethiopian (5.68). Sumatran green coffee beans, which contained the lowest total CQA, exhibited the highest pH—the lowest acidity. However, no significant correlation between total CQA and pH was observed in the other coffee brands.

In decreasing order, total CQA concentration in commercial roasted coffee beans was Nicaraguan (7.07 ± 0.16 mg/g) > Guatemalan > Ethiopian > Colombian > Sumatran > Papuan > Mexican (2.05 ± 0.07 mg/g). The decreasing order of pH of samples from commercial roasted coffee beans was Mexican (5.79) > Papuan, Ethiopian > Sumatran > Colombian > Guatemalan > Nicaraguan (5.41). Mexican roasted coffee beans, which contained the lowest total CQA, exhibited the highest pH—the lowest acidity. On the other hand, Nicaraguan roasted coffee beans, which contained the highest total CQA, showed the lowest pH—the highest acidity. In the case of commercial roasted coffee, a general correlation between total CQA and pH was observed.

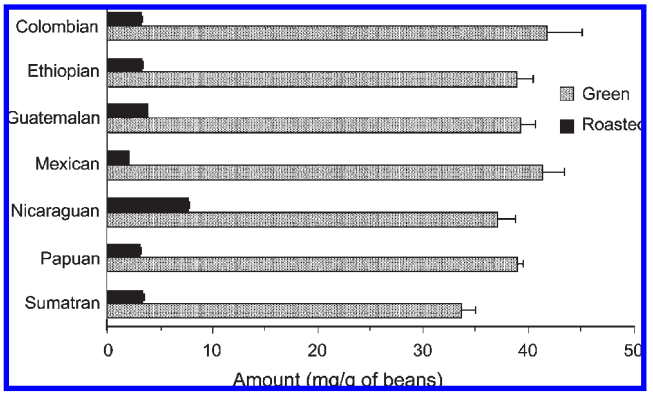

Figure 2. Total chlorogenic acids found in commercial green and roasted beans.

In green beans, 5-CQA was found in the greatest amount ranging from 30.02 ± 0.47 mg/g (Mexican) to 24.27 ± 1.05 mg/g (Sumatran), followed by 4-CQA ranging from 4.32 ± 0.08 mg/g (Papuan) to 2.97 ± 0.15 mg/g (Ethiopian). The general decreasing order of CQA isomers was 5-CQA > 4-CQA > 3-CQA > 3,5-diCQA > 4,5-diCQA > 5-FQA > 3,4-diCQA > 4-FQA. In roasted beans, as is seen in the case of total CQA levels, the amount of each CQA reduced significantly. For example, 5-CQA in Mexican green beans reduced from 30.02 ± 0.47 to 0.86 ± 0.01 mg/g. It is obvious that the roasting process reduced the amount of CQA present considerably. However, the rate of CQA reduction varied among coffee beans, ranging from 95.1% (Mexican) to 80.7% (Nicaraguan). As mentioned above, the content of CQA in roasted coffee beans was influenced by the roasting time and condition (*15*, *16*). However, roasting conditions used for the commercial coffee beans used for the above study were not known. Therefore, various green coffee beans were roasted under different conditions to investigate the role of roasting conditions in CQA content in roasted coffee beans. Caffeine content increased slightly in all brands after roasting.

Figure 3 shows the total amount of CQA found in various green coffee beans and in various roasted coffees treated under different conditions. Total CQA content was reduced significantly in accordance with the intensity of conditions. Total CQA found in green coffee beans was 86.42 ± 2.04 mg/g in Panamanian, 69.02 ± 2.36 mg/g in Ethiopian, 63.96 ± 0.97 mg/g in Sumatran, and 61.15 ± 1.40 mg/g in Nicaraguan. The reduction rate of total CQA was calculated as follows:

$$\text{reduction rate}\ (\%) = \frac{\text{total CQA in green beans} - \text{total CQA in roasted beans}}{\text{total CQA in green beans}} \times 100$$

In the present study, the reduction rates for city roast (250 °C, 17 min) and French roast (250 °C, 21 min) in all four samples were > 99%, whereas that for light roast (230 °C, 12 min) ranged from

Table 2. Chlorogenic Acids and Caffeine Content (Milligrams per Gram of Coffee Beans, w/w Dry Matter Basis) in Commercial Green Coffee Beans (Mean ± SD, *n* = 3) along with pH

compound	Colombian	Ethiopian	Guatemalan	Mexican	Nicaraguan	Papuan	Sumatran
3-CQA	2.45 ± 0.18	1.76 ± 0.09	2.26 ± 0.10	2.57 ± 0.14	2.65 ± 0.05	3.25 ± 0.06	2.57 ± 0.11
5-CQA	29.64 ± 2.08	29.39 ± 1.07	28.76 ± 0.99	30.02 ± 0.47	26.20 ± 0.20	26.76 ± 0.30	24.27 ± 1.05
4-CQA	3.73 ± 0.24	2.97 ± 0.15	3.46 ± 0.19	4.28 ± 0.16	3.76 ± 0.10	4.32 ± 0.08	3.57 ± 0.12
5-FQA	1.04 ± 0.05	0.92 ± 0.10	0.95 ± 0.09	0.86 ± 0.03	0.83 ± 0.01	0.73 ± 0.00	0.92 ± 0.02
4-FQA	0.15 ± 0.01	0.15 ± 0.00	0.14 ± 0.01	0.15 ± 0.01	0.18 ± 0.00	0.15 ± 0.01	0.17 ± 0.01
3,4-diCQA	0.85 ± 0.15	0.60 ± 0.05	0.77 ± 0.03	0.81 ± 0.04	0.67 ± 0.09	0.94 ± 0.02	0.87 ± 0.04
3,5-diCQA	2.35 ± 0.30	1.89 ± 0.11	1.85 ± 0.06	1.68 ± 0.10	1.51 ± 0.22	1.38 ± 0.02	1.14 ± 0.06
4,5-diCQA	1.43 ± 0.32	0.98 ± 0.08	1.13 ± 0.09	1.10 ± 0.10	0.90 ± 0.15	1.15 ± 0.03	0.92 ± 0.09
pH	5.78	5.68	5.70	5.73	5.78	5.84	5.85
caffeine	10.54 ± 0.19	8.27 ± 0.28	9.28 ± 0.69	8.95 ± 0.36	9.84 ± 0.41	9.68 ± 0.13	7.53 ± 0.38

Table 3. Chlorogenic Acids and Caffeine Content (Milligrams per Gram of Coffee Beans, w/w Dry Matter Basis) in Commercial Roasted Coffee Beans (Mean ± SD, *n* = 3) along with pH

compound	Colombian	Ethiopian	Guatemalan	Mexican	Nicaraguan	Papuan	Sumatran
3-CQA	0.78 ± 0.03	1.64 ± 0.02	0.94 ± 0.01	0.51 ± 0.01	1.69 ± 0.04	0.66 ± 0.03	0.69 ± 0.01
5-CQA	1.42 ± 0.01	1.08 ± 0.05	1.67 ± 0.05	0.86 ± 0.01	3.08 ± 0.06	1.10 ± 0.04	1.18 ± 0.00
4-CQA	0.86 ± 0.04	0.68 ± 0.01	1.02 ± 0.02	0.56 ± 0.02	1.86 ± 0.04	0.74 ± 0.02	0.77 ± 0.00
5-FQA	0.14 ± 0.00	0.10 ± 0.02	0.09 ± 0.00	0.06 ± 0.02	0.13 ± 0.01	0.05 ± 0.01	0.08 ± 0.01
4-FQA	0.08 ± 0.00	0.06 ± 0.01	0.09 ± 0.00	0.06 ± 0.01	0.12 ± 0.01	0.06 ± 0.02	0.09 ± 0.00
3,4-diCQA	0.04 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.00 ± 0.00	0.08 ± 0.00	0.02 ± 0.01	0.02 ± 0.00
3,5-diCQA	0.02 ± 0.00	0.00 ± 0.00	0.02 ± 0.00	0.00 ± 0.00	0.05 ± 0.00	0.00 ± 0.00	0.01 ± 0.01
4,5-diCQA	0.01 ± 0.01	0.00 ± 0.00	0.02 ± 0.00	0.00 ± 0.00	0.06 ± 0.00	0.11 ± 0.00	0.06 ± 0.00
pH	5.66	5.73	5.61	5.79	5.41	5.73	5.67
caffeine	11.86 ± 0.20	9.38 ± 0.27	10.41 ± 0.03	9.99 ± 0.29	10.03 ± 0.18	10.42 ± 0.32	10.33 ± 0.06

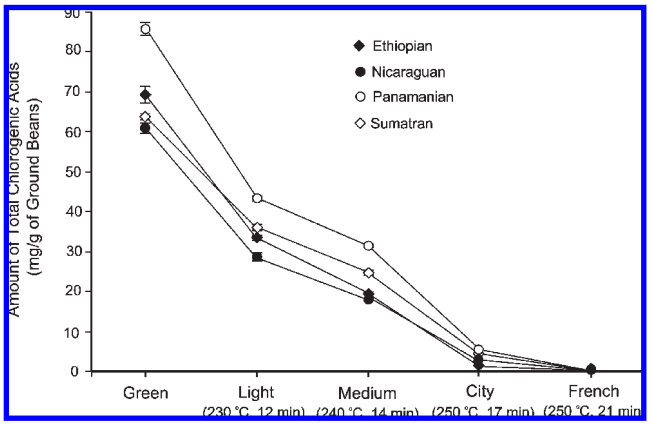

Figure 3. Total chlorogenic acids found in various green coffee beans and in various roasted coffees treated under different conditions.

Table 4. Chlorogenic Acids and Caffeine Content (Milligrams per Gram of Coffee Beans, w/w Dry Matter Basis) in Ethiopian Green Coffee Beans and Coffee Beans Roasted at Different Conditions (Mean ± SD, $n = 3$) along with pH

compound	green	light roast	medium roast	city roast	French roast
3-CQA	2.08 ± 0.05	5.45 ± 0.10	3.37 ± 0.07	0.38 ± 0.01	0.07 ± 0.01
5-CQA	50.70 ± 1.61	15.11 ± 0.35	9.27 ± 0.18	0.79 ± 0.01	0.16 ± 0.01
4-CQA	4.28 ± 0.13	7.56 ± 0.23	4.87 ± 0.10	0.59 ± 0.02	0.11 ± 0.01
4-FQA	3.58 ± 0.08	1.28 ± 0.03	0.89 ± 0.02	–[a]	–
5-FQA	0.29 ± 0.00	0.56 ± 0.02	0.42 ± 0.01	–	–
3,4-diCQA	1.01 ± 0.05	0.65 ± 0.01	0.29 ± 0.01	–	–
3,5-diCQA	5.75 ± 0.30	0.56 ± 0.00	0.21 ± 0.03	–	–
4,5-diCQA	1.33 ± 0.14	0.92 ± 0.01	0.40 ± 0.01	–	–
total CQA	69.09 ± 2.36	32.09 ± 0.75	19.72 ± 0.43	1.76 ± 0.04	0.34 ± 0.03
pH	5.65	4.86	5.01	5.88	6.18
caffeine	12.75 ± 0.35	12.05 ± 0.42	12.52 ± 0.28	13.42 ± 0.68	13.31 ± 0.31

[a] Trace or not detected.

45.2% (Sumatran) to 54.0% (Nicaraguan). The results on the reduction rates were similar to the previous report (*20*). In that previous paper, the total CQA in green coffee beans was reduced significantly by roasting at 205 °C for four different time periods: light, 7 min for Arabica and 5 min for Robusta; medium, 10 min for Arabica and 7 min for Robusta; dark, 13 min for Arabica and 14 for Robusta; or very dark, 19 min for Arabica and 16 min for Robusta. The reduction rates in this study were 88.8 and 93.0% for dark and 96.5 and 98.0% for very dark in Arabica and Robusta coffees, respectively. The reduction rates for medium roast (240 °C, 14 min) in the present study, which ranged from 61.3% (Sumatran) to 71.5% (Ethiopian), were similar to those for light (60.9% in Arabica, 59.7% in Robusta) and medium (67.7% in Arabica, 76.4% in Robusta) in the previous paper (*20*).

Amounts of each CQA and the caffeine content in green coffee beans and coffee beans roasted under different conditions are shown in **Tables 4** (Ethiopian), **5** (Nicaraguan), **6** (Panamanian), and **7** (Sumatran) along with pH. In green coffee beans, the decreasing order of CQA isomers was CQAs > diCQAs > FQAs. 5-CQA content was greatest in this test group, ranging from 50.70 ± 1.61 mg/g (Ethiopian) to 40.15 ± 0.71 mg/g (Panamanian). Among CQA found in coffee beans, 5-CQA has also been reported as the highest content (*5*, *19*). For example, 5-CQA found in the Arabica and Robusta green beans comprised 66 and 56% of total CQA, respectively (*20*). In the present study, percentages of 5-CQA in total CQA of green coffee beans were 73.4% for Ethiopian, 65.7% for Nicaraguan, 46.5% for Panamanian, and 65.5% in Sumatran.

It is interesting that 4-CQA increased in Ethiopian, Nicaraguan, and Sumatran coffee beans in the light roast treatment,

Table 5. Chlorogenic Acids and Caffeine Content (Milligrams per Gram of Coffee Beans, w/w Dry Matter Basis) in Nicaraguan Green Coffee Beans and Coffee Beans Roasted at Different Conditions (Mean ± SD, $n = 3$) along with pH

compound	green	light roast	medium roast	city roast	French roast
3-CQA	3.52 ± 0.08	4.65 ± 0.17	3.50 ± 0.06	0.50 ± 0.01	0.09 ± 0.00
5-CQA	40.19 ± 0.84	12.22 ± 0.41	8.19 ± 0.22	1.08 ± 0.04	0.21 ± 0.01
4-CQA	5.96 ± 0.11	7.12 ± 0.23	4.90 ± 0.17	0.87 ± 0.04	0.17 ± 0.00
4-FQA	3.52 ± 0.08	1.51 ± 0.05	1.00 ± 0.05	0.31 ± 0.07	–[a]
5-FQA	0.48 ± 0.03	0.65 ± 0.02	0.30 ± 0.02	0.13 ± 0.05	–
3,4-diCQA	1.59 ± 0.04	0.64 ± 0.03	0.33 ± 0.01	–	–
3,5-diCQA	3.34 ± 0.14	0.43 ± 0.03	0.18 ± 0.01	–	–
4,5-diCQA	2.55 ± 0.08	0.90 ± 0.05	0.44 ± 0.01	–	–
total CQA	61.15 ± 1.40	28.12 ± 0.99	18.84 ± 0.55	2.84 ± 0.21	0.47 ± 0.01
pH	5.76	4.90	5.05	5.81	6.12
caffeine	13.68 ± 0.23	13.24 ± 0.42	13.84 ± 0.42	14.84 ± 0.76	15.06 ± 0.37

[a] Trace or not detected.

Table 6. Chlorogenic Acids and Caffeine Content (Milligrams per Gram of Coffee Beans, w/w Dry Matter Basis) in Panamanian Green Coffee Beans and Coffee Beans Roasted at Different Conditions (Mean ± SD, $n = 3$) along with pH

compound	green	light roast	medium roast	city roast	French roast
3-CQA	10.18 ± 0.14	6.80 ± 0.11	4.59 ± 0.05	0.55 ± 0.01	0.10 ± 0.00
5-CQA	40.15 ± 0.71	15.88 ± 0.25	11.04 ± 0.12	1.17 ± 0.02	0.23 ± 0.01
4-CQA	13.14 ± 0.13	10.50 ± 0.12	7.54 ± 0.14	1.17 ± 0.04	0.13 ± 0.03
4-FQA	10.43 ± 0.14	4.55 ± 0.08	3.62 ± 0.06	0.87 ± 0.02	–[a]
5-FQA	1.27 ± 0.03	2.65 ± 0.04	2.74 ± 0.01	0.69 ± 0.01	–
3,4-diCQA	4.07 ± 0.25	1.48 ± 0.02	0.74 ± 0.01	–	–
3,5-diCQA	3.41 ± 0.32	1.01 ± 0.02	0.53 ± 0.02	–	–
4,5-diCQA	3.77 ± 0.32	1.77 ± 0.02	0.94 ± 0.02	–	–
total CQA	86.42 ± 2.04	44.64 ± 0.66	31.74 ± 0.43	4.45 ± 0.10	0.46 ± 0.04
pH	5.88	5.23	5.18	5.82	6.17
caffeine	23.38 ± 0.50	20.44 ± 0.30	21.33 ± 0.38	25.00 ± 0.54	25.15 ± 0.60

[a] Trace or not detected.

Table 7. Chlorogenic Acids and Caffeine Content (Milligrams per Gram of Coffee Beans, w/w Dry Matter Basis) in Sumatran Green Coffee Beans and Coffee Beans Roasted at Different Conditions (Mean ± SD, $n = 3$) along with pH

compound	green	light roast	medium roast	city roast	French roast
3-CQA	3.59 ± 0.03	5.83 ± 0.11	3.96 ± 0.10	0.72 ± 0.01	0.13 ± 0.01
5-CQA	41.65 ± 0.38	14.74 ± 0.34	10.11 ± 0.28	1.57 ± 0.01	0.30 ± 0.02
4-CQA	5.46 ± 0.04	8.30 ± 0.22	5.96 ± 0.22	1.20 ± 0.01	0.25 ± 0.01
4-FQA	3.95 ± 0.05	1.72 ± 0.03	1.56 ± 0.06	0.45 ± 0.00	–[a]
5-FQA	0.43 ± 0.01	1.27 ± 0.01	1.60 ± 0.05	0.59 ± 0.01	–
3,4-diCQA	2.02 ± 0.08	1.03 ± 0.04	0.52 ± 0.02	–	–
3,5-diCQA	3.74 ± 0.24	0.77 ± 0.02	0.36 ± 0.02	–	–
4,5-diCQA	3.12 ± 0.14	1.37 ± 0.04	0.70 ± 0.02	–	–
total CQA	63.96 ± 0.97	35.03 ± 0.82	24.77 ± 0.77	4.53 ± 0.04	0.68 ± 0.04
pH	5.83	5.01	4.91	5.68	6.09
caffeine	12.98 ± 0.26	12.22 ± 0.30	13.37 ± 0.58	14.44 ± 0.28	15.05 ± 0.65

[a] Trace or not detected.

suggesting that some CQA increase by heat treatment. For example, 4-CQA in Ethiopian (4.28 ± 0.13 mg/g in green beans) almost doubled in light-roasted beans (7.56 ± 0.23 mg/g). diCQA isomers reduced to trace or nondetected levels under city and French roast treatments in all four coffee samples.

Some CQA are known to be transformed into CQA lactones in coffee beans while roasting. It was suggested that roasting causes isomerization of CQA existing in green coffee beans prior to the formation of lactones (*24*, *25*). However, the study of CQA lactones was not within the scope of the present study.

Caffeine content increased slightly under the intense conditions of city and French roasts, but no significant change was observed.

The results of the present study suggest that roasting conditions play an important role in the CQA content of the final coffee product. It can be estimated that the commercial roasted coffee used in the present study was roasted somewhere between medium and city roasting conditions. The results of the present study suggest that CQA concentration in roasted coffee, which plays an important role in the quality of brewed coffee taste, was influenced by the roasting condition. The presence of certain levels of CQA in roasted coffee is also important because of their medicinal activities. CQA have been reported as biologically active components of various natural plants, including plumbago (*26*), Himalayan rhododendrons (*27*), *Gardenia jasminoides* fruits (*28*), chokeberry fruit (*29*), and coffee beans (*5*). High CQA content coffee seems to be better for medicinal purpose. However, acid reflux symptoms may be caused by the acidic components, including CQA, of coffee (*30*). Therefore, it is extremely important to prepare coffee in a way that has low enough levels of CQA to prevent acid reflux yet a sufficient amount for medicinal purposes. In fact, a previous study indicates that 5-CQA, which is the most abundant CQA in coffee, showed moderate antioxidant activity at the level of 10 μg/mL but slight pro-oxidant activity at the level of 100 μg/mL (*31*) in the MA-GC antioxidant assay (*32*). These results suggest roughly that a CQA content of 50−60 μg/mL in brewed coffee is optimal to expect medicinal activity but not to trigger acid reflux. However, more investigation on the toxicity and medicinal activity of coffee components to clarify the risks and benefits of coffee drinking is in order.

ABBREVIATIONS USED

CQA, chlorogenic acids; 3-CQA, 3-caffeoylquinic acid; 5-CQA, 5-caffeoylquinic acid; 3-FQA, 3-feruloylquinic acid; 4-CQA, 4-caffeoylquinic acid; 5-FQA, 5-feruloylquinic acid; 4-FQA, 4-feruloylquinic acid; 3,4-diCQA, 3,4-dicaffeoylquinic acid; 3,5-diCQA, 3,5-dicaffeoylquinic acid; 4,5-diCQA, 4,5-dicaffeoylquinic acid; HPLC, high-performance liquid chromatography; MA-GC, malonaldehyde gas chromatography; SD, standard deviation.

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