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Chlorogenic acid and caffeine contents in various commercial brewed coffees

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Abstract

Twelve commercial brewed coffees (seven regular and five decaffeinated) were analyzed for chlorogenic acids (CGA) and caffeine by HPLC. Their pH and UV–Vis absorbances were also measured. The CGAs identified were three caffeolylquinic acids (3-CQA, 4-CQA, and 5-CQA), three feruloylquinic acids (3-FQA, 4-FQA, and 5-FQA), and three dicaffeoylquinic acids (3,4-diCQA, 3,5-diCQA, and 4,5-diCQA). The total CGAs ranged from 5.26 mg/g to 17.1 mg/g in regular coffees and from 2.10 mg/g to 16.1 mg/g in decaffeinated coffees. Among CGA, 5-CQA was present at the highest level, ranging from 2.13 mg/g to 7.06 mg/g coffee, and comprising 36–42% and 37–39% of the total CGA in the regular and decaffeinated coffees, respectively. CGA isomer contents were, in decreasing order, 5-CQA > 4-CQA > 3-CQA > 5-FQA > 4-FQA > 3-FQA > 3,4-diCQA > 4,5-diCQA, 3,5-diCQA. The caffeine content in regular and decaffeinated coffees ranged from 10.9 mg/g to 16.5 mg/g and from 0.34 mg/g to 0.47 mg/g, respectively. The pH of regular and decaffeinated coffees ranged from 4.95 to 5.99 and from 5.14 to 5.80, respectively. The relationship between the pH and the UV–Vis absorbance at 325 nm was moderately correlated ($R^2 = 0.7829$, $p < 0.001$, $n = 12$).

Keywords: Acid contents; Brewed coffee; Caffeine; Chlorogenic acids

1. Introduction

Coffee is one of the world's most popular beverages. It is also the most important traded commodity in the world after oil (Production & Consumption, 2006). World coffee production grew by over 100% from 1950 to 1990 and is projected to grow by 0.5–1.9% by 2010. Global output is expected to reach 7.0 million tons by 2010. World consumption of coffee is projected to increase by 0.4% annually from 6.7 million tons in 1998–2000 to 6.9 million tons in 2010 (Coffee, 2006).

There have been numerous reports on diseases associated with coffee consumption (Sandler, 1983; Schilter, Cavin, Tritscher, & Constable, 2001). Coffee drinking, however, does not always have exclusively non-beneficial results. One recent review article stated that epidemiological and experimental studies have shown positive effects of regular coffee drinking on various aspects of health, such as psychoactive responses (alertness, mood change), neurological conditions (infant hyperactivity, Parkinson's disease), metabolic disorders (diabetes, gallstones), and gonad and liver function (Dorea & da Costa, 2005).

The majority of consumers' concerns about coffee drinking are, however, the acid reflux symptoms caused by coffee's acidic components, such as chlorogenic acids (CGA), and doctors tend to recommend patients with acid reflux to limit their coffee intake. CGAs are well known secondary metabolites in green coffee beans and are known to contribute to coffee's bitterness (Campa, Doulbeau, Dussert, Hamon, & Noirot, 2005). There have been many reports on the presence of CGA in green coffee beans (Clifford, 1979; Van der Stegen & Van Duijn, 1980). For example, the content of CGA in various green coffee beans (21

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species) from Cameroon and Congo ranged from 0.8% to 11.9% on a dry matter basis (Campa et al., 2005). The CGA content in brewed coffee may be influenced by the kind of coffee beans used because Arabica beans contain less CGA than Robusta beans (Ky et al., 2001). Most commercial brands of coffee are, however, made up of both Arabica and Robusta beans. The roasting method might also play an important role in the CGA content of the final coffee product. For example, the light medium roasting condition was found to result in the highest amount of transformation from CGA to the corresponding lactones, suggesting that this process reduced the amount of CGA in coffee (Farah, de Paulis, Trugo, & Martin, 2005). The amounts of seven CGAs in green coffees were significantly reduced by the degradation occurring during the roasting process (Trugo & Macrae, 1984). The preparation processes, including roasting, may, thus, play an important role in the CGA content of the final product. In the present study, therefore, CGA levels in various commercial coffees were investigated.

2. Materials and methods

2.1. Coffee samples and chemicals

Various brands of commercial ground-roasted coffees were bought from a local market. Caffeine was purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO). Chlorogenic acids (CGA) were bought from Cayman Chemical Co. (Ann Arbor, MI) or a gift from TAKATA Koryo Co., Ltd. (Osaka, Japan). 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 (20 mM) and CGA (20 mM) were prepared in methanol for preparation of standard solutions and spike analysis.

2.2. Preparation of brewed coffee samples

Ground-roasted coffee (12.5 g) was brewed with 450 ml of deionized water using a Mr. Coffee NCX-20 model coffee maker (Sunbeam Product, Inc., Boca Raton, FL) equipped with a paper filter. The brewed coffee was immediately cooled to room temperature in an ice bath, after which the samples were stored at 5 °C until required for pH determination and analysis for caffeine and CGA.

2.3. pH and color measurement

The pH of each brewed coffee sample was measured with a Corning pH meter 430 (Corning, NY). The brewed coffee samples (100 μl) were diluted 10-fold and 100-fold with purified water and the absorbances of the resulting solutions were measured at $\lambda = 276$, 325, and 420 nm with a Hewlett Packard 8452A Diode Array Spectrophotometer running UV–Visible Chemstation software (Agilent Technologies, 1995–2000). Water was used as a blank.

2.4. Analysis of caffeine and CGA in brewed coffee samples

Brewed coffee samples were treated with Carrez reagents I and II to eliminate polymeric components according to a previously reported method (Ito et al., 1983;Rincon, Martinez, & Delgado, 2003). Each brewed coffee sample (3 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. The precipitate was separated by centrifuging at 5000 rpm for 10 min. The solution was then decanted and filtered with a Acrodisc Syringe Filter with 0.2 μm HT Tuffryn membrane (Pall Corporation, Ann Arbor, MI).

Quantitative analyses of caffeine and CGA were performed using an Agilent 1100 model HPLC system equipped with a Zorbax Eclipse XDB C-18 5μ column (150 mm × 4.6 mm i.d.) and a multiple wavelength detector. Mobile phase A was 10 mM citric acid and mobile phase B was methanol. The gradient mode was initially set at A/B ratio of 85/15 from 0 to 5 min, then linearly increased to 60/40 at 40 to 85 min. The flow rate was 1.0 ml/min. The detector was set at 325 nm for CGA and at 276 nm for caffeine; injection volume was 5 μl.

Concentrations of caffeine, CGA, caffeic acid and ferulic acid were calculated using the regression equation of their

Table 1
pH and UV absorbance of brewed coffees

Brand	pH[a]		UV Absorbance at $\lambda =$ [a]					
			276 nm		325 nm		420 nm	
	Regular	Decaffeinated	Regular	Decaffeinated	Regular	Decaffeinated	Regular	Decaffeinated
A	5.99 ± 0.02	5.80 ± 0.01	0.496 ± 0.001	0.298 ± 0.001	0.306 ± 0.001	0.220 ± 0.001	0.273 ± 0.001	0.283 ± 0.004
B	5.22 ± 0.02	5.66 ± 0.01	0.720 ± 0.016	0.406 ± 0.003	0.513 ± 0.011	0.428 ± 0.002	0.397 ± 0.001	0.363 ± 0.003
C	5.26 ± 0.02	5.14 ± 0.01	0.882 ± 0.001	0.634 ± 0.001	0.712 ± 0.001	0.686 ± 0.001	0.458 ± 0.001	0.482 ± 0.005
D	5.17 ± 0.00	5.22 ± 0.01	0.738 ± 0.002	0.559 ± 0.001	0.577 ± 0.001	0.620 ± 0.001	0.384 ± 0.001	0.396 ± 0.003
E	5.12 ± 0.00	5.22 ± 0.01	0.872 ± 0.002	0.553 ± 0.001	0.774 ± 0.001	0.632 ± 0.001	0.370 ± 0.001	0.365 ± 0.001
F	4.95 ± 0.00	–	0.710 ± 0.003	–	0.621 ± 0.002	–	0.369 ± 0.001	–
G	5.21 ± 0.01	–	0.669 ± 0.001	–	0.575 ± 0.001	–	0.334 ± 0.001	–

–: Commercial samples were not available.
[a] Values are means ± SD ($n = 3$).