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The effect of processing on chlorogenic acid content of commercially available coffee

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ABSTRACT

Chlorogenic acids (CGA) are a class of polyphenols noted for their health benefits. These compounds were identified and quantified, using LC–MS and HPLC, in commercially available coffees which varied in processing conditions. Analysis of ground and instant coffees indicated the presence of caffeoylquinic acids (CQA), feruloylquinic acids (FQA) and dicaffeoylquinic acids (diCQA) in all 18 samples tested. 5-CQA was present at the highest levels, between 25 and 30% of total CGA; subsequent relative quantities were: 4-CQA > 3-CQA > 5-FQA > 4-FQA > diCQA (sum of 3,4, 3,5 and 4,5-diCQA). CGA content varied greatly (27.33–121.25 mg/200 ml coffee brew), driven primarily by the degree of coffee bean roasting (a high amount of roasting had a detrimental effect on CGA content). These results highlight the broad range of CGA quantity in commercial coffee and demonstrate that coffee choice is important in delivering optimum CGA intake to consumers.

1. Introduction

Coffee is an extremely popular beverage throughout the world and is the third most commonly consumed after only water and tea (Wang & Ho, 2009). As well as being a rich source of methylxanthines, in particular caffeine (Bunker & McWilliams, 1979), it is also considered to contain relatively high levels of hydroxycinnamates, particularly chlorogenic acids (CGA), which have been noted for their health benefits (Tavares et al., 2012; Vita, 2005; Yang, Wang, Lu, & Picinich, 2009). CGA consists of a quinic acid moiety esterified to one or more hydroxycinnamic acids and to date around 45 CGA have been identified in coffee (Clifford & Jarvis, 1988; Clifford, Johnston, Knight, & Kuhnert, 2003; Clifford, Knight, Surucu, & Kuhnert, 2006; Clifford, Marks, Knight, & Kuhnert, 2006). A 200 ml serving of coffee delivers approximately 15–325 mg of CGA (Richelle, Tavazzi, & Offord, 2001), contributing between 0.5 and 1.0 g intake per day in regular coffee drinkers (del Castillo, Ames, & Gordon, 2002). The most abundant hydroxycinnamic acid derivatives in coffee are quinic acid esters of caffeic (one or two moieties per molecule) and ferulic acid (Fig. 1). Although data are limited, studies suggest that CGA may possess potential health effects, including an ability to reduce the risk of cardiovascular disease (Mubarak et al., 2012) and type two diabetes (van Dijk et al., 2009), whilst there are suggested improvements in cognitive function (Cropley et al., 2012).

Although data indicate that coffee is capable of delivering relatively high amounts of these potentially beneficial compounds, there is limited information regarding the influence of coffee processing on precise levels of CGA delivered per cup. There are a number of processing steps in coffee production which may have a significant impact on CGA content, such as bean fermentation, bean roasting, freeze or spray drying (in the case of instant coffee), decaffeination and/or blending (with non-coffee components). Amongst these, the roasting stage has the most profound effect on the chemical composition, as the low moisture content of the bean and high temperatures facilitate the Maillard reaction; a complex chain of reactions known to lead to many and varying aroma characteristics associated with coffee. It has been reported that CGA are unstable at high temperatures (Dawidowicz & Typek, 2010; Dawidowicz & Typek, 2011), which is likely to be responsible for roasting having a detrimental effect on CGA content (Farah, de Paulis, Trugo, & Martin, 2005; Moon, Yoo, & Shibamoto, 2009; Perrone, Farah, Donangelo, de Paulis, & Martin, 2008; Trugo & Macrae, 1984). Despite there being information of the effects of bean roasting on CGA levels, data relating to the influence of other processing conditions on CGA are limited, and investigations using commercial coffee available in retail outlets, have not been reported. The aim of this study was to investigate CGA levels of a range of commercial coffee brews, which have been subject to different processing and preparation methods in order to understand the potential variation in the amount of CGA consumed by coffee drinkers.

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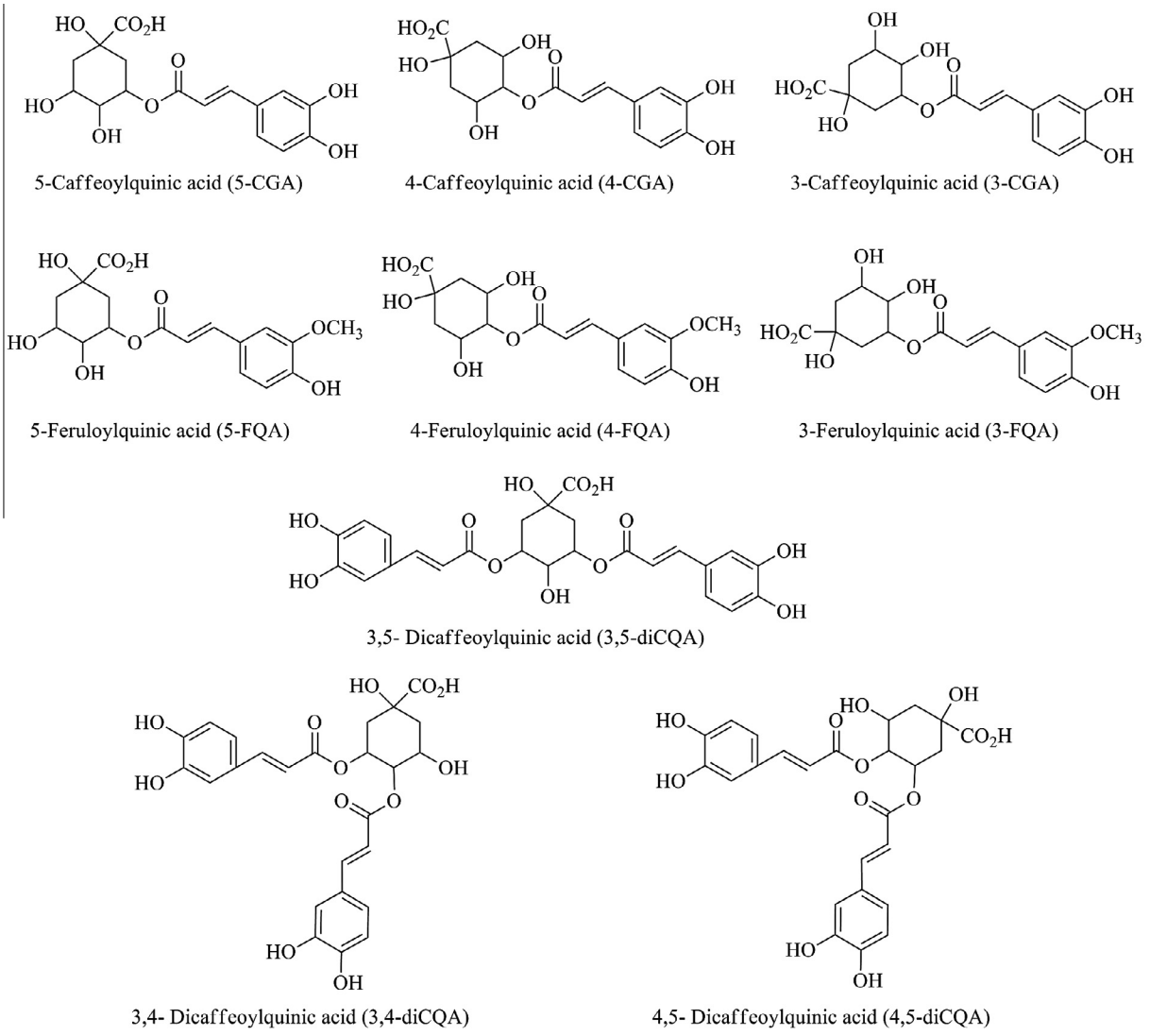

Fig. 1. Structural representation of the major chlorogenic acids found in coffee.

2. Materials and methods

2.1. Chemicals and reagents

5-Caffeoylquinic acid (5-CQA), crystallised zinc acetate, glacial acetic acid and potassium ferrocyanide trihydrate, were all obtained from Sigma–Aldrich (Dorset, UK). Ethanol, HPLC grade; methanol, acetonitrile and hydrochloric acid, LC–MS grade; formic acid, acetonitrile, methanol and water were from Fischer Scientific (Loughborough, UK). Deionised water was prepared using a Purite dispenser.

2.2. Coffee sample preparation

The coffee samples were obtained from two local supermarkets (Tables 1 and 2). Pre-ground coffee (20 g) was extracted by adding 900 ml boiled distilled water (left to stand for 20 s) for 4 min in an 8 cup caffetiere, before plunging through the metal mesh filter. Instant coffee (0.45 g) was extracted by addition of 50 ml of boiled distilled water. All coffee samples were placed on ice immediately after preparation. Prior to either LC–MS^n or HPLC analysis, 1 ml of Carrez I solution (1 M crystallised zinc acetate, acidified with glacial acetic acid), 1 ml Carrez II solution (250 mM potassium ferrocyanide trihydrate) and 0.8 ml ethanol (100%) was added to 4 ml of the coffee extracts for clarification. The samples were vortexed and left to stand for 10 min after which they were centrifuged at 930*g* for 10 min then filtered through a 0.45 μm syringe filter. All extractions were carried out in triplicate for each coffee. Quantities were expressed as 5-CQA equivalents per 200 ml cup, assuming 1.8 g of instant coffee and 11 g of fresh coffee is used, as recommended for domestic use.

Table 1
Sainsbury's pre-ground coffee details.

Name[a]	Roast grade[b]	% *C. arabica*: *C. robusta*	Other
Breakfast	2	100:0	
All day	3	95:5	
Viennese style	3	85:15	12.5% fig
Italian style	4	95:5	
New York style	4	100:0	50% Decaffeinated
French style	4	40:60	45% Chicory
Continental style	5	80:20	
After dinner	5	70:30	

[a] Supermarkets own label.
[b] Roast grade as established by manufacturer.

Table 2
Instant coffee details.

Brand	Name	Other
Nescafé	Gold blend	Golden roast
	Gold blend decaff	Golden roast without caffeine
	Original	Medium-dark roast
	Original decaff	Medium-dark roast without caffeine
	Fine	
	Green blend	Blend of unroasted and roasted beans
Morrisons[a]	Gold	
	Gold decaffeinated	
	Full	
	Full decaffeinated	

[a] Supermarkets own label.

2.3. Liquid chromatography–mass spectrometry (LC–MS^n)

The coffee was analysed by LC–MS^n utilising electrospray ionisation to identify the principle chlorogenic acids in the extracts. LC–MS analyses were performed using an Agilent 1200 Series LC system (Agilent, Palo Alto, CA) equipped with a binary pump, degasser, auto-sampler, thermostat, column heater, photodiode array detector and an Agilent 1100 Series LC/MSD mass trap spectrometer. Separation of samples was achieved using a Zorbax SB C18 column (2·1 × 100 mm; 1·8 μm; Agilent, Santa Clara, CA, USA) and HPLC conditions were as follows: injection volume, 10 μl; column temperature, 25 °C; binary mobile system: (A) 0·1% of aqueous formic acid and (B) 0·1% of formic acid in acetonitrile; flow rate, 0·2 ml/min. A series of linear gradients was used for separation (min/% B): 0/0, 5/4, 40/25, 55/50 and 60/50. MS was performed in the negative ion mode (scan range, m/z 100–800 Da; source temperature, 350 °C). The eluent was monitored by photodiode array detection at 254, 280, 320, 370 and 520 nm and spectra of products were obtained over the 220–600 nm range. All data was analysed using Bruker Daltonics software. Compounds were identified in all of the coffee extracts using three MS fragmentations (Table 3) and by comparing the data with those published by Clifford et al. (2003).

2.4. High performance liquid chromatography (HPLC)

Coffee samples were analysed by HPLC to quantify chlorogenic acids using an Agilent 1100 Series LC fitted with a C_{18} Nova Pak® column (250 × 4.6 mm I.D., 5 μm particle size) and a C_{18} Nova Pak® guard column (Waters Ltd., Elstree, UK). The mobile phases consisted of 5 N hydrochloric acid (0.1%) in 95% water (phase A) and 5% methanol and 5 N hydrochloric acid (0.1%) in 50% acetonitrile and 50% water (phase B) pumped through the column at 0.7 ml min^{-1}. An aliquot of the sample (50 μl) was injected and separated using a gradient system (min/% B): 0/5, 5/5, 40/50, 55/100, 59.9/100, 60/5. The eluent was monitored by photodiode array detection at 254, 280, 320, 370 and 520 nm and spectra of products obtained over the 220–600 nm range. Quantification of CGA was obtained at 320 nm. A standard curve using 5-CQA (0.1–0.6 mM) was constructed with a correlation coefficient of >0.98. All data were analysed using Agilent Chem Station software.

3. Results and discussion

HPLC analysis of the coffee samples indicated the presence of 8 major phenolics acids in all coffee extracts (Fig. 2; 'All Day' coffee given as an example). Using LC–MS^n these eight compounds were identified from their MS spectra (after three MS fragmentations) to be 3, 4 and 5-CQA, 4 and 5-FQA and 3,4, 3,5 and 4,5-diCQA (Table 3). Quantification of CGA content in 18 commercial coffees was expressed as 5-CQA equivalents (mg per 200 ml coffee) in order to allow comparison between instant and ground coffee samples (Tables 4 and 5). Good reproducibility was seen between replicate analyses with all coefficients of variance being less than 8% (average 3%), with the exception of compounds present in small amounts (namely diCQA). Our data indicated that the most abundant phenolics in all coffee samples were caffeoylquinic acids (CQA) with 5-CQA accounting for between 25% and 30% of the total CGA in all of the coffee samples. Quantitatively, the subsequent phenolics were detected in the following amounts in freshly brewed coffee: 4-CQA > 3-CQA > 5-FQA > 4-FQA with the diCQA contributing the least to the total CGA, the sum of all three isomers amounting to just 1.6% of the total chlorogenic acid (Table 4). The same pattern was observed in instant coffee, although, diCQA contributed more to the total CGA at 6% (Table 5).

Information supplied on the front of pack by the manufacturers with regards to the extent of bean roasting (1–5, with '1' being the lowest roast and '5' the most roasted) for ground coffee allowed an approximate assessment of how the extent of roasting influences overall chlorogenic acid content (although it is unclear if a linear relationship between grade and roast extent exists in practice). Specific roasting processes and other variables such as coffee variety and country of origin are unlikely to be identical, and are known to influence CGA content (Clifford and Jarvis, 1988) and may contribute to batch to batch variation. Despite this, our data indicate that the greater the extent to which the coffee has been roasted, the lower the content of CGA; a strong inverse correlation was observed ($r^2 = 0.7$, $p < 0.0001$) (Fig. 3). Our data are in agreement with other studies that have investigated such parameters, although these studies investigate non-commercial coffee or coffees not prepared or extracted to give a representation of the CGA level consumed during standard preparation outside of laboratory conditions (Farah, de Paulis, Trugo, et al., 2005; Moon et al., 2009; Perrone et al., 2008; Trugo and Macrae, 1984). There were some exceptions to this roast/CGA relationship in our sample set, for example, levels of CGA in the two grade 3 coffees ('Viennese' and 'All Day') did not match, potentially reflecting the different bean varieties (C. Robusta versus C. Arabica) (Ky et al., 2001) and other added ingredients ('Viennese' coffee contained

Table 3
Negative ion MS^3 fragmentation data for identification of chlorogenic acids.

Compound	Retention time (min)	MS^1	MS^2				MS^3			
		Parent ion	Base peak (m/z)	Secondary peaks (m/z)			Base peak (m/z)	Secondary peaks (m/z)		
3-CQA	19.1	353.1	190.7	178.7	134.8		126.8	110.7		
4-CQA	25.9	353.2	172.9	178.8	190.8	134.9	154.7	110.8	92.8	
5-CQA	24.8	353.2	190.8	179			126.7	92.7	172.7	
4-FQA	35.2	367.1	178.8	190.9						
5-FQA	32.1	367.2	190.8	172.9	192.8					
3,4-diCQA	41.5	514.9	352.8	334.9	172.7		172.7	178.6	190.7	134.7
3,5-di-CQA	42.3	514.9	352.9				190.7	178.3		172.7
4,5-diCQA	45.6	514.8	352.8				172.7	178.7	190.7	134.7

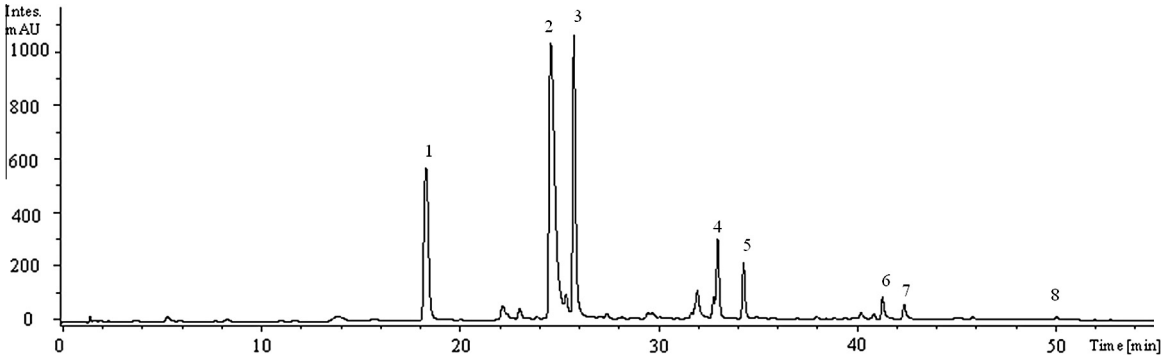

Fig. 2. Example HPLC chromatogram of All Day pre ground coffee (20 g) extracted with 900 ml boiled distilled water for 4 min in an 8 cup caffetiere at 320 nm (1) 3-CQA, (2) 5-CQA, (3) 4-CQA, (4) 5-FQA, (5) 4-FQA, (6) 3,4-diCQA, (7) 3,5-diCQA, (8) 4,5- diCQA.

Table 4
Chlorogenic acid content of commercial fresh ground coffee.

Coffee[b]	Concentration (mg/200 mL cup of brewed coffee)[a]									
	5-CQA	4-CQA	3-CQA	5-FQA	4-FQA	3,4-diCQA	3,5-diCQA	4,5-diCQA	Total	Rank[c]
Breakfast (2)	23.78	14.23	11.92	6.73	2.55	0.44	0.28	0.12	94.47	1
All day (3)	23.41	12.30	10.15	6.13	2.82	0.19	0.23	0.20	79.20	2
Viennese (3)	18.02	9.15	8.20	3.50	2.08	0.28	0.05	0.22	59.29	4
Italian (4)	19.12	10.88	8.85	6.43	3.06	0.14	0.16	0.20	70.90	3
New York (4)	14.40	8.30	6.49	4.72	2.13	0.27	0.06	0.09	52.0	5
French (4)	8.19	4.12	3.66	1.88	1.04	ND	0.24	ND	27.33	8
Continental (5)	8.25	4.46	4.13	3.00	1.76	ND	ND	0.41	31.45	7
After dinner (5)	9.95	5.56	5.09	2.92	1.91	0.34	0.08	0.53	37.68	6

[a] Values are means ($n = 3$).
[b] Commercial roast grade in brackets.
[c] Ranked in order of highest total CGA.

Table 5
Chlorogenic acid content of commercial instant coffee.

Coffee	Concentration (mg/200 mL cup of brewed coffee)[a]									
	5-CQA	4-CQA	3-CQA	5-FQA	4-FQA	3,4-diCQA	3,5-diCQA	4,5-diCQA	Total	Rank[b]
Nescafé fine	21.17	13.62	12.29	2.83	1.56	0.55	0.44	0.10	76.51	2
Nescafé green	41.05	17.12	16.26	2.78	2.09	2.27	2.07	1.22	121.25	1
Nescafé gold	14.39	8.64	8.37	2.11	0.88	0.36	0.49	0.30	50.78	5
Nescafé gold decaf	11.54	7.29	7.31	2.00	0.72	0.72	0.47	0.28	43.26	9
Nescafé original	14.29	8.68	8.41	1.69	0.45	1.01	0.58	0.35	50.67	6
Nescafé original decaf	15.52	9.71	9.13	1.80	0.60	0.95	0.54	0.40	55.24	3
Morrisons gold	12.65	8.72	9.19	0.54	0.88	0.86	0.55	0.75	48.79	7
Morrisons gold decaf	14.10	9.47	9.68	ND	2.04	1.11	0.72	0.72	54.06	4
Morrisons full	9.45	6.67	6.47	0.87	1.68	0.51	0.28	ND	37.04	10
Morrisons full decaf	11.28	7.44	7.42	0.88	2.67	0.74	0.48	0.50	44.88	8

[a] Values are means ($n = 3$).
[b] Ranked in order of highest total CGA.

12.5% fig) (Veberic, Colaric, & Stampar, 2008). Furthermore, although raw chicory roots present at 45% in the 'French' coffee contain CGA (Clifford, Shutler, Thomas, & Ohiokpehai, 1987) levels are much lower than in coffee itself, therefore causing this product to contain less CGA than it otherwise would have.

With regards to the instant coffee, Nescafé Green Blend coffee contains a proportion of green, unroasted coffee and in line with the trend seen with the ground coffee, this coffee had significantly higher total CGA levels ($p < 0.05$) than all of the other instant coffees tested. A clear explanation as to why roasting has such a detrimental effect on CGA is yet to be established, however thermal decomposition of CGA has previously been described, although in aqueous conditions (Dawidowicz and Typek, 2010). Another possibility is that during prolonged heating in dry conditions and at high temperatures, CGA may interact with Maillard reaction intermediates, as has been observed with other polyphenols in model systems (Jiang, Chiaro, Maddali, Prabhu, & Peterson, 2009; Totlani & Peterson, 2005; Totlani & Peterson, 2006).

Assessment of the instant coffees could not easily be made due to a lack of manufacturer information. However, visual assessment allowed division of the instant coffees into three groups: Morrisons Full/Nescafé Original, Morrisons Gold/Nescafé Gold Blend and Nescafé Fine. There was no significant difference between the Morrisons Gold/Nescafé Gold and the Morrisons Full/Nescafé Original coffee in terms of CGA levels. However, the Nescafé Fine coffee contained at least 20 mg CGA/200 ml cup more than the average content of the other two groups (Table 5). In terms of the amount of CGA delivered by instant coffee compared to fresh coffee (prepared by caffetiere), there was less than a 2 mg difference per 200 ml, indicating that although instant coffee is subject to a higher degree of processing, the coffee we assessed is capable of delivering similar amounts of CGA per serving.

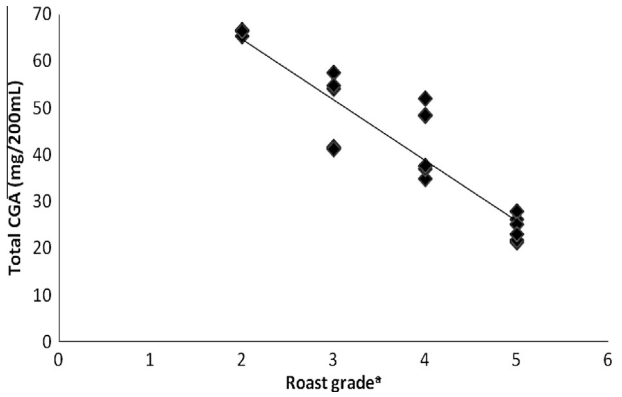

Fig. 3. Correlation between roast grade and total chlorogenic acid/200 ml brewed coffee. $R^2 = 0.8$, $p < 0.0001$. [1]Roast grade as established by manufacture with '1' being the lowest and '5' being the most roasted.

With respect to how decaffeination affects CGA amounts, our data indicate that 3 of the 4 decaffeinated instant coffee varieties appeared to contain more total CGA than their caffeinated equivalents, although statistical analysis of the CGA content for caffeinated versus decaffeinated coffee (by a two tailed t-test), showed no significant difference between the two coffee sets. In addition, with regards to the 'New York' ground coffee, the CGA content of this product also does not seem to be affected by the fact that the coffee is 50% decaffeinated. These data are contradictory to previous work (Farah, de Paulis, Moreira, Trugo, & Martin, 2005), although such data may have been influenced by a specific method used to extract caffeine from coffee. Recent commercial methods, such as supercritical liquid carbon dioxide extraction extract less CGA (Azevedo, Mazzafera, Mohamed, Melo, & Kieckbusch, 2008) thus resulting in less loss during extraction. In addition, our data may have been affected from batch to batch variation and would benefit from a more extensive sample size.

4. Conclusion

In conclusion, these data demonstrate that when preparing commercial coffee as per the manufacturers' guidelines, processing conditions are relevant when calculating the overall level of CGA ingested. Coffees which were roasted to a lesser extent or which contained a proportion of unroasted coffee were favourable with regards to CGA content, whilst there was no difference in CGA level per serving between instant coffee and coffee made by a caffetiere in this sample set. Furthermore, decaffeination seemed to have little or no effect on the CGA content per serving of coffee, although to confirm these predictions it would be necessary decaffeinate a single bean variety and assess CGA levels prior to and after the decaffeination process. The CGA content of the coffee samples analysed ranged from 27.33 to 121.25 mg/200 ml coffee, demonstrating that coffee selection may have a profound influence on an individual's intake of CGA. This may be relevant in light of studies suggesting that CGA may be beneficial to vascular health (Buscemi et al., 2009), where intakes of 400 mg of CGA may reduce systolic and diastolic blood pressure in healthy humans (Mubarak et al., 2012). As a consequence, coffee selection may have a large influence on the potential health potential of coffee intake.

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