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A Study of the Effect of Roasting on the Chlorogenic Acid Composition of Coffee Using HPLC

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ABSTRACT

A method, based on HPLC, described in our previous publication for the analysis of chlorogenic acids in instant coffee, was used in a study of the effect of roasting on the chlorogenic acid composition of Arabica and Robusta coffee. The degradation of seven chlorogenic acids was followed during roasting. Losses of about 60% were observed when mild roasting conditions were used and almost 100% after severe roasting. Considerable differences in degradation rates of individual isomers were observed so that the composition of chlorogenic acids changed throughout the roasting process. Thus the degree of roasting may have a direct influence on the final product flavour as the individual isomers have different sensory properties.

INTRODUCTION

Chlorogenic acid is a trivial name used to describe a range of phenolic acids found in plant materials, including coffee. Chlorogenic acid was first identified as 3-caffeoylquinic acid (Fisher & Dangschat, 1932) and more recently its structure has been designated as 5-caffeoylquinic acid, according to the IUPAC (1976) nomenclature. However, currently, the

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term chlorogenic acid includes at least five groups of isomers of which caffeoylquinic acids (CQA), dicaffeoylquinic acids (diCQA) and feruloylquinic acids (FQA) are the major ones present in coffee (Clifford & Wright, 1976). The determination of the levels of individual chlorogenic acids in coffee and the study of their transformation during coffee processing are important for establishing correlations between the chemical composition and sensory attributes of coffee products and also for quality-control purposes. Studies on the degradation of some chlorogenic acids during coffee roasting have been reported using chromatographic techniques such as paper chromatography (Pictet & Brandenberger, 1960) and gas liquid chromatography (Kung *et al.*, 1967). More recently, high-performance liquid chromatography (HPLC) has shown better resolution of the chlorogenic acids and, as an additional advantage, it avoids the derivatization step, necessary for GLC (van der Stegen & van Duijn, 1980; Trugo & Macrae, 1984). In a recent study, HPLC was used for the determination of five chlorogenic acids in green (Maier & Grimsehl, 1982*a*) and roasted coffee (Maier & Grimsehl, 1982*b*). In the present work the range of chlorogenic acids analysed was extended and diagrams showing the rate of degradation of individual isomers are presented.

MATERIALS AND METHODS

Sample preparation

Green Arabica (Guatemala) and green Robusta (Uganda) coffee beans were supplied by the coffee industry. One part (5 kg) of the same batch of each Arabica and Robusta coffees were industrially roasted in a Probat pilot roaster at 205 °C. Four different degrees of roasting were obtained and classified according to their colour. The roasting time was compared after the roaster had recovered the roasting temperature. The time to recover the temperature of roasting (205 °C) was 4–5 min for the Robusta and 3–4 min for the Arabica coffee. The coffee samples were then ground in a laboratory scale mill (Brook Motors Ltd, Great Britain) and sieved to pass through a 0·841 mm sieve. The ground coffee (approximately 0·2 g for green and 2 g for roasted) was extracted by shaking with hot water (10 ml) for 15 min in a boiling water bath using a 50 ml stoppered centrifuge tube. The mixture was centrifuged for 10 min (1500 *g*), the

supernatant transferred to a 100 ml volumetric flask and the residue re-extracted twice as above. Carrez solution (Pearson, 1976) (1 ml of each component for the green and 2 ml for the roasted coffee) was added to the combined extracts, the mixture made up to volume, stirred and allowed to stand for 10 min. This mixture was then filtered under gravity (Whatman No. 1 filter paper) and the filtrate used directly for chromatography.

Chromatography

The chromatographic method and all analytical conditions were the same as described previously (Trugo & Macrae, 1984).

RESULTS AND DISCUSSION

The characteristics of the coffee samples used in this study are shown in Table 1. Seven chlorogenic acids were quantified in the green and roasted samples, including the caffeoylquinic acids and also the major isomer of the feruloylquinic acid group (5-feruloylquinic acid). The extraction procedure using 40% (v/v) aqueous methanol, which proved successful for the determination of chlorogenic acids in instant coffees (Trugo & Macrae, 1984), produced low recoveries, particularly for the dicaffeoylquinic acids, when green and roasted coffees were studied. However,

TABLE 1
Roasting Characteristics of the Arabica and Robusta Coffees

Type of Roast	*Arabica coffee*			*Robusta coffee*		
	Roasting time (min)	*Roasting loss (%)*[a]	*Moisture (g %)*[b]	*Roasting time (min)*	*Roasting loss (%)*[a]	*Moisture (g %)*[b]
Light	7	3·8	2·1	5	2·4	2·3
Medium	10	3·7	2·1	7	4·0	1·9
Dark	13	10·0	1·8	14	8·3	1·8
Very dark	19	9·8	1·7	16	7·8	1·3

[a] Dry matter basis.
[b] Moisture content of green beans: Arabica, 8·4%; Robusta, 7·9% (determined by the vacuum oven method (Pearson, 1976)).

improved recoveries were achieved when these samples were exhaustively extracted (three times) with hot water (100 °C). Subsequent clearing of these aqueous extracts with Carrez solution (Pearson, 1976) did not result in a significant loss of chlorogenic acids, as for the instant coffee extracts (Trugo & Macrae, 1984). The use of a purely aqueous extract also avoids the adverse effect of high concentrations of a more hydrophobic solvent in the injected sample. This can lead to distortion of the chromatographic peaks, a phenomenon which was observed in this work and which has been well documented in other applications (Tsimidou & Macrae, 1984). The separation of 4-caffeoylquinic and 3-feruloylquinic acids was not adequate and they were included in the same chromatographic peak. However, as 3-feruloylquinic acid is present in coffee only at very low levels (van der Stegen & van Duijn, 1980) compared to the caffeoylquinic acids, the error introduced in the quantification of 4-caffeoylquinic acid will not alter significantly the results for the proportional distribution of the caffeoylquinic acid isomers in the samples.

The results obtained for the green coffees are presented in Table 2. The Arabica coffee showed considerably lower levels of chlorogenic acids than the Robusta coffee with 5-caffeoylquinic acid being the major component in both coffees. This isomer represented about 66% of the total chlorogenic acids in the Arabica and about 56% in the Robusta green coffee. The caffeoylquinic acid isomers were always present in much higher proportions than the other group of isomers. In the green Arabica the level of 3,5-dicaffeoylquinic acid was significantly higher than the other isomers of this group but in the Robusta green coffee there was little difference in the distribution of these isomers. The amount of 5-feruloylquinic acid in the green Robusta coffee was more than double that found in the Arabica sample but in both cases it represented only a small fraction of the total. These observations as to the relative amounts of individual isomers within each group of chlorogenic acids are similar to those reported by other workers (van der Stegen & van Duijn, 1980; Maier & Grimsehl, 1982*a*).

After roasting, considerable change in the chlorogenic acid composition occurred in both coffee samples. In the Arabica coffee the level of 5-caffeoylquinic acid decreased steadily after light roasting while 4-caffeoylquinic acid decreased only slightly and the 3-caffeoylquinic acid actually increased (Fig. 1A). This increase of the 3-isomer after roasting has also been observed by Kung *et al.* (1967) and Maier & Grimsehl (1982*b*). Formation of 3-caffeoylquinic acid on roasting can logically

TABLE 2

Content of Chlorogenic Acids in Green and Roasted Coffees and Percentage Loss During Roasting[a]

Coffee	*Chlorogenic acids*	*Green coffee*	*Type of roasting*[b]							
			Light	*Loss*	*Medium*	*Loss*	*Dark*	*Loss*	*Very dark*	*Loss*
Arabica (Guatemala)	3-CQA	4·59	4·85	−5·7	4·02	12·4	1·59	65·4	0·53	88·5
	4-CQA[c]	7·68	6·86	10·7	5·70	25·8	2·26	70·6	0·71	90·8
	5-CQA	45·34	12·08	73·4	10·12	77·7	3·25	92·8	0·98	97·8
	Total CQA	57·61	23·78	58·7	19·84	65·6	7·10	87·7	2·22	96·1
	5-FQA	2·49	0·86	65·5	0·84	66·3	0·30	88·0	0·08	96·8
	3,4-diCQA	2·13	0·77	63·8	0·52	75·6	0·12	94·4	n.d.[d]	100
	3,5-diCQA	4·95	0·63	87·3	0·44	91·1	0·06	98·8	0·04	99·2
	4,5-diCQA	1·59	0·84	45·2	0·57	64·2	0·13	91·8	0·08	95·0
	Total diCQA	8·67	2·24	74·2	1·53	82·4	0·31	96·4	0·12	98·6
	Total	68·77	26·88	60·9	22·21	67·7	7·71	88·8	2·42	96·5
Robusta (Uganda)	3-CQA	7·32	6·81	7·0	4·10	44·0	1·26	82·8	0·35	95·2
	4-CQA[c]	11·25	9·52	15·4	5·95	47·1	1·84	83·6	0·53	95·3
	5-CQA	49·66	13·87	72·1	7·77	84·4	2·07	95·8	0·53	98·9
	Total CQA	68·23	30·20	55·7	17·82	73·9	5·17	92·4	1·41	97·9
	5-FQA	6·04	2·39	60·4	1·50	75·2	0·46	92·4	0·11	98·2
	3,4-diCQA	5·05	1·02	79·8	0·45	91·1	0·14	97·2	n.d.	100
	3,5-diCQA	4·61	0·83	82·0	0·36	92·2	0·08	98·3	n.d.	100
	4,5-diCQA	4·11	1·00	75·7	0·61	85·2	0·30	92·7	0·24	94·2
	Total diCQA	13·77	2·85	79·3	1·42	89·7	0·52	96·2	0·24	98·3
	Total	88·04	35·44	59·7	20·74	76·4	6·15	93·0	1·76	98·0

[a] Results are average of duplicate determinations expressed in $g\,kg^{-1}$ on a dry green bean basis.

[b] Roasting conditions as in Table 1.

[c] Values correspond to 4-CQA plus 3-FQA.

[d] n.d.—Not detected.

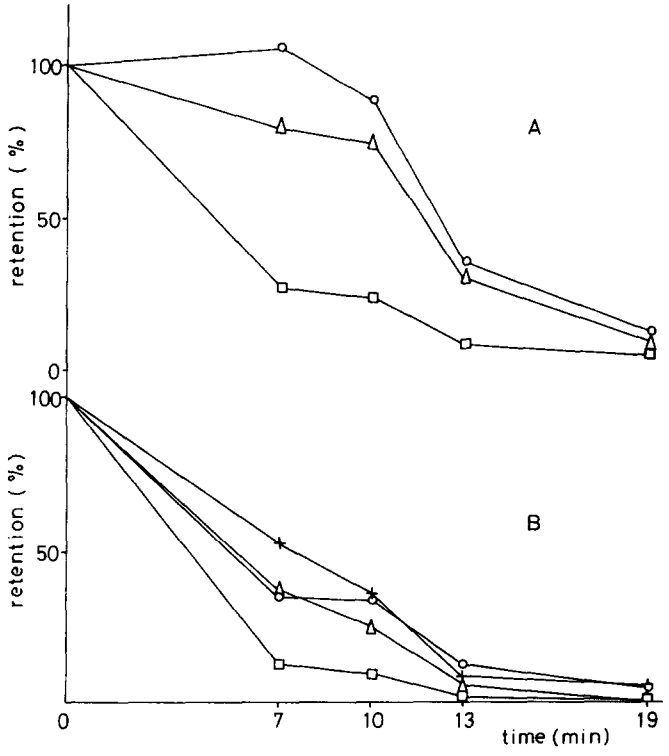

Fig. 1. Degradation of chlorogenic acids during roasting of Arabica (Guatemala) coffee. (A)—(○) 3-caffeoylquinic acid; (△) 4-caffeoylquinic acid + 3-feruloylquinic acid; (□) 5-caffeoylquinic acid. (B)—(+) 4,5-dicaffeoylquinic acid; (□) 3,5-dicaffeoylquinic acid; (△) 3,4-dicaffeoylquinic acid; (○) 5-feruloylquinic acid.

arise from either isomerisation of the 5-isomer, which is present in much larger amounts, or from partial decomposition of the dicaffeoylquinic acids. Under the conditions prevalent during roasting, i.e. low water content and moderate acidity, the latter would seem more likely and the 3,5-isomer would appear to be the more likely source as it was present in larger amounts than the 3,4-isomer. This is supported by the fact that this compound decreased its level sharply during the roasting process (Fig. 1B). In the Robusta coffee, 5-caffeoylquinic acid decomposed more rapidly than the 3- and 4-isomers (Fig. 2A), with levels of all the isomers decreasing immediately even under mild roasting conditions, in contrast to the Arabica sample.

Little difference was observed in the rates of degradation of the

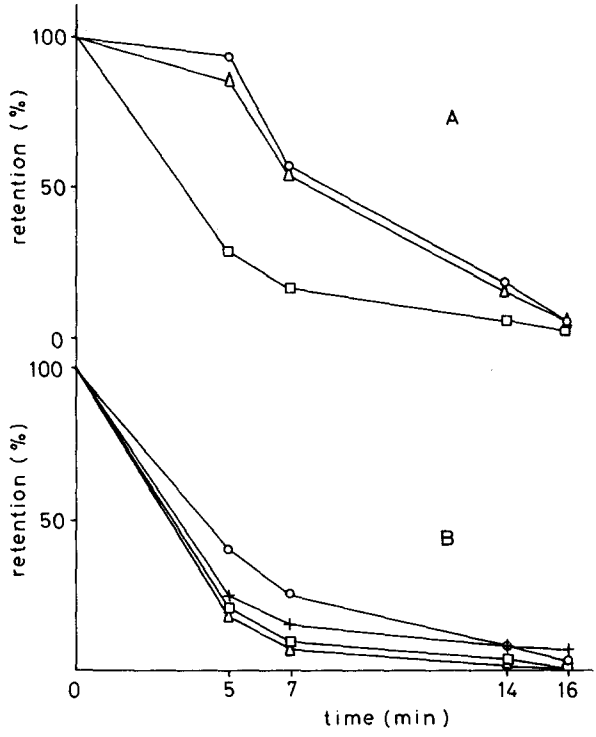

Fig. 2. Degradation of chlorogenic acids during roasting of Robusta (Uganda) coffee. (A)—(○) 3-caffeoylquinic acid; (△) 4-caffeoylquinic acid + 3-feruloylquinic acid; (□) 5-caffeoylquinic acid. (B)—(+) 4,5-dicaffeoylquinic acid; (△) 3,5-dicaffeoylquinic acid; (□) 3,4-dicaffeoylquinic acid; (○) 5-feruloylquinic acid.

dicaffeoylquinic acids. However, the 5-feruloylquinic acid did degrade at a slower rate compared to the dicaffeoylquinic or caffeoylquinic acids (Fig. 2). The relative stability of feruloylquinic acids has been noted by Pictet and Rehacek (1983) although there is no simple explanation as to why this should be so. Reports have also been made of increases in the levels of 3-feruloylquinic acid and 4-feruloylquinic acid in certain lightly roasted samples (van der Stegen & van Duijn, 1980) but this was not confirmed in the present work as these isomers were not individually quantified. Indeed these apparent increases may be due to inadequately resolved peaks as, at least in the case of the 4-feruloylquinic acid, van der Stegen & van Duijn (1980) show evidence of unidentified co-eluted material. The thermal stability of individual isomers appears to be

influenced by the coffee species with Robusta showing consistently faşter rates of degradation than the Arabica coffee (Figs 1 and 2).

The caffeoylquinic acids which were present at higher levels in the green and lightly roasted Robusta coffee were, in contrast, higher in the more highly roasted Arabica coffee. However, the total dicaffeoylquinic acids were always higher in the Robusta samples with the 4,5-isomer being the major contributor. It is interesting to note that even with these considerable differences in rates of loss of individual chlorogenic acids between the two coffees, particularly under mild roasting conditions, the percentage losses of the total chlorogenic acids were similar (Table 2).

Since it is generally accepted that Robusta coffees are inferior in quality to Arabicas and, if chlorogenic acids actually provide any significant sensory contribution to the beverage, it appears that the dicaffeoylquinic acids and also the feruloylquinic acids (in this case 5-feruloylquinic acid) are the main chlorogenic acids responsible for this property. Assuming that the dicaffeoylquinic acid isomers have the same sensory threshold and knowing that these isomers have a 'peculiar lingering metallic taste' (Clifford & Ohiokpehai, 1983) that may influence coffee acceptability, then 4,5-dicaffeoylquinic acid may play a major role in this negative sensory effect, since its level was always higher in the Robusta coffee.

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