Changes of Antioxidant Capacity of Robusta Coffee during Roasting

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Abstract: The *in vitro* radical scavenging capacity of the roasted and ground coffee is generally known as well as the published results of lowering the incidence of various diseases by regular intake of coffee. The antioxidant capacity of coffee is based mainly on the phenols, but during the roasting phenols are degraded and new products with antioxidant capacity are formed. A major contributor to the antioxidant activity was identified as N-methylpyridinium, which is formed during the roasting by degradation of trigonelline, the degradation is about 50% of trigonelline content and the concentration of N-methylpyridinium in roasted coffee is up to 0.25% on a dry weight basis. These literature data were verified within the processing plant experiment, during the usual roasting procedure of Robusta coffee the following parameters were analysed: humidity, water activity, total antioxidant capacity, total phenols, chlorogenic acid and trigonelline content, and colour (L^*, a^*, b^*). The changes of the evaluated parameters were correlated to each other. During the roasting the total antioxidant capacity (TAC) decreased to about one half of original level in the beginning stages of roasting, another decrease continued during the storage of roasted coffee at about 10% within the year. The degradation of trigonelline, neither the content of chlorogenic acid or total phenols did not correlate with TAC in samples during the roasting and storage.

Keywords: coffee; antioxidant capacity; trigonelline; chlorogenic acid

INTRODUCTION

Coffee is one of the most popular beverages consumed daily throughout the world. Recent studies have indicated that the coffee constituents like caffeine, the phenolic compounds, chlorogenic acids and hydroxycinnamic acids, or the compounds formed from Maillard reactions, like melanoidins, have antioxidant properties. According to Svilaas coffee based drinks contribute to 64% of the total antioxidant intake, followed by fruits, berries, tea, wines, cereals and vegetables (Svilaas *et al*. 2004).

Green coffee beans are rich in the phenolic compounds exemplified by chlorogenic acid, caffeic acid, ferulic acid and *p*-coumaric acid. Coffee is the major source of chlorogenic acid in the human diet. On the basis of 10 g of coffee per cup of brew, a cup contains 15–325 mg of chlorogenic acids; daily intake of coffee drinkers is 0.5–1.0 g, whereas coffee abstainers typically ingest < 100 mg/day (Richelle *et al.* 2001; Castillo *et al*. 2002). Roasting markedly affects the composition of coffee. Roasting is comprised of two consecutive phases. The first phase corresponds to the drying (bean's temperature below 160°C) and the second phase is the roasting (bean's temperature between 160 and 260°C). In this second phase, pyrolytic reactions start at 190°C causing oxidation, reduction, hydrolysis, polymerisation, decarboxylation and many other chemical changes, leading to the formation of substances essential to give among other, the sensory qualities of the coffee. The moisture loss and chemical reactions are accom-

panied by important changes in colour, volume, mass, form, bean pop, pH and density, volatile components and CO_2 generates, a part of which escapes and other part is retained in the cells of the beans. After this second phase, the beans must be rapidly cooled to stop the reactions (using water or air as cooling agent) and to prevent an excessive roast which alter the quality of the product. During the process, several parameters can be used as indicators to determine the degree of roasting (aroma, flavour, colour, bean's temperature, pH, chemical composition, bean pop, mass loss, gas composition and volume) (Hernandez *et al*. 2007). Although compounds with antioxidant properties are lost during roasting of coffee beans, the overall antioxidant properties of coffee brews can be maintained, or even enhanced, by the development of compounds possessing antioxidant activity, including Maillard reaction products (Castillo *et al.* 2002).

A major contributor to the antioxidant activity was identified as *N*-methylpyridinium. The levels of 1-methylpyridinium in roasted and ground coffee are positively correlated to the degree of roasting (Stadler *et al*. 2002a,b). Methylpyridinium is not present in raw coffee beans but it is formed during the roasting process from its chemical precursor, trigonelline, which is common in raw coffee beans. Trigonelline is the second most abundant alkaloid in green coffee and reaches levels in *Coffea arabica* and *Coffea canephora* var. *robusta* from 7.9 to 10.6 g/kg and from 6.6 to 6.8 g/kg, respectively (Stennert & Maier 1994).

The aim of the presented work was to evaluate the influence of the roasting degree and storage conditions on the changes of the overall antioxidant capacity and other parameters of the low-end Robusta coffee.

MATERIAL AND METHODS

Samples. Coffee beans (blend of Robusta from Vietnam, Guinea, Uganda, Indonesia) were conventionally roasted. The samples of coffee were taken during the roasting: 5 minute (160°C), 10 min (225°C), 12 min (cooling), 30 min (storage tank). The coffee beans were finely ground prepared by solid-liquid extraction with deionised water. The coffee powder (0.5 g) was mixed with 100 ml deionised water at 90°C and extracted for 10 minutes. The samples were then filtered through Whatman No. 1 filter paper and a microfilter (0.45 μm). All analyses were performed with freshly prepared coffee brews.

Methods. The total antioxidant capacity (TAC) was measured by 2,2-diphenyl-1-picrylhydrazyl (DPPH). The total polyphenols content was determined using the Folin-Ciocalteu method. The total antioxidant capacity and the content of polyphenols were expressed in milligrams of chlorogenic acid. The content of chlorogenic acid (CGA) and trigonelline was measured with HPLC. HPLC analyses were performed with a Dionex Summit Chromatograph, equipped with 250 × 4.6 mm Synergi 4 μm Hydro-RP, 80 A, Phenomenex column and UV-VIS detector. Elution was carried out with two solvents, 5mM KH_2PO_4 in redistilled water (A) and mixture of 80% methanol and 5mM KH_2PO_4 (B). The samples were eluted for 20 min at a flow rate of 1 ml per min, with a gradient. The column temperature was 20°C and UV detection was at 265 nm for trigonelline and 325 nm for CGA. Sample's moisture was determined by drying at 103 ± 2°C until constant weight, in order to express the results on a dry weight basis (dwb). Colour analysis of the ground coffee was carried out using a tristimulus colorimeter Minolta CM-2600d spectrophotometer (Minolta, Osaka, Japan). Colour was expressed in L^*, a^*, b^* Cielab scale parameters. Colour change was described as $\Delta E = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$. Water activity was measured by the chilled mirror dew point method. The Experimental results were expressed as means ± SD of three parallel replicates.

RESULTS AND DISCUSSION

Coffee is believed to be the most important source of natural antioxidants in the diet. The recent studies suggest that the most important antioxidant in coffee is methylpyridinium which is formed by degradation of trigonelline during the roasting process (Stennert & Maier 1994; Stadler *et al*. 2002a, b). The several parameters including trigonelline, chlorogenic acid, the total polyphenols content and the total antioxidant capacity were followed during the roasting and subsequent storage of the Robusta coffee. The results are given in Figure 1 and in Table 1, there are summarised the changes in the water content, the water activity, and colour during the roasting and storage of coffee. From the results it is

Table 1. The changes of moisture, water activity and Cielab scale parameters during the roasting of coffee beans

Blend of green beans Robusta		H_2O	a_w	Colour parameters			
				L^*	a^*	b^*	ΔE
Green beans		11.62 ± 0.03	0.638 ± 0.006	46.90 ± 2.05	4.00 ± 0.28	11.62 ± 0.03	0.00
Roasting	5 min at 160°C	7.06 ± 0.05	0.372 ± 0.004	56.03 ± 1.43	4.41 ± 0.18	7.06 ± 0.05	9.47
	10 min at 215°C	2.08 ± 0.03	0.058 ± 0.001	38.59 ± 2.40	8.74 ± 0.71	2.08 ± 0.03	9.78
	12 min after water cooling	4.16 ± 0.02	0.242 ± 0.001	37.33 ± 3.36	8.08 ± 1.02	4.16 ± 0.02	11.17
	20 min storage tank	4.79 ± 0.03	0.278 ± 0.003	34.59 ± 1.75	8.03 ± 0.96	4.79 ± 0.03	13.48
Storage	11 days at 20°C	4.59 ± 0.03	0.284 ± 0.001	35.12 ± 2.04	8.23 ± 0.88	4.59 ± 0.03	13.13
	6 months at 20°C	4.28 ± 0.03	0.337 ± 0.002	36.25 ± 3.21	8.47 ± 1.04	4.28 ± 0.03	11.93
	1 year at 20°C	5.00 ± 0.03	0.419 ± 0.004	37.56 ± 2.46	7.96 ± 0.68	5.00 ± 0.03	10.82

Table 2. The correlation matrix (r – the linear correlation coefficient) of the followed markers during the roasting and storage of coffee beans

r	H_2O	a_w	L^*	a^*	b^*	ΔE	PPH	CGA	TRIG	TAC
H_2O		0.92	0.61	–0.90	0.58	–0.83	0.91	0.75	0.59	0.67
a_w	0.92		0.43	–0.74	0.37	–0.68	0.73	0.53	0.24	0.50
L^*	0.61	0.58		–0.89	0.97	–0.56	0.42	0.97	0.73	0.24
a^*	–0.90	–0.74	–0.89		–0.86	0.76	–0.79	–0.96	–0.77	–0.52
b^*	0.58	0.37	0.97	–0.86		–0.57	0.54	0.96	0.78	0.39
ΔE	–0.83	–0.68	–0.56	0.76	–0.57		–0.93	–0.69	–0.65	–0.69
PPH	0.91	0.73	0.50	–0.79	0.54	–0.93		0.69	0.71	0.86
CGA	0.75	0.53	0.97	–0.96	0.96	–0.69	0.69		0.84	0.46
TRIG	0.59	0.24	0.73	–0.77	0.78	–0.65	0.71	0.84		0.58
TAC	0.67	0.50	0.24	–0.52	0.39	–0.69	0.86	0.46	0.58	

$r_{(crit)} = 0.63$; $n = 8$, $P < 0.05$

H_2O – moisture (%); a_w – water activity at 20°C; L^*, a^*, b^*, ΔE – Cielab scale parameters; PPH – polyphenols (mg CGA/g dwb); CGA – chlorogenic acid (mg/g dwb); TRIG – trigonelline (mg/g dwb); TAC – total antioxidant capacity (mg CGA/g dwb); dwb – dry weight basis

obvious that the total antioxidant capacity (TAC) decreased within the beginning period of roasting, than the value varied around the 50% of the initial level. No trends were observed in the total polyphenols content, probably due to the not very specific analytical procedure, but the content of chlorogenic acid increased in the beginning stage of roasting due to the decomposition of phenolic acids and then it decreased also during the subsequent storage of roasted beans. The trigonelline content also decreased, the content in the roasted beans was about 50% of its initial value in green coffee. The correlation matrix was calculated for the all followed parameters, surprisingly the TAC correlated neither with chlorogenic acid content nor with polyphenols. The correlation was found between the TAC and the trigonelline content, but surprisingly positive and the TAC value correlated also with water content in coffee and colour. In spite of the published data the formation of new antioxidants (expressed as the TAC by the DPPH reaction) during the roasting of Robusta coffee was not so important as degradation of natural antioxidants in green coffee

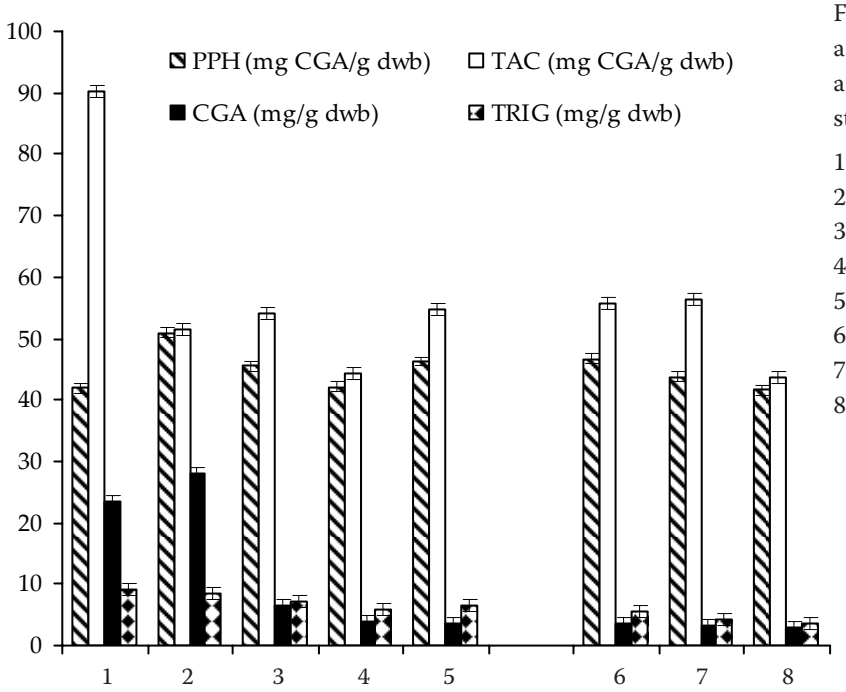

Figure 1. The changes of polyphenols, antioxidant capacity, chlorogenic acid and trigonelline during the roasting and storage of coffee beans

1 – green beans
2 – roasting – 5 min at 160°C
3 – roasting – 10 min at 215°C
4 – roasting – 12 min after water cooling
5 – roasting – 20 min storage tank
6 – storage – 11 days at 20°C
7 – storage – 6 months at 20°C
8 – storage – 1 year at 20°C

beans. The TAC decreased to the about half level and the slow decrease continued also during the storage of roasted coffee beans.

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