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Influence of torrefacto roast on antioxidant and pro-oxidant activity of coffee

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Abstract

The addition of sugar at the end of the torrefacto roasting process may influence the antioxidant and pro-oxidant properties of coffee because sugar is one of the main precursors the Maillard reaction. The aim of the work was to study and to compare the antioxidant and pro-oxidant properties of some commercial roasted coffees which are selected to represent conventional roasted arabica coffee and arabica/robusta blends, and torrefacto roasted blends. Higher antioxidant activity was observed in Colombian coffees than in conventional roasted coffee blends. On the other hand, when the percentage of torrefacto coffee was increased, an increase of the antioxidant activity and a slight tendency to decrease the pro-oxidant activity were observed. Moreover, principal component analysis allowed separation of: (a) brands by PC1 (46.9%), characterised by colour parameters defined by roasting degree and (b) torrefacto roasted blends by PC2 (33.7%), characterised by antioxidant/pro-oxidant activity.

Keywords: Coffee; Antioxidant activity; Pro-oxidant activity; Torrefacto roast; Color; Maillard reaction

1. Introduction

Following the disclosure of epidemiological associations between diet and health, in recent years increased attention has been paid to those foods potentially exerting antioxidant capacity. In heat-treated foods, such as coffee and related beverages, this property is generally the result of the contribution of both natural and heat-induced antioxidants. In fact, during very intense heat treatments, such as the roasting of coffee, the loss of antioxidant activity of natural antioxidants – mainly represented by polyphenols – by progressive thermal degradation, has been found to be minimised by the formation of Maillard reaction products (MRPs). Thus, the total antioxidant properties of coffee brews may be maintained or even enhanced (Daglia, Papetti, Gregotti, Berte, & Gazzani, 2000; Nicoli, Anese, Parpinel, Franceschi, & Lerici, 1997a; Nicoli, Anese, & Parpinel, 1999). Beyond their influence on colour and aroma, MRPs were found to affect the oxidative stability of many processed foods and to play an important role as health protecting factors (Ames, 1988; O'Brien & Morrissey, 1989; Rizzi, 1994). Since the development of the Maillard reaction seems to play a key counter balancing role in the thermal degradation of naturally occurring phenolics, the overall antioxidant capacity of roasted coffee is expected to depend strictly on the extent of the Maillard reaction developed during roasting (Andueza, Cid, & Nicoli, 2004). Moreover, positive correlation between colour and antioxidant properties has been found in the case of the development of Maillard reactions in model systems and in other food products (Manzocco,

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Calligaris, Mastrocola, Nicoli, & Lerici, 2001), but not in coffee (Nicoli et al., 1997a).

On the other hand, coffee was demonstrated to act in vitro as a pro-oxidant (Turesky, Stadler, & Leong-Moergenthaler, 1993). In fact, pro-oxidant molecules formation has been observed in model systems and foods during the early phases of Maillard browning (Nicoli et al., 1997a; Roberts & Lloyd, 1997) while, in the advanced stages, antioxidant products seem to prevail (Manzocco et al., 2001). In addition, Turesky et al. (1993) proposed that some pro-oxidant compound formation appears to result from polyphenolic thermal degradation products of chlorogenic and caffeic acids in model systems.

The addition of sugar at the end of the torrefacto roasting process may influence the antioxidant and pro-oxidant properties of coffee because sugar is one of the main precursors in the Maillard reaction. Some authors (Andueza et al., 2004) have observed high antioxidant activity in torrefacto coffees, but no studies on torrefacto roasted commercial blends have been reported. Furthermore, the variety of coffee could also have an influence on the antioxidant and pro-oxidant activities because of different contents of polyphenolic compounds, such as chlorogenic acids (Richelle, Tavazzi, & Offord, 2001). From the commercial point of view, arabica coffee *(Coffea arabica)* is the most highly produced variety in the world (62%), whereas robusta coffee (*Coffea canephora var. Robusta*) has been responsible for 38% of the produced coffee on the world market during the past year (ICO, 2004). Blends of arabica and robusta coffees are commonly used by consumers. However, most of studies focus on one variety of controlled roasted coffees, which are very useful for understanding the reactions and their consequences, but less for consumers.

Therefore, the aim of the present work was to study and to compare the antioxidant and pro-oxidant properties of some commercial roasted coffees, which are selected to represent conventional roasted arabica coffee and arabica/robusta blends, and torrefacto roasted blends.

2. Materials and methods

2.1. Chemicals and reagents

The methanol used was of spectrophotometric grade from Panreac (Barcelona, Spain). 2,2-Diphenyl-1-picrylhydrazyl (DPPH·) was from Aldrich (St. Quentin Fallavier, France).

2.2. Coffee samples

Eleven commercial roasted coffee samples were purchased in a local market: two pure *C. arabica* from Colombia (0Co), three conventional roasted coffees (0), two blends with 30% torrefacto roasted coffee (30), two blends with 50% torrefacto roasted coffee (50) and two 100% torrefacto roasted coffees (100). Four brands (A, B, C, D) were chosen among those most consumed. Two batches of each coffee sample were analysed. All coffees were stored under similar conditions before and during analysis.

2.3. Sample preparation

Coffee extract was obtained by solid-liquid extraction, using deionized water at 100 °C, under nitrogen atmosphere. The ratio between coffee and water was 10/100 (g/ml). The extraction time was 10 min. The extract was immediately cooled in cold running water and filtered through Whatman No. 4 filter paper.

2.4. Colour analysis

Colour analysis was carried out both on ground roasted coffees and their extracts using a tristimulus colorimeter (Chromameter-2 CR-200, Minolta, Osaka, Japan). The instrument was standardised against a white tile before sample measurements. Colour was expressed in L^*, a^* and b^* Cielab scale parameters.

2.5. Antioxidant activity

The antioxidant activity was measured by using the DPPH· (2,2-diphenyl-1-picrylhydrazyl) decolorization assay (Brand-Williams, Cuvelier, & Berset, 1995). A 6.1×10^{-5} M DPPH· methanol solution was prepared immediately before use. The DPPH· solution was adjusted with methanol to an absorbance of 0.7 (±0.02) at 515 nm in a 1-cm cuvette at 25 °C (Lambda 25 UV–Vis spectrophotometer, Perkin–Elmer Instruments, Madrid, Spain). Coffee extracts were diluted 1:50 in water prior to analysis. Samples (20 μl) were added to DPPH· solution (1.98 ml). After mixing, the absorbance was measured at 515 nm after exactly 1 min, and then every minute for 18 min, with incubation at 25 °C. Reaction rates were calculated using the equation proposed by Manzocco, Anese, and Nicoli (1998).

$1/\mathrm{Abs}^3 - 1/\mathrm{Abs}_0^3 = -3kt$, where k is the DPPH· bleaching rate, Abs_0^3 is the initial absorbance value, and Abs^3 is the absorbance at increasing time, t. The antioxidant activity was expressed as slope obtained from the equation ($-\mathrm{Abs}^3\ \mathrm{min}^{-1}$) per g of sample.

2.6. Pro-oxidant activity

The pro-oxidant activity was determined using crocin as a radical quencher, according to the method described by Manzocco, Calligaris, and Nicoli (2002). Crocin was isolated from commercial saffron. Saffron (0.6

g), previously washed with ethyl ether, was extracted with methanol. The crocin solution was adjusted with 0.1 M phosphate buffer, (pH 7.0) to an absorbance of 1.8 (±0.02) at 443 nm in a 3-ml capacity cuvette (1 cm length) at 40 °C (Lambda 25 UV–Vis spectrophotometer Perkin–Elmer Instruments, Madrid, Spain). Coffee extracts were diluted 1:50 in water prior to analysis. Samples (20 μl) were added to crocin solution (1.9 ml) together with phosphate buffer (80 μl). Absorbance was monitored at 443 nm for 10 min. The decrease in absorption at 443 nm, 5 min after addition of sample, was used for calculation of the pro-oxidant capacity. The pro-oxidant activity was expressed as the decrease in crocin absorbance at 443 nm after 5 min of reaction per g of sample ($\Delta OD_{5\,min}\ g^{-1}$).

2.7. Redox potential

The redox potential measurements of the coffee samples were made with a platinum indicating electrode connected to a voltmeter (mod. 2002, Crison, Spain). Calibration was performed against 220 and 468 mV redox standard solutions at room temperature (Crison, Spain). Electrodes were placed in a 50-ml 3-neck flask containing a volume of 16 ml of coffee extract sample, together with 20 ml of deionized water. Prior to analysis, oxygen was removed from the system by continuous nitrogen flushing for a period of 10 min. Milivolt values were recorded for at least 15 min at room temperature, until a stable potential was reached. A stable redox potential was arbitrarily defined as a change of less than 1 mV in a 3-min period.

2.8. Statistical analysis

Each coffee sample was analysed in triplicate. All results are shown as means and standard deviations. Analysis of variance (ANOVA) was applied to the colour data, antioxidant activity, pro-oxidant activity and redox potential. Tukeys test was applied test a posteriori with a level of significance of 95%. Principal component analysis (PCA) was applied to the analytical data (based on the Pearson correlation matrix) to observe differences among coffees samples. Principal components (PC) with eigenvalues greater than 1 were selected. All statistical analyses were performed using the SPSS v.11.0 software package.

3. Results and discussion

The results of colour parameters of ground coffee samples and coffee extracts are shown in Tables 1 and 2, respectively. The L^* parameter indicates lightness and a^* and b^* are the chromaticity coordinates and indicate red ($+a^*$) and yellow ($+b^*$). L^* and b^* results were

Table 1
Colour data of ground roasted coffees

	L^*	a^*	b^*
0Co A	24.16 ± 0.54^{c}	12.17 ± 0.25^{c}	13.61 ± 0.16^{d}
0Co B	23.19 ± 0.13^{b}	11.20 ± 0.05^{b}	12.16 ± 0.11^{c}
0A	24.50 ± 0.50^{c}	11.19 ± 0.16^{b}	13.36 ± 0.33^{d}
0B	26.16 ± 0.33^{d}	12.54 ± 0.27^{cd}	15.68 ± 0.43^{f}
0C	22.92 ± 0.45^{b}	10.05 ± 0.17^{a}	11.15 ± 0.36^{b}
30B	26.58 ± 0.86^{d}	12.78 ± 0.39^{d}	16.37 ± 0.56^{g}
30D	24.88 ± 0.27^{c}	11.40 ± 0.23^{b}	14.15 ± 0.30^{e}
50A	24.83 ± 0.52^{c}	11.29 ± 0.13^{b}	13.77 ± 0.21^{de}
50C	21.90 ± 0.62^{a}	9.78 ± 0.53^{a}	10.39 ± 0.36^{a}
100B	30.86 ± 0.55^{e}	12.64 ± 0.09^{d}	20.42 ± 0.26^{h}
100C	22.45 ± 0.24^{ab}	11.28 ± 0.07^{b}	12.63 ± 0.09^{c}

In each column, different superscripts indicate significant differences ($p < 0.05$) among coffee samples. Results are shown as means ± standard deviations ($n = 6$).

Table 2
Colour data of coffee extracts

	L^*	a^*	b^*
0Co A	21.00 ± 0.34^{ab}	0.58 ± 0.04^{c}	0.53 ± 0.06^{ab}
0Co B	21.64 ± 1.29^{b}	0.71 ± 0.03^{d}	0.63 ± 0.04^{cd}
0A	20.59 ± 0.01^{ab}	0.84 ± 0.05^{e}	0.82 ± 0.04^{f}
0B	23.10 ± 1.59^{c}	0.46 ± 0.02^{b}	0.33 ± 0.03^{b}
0C	20.69 ± 0.24^{ab}	0.36 ± 0.02^{a}	0.30 ± 0.04^{a}
30B	20.67 ± 0.33^{ab}	0.46 ± 0.03^{b}	0.62 ± 0.09^{cd}
30D	19.73 ± 0.61^{a}	0.49 ± 0.01^{b}	0.66 ± 0.08^{cde}
50A	20.38 ± 0.05^{ab}	0.46 ± 0.03^{b}	0.27 ± 0.04^{a}
50C	20.58 ± 0.56^{ab}	0.48 ± 0.03^{b}	0.70 ± 0.02^{de}
100B	20.15 ± 0.00^{a}	0.57 ± 0.02^{c}	0.71 ± 0.02^{e}
100C	20.06 ± 0.01^{a}	0.49 ± 0.06^{b}	0.60 ± 0.03^{bc}

In each column, different superscripts indicate significant differences ($p < 0.05$) among coffee samples. Results are shown as means ± standard deviations ($n = 6$).

statistically similar in A ground roasted coffee samples, whereas statistical differences were found in B and C coffees. Nicoli, Anese, Manzocco, and Lerici (1997b) observed that there was a tendency to decrease L^*, a^* and b^* results with roasting because of the brown colour development. In our work, a slight tendency to increase in L^* and b^* parameters with torrefacto percentage, within each brand except C, was found. This might be due to a lower roasting degree (to avoid an excess of burnt caramel in torrefacto). Colour parameters of coffee extracts were lower than ground roasted coffees, and similar among different samples; a^* and b^* results were very close to zero.

The antioxidant capacity was evaluated by chain-breaking activity that allows evaluation of the quenching rate of coffee compounds toward a reference radical ($DPPH^{\cdot}$). The results are shown in Fig. 1. Higher antioxidant activity was observed in Colombian coffees (0Co)

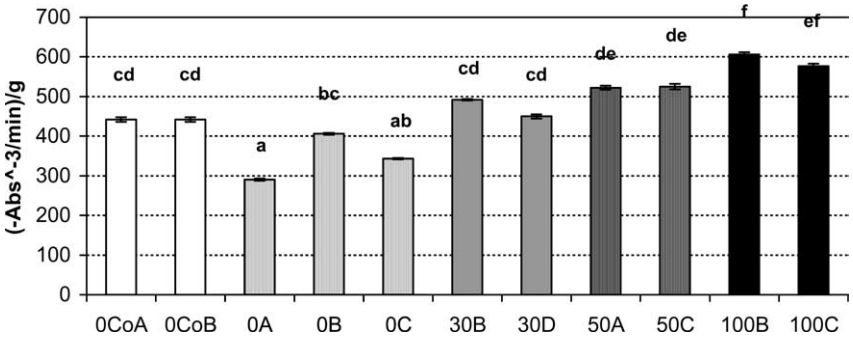

Fig. 1. Antioxidant activity of coffee.

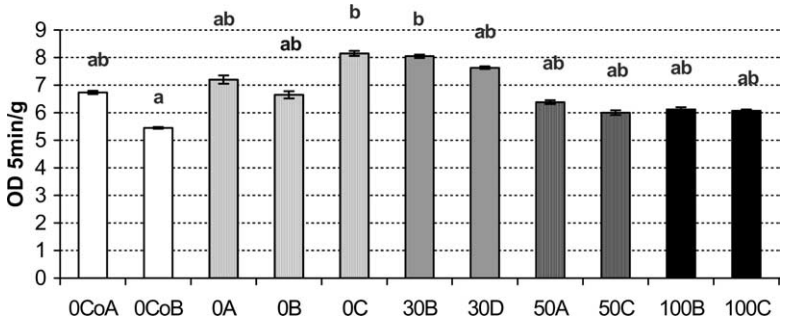

Fig. 2. Pro-oxidant activity of coffee.

than in conventional roasted coffee blends (0). Due to the presence of Robusta coffee, which usually have higher amounts of chlorogenic acids (Illy & Viani, 1995) a higher antioxidant activity had been expected in conventional roasted blends (0). However, roasting process could produce a greater decrease in polyphenolic compounds in Robusta coffees than in Arabica (Colombia) ones (Richelle et al., 2001). On the other hand, Steinhart, Luger, and Piost (2001) reported higher values of antioxidant activity in Colombian roasted than in raw coffees, possibly because of the formation of MRPs. Both hypotheses could explain the higher antioxidant capacity results in 0Co. In blends, antioxidant activity was increased with the percentage of torrefacto coffee. This could be because addition of sugar in the roasting process has a great effect on the rate of the Maillard reaction and, consequently, in the formation of MRPs because carbohydrates, together with proteins are the major precursors of melanoidin formation, of partially responsible for the antioxidant capacity of coffee.

The pro-oxidant capacity was evaluated by the crocin-bleaching test and these results are shown in Fig. 2. The assessment of pro-oxidant activity by crocin bleaching allows evaluation of the quenching rate of coffee compounds toward a reference radical quencher (crocin). Notably, the noted that 0CoB coffee sample showed the lowest pro-oxidant capacity. In blends, there was a slight tendency to decrease the pro-oxidant activity with increasing percentage of torrefacto coffee. Highly reactive radicals are formed in the early phases of the Maillard reaction, just prior to the Amadori rearrangement, whereas strong antiradical properties are

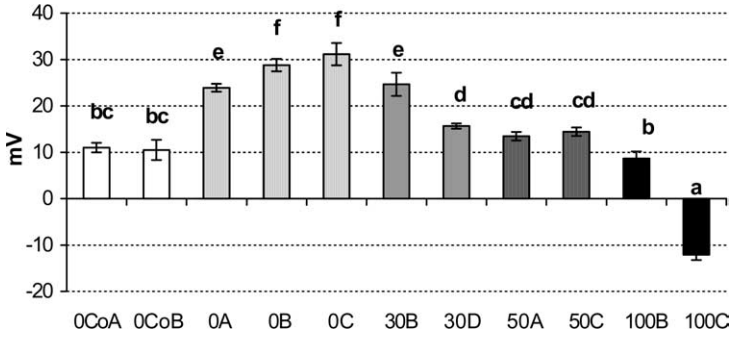

Fig. 3. Redox potential values of coffee.

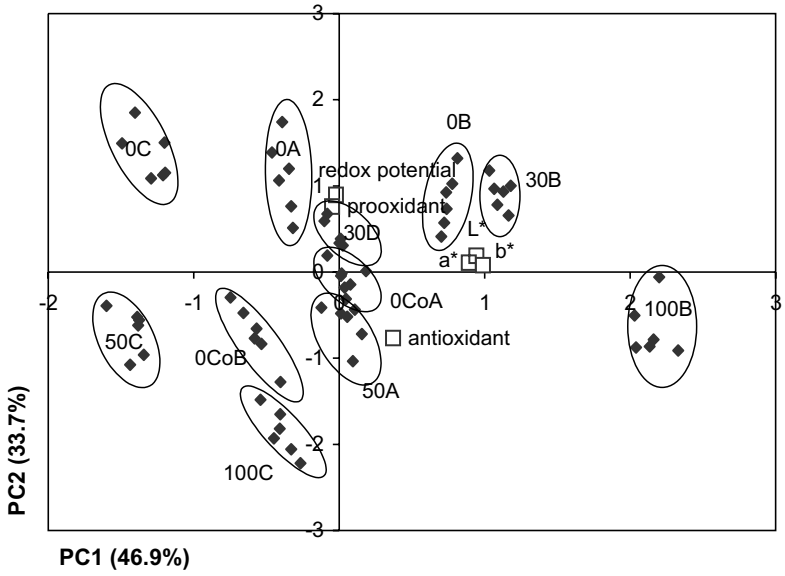

Fig. 4. Principal component analysis of the coffee samples.

attributable to the high molecular weight brown compounds formed in the advanced phases of the reaction (Manzocco et al., 2002). Therefore, when the roasting process had been completed, pro-oxidant radicals could be quenched by the MRPs, thus reducing pro-oxidant activity in the torrefacto roast.

Redox potential indicates the oxidation/reduction efficiency of all the antioxidants, including the slow ones, and pro-oxidants in coffee. Redox potential results are shown in Fig. 3. Significantly ($p < 0.05$) lower redox potential results were observed in Colombian coffees (0Co) versus conventional roasted blends (0) according to the higher antioxidant capacity previously discussed. In blends, there was a tendency to decrease the redox potential with increasing percentage of torrefacto coffee, suggesting an increase of the overall antioxidant activity.

Two principal components (PC), with eigenvalues greater than 1 were selected by PCA. PC1 and PC2 explained 80.6% of the total variance. Fig. 4 shows bidimensional representations of PC1 and PC2 scores for all the variables and coffee samples. PC1, which explained 46.9% of total variance, is mainly characterised by colour parameters of ground roasted coffees. Brand C samples are shown on the left half graphic, A around the middle and B, with the exception of Colombian (0CoB), on the right. As mentional, Nicoli et al. (1997b) observed lower L^*, a^* and b^* results with higher roasting degree. For that reason, brand C samples might have higher roasting degrees and brand B coffees lower. Some roasting companies usually apply higher roasting degree to Colombian coffees to decrease their high acidity index. This could explain the movement of 0CoB sample to the left.

PC2, which explained 33.7% of total variance, is characterised by antioxidant/pro-oxidant activity. Conventional roasted coffees are shown at the top of the Figure because of their low antioxidant activity. However, those samples with more than 50% of torrefacto roasted coffees are shown at the bottom, having the highest antioxidant activity. Among torrefacto roasted coffees, it can be observed that 100B had less antioxidant capacity than 100C, maybe because it was less roasted producing less MRPs.

In conclusion, coffee blends with high percentages of torrefacto roast had stronger antioxidant activities maybe because sugar addition could contribute to the formation of MRPs during roasting. At the same time, roast degree and, consequently, colour parameters could also influence the antioxidant/pro-oxidant activity of coffee, but linear correlations were not observed and both groups of parameters were represented in different principal components.

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References

Ames, J. M. (1988). The Maillard browning reaction-an update. *Chemistry and Industry, 5*, 558–561.

Andueza, S., Cid, C., & Nicoli, M. C. (2004). Comparison of antioxidant and prooxidant activity in coffee beverages prepared with conventional and "Torrefacto" coffee. *Lebensmittel-Wissenschaft und-Technologie, 37*, 893–897.

Brand-Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. *Lebensmittel-Wissenschaft und-Technologie, 28*, 25–30.

Daglia, M., Papetti, A., Gregotti, C., Berte, F., & Gazzani, G. (2000). In vitro antioxidant and ex vivo protective activities of green and roasted coffee. *Journal of Agricultural and Food Chemistry, 48*, 1449–1454.

ICO. (2004). Exports by exporting countries to all destinations March 2004. Market Information. (On line). In http://www.ico.org/frameset/traset.htm.

Illy, A., & Viani, R. (1995). Espresso coffee: The chemistry of quality. In A. Illy & R. Viani (Eds.). London: Academic Press Limited.

Manzocco, L., Anese, M., & Nicoli, M. C. (1998). Antioxidant properties of tea extracts as affected by processing. *Lebensmittel-Wissenschaft und-Technologie, 31*, 694–698.

Manzocco, L., Calligaris, S., Mastrocola, D., Nicoli, M. C., & Lerici, C. R. (2001). Review of non-enzymatic browning and antioxidant capacity in processed foods. *Trends in Food Science and Technology, 11*, 340–346.

Manzocco, L., Calligaris, S., & Nicoli, M. C. (2002). Assessment of pro-oxidant activity of foods by kinetic analysis of crocin bleaching. *Journal of Agricultural and Food Chemistry, 50*, 2767–2771.

Nicoli, M. C., Anese, M., Parpinel, M., Franceschi, S., & Lerici, C. R. (1997a). Loss and/or formation of antioxidants during food processing and storage. *Cancer Letters, 114*, 71–74.

Nicoli, M. C., Anese, M., Manzocco, L., & Lerici, C. R. (1997b). Antioxidant properties of coffee brews in relation to the roasting degree. *Lebensmittel-Wissenschaft und-Technologie, 30*, 292–297.

Nicoli, M. C., Anese, M., & Parpinel, M. (1999). Influence of processing on the antioxidant properties of fruit and vegetables. *Trends in Food Science and Technology, 10*, 94–100.

O'Brien, J., & Morrissey, P. A. (1989). Nutritional and toxicological aspects of the Maillard reaction in food. *Critical Reviews in Food Science and Nutrition, 28*, 211–248.

Richelle, M., Tavazzi, I., & Offord, E. (2001). Comparison of the antioxidant activity of commonly consumed polyphenolic beverages (coffee, cocoa and tea) prepared per cup serving. *Journal of Agricultural and Food Chemistry, 49*, 3438–3442.

Rizzi, G. P. (1994). The Maillard reaction in foods. In T. P. Labuza, G. A. Reineccius, V. M. Monnier, J. O'Brien, & J. W. Baynes (Eds.), *Maillard reaction in chemistry, food and health* (pp. 11–19). Cambridge: Royal Society of Chemistry.

Roberts, R. L., & Lloyd, R. V. (1997). Free radical formation from secondary amines in the Maillard reaction. *Journal of Agricultural and Food Chemistry, 45*, 2413–2418.

Steinhart, H., Luger, A., & Piost, J. (2001). Antioxidative Effect of Coffee Melanoidins. *Proceedings of the 19th Colloquium ASIC, Trieste*, in CD.

Turesky, R. J., Stadler, R. H., & Leong-Moergenthaler, P. M. (1993). The pro- and antioxidative effects of coffee and its impact on health. *Proceedings of the 15th Colloquium ASIC, Montpellier* (pp. 426–431).