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Review on Coffee Antioxidant and Its Health Benefit

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Abstract
Coffee has been for decades the most commercialized food product and most widely consumed beverage in the world. Antioxidants prevent oxidation of other molecules in our body. Coffee shows the greatest antioxidant activity and major source of antioxidants. Antioxidant content can be maintained or even enhanced by the formation of compounds with antioxidant activity (AA) such as Maillard reaction products. AA of coffee brews is strongly affected by coffee roasting process. Measuring antioxidant activity of coffee would help assess their potential as a source of natural antioxidants. Reviewing AA of coffee is the aim of this seminar paper. AA coffee can be measured by various chemical and physicochemical methods. Coffee is the most antioxidant rich beverages. Roasted coffee brews showed a greater oxygen scavenging capacity than the crude coffee brew. These results suggested that the changes in the antioxidant properties of the coffee brews may be attributed to a further development at any degree of roasting. AA of semi dry and natural coffees was quite similar. Redox potential values of coffee brews during storage at 30°C under ordinary atmosphere greatly increased in the first few days. Contribution of non-phenolic fraction to the overall AA of coffee brew is much lower than that of the phenolic fraction. Evaluation of antioxidant content of local coffee is very important for coffee value addition.

1. Introduction

Coffee has been for decades the most commercialized food product and most widely consumed beverages in the world due to its sensory characteristics, stimulating and beneficial health effects (Pérez-Martínez *et al.,* 2010). It ranks second after petroleum in international trade to earn foreign exchange in many agriculture oriented countries (Ramalakshmi *et al.,* 2008). It is considered a functional food, primarily due to its high content of compounds that exert antioxidant and other beneficial biological properties. The characteristic flavor and richness of coffee aroma make it a unique beverage, with almost a thousand volatile compounds identified in roasted coffee (Yeretzian *et al.,* 2003). Its unique flavor has been intensively studied since the beginning of this century. The number of volatile chemicals identified in coffee has reached almost 1000 (Shibamoto, 1992).

Coffee consumption is progressively increasing in the world due to its distinct taste and aroma. Coffee is consumed for its refreshing and stimulating effect which has a complex chemical mixture composed of several chemicals. It is responsible for a number of bioactivities and a number of compounds accounting for these effects. Few of the significant bioactivities documented are AA, anticarcinogenic activity, antimutagenic activity etc.

Antioxidants are powerful substances prohibit or prevent the oxidation of other molecules in our body. Oxidation is a chemical reaction that can produce free radicals, leading to chain reactions that may damage cells. Antioxidants are very important to good health, because if free radicals are left unchallenged, they can cause a wide range of illnesses and chronic diseases. Antioxidants are organic molecules which can prevent or delay the progress of lipid oxidation. Their ability to do this is based mainly on their phenol-derived structure. Recently, the interest in using antioxidants of natural origin in food has increased, because they also appear to be suitable antioxidants for the prevention of diseases associated with the process of lipid peroxidation (Valenzuela *et al*., 2003). Hydroxycinnamic acid compounds have been described as chain-breaking antioxidants, probably acting through radical-scavenging, which is related to their hydrogen-donating capacity, and their ability to stabilise the resulting phenoxyl radical (Siquet *et al*., 2006).

Coffee shows the greatest total AA and has been reported to be the major source of antioxidants (Vinson *et al.,* 2005). Coffee, one of the most popular beverages worldwide, is a major contributor of phytochemicals in the diet and contributes more than 50% of dietary antioxidants in many countries (Ingvild *et al.,* 2010). Coffee is a natural source of antioxidants because of its phenolic compound content, of which Chlorogenic acids (CGA) are the most prevalent (Clifford, 2000).

AA of coffee brews is strongly affected by the coffee roasting process. It leads to profound changes in the chemical composition of coffee, such as protein, amino acids, reducing sugars, sucrose, trigonelline (TRG), CGA and water decreasing and melanoidins formation, many of which are due to the Maillard reaction. It occurs when sugars condense with free amino acids, peptides or proteins, and leads to the formation of a wide variety of compounds reported to possess antioxidant activity (Nicoli *et al.,* 1999). Some phenolic antioxidants naturally occurring in coffee decreases during roasting process (Delgado-Andrade and Morales, 2005). Antioxidant content can be maintained or even enhanced by the formation of compounds with AA such as Maillard reaction products (Del Castillo *et al.,* 2005). Major CGA compounds present in coffee are differentially absorbed and/or metabolized in humans, with a large inter-individual variation. According to (Monteiro *et al.,* 2007), urine does

not appear to be a major excretion pathway of intact CGA compounds in humans.

Coffee is considered as a functional beverage with the potential health benefits due to their radical scavenging capabilities, which are contributed by a diverse array of phenolic components. Phenolic acids, especially CGA, which is found abundantly in coffee beans, could assert neuroprotective effects that may prevent diseases like Alzheimer's disease (Vignoli *et al.,* 2011). Phenolic components of coffee beans contribute not only to the bitterness and astringency but more importantly, the antioxidant capabilities of the beverage. AA of coffee measuring helps to assess their potential as a source of natural antioxidants.

The objective of this seminar is to review available information on antioxidant of coffee; coffee consumption and its antioxidant health benefit and also effect of coffee origin, processing and roasting on antioxidant content coffee.

2. Biochemical Composition of Coffee, Antioxidant and Its Health Benefit

Biochemical compounds are metabolic products and they confer adaptive properties to plants. Green coffee beans contain a wide range of different chemical compounds which react and interact at all stages of coffee processing to produce a final product with an even greater diversity and complexity of structure (Kathurima et al., 2010). Chemical composition of green coffee depends primarily on genetic aspects (species) and on physiologic aspects such as degree of maturation (Farah, 2012). In addition to these intrinsic factors, extrinsic factors such as soil composition, climate, agricultural practices, and storage conditions affect seed physiology and chemical composition, but to a lesser extent. More than 950 compounds have been identified after roasting in different types of coffee, depending on their origin, degree of roasting, and analytical methods used (Yeretzian *et al.,* 2003).

In Arabica coffee substantial variation was also observed in green bean caffeine, CGA, sucrose and TRG contents (Silvarolla *et al.,* 2004), tree size and shape, bean size, shape and colour and cup quality. Caffeine, CGA, sucrose and TRG have been used for characterization of coffee species as well as varieties within a species (Bicchi *et al*., 1995). Caffeine is a mild stimulant, which acts on the central nervous system and increases the metabolic rate. Consumption of caffeine equivalent to that found in a couple of cups of coffee has been shown to improve alertness and enhance concentration. Chemically, caffeine remains stable during coffee roasting except for minute amounts that sublime although roasting has been reported to cause a reduction in caffeine content (Hecˇimovic *et al.,* 2011).

2.1. Methods of Measuring AA and Its Content in Coffee

The AA is measured by various chemical and physicochemical methods. All those methods are most often based on the direct or indirect measurement of reaction rate. Based on oxygen intake; formation of oxidation products and uptake or binding of free radicals three methods could be distinguished. In the cases of oxygen intake and formation of oxidation products AA is determined based on the degree of inhibition or intake rate for reagents or the products formed.

Primary methods for AA measurements are oxygen radical absorbance capacity (ORAC); total radical trapping antioxidant parameter (TRAP); ferric reducing antioxidant power (FRAP); (Randox)- trolox equivalent antioxidant capacity (TEAC); 2,2-azinobis(3-ethylbenzthiazoline)-6-sulfonic acid (ABTS) and thiobarbituric acid reactive substance (TBARS). In all of these methods AA depends on multiple parameters, including time, temperature, nature of the substance, concentration of the antioxidants and other compounds, etc. AA cannot be measured directly what is typically measured is the effect of the antioxidants on the degree of oxidation. AA is most often measured based on long living synthetic free radicals (ABTS, DPPH, etc.). Lots of synonymous terms have been proposed, including “antioxidant ability”, “antioxidant power”, “antioxidant activity”, and “antioxidant capacity”. All of these terms are related to the antioxidant concentration.

2.2. Coffee Consumption and Its Antioxidant Health Benefit

Green coffee beans contain large amount of polyphenolic antioxidants, such as clorogenic, caffeic, ferulic and n-coumaric acids. Coffee roasting significantly alters the composition of polyphenols due to Mailard reaction. The most antioxidant rich beverages are: coffee 200- 250mg/cup; tea 100- 400mg/cup (Menscikova et al., 2006). Intake of these drinks makes a significant contribution to the total amount of antioxidants consumed by people. A cup of coffee which contains 10 g of roasted coffee powder may have 15 to 325 mg of Chlorogenic acids. Ferulic acid presedted in coffee has anti inflammatory, anti allergic, antibacterial, and antiviral effect (Prior et al., 2003). Pharmacological properties of ferulic acid are related to its high AA, in particular, its ability to inhibit lipid peroxidation in biological membranes. In one study, it has been shown that ferulic acid at a concentration of 10^{-3} mol/L in a perfusion solution reduces arrhythmia (Dyakov et al., 2005).

Coffee beverage is known for antioxidant properties of its components caffeine, CGA, hydroxycinnamic acids and melanoidins (Vignoli, et al., 2011). Melanoidins from coffee showed higher AA than those isolated from other sources, such as beer (Morales and Jiménez-Pérez, 2004). Thus, as mentioned above, the antioxidant

capacity of coffee is associated to the presence of both natural compounds and substances developed during roasting. Antioxidants of the hydroxycinnamic acids group, such as combined or conjugated forms of caffeic, chlorogenic, coumaric, ferulic and sinapic acids, are also found in coffee beverage (Manach et al., 2004).

In one study the bioavailability of CGAs in 2 types of coffees and the effects of their consumption on the plasma antioxidant capacity were evaluated. After coffee consumption (1 h and 8 wk), antioxidant concentrations increased. At 1 h after consumption, the plasma AC in the control group was significantly lower than the baseline value (553) and significantly increased in the MCGA (618) and HCGA (590) groups (Table 1) (Agudelo-Ochoa et al., 2016). Both coffees, which contained CGAs and were low in diterpenes and caffeine, provided bio-available CGAs and had a positive acute effect on the plasma antioxidant capacity in healthy adults. Regarding the bioavailability of the CGAs in coffee and their effects on the AC in healthy adults suggest an acute positive effect that tends to decrease as the metabolites are eliminated by the body. The fact that the plasma antioxidant capacity increased 1 h after the consumption of the 2 coffee beverages (MCGA and HCGA) and significantly increased after the consumption of the MCGA coffee suggests that other substances with antioxidant properties may have been generated during the roasting process, which differed for the 2 coffees.

Table 1: Antioxidant capacity of plasma after coffee consumption

Intervention	Control	MCGA	HCGA
Baseline	562 ± 70.8	584 ± 63.6	563 ± 78.5
1 h	553 ± 71.6[b]	618 ± 59.9[a]	590 ± 81.3[a,b]
8 week	519 ± 80.3[a]	552 ± 59.3[a]	533 ± 71.0[a]

Labeled means in a row without a common letter differ significantly.
HCGA, high content chlorogenic acid t; MCCGA, medium content chlorogenic acid
Source: Agudelo-Ochoa, et al., 2016

2.3. Comparison of Coffee Antioxidant Activity with Other Drinks

Comparison on the AA between coffee and various (non-alcoholic and alcoholic) beverages is summarized Table 2. According to Pellegrini et al (2003) finding coffee based drinks had large amount of antioxidant activity. It should be noted that figures provided for green and black tea as well as for beer are understated. Accordingly, the antioxidant activity of cognac is smaller than whisky. This is an induction of coffee is the major source of antioxidant. Melanoidins from coffee showed higher antioxidant activity than those isolated from other sources, such as beer (Morales and Jiménez-Pérez, 2004).

Coffee provides a very significant portion of daily intake of antioxidants established for humans. The comparison of coffee, tea and cocoa in terms of total antioxidant content is presented in Table 3. The data suggested that in terms of antioxidant capacity coffee is comparable with tea, which can be attributed to higher consumption rates of these products. Antioxidant activity of coffee, tea, and cocoa are the most widely consumed beverages containing polyphenolic antioxidants were compared (Yashin *et al.,* 2009).

The AA of the beverage is represented by the increase of the lag time (lag time of LDL in the presence of coffee beverage with respect to the lag time of control LDL). Table 4 shows the effect of the roasting degree of Arabica and Robusta coffee beans on their AA (Richelle *et al.,* 2001). The AA of Robusta green coffee is significantly higher than that of Arabica. However, this difference virtually disappears after light roasting; and after dark roasting Arabica coffee even exceeds Robusta coffee with regards to antioxidant activity.

Table 2**:** Antioxidant activity of coffee and other drinks

No.	Beverages	AA determined by different methods		
		FRAP (mol Fe^{2+}/L)	TRAP (mol Trolox/L)	TEAC (mol Trolox/L)
1	Coffee (Espresso)	129.4	66 .0	36.5
2	Coffee (Instant)	108.6	52.4	32.5
3	Coffee (Extract)	96.4	59.6	30.3
4	Coffee (Espresso, Decaffeinated)	93.0	45.8	27.0
5	. Red wine	31.5	14.8	11.4
6	Green Tea	18.0	7.6	6.0
7	Black Tea	10.1	4.9	3.6
8	Rose wine	8.3	2.2	2.4
9	White wine	3.7	2.1	1.7
10	Whisky	3.4	2.3	1.7
11	Cognac	2.2 1	1.5	1.3
12	Beer	2.8	–	1.0

FRAP= ferric reducing antioxidant power; TRAP= total radical-trapping antioxidant parameter; TEAC= trolox equivalent antioxidant capacity.
Source: Pellegrini, et al, 2003

Table 3: Total antioxidant content of different beverages

Beverage	One time consumption rate, in grams	TAC, mg/g
Coffee	7 -10	150 - 300
Green tea	2	150 – 300
Black tea	2	110 - 200
Cocoa	10	200 -250

Source: Yashin et al., 2009

Table 4: Antioxidant activity of green and roasted Arabica and Robusta coffee beans

Type of coffee	Increase of lag time, min	
	Arabica	Robusta
Green	366 ± 74	643 ± 68
Light roasted	284 ± 80	294 ± 41
Medium roasted	206 ± 30	190 ± 39
Dark roasted	168 ± 23	134 ± 34

Source: Richelle, et al., 2001

2.4. Coffee Brews Antioxidant Activity by Different Methods

Antioxidant properties of melanoidins in coffee brews from different roasting degrees by applying different antioxidant methods and the specific AA associated with bonded melanoidins compounds were evaluated. Instant coffees produced from roasted coffee beans were used in three different roasting degrees (light, medium and dark). Then one gram of the different instant coffees was re-suspended in 100 mL of hot water (50- 60 °C) for 3 min while continuously stirring. The coffee brews obtained were then filtered and stored at 4 °C until analyses were shortly performed. Filtrates, corresponding to the low molecular weight (LMW) fraction non-covalently linked to the melanoidins skeleton, were also preserved. AA of coffee brews (CB), melanoidins (M), pure melanoidins (PM), and bounded melanoidin compounds (BMC) were tested using the 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,2-azobis-(3- ethylbenzothiazoline-6-sulfonic acid) (ABTS), and ferric reducing power (FRAP) methods. AA of light, medium and dark coffee brews manifested the same pattern in the three methods used (Tables 5-7), with stability of AA in light dark and medium but decreasing around a 35% in light sample ($P < 0.05$). As the roasting degree decreased from dark to light a higher extent of the non enzymatic browning reaction is expected in more severely roasted coffee beans (Delgado-Andrade *et al.,* 2005).

The maintenance of AA in dark and medium samples could be explained by the contribution of a higher melanoidins fraction in those coffees, whereas that fraction in light is still low and therefore has a lower contribution to the antioxidant capacity (Delgado-Andrade *et al.,* 2005). Development of browning is associated with an increase in the antioxidant properties in systems where the Maillard reaction is the prevalent reaction (Nicoli *et al.,* 2004). In this sense, although the major presence of still intact phenolic compounds in light sample could be enough to reach similar values of activity, some authors have described enhancement of the antioxidant properties of coffee brews by the appearance of Maillard reaction products possessing antioxidant capacity.

Table 5: Antioxidant Activity Determined by the DPPH Method[a]

Sample	$TEAC_{DPPH}$[b]				$CEAC_{DPPH}$[c]			
	CB	M	PM	BMC	CB	M	PM	BMC
Dark	428 ± 1	374 ± 3	144 ± 3	196 ± 1	502 ± 2	430 ± 4	125 ± 3	585 ± 1
Medium	419 ± 5	248 ± 3	157 ± 3	255 ±1	491 ± 7	262 ± 4	142 ± 4	781 ± 3
Light	325 ± 3	323 ± 8	160 ± 1	283 ± 1	366 ± 5	362 ± 11	145 ± 1	874 ± 5

Source: Delgado-Andrade et al., 2005

Table 6: Antioxidant Activity Determined by the ABTS Method[a]

Sample	$TEAC_{ABTS}$[b]				$CEAC_{ABTS}$[c]			
	CB	M	PM	BMC	CB	M	PM	BMC
Dark	1195 ± 12	699 ± 4	163 ± 21	937 ± 8	1361 ± 12	868 ± 4	335 ± 21	1104 ± 8
Medium	1206 ± 7	530 ± 8	140 ± 28	978 ±11	1372 ± 7	699 ± 8	312 ± 28	1145 ± 11
Light	616 ± 11	690 ± 13	137 ± 17	969 ± 9	770 ± 11	859 ± 13	310 ± 16	1137 ± 8

Source: Delgado-Andrade et al., 2005

Table 7: Antioxidant Activity Determined by the FRAP Method[a]

Sample	TEAC $_{FRAP}$[b]				CEAC $_{FRAP}$[c]			
	CB	M	PM	BMC	CB	M	PM	BMC
Dark	314 ± 2	273 ± 6	54 ± 1	384 ± 24	211 ± 1	187 ± 3	55 ± 1	254 ± 15
Medium	296 ± 11	176 ± 9	69 ± 4	508 ±3	201 ± 6	128 ± 6	64 ± 2	328 ± 1
Light	225 ± 3	255 ± 8	71 ± 3	598 ± 29	158 ± 1	176 ± 4	62 ± 3	382 ± 18

a CB, coffee brew; M, melanoidin; PM, pure melanoidin; BMC, bonded melanoidin compound. Values are mean ± S. D. b Data expressed as µ mol equiv of trolox/g of sample. c Data expressed as µ mol equiv of CGA/g of sample.
Source: Delgado-Andrade et al., 2005

2.5. Biochemical Components and Beverage Quality of Shaded Coffee

Coffee beverage quality is an important sensory attribute and is used as a measure for price determination. To investigate effect of shading levels on biochemical components and beverage quality of coffee variety study was conducted. Coffee samples for analysis were taken from composite of fully ripe cherries from four trees in each of the five treatments. Samples were processed using wet method. Seven sensory variables were evaluated on a 10-point scale. Caffeine, oil, TRG, total CGA, and sucrose were analyzed in green coffee samples and quantified on percent dry weight basis. Contents of TRG and sucrose were significantly higher in full sun while oil and caffeine content were significantly higher in the shaded coffee (Table 8) (Odeny *et al.,* 2016).

Shade enhanced the CGA content (Morais *et al.,* 2006). Positive effect of shade on biochemical components that enhance quality has been attributed to the larger bean size brought about by delayed ripening and hence better bean filling (Vaast et al., 2007). Shade levels had a significant effect on (Table 9). Shade levels significantly affected acidity, balance and biochemical components of the coffee. Shaded coffee had significantly higher levels oil, caffeine while coffee in full sun had significantly higher levels of TGR and sucrose. Generally, shaded coffee recorded higher acidity and balance. The results indicate that shade has potential to improve coffee quality.

Table 8: Biochemical components in green coffee under different shade levels

Shade level-Distance from tree(m)	Biochemical componentes				
	Oil	Caffeine	Trigonelline	Sucrose	CGA
0 - 1.5	16.75	1.22	0.77	8.22	5.37
1.5 - 3.0	16.59	1.03	1.01	8.42	6.19
3.0 - 4.5	16.54	0.99	0.93	8.09	6.05
4.5 - 6.0	16.57	0.94	0.94	8.67	6.26
Full sun	16.30	0.87	1.11	8.76	6.28
LSD (Shade level)	0.21	0.05	0.06	0.29	0.40
CV (%)	1.05	3.79	5.44	2.75	5.35

Source: Odeny, et al., 2016

Table 9: Sensory characteristics of coffee under different shade levels

Shade level-Distance from tree(m)	Sensory variables						
	Fragrance	Flavour	After taste	Acidity	Body	Balance	Overall
0 - 1.5	7.55	7.62	7.62	7.77	7.57	7.57	7.54
1.5 - 3.0	7.52	7.62	7.57	7.61	7.60	7.54	7.49
3.0 - 4.5	7.54	7.52	7.54	7.70	7.58	7.56	7.50
4.5 - 6.0	7.57	7.63	7.56	7.79	7.70	7.58	7.61
Full sun	7.56	7.48	7.52	7.56	7.57	7.54	7.54
LSD (Shade level)	NS	NS	NS	0.11	NS	NS	NS
CV (%)	1.85	2.61	2.44	2.38	2.65	1.91	2.26

The sensory characteristics are measured on a scale of 1- 10, with 10 being the best score.
Source: Odeny, et al., 2016

2.6. Effect of Roasting on Antioxidant Properties of Coffee Brews

Antioxidant properties of coffee in relation to roasting degree were studied. In order to obtain coffee beans (*Coffea arabica*) with different degrees of roasting, green coffee beans were roasted for 8, 10, 15 and 20 min to obtained medium, medium-dark dark and dark roasted coffee respectively. The roasting samples were ground in a mill immediately after the roasting process had been completed. Coffee brews were obtained by solid–liquid extraction with deionized water. The ratio between coffee powder and water was 1:10 w/w. The mixtures of coffee powder and water were introduced in screw capped flasks and then placed in a water-bath at 100 °C for

15 min. Particularly the extent of the chain-breaking activity and oxygen scavenging properties of Maillard reaction products contained in coffee brews were evaluated. Percentages of oxygen uptake/min/gm dry matter vs. roasting time were expressed. As a result the highest antioxidant properties were found for the medium-dark roasted coffee brews.

Oxygen scavenging properties of coffee brews in relation to roasting time was shown in Fig. 1 All the roasted coffee brews showed a greater oxygen scavenging capacity than the crude coffee brew (Nicoli *et al.,* 1997). The oxygen uptake of the crude coffee brew can be attributed to the phenolic compounds, such as caffeic acid and chlorogenic acid, which are naturally present in the crude coffee beans. Dramatically higher oxygen scavenging properties of the roasted coffee brews can be attributed to the Maillard reaction products (MRPs) formed during thermal treatment. Oxygen consumption did not increase linearly with increasing roasting time, but a maximum for the 10-min roasted coffee brew was observed. For longer roasting times, the oxygen uptake showed a slight decrease. Oxygen scavenging properties of coffee brews are related to a dynamic evolution of MRPs during roasting.

Overall antioxidant effect of coffee brews, the stability to oxidation of a soybean oil sample in the presence or absence of coffee extracts was carried out. Table 10 shows the differences in the induction times to oxidation between the oil sample, taken as a reference, and the mixtures of oil and coffee brew. These results confirmed that the MRPs with the highest antioxidant properties are formed during the intermediate stages of the roasting process. Coffee brews show strong overall antioxidant properties, which may mainly be attributed to the MRPs formed during the roasting process. These compounds can act both as primary and secondary antioxidants. The antioxidant properties of coffee could be considered responsible for the low oxidation rate of lipids contained in roasted coffee. It can also be hypothesized that the antioxidant properties of coffee MRPs could exhibit positive effects on human health (Nicoli *et al.,* 1997).

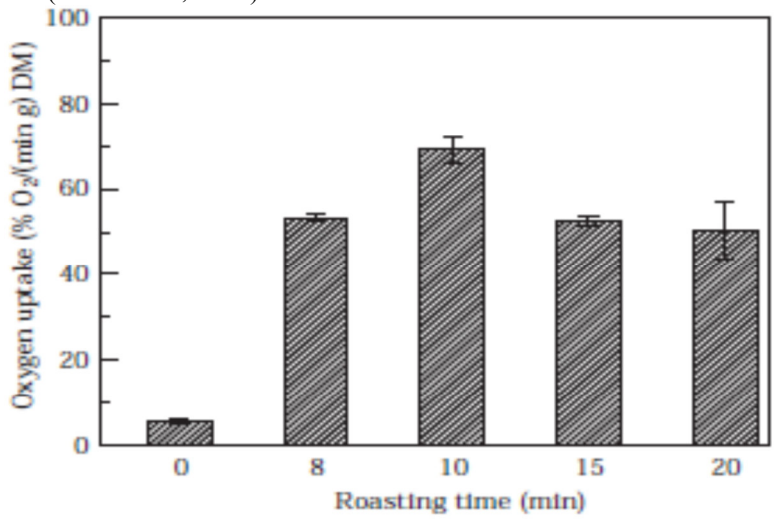

Fig. 1: Oxygen scavenging properties of coffee brews expressed as percentage of oxygen uptake/min/g dry matter as a function of the roasting time
Source: Nicoli et al., 1997

Table 10: Evaluation of the overall antioxidant activity of coffee brews

Roasting time (min)	D induction time (h)*a*	
	x	S*x*
0	1.5	0.2
8	6.4	0.5
10	5.1	0.1
15	4.8	0.2
20	4.7	0.1

*a*Mean values (*x*) and standard deviations (s*x*) of five measurements.
Data are expressed as the differences in the induction times to oxidation between an oil sample, taken as reference, and the oil–coffee brew mixtures.
Source: Nicoli, et al., 1997

The antioxidant properties of green and roasted coffee, in relation to coffee origin and degree of roasting (light, medium, dark), were investigated. These properties were evaluated by determining its antioxidant activity. The AA of coffee solutions based on coupled oxidation of *â*-carotene and linoleic acid were evaluated. The in vitro AA showed very similar profiles and values during the roasting process. All green coffee solutions showed

an immediate, strong activity which nevertheless increased with time of reaction (Maria *et al.,* 2000). At the end of the monitoring period (30 min), all the green coffee solutions decreased the lipid peroxidation rate in a model system to at least 90%. Considered in terms of the degree of roasting, AA values were higher for green coffee, decreased slightly with light roasting, and then increased with stronger roasting although they never exceeded AA values of green coffee (Table 11).

AA depending on the degree of roasting can probably be attributed to the loss of polyphenolic compounds occurring in green coffee during light roasting and to the successive formation of other antioxidant compounds such as Maillard reaction products (MRP) or pyrolysis products (less active ex vivo), when more severe thermal conditions are applied. The antioxidant compounds naturally occurring in green coffee were found to be very active in the chemical test. These compounds were found to be far less active in biological systems, where the compounds generated during roasting were found to be highly protective.

Table 11: Antioxidant activity green and roasted *C. arabica* of different origin

origin	Degree of roasting	AA%		
		10 min	20 min	30 min
Brazil	Green	84	86	89
	Light roasted	62	73	76
	Medium roasted	75	78	84
	Dark roasted	72	82	86
Colombia	Green	82	89	92
	Light roasted	70	74	80
	Medium roasted	69	83	87
	Dark roasted	75	80	87
Costa Rica	Green	84	88	92
	Light roasted	65	75	82
	Medium roasted	72	80	85
	Dark roasted	69	82	86

Source: Maria et al., 2000

2.7. Coffee Origins Effect in Antioxidant capacity of brew

Free radical scavenging activities and the antioxidant capacities of 14 coffees from different countries of origin prepared in three commonly used ways (espresso, filter and Italian coffee) were evaluated. The H_2O_2 scavenging capacity was analysed in freshly made coffee and 6 h later, the antioxidant activity slightly increasing with time (Parras *et al.,* 2007). The filtered coffee showed a greater capacity to react with H_2O_2 ($p < 0.05$) than the Italian and espresso coffees. All the coffee samples improved the oxidative stability of butter (Rancimat test), espresso and Italian coffee providing greater protection than the filtered beverages (Table 13).

There was decreasing antioxidant capacity in order of ranking for samples: Vietnam, Uganda, Nicaragua, Colombia, Brazil, ‘‘caracolillo’’, Puerto Rico, Guatemala, Kenya, Papua, decaffeinated Colombia, Ethiopia, Jamaica, and decaffeinated Brazil. Table 12 shows the inhibition of lipid peroxidation in the presence of coffee beverages from different origins compared with the activity of standards (typical coffee compounds and common food additives). All the coffees studied, regardless of origin, were very effective scavengers of lipoperoxyl radicals, in the following decreasing order: Colombia (decaffeinated), Uganda, Papua, Jamaica, ‘‘Caracolillo’’, Ethiopia, Kenya, Puerto Rico, Nicaragua, Colombia, Brazil (decaffeinated), Vietnan, Brazil, Guatemala, with no significant differences between them ($p < 0.05$). Both decaffeinated coffees (Colombia and Brazil) exhibited higher scavenging capacity than the equivalent coffees containing caffeine from the same origin. All the coffee samples analyzed showed higher antioxidant activity than typical coffee compounds.

Table 13 shows antioxidant activity value at 6 min and 24 h obtained for coffees from different origins. The results are Vietnam, Uganda, Nicaragua, Colombia, Brazil, ‘‘caracolillo’’, Puerto Rico, Guatemala, Kenya, Papua, decaffeinated Colombia, Ethiopia, Jamaica, and decaffeinated Brazil, in decreasing order for samples at 6 min. Decaffeinated coffees (Colombia and Brazil) show lower antioxidant activity values than their equivalents with caffeine. The antioxidant activity values (24 h) shown by the coffee beverages were, in decreasing order, Vietnam, Nicaragua, Brazil, Guatemala, ‘‘caracolillo’’, Colombia, Puerto Rico, Uganda, decaffeinated Brazil, decaffeinated Colombia, Ethiopia, Jamaica, Kenya, and Papua. Decaffeinated Colombia and Brazil were slightly less effective of antioxidant activity scavengers than that their equivalents containing caffeine. Filter and Italian coffee analyzed after 6 min exhibited higher TEAC value than espresso coffees (Parras *et al.,* 2007).

Table 12: Inhibition percentage of peroxidation by coffee origin and ways of used

Coffee origin	Ways of coffee used		
	Filter coffee	Italian coffee	Espresso coffee
Guatemala	73.1 ± 4	77.2 ± 3	78.1 ± 3
Nicaragua	76.0± 2	78.0± 3	79.1 ± 3
Colombia	74.2± 4	79.2 ± 3	80.1 ± 4
Colombia (decaffeinated)	85.0 ± 3	81.1 ± 4	78.2 ± 4
Vietnam	78.0 ± 1	77.2 ± 2	76.4± 2
Papua	81.3 ± 2	81.2 ± 4	77.1 ± 3
Ethiopia	77.0 ± 3	80.1 ± 2	78.2 ± 2
Brazil	76.0 ± 1	77.1 ± 1	77.0 ± 1
Brazil (decaffeinated)	80.0 ± 3	74.2 ± 4	78.1 ± 3
‘‘Caracolillo’’ Puerto Rico	79.1 ± 2	79.1 ± 1	77.1 ± 2
Puerto Rico	77.2 ± 2	79.2 ± 2	78.0 ± 1
Kenya	78.0 ± 1	78.1 ± 1	79.3 ± 1
Jamaica	79.4 ± 2	80.2 ± 1	78.1 ± 1
Uganda	82.1 ± 2	82.0 ± 1	79.1 ± 3

Source: Parras et al., 2007

Table 13: Scavenging of antioxidant activity of different origin coffee by ways of coffee used

Coffee origin	Ways of coffee used					
	Filter coffee		Italian coffee		Espresso coffee	
	6 min	24 h	6 min	24 h	6 min	24 h
Guatemala	10.32 ± 0.04	12.92 ± 0.02	10.21 ± 0.05	12.46 ± 0.04	8.67 ± 0.01	11.11 ± 0.07
Nicaragua	12.29 ± 0.07	13.46 ± 0.07	11.51 ± 0.06	12.42 ± 0.01	8.74 ± 0.02	11.23 ± 0.03
Colombia	12.13 ± 0.04	13.40 ± 0.03	10.34 ± 0.01	11.63 ± 0.02	8.60 ± 0.03	10.99 ± 0.06
Colombia (decaffeinated)	8.06 ± 0.07	12.91 ± 0.07	10.85 ± 0.03	11.95 ± 0.05	8.54 ± 0.06	10.32 ± 0.02
Vietnam	11.90 ± 0.03	13.41 ± 0.01	12.82 ± 0.05	12.32 ± 0.05	11.42 ± 0.07	11.23 ± 0.01
Papua	10.07 ± 0.07	13.10 ± 0.06	10.42 ± 0.01	11.76 ± 0.01	7.31 ± 0.07	9.46 ± 0.07
Ethiopia	9.80 ± 0.07	13.07 ± 0.02	8.77 ± 0.04	11.21 ± 0.04	8.23 ± 0.02	10.76 ± 0.07
Brazil	10.63 ± 0.07	13.54 ± 0.07	10.91 ± 0.04	12.02 ± 0.01	9.38 ± 0.02	11.24 ± 0.07
Brazil (decaffeinated)	7.75 ± 0.07	12.95 ± 0.07	9.68 ± 0.05	11.78 ± 0.05	7.80 ± 0.01	10.59 ± 0.01
‘Caracolillo’ Puerto Rico	10.91 ± 0.06	13.33 ± 0.04	11.00 ± 0.01	12.08 ± 0.05	8.46 ± 0.03	10.84 ± 0.01
Puerto Rico	9.54 ± 0.07	13.27 ± 0.07	10.66 ± 0.02	11.67 ± 0.02	9.20 ± 0.04	11.04 ± 0.04
Kenya	10.69 ± 0.07	13.11 ± 0.07	10.28 ± 0.02	11.39 ± 0.02	7.36 ± 0.04	9.96 ± 0.04
Jamaica	8.82 ± 0.07	12.93 ± 0.05	9.51 ± 0.05	11.51 ± 0.01	6.97 ± 0.02	10.42 ± 0.06
Uganda	10.95 ± 0.07	13.38 ± 0.05	11.85 ± 0.05	11.75 ± 0.03	10.51 ± 0.04	10.84 ± 0.05

b TEAC is the micromolar concentration of a Trolox solution having the antioxidant capacity equivalent to the dilution of the substance under investigation.
Source: Parras et al., 2007

2.8. Antioxidant Properties of Ready to Drink Coffee Brews

Some technological variables influences on changes of antioxidant capacity of ready to drink coffee brews. To investigate influence of roasting degree and packaging atmosphere on the changes of the overall antioxidant capacity of ready-to-drink coffee brews, which were prepared from light, medium and dark roasted coffee beans was conducted. Results showed that, depending on the roasting degree as well as on the packaging conditions adopted, redox reactions, which can take place during storage, are responsible for significant changes in the overall antioxidant capacity of the product. In particular, the redox potential of air-packaged coffee brews, obtained from light- and medium-roasted beans, showed maximum values after 2 days of storage, which corresponded to a minimum in the chain breaking activity, while, in the case of the dark-roasted sample packaged under ordinary atmosphere, both the redox potential and the chain-breaking activity showed a maximum around 2-3 days of storage. In contrast, in the absence of oxygen, the coffee brews maintained the initial reducing properties over all the storage time, although the radical-scavenging activity values changed in a way very similar to that of the air-packaged sample. These results suggested that the changes in the antioxidant properties of the coffee brews may be attributed to a further development of the Maillard reaction during storage (Anese and Nicoli 2003).

Chain breaking activity and redox potential values of freshly prepared light, medium, and dark roasted coffee brews as well as of the green coffee one are shown in Table 12. The roasting process seems to slightly

affect the chain-breaking activity (Anese, and Nicoli, 2003). Chain-breaking activity slightly increased as the roasting degree increased. As already pointed out, though the naturally occurring phenols, such as caffeic acid and chlorogenic acid, are the principal antioxidants of unroasted coffee (Clifford, M. N. 1979), the antioxidant properties of the roasted coffee brews are mainly attributed to the Maillard reaction products (MRPs), which are formed during the heating process.

Redox potential values of coffee brews during storage at 30°C under ordinary atmosphere greatly increased in the first few days. After a prolonged storage time, a significant decrease in the redox potential was observed. At the beginning of storage, coffee brews lost a portion of their initial reservoir of antioxidants, which, however, progressively increased with aging. Maximum redox potential were observed for both light and medium roasted samples, corresponded to minimum in chain breaking activity values (Figure 2a, b). In contrast, in case of dark roasted sample, radical scavenging properties significantly increased in the first 2 days of storage, while after a prolonged storage time, no further increase was observed (Figure 2c). It must be pointed out that the dark-roasted sample always had higher reducing and chain breaking properties than light and medium roasted ones at corresponding storage times.

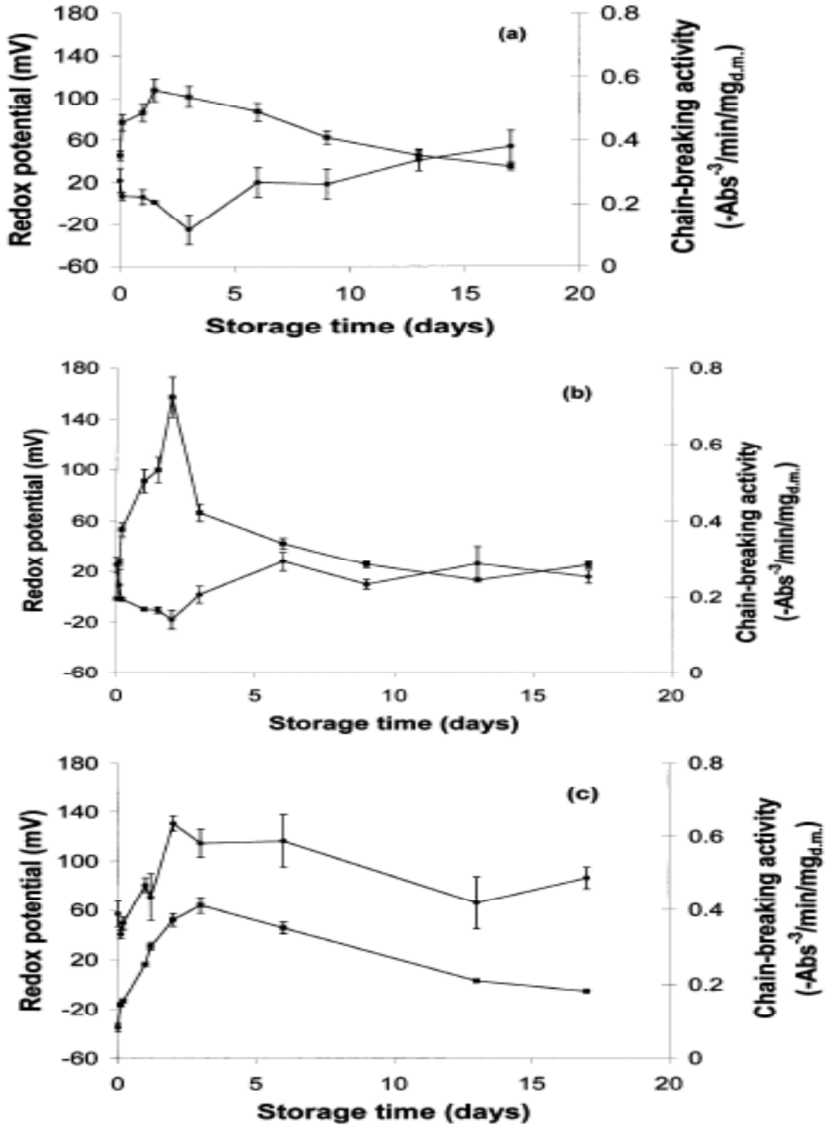

Fig. 2: Changes in chain-breaking activity (•, right *y*-axis) and redox potential (•, left *y*-axis) values of (a) light-, (b) medium-, and (c) dark roasted coffee brews during storage at 30 °C in ordinary atmosphere.
Source: Anese and Nicoli 2003

Table14: Chain-Breaking Activity of green and differently Roasted Coffee Brews

Degree of roasting	Chain-breaking activity[a] ($-Abs^{-3}/min/mg_{d.m.}$)
Green coffee	0.321 ± 0.011^{a}
Light roast	0.273 ± 0.038^{a}
Medium roast	0.284 ± 0.022^{a}
Dark roast	0.390 ± 0.035^{b}

[a]Chain-breaking activity values are presented as the mean ± SD (*n*) 3). Means in the same column with different letters are significantly different ($P < 0.05$).
Source: Anese and Nicoli, 2003

2.9. Effect of Processing and Roasting on Antioxidant Activity of Coffee Brews

Coffee beverage is a very complex mixture of several chemicals which are either naturally occurring or induced by the roasting process. Green beans contain a variety and large amount of phenolic acids. Differences in green bean composition, roasting conditions, and extraction procedures adopted for the coffee beverages preparation result in great diversity of the chemical composition of the final product Borrelli *et al.,* 2002), which could account for differences in the biological activities of coffee brews.

Effect of processing and roasting on the antioxidant activity of coffee beverages prepared as commonly consumed coffee was evaluated in different concentrations of coffee brews. All of the coffee brews presented a high antioxidant activity in all tested concentrations, but the antioxidant activity decreased with roasting (Duarte *et al.,* 2005). At any degree of roasting, the antioxidant activity of semi-dry and natural coffees were quite similar, except for the dark natural, that showed a significantly lesser antioxidant activity than the other samples ($p<0.05$).

The data presented here (Table 15) suggest that the antioxidant activity of coffee brews decrease with roasting, and it can be attributed, at least in part, to the loss of phenolic compounds during the roasting process. The coffee that presented the lower antioxidant activity was the dark natural. The behavior of antioxidant activity depending on the degree of roasting can probably be attributed to the loss of polyphenolic compounds, and to the successive formation of other antioxidant compounds, such as Maillard reaction products, which are lost or undergone pyrolysis when more severe thermal conditions are applied.

Table 15: Processing, roasting and brew concentration effect on Antioxidant activity

Processing	Concentration(PPM)	Antioxidant activity		
		Light	Medium	Dark
Semi-dry	10000	10.77^{a}	5.58^{a}	5.51^{a}
	20000	18.47^{b}	15.39^{b}	12.37^{b}
	30000	28.50^{c}	29.91^{c}	24.79^{c}
	40000	37.05^{d}	38.12^{d}	36.36^{d}
Dry	10000	10.46^{a}	7.08^{a}	5.27^{a}
	20000	19.73^{b}	14.51^{b}	12.48^{b}
	30000	37.12^{c}	29.30^{c}	22.30^{c}
	40000	43.79^{d}	40.04^{d}	29.27^{d}

The data are mean values of five analysis; when followed by different letters they differ significantly by Tukey test ($p<0.01$)
Source: Duarte et al., 2005

3. Conclusion

Antioxidants are powerful substances prohibit or prevent the oxidation of other molecules in our body. Antioxidants are very important to good health, because if free radicals are left unchallenged, they can cause a wide range of illnesses and chronic diseases. Human interest in using antioxidants of natural origin in food has increased, because they also appear to be suitable antioxidants for the prevention of diseases associated with the process of lipid peroxidation.

Coffee is major source of antioxidant hot beverage. The antioxidant activity of coffee is affected by processing and roasting. Coffee variety influences in the antioxidant capacity of coffee due to the percentage of poliphenolics compounds. The antioxidant activity of Robusta green coffee is significantly higher than that of Arabica. However, the antioxidant capacity of roasted coffees is mainly due to Maillard reaction products formed during roasting process. Antioxidant capacity increases due to the higher formation of Maillard reaction products but decreased lastly.

Many chemical changes occur during coffee roasting; among which the activation of Maillard reaction and degradation of polyphenols. The Maillard reaction causes antioxidant activity increase in extracts from light and medium roasted coffee. At higher roasting intensities, the thermal degradation of polyphenols causes antioxidant activity to decrease and this process is not counter balanced by further MRP formation. In all cases, the

contribution of the non-phenolic fraction to the overall antioxidant activity of the brew is much lower than that of the phenolic fraction. The antioxidant activity changes in brews from medium and dark roasted coffee are negatively influenced by the intensity of thermal process and seem to be much more dependent on roasting severity than on the type of coffee.

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