

ORIGINAL ARTICLE

ASSESSING POLYPHENOLS CONTENT AND ANTIOXIDANT ACTIVITY IN COFFEE BEANS ACCORDING TO ORIGIN AND THE DEGREE OF ROASTING

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ABSTRACT

Background. The roasting stage constitutes a key component in the manufacturing process of natural coffee because temperature elicits changes in bioactive compounds such as polyphenols and that Maillard-reaction compounds appear, thus affecting the product's sensory and antioxidant properties. Actual contents of these compounds may depend on which region the coffee is cultivated as well as the extent to which the beans are roasted.

Objectives. To determine polyphenols content and antioxidant activity in the 'Arabica' coffee type coming from various world regions of its cultivation and which have undergone industrial roasting. Also to establish which coffee, taking into account the degree of roasting (ie. light, medium and strong), is nutritionally the most beneficial.

Materials and Methods. The study material was natural coffee beans (100% Arabica) roasted to various degrees, as aforementioned, that had been cultivated in Brazil, Ethiopia, Columbia and India. Polyphenols were measured in the coffee beans by spectrophotometric means based on the Folin-Ciocalteu reaction, whereas antioxidant activity was measured colourimetrically using ABTS⁺ cat-ionic radicals.

Results. Polyphenol content and antioxidant activity were found to depend both on the coffee's origin and degree of roasting. Longer roasting times resulted in greater polyphenol degradation. The highest polyphenol concentrations were found in lightly roasted coffee, ranging 39.27 to 43.0 mg/g, whereas levels in medium and strongly roasted coffee respectively ranged 34.06 to 38.43 mg/g and 29.21 to 36.89 mg/g. Antioxidant activity however significantly rose with the degree of roasting, where strongly roasted coffee had higher such activity than lightly roasted coffee. This can be explained by the formation of Maillard-reaction compounds during roasting, leading then to the formation of antioxidant melanoidin compounds which, to a large extent, compensate for the decrease in polyphenols during roasting.

Conclusions. Polyphenols levels and antioxidant activities in the studied Arabica coffee beans that had undergone roasting depended on the cultivation region of the world. Longer roasting caused a significant decline in polyphenols compound levels (from 7.3% to 32.1%) in the coffee beans. Antioxidant activities of coffee increased with roasting, despite reduced levels of natural antioxidants. From a nutritional standpoint, the most favoured coffees are those lightly or medium roasted.

Key words: coffee, polyphenols, antioxidant activity, Arabica, roasting

STRESZCZENIE

Wprowadzenie. Kluczowym procesem w czasie produkcji kawy naturalnej jest etap prażenia, w wyniku którego pod wpływem wysokiej temperatury w ziarnach kawy zachodzą zmiany zawartości związków bioaktywnych, takich jak polifenole, powstają związki Maillarda, mające wpływ na ich właściwości sensoryczne oraz właściwości antyoksydacyjne. Zawartość tych związków może zależeć od rejonu upraw kaw, a także od zastosowanego procesu prażenia.

Cel badań. Celem niniejszych badań była ocena zawartości polifenoli oraz aktywności antyoksydacyjnej kaw rodzaju Arabika pochodzących z różnych rejonów upraw, poddanych procesowi prażenia, stosowanych w warunkach przemysłowych, a także określenie jaki czas prażenia kawy jest najkorzystniejszy dla produktu z żywieniowego punktu widzenia.

Materiał i metody. Materiał do badań stanowiły ziarna kawy naturalnej (100% Arabika) o różnym stopniu prażenia: lekko, średnio i mocno prażone, pochodzące z czterech różnych rejonów upraw: z Brazylii, Etiopii, Kolumbii i Indii. W pracy oznaczono zawartość polifenoli metodą spektrofotometryczną z wykorzystaniem odczynnika Folina-Ciocalteu'a oraz aktywność antyoksydacyjną przy zastosowaniu metody kolorymetrycznej z wykorzystaniem kationorodników ABTS⁺.

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Wyniki. Przeprowadzone badania wykazały wpływ zarówno pochodzenia kaw, jak i procesu ich prażenia na zawartość polifenoli i ich właściwości antyoksydacyjne. Proces prażenia powodował degradację polifenoli ze względu na termolabilny charakter tych związków. Największą zwartość polifenoli zaobserwowano w kawie lekko prażonej, a wraz ze wzrostem stopnia prażenia zawartość polifenoli istotnie malała. W zależności od stopnia prażenia wynosiła odpowiednio 39,27-43,00 mg kwasu galusowego/g dla kaw słabo prażonych, 34,06-38,43 mg/g dla kaw średnio prażonych i 29,21-36,89 mg/g dla kaw mocno prażonych. Wykazano, że wraz ze wzrostem stopnia prażenia kawy następuje obserwuje się istotny wzrost aktywności antyoksydacyjnej. Kawy mocno prażone cechowały się wyższą aktywnością antyoksydacyjną niż słabo prażone. Można to tłumaczyć faktem, że w czasie prażenia zachodzą reakcje *Maillarda*, które prowadzą do powstania melanoidynów, związków o charakterze antyoksydacyjnym, które w znacznym stopniu kompensują ubytek polifenoli w czasie prażenia.

Wnioski. Zawartość polifenoli w ziarnach kawy Arabika oraz ich właściwości antyoksydacyjne zależą w znacznym stopniu od ich pochodzenia (rejonu uprawy). Proces prażenia powoduje znaczne (od 7,3% do 32,1%) obniżenie zwartości związków polifenolowych w kawach, co jest związane z termolabilnym charakterem tych związków. W wyniku prażenia właściwości przeciwutleniające kaw zostają istotnie zwiększone, pomimo znacznego spadku naturalnych przeciwutleniaczy. Z żywieniowego punktu widzenia najkorzystniejsze jest spożywanie kawy o krótkim lub średnim czasie prażenia.

Słowa kluczowe: kawa, polifenole, aktywność antyoksydacyjna, Arabika, prażenie

INTRODUCTION

Coffee is rich in high-antioxidant activity compounds like polyphenols, chiefly chlorogenic acid and its degradation products (ie. ferulic, coumaric and caffeic acids), together with melanoidin compounds derived from the Maillard reaction [22, 25]. Consuming coffee has a large effect on the overall intake of antioxidants via the human diet, where it constitutes an important source of chlorogenic acid. Daily intakes of this compound for coffee drinkers range from 0.5 to 1.0 g, whilst they are < 0.1g daily for non-coffee drinkers [8]. Polyphenolic compounds, such as caffeic, quinic and chlorogenic acids, present in coffee exhibit a broad spectrum of activity within the human body. They demonstrate, inter alia, antioxidant properties, anti-carcinogenic effects, inhibit the oxidation of LDL cholesterol and prevent atherosclerotic lesions forming in blood vessels as well as showing anti-inflammatory and antibacterial properties. Chlorogenic acid exhibits antiviral and hypoglycaemic properties [4, 23, 27, 28]. Coffee's antioxidant potential comes not only from its natural compounds but also from those that arise during processing. The literature indicates that the antioxidant activity of green coffee (Arabika and Robusta) is lower than in both lightly roasted coffee [1, 8] and that medium roasted [19]. Such effects are due to phenolic compounds being released under medium roasting [1], as well as to the action of the non-phenolic fraction. Antioxidant properties are maintained or even elevated, despite significant decreases in natural antioxidant concentrations arising from thermal processes [15]. Roasting evokes several changes in the constituents of coffee beans through modification or degradation. During roasting, high temperatures result in polyphenol degradation [8, 13]. Chlorogenic, malic and citric acid levels become decreased, whilst quinic

acid increases due to chlorogenic acid degradation [6]. Thermal degradation of chlorogenic acid gives rise to phenolic compounds, such as chlorogenic acid lactones, which increase the bitter taste of coffee brews [9]. Indeed, the effect of heat leads to significant changes in the chemical, physical, structural and sensory properties of coffee [5]. Roasting coffee beans is very important in the coffee manufacturing process, as it is a key step for achieving the coffee's appropriate taste, aroma and colour [4]. During roasting, Maillard's reactions generate, a variety of compounds that create the aroma of coffee and the melanoidins responsible for its colour [26]. Indeed, coffee bean colour is a frequently used parameter for describing their degree of roasting and is classified according to light, medium and dark qualities. As the extent of roasting increases, the coffee bean colour changes from green-yellow to beige, brown to dark brown and then to brown-black [2]. The organoleptic properties of coffee are also significantly affected by the temperature and duration of the roasting process. Nevertheless, there is still no standardised definition for the different degrees of coffee roasting, and its parameters are selected depending on the desired properties of the final product. Roasting temperatures used, range from 160 to 240°C for durations of 8 to 24 minutes. The bright type of roasting coffee is characterised by bright cinnamon-coloured grains with a matt surface, obtained by short roasting and/or at lower temperatures. Such a shortly roasted coffee gives a mildly spicy brew. Medium-roasted coffee is obtained through adopting a medium roasting duration and/or moderate temperatures, where the resulting brews possess a most harmonious flavour with a hint of bread and nutmeg [17]. A long roasting of coffee at high temperatures leads to dark types, where coffee beans acquire an almost black colour and their surfaces

becomes shiny. This coffee type has an intense and bitter aroma, and in the case of very dark coffee the aroma is strongly roasted and bitter [2]. Melanoidins are formed by the reaction of sugars and amino acids during the Maillard reaction and from caramelisation of sugars by non-enzymatic browning reactions [4, 26]. These are high molecular weight compounds with a high molecular complexity [4]. Melanoidins raise the antioxidant potential of coffee [22, 19, 8]. Levels of melanoidin in coffee are linked to the intensity of the roasting process; the more intense the temperature then the higher the levels become, but they are of lower the molecular weight compared to those found in lightly roasted coffee [10]. Melanoidins possess antioxidant properties, elicit anti-mutagenic effects, lower cholesterol, have antagonist action against Helicobacter pylori, have low bioavailability and are digested only to small extents [10, 12]. Literature reports on the anti-mutagenic effect of roasted coffee and melanoidin compounds are however equivocal. For cases of colonic, liver and breast cancers, their protective effects have not been excluded, whereas for bladder and lung tumours outcomes are equivocal [27].

Because polyphenols and other antioxidant compounds play such important roles, as aforementioned, choosing the most desirable processing conditions is required for keeping the highest possible content of these valuable ingredients, whilst maintaining a high antioxidant activity of the coffee.

The purpose of this study was to determine the content of polyphenols and the antioxidant activity of Arabica coffees originating from various regions of cultivation and under varying roasting regimens, (ie. mildly, medium or strongly roasted), in order to elucidate which is the most beneficial from a nutritional point of view.

MATERIALS AND METHODS

The study raw material comprised four categories of natural coffee beans (100% Arabica) originating respectively from different world regions: Brazil, Ethiopia, Colombia and India. Each were subjected to the three different conditions of roasting: light, medium and strongly roasted. Coffee was roasted under industrial conditions at 220 °C. The duration of lightly roasted coffee was 17 minutes, for medium roasting 20 minutes and for strongly roasting 24 minutes. Study methods measured antioxidant properties, polyphenols content, dry matter and water activity. The coffee beans were ground in a coffee grinder for 25 ± 3 seconds. Coffee brews were prepared by pouring in deionized water at 94 ± 2 °C, with brewing lasting 5 minutes [14]. Antioxidant properties were determined spectrophotometrically using synthetic ABTS⁺ radicals according to the method described by *Pellegrini* et al. [16]. Another spectrophotometric method, using Folina-Ciocalteu reagent [21], was used for measuring polyphenols content. Statistical analyses were performed by Analysis of Variance using the Tuckey, Shapiro-Wilk and Bartlett tests.

RESULTS

The dry matter content and water activity of the tested coffee beans from different cultivation regions are shown on Table 1, divided according to the roasting processes used. The dry matter content for each type of coffee was high (96.41-98.26%), which reflected the low water activity found (0.30-0.41). There was a small, but statistically significant difference in the dry matter content between instances of low and high degrees of roasting. Coffee beans varied in colour depending on the degree of roasting; Figure 1, where the slightly roasted coffees had lighter colours than the strongly roasted ones, whose colours were dark brown.

decording to the degree of rousing					
	Brazil	Columbia	Ethiopia	India	
Degree of roasting					
Dry matter content (%)					
Lightly	97.42±0.09 A a	96.65±0.00 A b	97.48±0.14 A a	97.48±0.06 A a	
Medium	97.84±0.02 B a	97.73±0.13 B a	97.53±0.00 A b	98.34±0.03 B c	
Strongly	97.86±0.06 B a	97.98±0.07 C b	98.60±0.06 B c	98.66±0.03 C c	
Water activity (a_w)					
Lightly	0.41±0.01 A a	0.40±0.00 A a	0.37±0.02 A b	0.36±0.01 A b	
Medium	0.41±0.01 A a	0.38±0.02 A a	0.37±0.01 A a	0.32±0.02 A b	
Strongly	0.41±0.01 A a	0.34±0.02 B b	0.30±0.03 B b	0.34±0.02 A b	

Table 1. Dry matter content (%) and water activity (a_w) of investigated coffee beans cultivated from different world regions according to the degree of roasting

*statistically significant differences according to the degree of roasting (in columns) denoted by capital letters A-C;

** statistically significant differences according to region of origin (in legends) denoted by lower-case letters a-d.



Figure 1. Natural coffee beans (100% Arabica) according to place of origin and degree of roasting.

Table 2. Average polyphenol content in coffee (in mg gallic acid/g) according to world cultivation region and the degree of roasting

Degree of roasting	Brazil	Columbia	Ethiopia	India
Lightly	39.27±0.13 A* a**	39.81±0.37 A a	43.00±0.37 A b	41.99±0.45 A b
Medium	34.06±0.69 B a	38.43±0.26 B b	36.83±0.64 B c	37.98±0.42 B d
Strongly	29.46±0.45 C a	36.89±0.21 C b	29.21±0.37 C a	34.98±0.38 C d
* (d + d + 1) = (d + 1)				

*statistically significant differences according to the degree of roasting (in columns) denoted by capital letters A-C;

** statistically significant differences according to region of origin (in legends) denoted by lower-case letters a-d.

Table 3.	Antioxidant	activities o	of investigated	roasted coffee b	peans (µmol	Trolox/g coffee)	ļ
			<u> </u>			<u> </u>	

Degree of roasting I	Brazil	Columbia	Ethiopia	India
Lightly	952.07± 7.63 A* a**	1010.62±4.94 A b	1028.02±3.63 A c	1172.01±4.94 A d
Medium 9	963.15±2.74 A a	1083.40±2.37 B b	1103.18±11.95 B c	1206.82±6.28 B d
Strongly 9	973.43±3.63 B a	1130.87±2.37 C b	1160.14±9.88 C c	1210.77±1.37 B d

*statistically significant differences according to the degree of roasting (in columns) denoted by capital letters A-C;

** statistically significant differences according to region of origin (in legends) denoted by lower-case letters a-d.



Figure 2. A comparison of changes in mean polyphenol content and antioxidant activities according to world region of cultivation (means for all groups)



Figure 3. A comparison of changes in mean polyphenol content and antioxidant activities according to the degree of roasting (mean for all groups)

Significant differences in total polyphenols content between coffees were observed, depending on the intensity of the roasting process (Table 2 and Figure 3). The highest levels of polyphenols were found in the lightly roasted coffee. Extending the roasting time caused a significant decrease in polyphenol content from 7.3% to 32.1%. The coffee's place of origin also significantly impacted on the polyphenol levels, within the roasting regimens. Lightly roasted coffee from Ethiopia and India had higher polyphenols compared to coffee from Brazil and Columbia. The smallest losses of polyphenols during roasting were observed for Columbian coffee, which also had the highest total polyphenols content. The highest decline in polyphenols content (32.1%) was recorded for Ethiopian coffee, which, after a strong roasting process, had the lowest content of polyphenols of all. In other coffees, the differences in polyphenols levels between lightly and strongly roasted ranged from 16.7-25%.

The comparisons of coffee antioxidant activity according to type and the degree of roasting are presented in Table 3 and Figure 2, where the coffee's origin significantly impacted the antioxidant activity. This was highest for Indian coffee but the lowest for Brazilian coffee. A greater increase in antioxidant activity was observed between the light and strong degrees of roasting for both Ethiopian and Columbian coffee (11.9-12.9%). However, for Brazilian and Indian coffee, only small but yet significant (though 2.2-3.3%) differences in antioxidant activity were found between the light and strong degrees of roasting.

DISCUSSION

High levels of polyphenols were measured in coffee beans ranging from 29.21 to 43.00 mg gallic acid /g which are higher than in various fruit raw materials; in particular, aronia (chokeberry), which has high levels of 15.865-20.595 mg/g [18]. Such values are however lower compared to the polyphenols content in green and black tea; respectively 240.73

mg/g and 164.65 mg/g [24]. Various studies measuring polyphenols contents in coffee have been focused mainly on comparing Robusta with Arabica coffee, where higher polyphenol revels were recorded in Robusta coffee than in Arabica coffee [8, 19, 25]. Our own studies conducted on Arabica coffee, (being the most popular type with consumers), indicated significant variations in polyphenol content according to the region of cultivation. Likewise, other studies have found that differences in polyphenols content may be related to region of origin and conditions of cultivating coffee growing as well as to other factors [7, 19]. Our presented measurements of polyphenols content are consistent with other studies [8, 19, 23, 25], which likewise demonstrated such levels in slightly roasted coffee. With increasing the degrees of roasting, the polyphenols content became considerably reduced, both for the Arabica coffee [23] and the mixture of Arabica and Robusta coffees [1]. During coffee roasting the degradation of polyphenols [8, 19, 22, 23], which are thermo-labile, are affected by temperature. The decrease in the polyphenols content coupled along with the increase in the degree of roasting is due to the thermo-labile nature of such compounds and to the high processing temperature, as well as the extended roasting time for subsequent stages. Polyphenols losses are undesirable because they are compounds with proven beneficial effects for human health. They also show anti-tumour properties, counteract atherosclerosis and LDL oxidation.

Besides fruits and vegetables, coffee also displays significant antioxidant activity and may thus be an important source of antioxidants [19]. Coffee's antioxidant potential is due to the presence of natural/ native antioxidant compounds, as well as antioxidant compounds that form upon roasting. The actual roasting process creates the high temperatures resulting in antioxidant degradation, *inter-alia*, the polyphenols. However contemporaneously, melanoidins are formed by the Maillard reaction, which increases the antioxidant potential of coffee [8, 19, 22]. The findings

from various studies concerning antioxidant properties of coffee have been quite diverse, where elevated antioxidant activity for higher degrees of roasting has been confirmed in studies by Liu and Kitts [11], Vignoli et al. [25] and Sánchez-González et al. [20]. The reasons for such variable study outcomes can be attributed to the formation of melanoidin compounds, which raise the antioxidant potential despite the decreasing polyphenol content. Nevertheless, other studies have not found any significant effects of roasting on antioxidant activity [23] nor any signs that long-lasting roasting at high temperatures causes decreasing antioxidant activity [1, 3, 8], when polyphenol degradation is not compensated by melanoidin formation [19, 22]. Amongst other coffees, this occurrence was observed for dark roasted Robusta coffee [25]. Such differences in outcome could of arisen by the different analytical methods used for measuring antioxidant activity, the different ways of brewing coffee and obtaining extracts and that the differing degrees of roasting lack of any standard definition; also different coffee varieties are another source of variation [19]. The origin of any analysed coffee beans is another vital factor affecting antioxidant activity, since depending on the type, different concentrations of those compounds occur that constitute reagents for Maillard's reaction, thereby conferring different antioxidant activities [19]. Increases in antioxidant activity, along with increases in the degree of roasting is not only due to the appearance of melanoidin but also to highly-active low molecular weight polyphenols becoming released [19].

CONCLUSIONS

- 1. Polyphenols content, as measured in Arabica coffee beans, is high and varies according to the coffee's region of cultivation. Significantly high levels of polyphenols were found in coffee originating from Ethiopia and India.
- Concentrations of polyphenols depended on the degree of coffee roasting which strongly affects the polyphenol content. When used at industrial conditions of 220 °C and a roasting time from 17 to 24 minutes, polyphenols levels in strongly roasted coffee decreased on average from 7.3% to 32.1% when compared to lightly roasted coffee.
- 3. Quite high antioxidant activities were found in the investigated Arabica roasted coffee which varied depending on its origin and the degree of roasting. Due to roasting, the antioxidant properties of coffee are significantly increased despite significant decreases in natural antioxidants.
- 4. From a dietary standpoint, taking into account both polyphenols content and antioxidant properties, most nutritional benefit is derived from drinking lightly or medium roasted coffee.

Conflict of interest

The authors declare none.

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