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Research Article

Coffee Spent as a Potential Source of Bioactive Compounds

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Abstract

The aim of this research was to evaluate coffee spent as a potential source of antioxidant compounds. 8 brands of coffee capsules, 6 brands of domestic 'moka' coffee, and 5 brands of bar coffee were analysed after the brewing process. Extraction was performed using water as a solvent. Total phenolic content, concentrations of caffeine and chlorogenic acids and antioxidant activity were measured. Within each type of coffee spent, the phenolic concentrations and the antioxidant activity showed a great variability. Concerning the mean values, the highest phenolic content was found in spent from bar coffee, followed by capsules, and domestic 'moka' while the antioxidant activity was in the following decreasing order: capsule, domestic 'moka', and bar coffee. Antioxidant activity measured through the DPPH assay was highly correlated with the contents of total phenolic and chlorogenic acids. Caffeine contributed to the antioxidant activity of the extracts.

Keywords: Antioxidant; Caffeine; Chlorogenic Acids; Coffee Spent; Extraction

Highlights

- Coffee spent was analysed as a potential source of antioxidant.
- Samples of coffee spent from capsules, domestic Moka, and bar were considered.
- Water was used as a solvent.
- The phenolic contents were spent from bar coffee > capsules > domestic Moka.
- Antioxidant activity was highly correlated with total phenolics and chlorogenic acids.

Introduction

With a world production of 145.1 million bags in the crop year 2012/2013 [1], coffee is the second most important commodity after petroleum [2].

Coffee is the beverage obtained by decoction or infusion of the roasted ground seeds (called coffee beans) of the homonymous plant. The contact between the coffee powder and the hot water or steam favours the release of aroma compounds and other coffee-bean constituents into the aqueous solution. Several species of the Coffea L. genus may be grown for the seeds even though Coffea arabica (known as Arabica coffee) and Coffea canephora var robusta (known as Robusta coffee) respectively account for 75 - 80% and 20% of the world production [3].

Coffee manufacturing includes several after harvesting: obtainment of the green coffee beans; roasting; eventually grinding; packing. The green coffee beans can be obtained through 2 methods: the dry method, in which the harvested cherries are sorted, to separate the unripe, overripe and damaged cherries, cleaned to remove soil and leaves, dried in the sun, and submitted to the removal of the outer layers (skin and pulp); the wet method, which differ from the dry method for the separation of the pulp that occurs before the drying stage. As alternatives to the traditional coffee, there are the instant coffee and the decaffeinated coffee types. Instant or soluble coffee is made from coffee beans roasted, ground, and submitted to extraction with hot water in order to recover the coffee flavour and aroma. Then, coffee extract is dried by spray-drying or by freeze-drying. The first process for decaffeinating coffee, invented by Ludwig Roselius in 1905, was based on the use of benzene to remove caffeine from pre-moistened, green coffee beans. Currently, there are 3 main decaffeination methods: water processing; direct solvent method; and supercritical carbon dioxide decaffeination). In all of them, the green beans are previously moistened in order to make the caffeine soluble.

The domestic preparation of coffee is mainly performed through the so-called 'moka pot', a stove-top or electric coffee maker, which produces the beverage by passing boiling water pressurized by steam through ground coffee. Recently, single-serve coffee containers have been increasingly used as a domestic method to produce single portions of coffee. A single-serve coffee container can consisted in one of the following item: a pod or pad, i.e. a paper filter that wrapped an appropriate amount of ground coffee; a capsule, in which the ground coffee is packed in a plastic or aluminium package; a bag, containing a mixture of instant coffee and ground roast coffee, to provide an instant coffee but preserving the flavour of the brewed coffee [4]. To produce the beverage, a single-serve coffee container must be inserted in a coffee machine. The professional production of coffee beverage requests a 'pump espresso maker' that first heats the water to temperatures around 85 - 92°C) and then forces it to pass through the ground coffee at the correct bar pressure.

Coffee is an important source of antioxidants. The mainly phenolics in the green coffee beans are represented by chlorogenic acids and related compounds (caffeoylquinic acids, dicaffeoylquinic acids, feruloylquinic acids, p-coumaroylquinic acids and mixed diesters of caffeic and ferulic acids with quinic acid). The chlorogenic acids composition of coffee varies during processing due to isomerization, hydrolysis, degradation into low molecular weight compounds, and transformation of part of chlorogenic acids into

quinolactones and melanoidins [5]. Coffee also contains caffeine, which is known to prevent the actions of free radicals since its superoxide anion-scavenging effects and the inhibitory activity of lipid peroxidation [6,7].

The solid residue remaining after extraction of the coffee brew is known as spent coffee. In the case of single-serve coffee containers, it consists of a mix of plastic, aluminium, and organic material (the spent coffee), which is difficult to recycle. Besides researches focused on new and less polluting containers, the need to reduce waste reduction and to protect the environments has stimulated the search for methods of using spent coffee.

The coffee spent still contains compounds with high antioxidant capacity and health benefits [8] that can be recovered and used as natural antioxidants. The aim of this work was to give an overview of the antioxidant potential of coffee spent deriving from coffee machine, domestic 'moka', and bar coffee. The novelty is represented by the use of water as a solvent, in order to perform an environmental friendly extraction.

Materials and Methods

Sources of coffee spent

The coffee spent samples were withdrawn after extraction of the coffee beverage from 8 brands of coffee capsules, 6 brands of domestic 'moka' coffee, and 5 brands of bar coffee.

Extraction of the phenolic fraction from coffee spent

Before extraction, coffee pods and capsules were opened to recover the coffee spent. The materials were dried in an oven at 60°C until 5% moisture content and stored for further extractions. Twenty grams of spent coffee were submitted to extraction using 50 mL of distilled water as a solvent. Extraction was performed at 80°C for 1h under stirring.

Analysis of the total phenolic content

The total phenolic compounds were determined according to the Folin-Ciocalteau method [9]. Quantification was based on a standard curve built with aqueous solutions of gallic acid (Extra-Synthese, Genay, France) having known concentrations.

The total phenolic content was expressed as milligrams of gallic acid equivalents per gram of material.

HPLC antioxidant profile

The HPLC-DAD analysis of the phenolic extracts was carried out according to the method of Trandafir., *et al.* [7] with some modifications. A HPLC binary system consisting of a degasser mod. G1322A, a binary pump mod. G1312A, an autosampler mod. G1329A equipped with a 20- L loop, and a diode array detector mod. G1315D (Agilent, Santa Clara, CA, USA) was used. The stationary phase was a C18-RP Gemini column (250 x 4,6 mm, 5 um, Phenomenex, Torrance, CA) thermostated at 20°C. The mobile phases for chromatographic analysis were solvent A (90%) represented by 2% of o-H_3PO_4 in bidistilled water and solvent B (10%) acetonitrile at constant flow rate of 1 mL/min. Identification of the antioxidant compounds was performed by comparing the spectra and the relative retention times of the sample peaks with those obtained by injection of pure standards. Quantification was made on the basis of calibration curves of the pure standards. Results were expressed as mg per g of material.

Evaluation of the antioxidant activity

The antioxidant activity of the phenolic extracts was evaluated on the basis of the scavenging activity of the ABTS (2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt) and DPPH (1,1-diphenyl 2-picrylhyorazyl free radical) stable radical, as described in Re., *et al.* [10] and Brand-Williams, Cuvelier, and Berset [11], respectively. Data were expressed as mg trolox eq/g (ABTS) and mmol trolox eq/g (DPPH).

Statistical Analysis

Each analysis was replicated at least three times. The averages and the standard deviations were calculated using Excel software V. 11.5.1 (Microsoft, Redmond, WA). The statistical treatment was performed using the package Statistica for Windows V. 8.0. (Statsoft Inc., Tulsa, OK), with the exception of data concerning the volatile compounds, which were treated through the SCAN software from Minitab Inc. (State College, PA, USA). The least significant difference (LSD) test ($p < 0.05$) and the one-way analysis of variance (ANOVA) were applied.

Results and Discussion

Phenolic contents of coffee spent from different sources

The total phenolic contents of the coffee spent samples as extracted by hot water are reported in table 1. Data are difficult to compare with those of the previous literature since extraction was generally performed using ethanol or methanol as solvents and, sometimes, microwave or ultrasound extraction were applied to improve the extraction process [12,13]. Other researchers used water as a solvent but only compared coffee spent samples obtained by an express machine [14] or compared the effectiveness of several solvents applied on one type of spent obtained by a cafeteria [8]. In the present work, the coffee wastes from difference sources were extracted with an environmentally friendly procedure to evaluate the recovery of antioxidants in such conditions and to obtain products usable without further purification as nutritional supplements, food and cosmetic additive. The mean total phenolic contents of the analysed coffee spent were 9.8, 9.5, and 4.6 mg/g for bar coffee, capsules, and domestic 'moka', respectively, although a great variability can be observed within each type of spent depending on coffee blend, brand, type of coffee machine or domestic 'moka', conditions of coffee production. These mean values were generally in agreement with the finding of other authors, in particular when water extraction procedures were applied. It is reasonable to suppose that the phenolic concentration of the coffee spent is related to the speed of coffee production. The slowest is coffee production (as in the domestic production), the lowest is the amount of phenolics that remains in the coffee spent.

Types of Coffee spent		TPC (mg gallic acid/g)	Antioxidant activity	
			ABTS (mg trolox eq/g)	DPPH (mmol trolox eq/g)
From capsules	1	9 ± 0.4 d	19.2 ± 1.2 d	4.6 ± 0.5 d
	2	5.4 ± 0.4 b	18.3 ± 4.2 d	2.3 ± 0.1 b
	3	6.3 ± 0.1 c	8.2 ± 0.6 a	2.4 ± 0.1 b
	4	9.3 ± 0.4 d	12.4 ± 0.7 c	3.4 ± 0.8 c
	5	14 ± 0.4 e	20.9 ± 2 d	6.9 ± 0.1 e
	6	14.7 ± 0.8 e,f	32.9 ± 5 e	6.9 ± 0.5 e
	7	4.2 ± 0.4 a	9.6 ± 0.3 b	1.7 ± 0.3 a
	8	14.7 ± 0.3 f	37.6 ± 4.6	4.8 ± 0.2 d
From domestic 'moka'	1	3.3 ± 0.8 c	5 ± 0.7 c	1.2 ± 0.1 b
	2	2.4 ± 0.2 b	3.4 ± 0.5 a	0.8 a
	3	2.6 ± 0.6 a,b,c	7.4 ± 1.2 d	1.3 ± 0.2 b
	4	1.8 ± 0.5 a	4 ± 0.3 b	0.7 ± 0.2 a
	5	10.5 ± 0.4 e	26.7 ± 4.9 f	5 ± 0.4 d
	6	7 ± 0.6 d	15 ± 0.6 e	3.2 ± 0.4 c
From bar coffee	1	3.9 ± 0.4 a	7.3 ± 1.2 a	1.6 ± 0.1 a
	2	9.8 ± 0.7 c	18.5 ± 1 b	3.4 ± 0.5 b
	3	14.1 ± 0.5 e	35.4 ± 1.7 d	5.7 ± 0.6 c
	4	8.1 ± 0.2 b	27.6 ± 0.9 c	3.7± 0.5 b
	5	12.9 ± 0.6 d	29 ± 5 c,d	5.5 ± 0.4 c

Table 1: Total phenolic content (TPC) and antioxidant activity of coffee spent.
In column, within each type of coffee spent, different letters indicate significant differences at $p < 0.05$ by LSD multiple range test.

Antioxidant activity of coffee spent from different sources

Concerning antioxidant activity measured through the ABTS assay (Table 1), the mean values were 16.6, 10.2, and 1.9 mg trolox eq/g respectively for capsule, domestic 'moka', and bar coffee spent. The results obtained by the application of the DPPH assay were the following (Table 1): 3.6, 2, and 4 respectively for capsule, domestic 'moka', and bar coffee spent. Antioxidant activity detected by ABTS assay was significantly higher if compared to that by DPPH assay and, in agreement with the findings of other authors [15], these results suggest a greater effectiveness of ABTS assay in evaluating antioxidant capacity in a variety of foods. Nevertheless, in the case of ABTS, the more polar the solvent is, the greater is the antioxidant activity value while DPPH is known as the assay in which the solvent influence was the weakest [16].

Further, although the antioxidant activity measured through both the assays was well correlated to the phenolic content, the stronger correlation was found for the DPPH assay with a R value of 0.96 ($p < 0.05$) against R equal to 0.90 for the ABTS assay.

Phenolic profile of coffee spent from different sources

The contents of caffeine and chlorogenic acids are listed in table 2. The mean concentrations of caffeine were 2.2, 2, and 0.6 mg/g for capsule, bar, and domestic 'moka' coffee spent, respectively. Concerning chlorogenic acids, the mean concentrations were the following: 0.6, 0.5, and 0.2 mg/g for capsule, bar, and domestic 'moka' coffee spent, respectively.

Types of Coffee spent		Caffeine (γ = 275 nm)	Chlorogenic acids (γ = 323 nm)
From capsules	1	1.2 c	0.7 c
	2	0.6 b	0.1 a
	3	1.4 d	0.5 b
	4	1.7 ± 0.3 e	0.5 b
	5	3.8 ± 0.3 f	1.3 ± 0.1 d
	6	4.4 ± 0.2 g	1.3 d
	7	0.1 a	n.d. a
	8	4.4 ± 0.3	0.8 c
From domestic 'moka'	1	0.4 c	n.d. a
	2	n.d. a	n.d. a
	3	0.2 b	0.1 a
	4	n.d. a	0.2 a
	5	1.4 ± 0.6 d	0.8 ± 0.1 b
	6	1.7 ± 0.1 d	0.2 a
FromBar Coffee	1	0.4 a	0.1 a
	2	0.4 ± 0.1 a	n.d. a
	3	4.9 ± 0.2 d	1.4 d
	4	1.2 b	0.5 b
	5	3 ± 0.1 c	0.7 c

Table 2: Phenolic profile of coffee spent. Data are expressed as mg/g.

In column, within each type of coffee spent, different letters indicate significant differences at $p < 0.05$ by LSD multiple range test.

n.d.: not detected

Antioxidant activity was correlated to the content in caffeine and chlorogenic acids with the following results: ABTS and caffeine, R = 0.83; ABTS and chlorogenic acids, R = 0.76; DPPH and caffeine, R = 0.86; DPPH and chlorogenic acids, R = 0.90. These findings taken together with the highest correlation values obtained with the antioxidant activity measured through the DPPH assay suggest that chlorogenic acids are the major contributors to the antioxidant capacity in coffee spent although also caffeine strongly contributed to it. In fact, it has been documented that the antioxidant capacity of chlorogenic acids a result of their ability to donate hydrogen atoms to reduce free radicals and to inhibit oxidation reactions. Then, chlorogenic acids are oxidized to respective phenoxyl radicals and these phenoxyl radicals are quickly stabilized by resonance stabilization [17]. Instead, caffeine exerts an important scavenging activity against several reactive oxygen species (•OH, $•OCH_3$, and other alkoxyl radicals) and that the main mechanism involved is the radical adduct formation [18].

Conclusion

This study indicated that water extracts of coffee residue contained concentrations of caffeine and chlorogenic acids able to exert significant antioxidant activity as measured through ABTS and DPPH assay. Coffee spent from capsule, domestic 'moka', and bar coffee showed different values of mean total phenolic concentration, also as a consequence of the different conditions of brewing (time, temperature, pressure). Caffeine was found in concentrations higher than those of chlorogenic acids, although the latter showed the highest correlations with the antioxidant activity of the coffee spent. Coffee spent from capsules showed the highest mean values of antioxidant activity among the three types of spent. This finding can encourage the attempt to find possible ways to recycle capsules in which the complexity of the packaging constituted by a mix of different materials is combined with the presence of organic waste.

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