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Crude ethanolic extract from spent coffee grounds: Volatile and functional properties

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ABSTRACT

Espresso capsule consumption and spent coffee ground (SCG) generation have increased, and the present study was undertaken to evaluate the volatile profile (VP), the antioxidant activity (AA) and the sun protection factor (SPF) of the Crude ethanolic extract obtained from the SCG in capsules. The extract yield was superior to the ether yield because a higher unsaponifiable matter (U.M.) amount was recovered by ethanol. The obtained VP (70 compounds) was typical of roasted coffee oil. Furthermore, chemometric analysis using principal components (PCA) discriminated the extracts and grouped the replicates for each sample, which showed the repeatability of the extraction process. The AA ranged from 18.4 to 23.6 (mg extract mg $DPPH^{\cdot -1}$) and the SPF from 2.27 to 2.76. The combination of the coffee VP, AA and SPF gave the *espresso* SCG's crude ethanolicextract, desirable properties that can be used in cosmetic and food industries.

1. Introduction

Agro-industrial waste reutilization has been adopted as alternative to improve emergent and sustainable technologies (Jones and Jew, 2007, Orioli et al., 2016) and increase the natural and rare ingredient supplies for industrial interests. Since new environmental rules for industrial waste disposal have become stricter, the reuse of residues may prove to be economically viable in agribusiness sectors (Ferrari et al., 2004; Paula et al., 2015).

Several substances found in the unsaponifiable fraction of lipids, which is obtained from agro-industrial residues, have biofunctionalities and are effective in disease prevention against cataracts, macular degeneration, diabetes, cardiovascular diseases, oxidative stress and some types of cancer (Nicolosi et al., 1997; Mussato et al., 2011). Furthermore, the lipid fraction contains volatile compounds of organoleptic interest whether they are bioactive or not (Oliveira et al., 2009).

Since 2000, the consumption of *espresso* coffee in capsules has increased and reached 20 billion units, and the sales of *espresso* coffee in capsules reached approximately 17 billion dollars in Europe in 2009 (Getty, 2010). In 2015, sales of coffee capsules in Brazil were nearly 0.5 billion dollars (1.4 billion Brazilian reais) (ABIC, 2015), which corresponded to approximately 3500 tonnes of spent coffee grounds (dry matter). By 2019, this number is estimated to be 7400 tonnes. The increase in consumption and residue generation encourages studies on new technological processes that can add value to the residues and provide economically feasible reutilization opportunities. Spent coffee grounds collected from coffee bars (SCG-1) or recovered from coffee capsules (SCG-2) were investigated as a potential source of phenolic compounds and energy (Zuorro & Lavecchia, 2012). According to these authors, the calorific values of the two coffee wastes were only marginally affected by the extraction procedure, which supports the potential use of the spent coffee ground to recovery the phenolic compounds and to produce pellets or other agglomerates for heating purposes from the extraction by product. Furthermore Casal et al., (2012), Magalhães et al., (2016) and Ballesteros et al., (2017) evaluated the use of coffee spent grounds as a source of bioactive substances to pharmaceutical, cosmetic and food industries applications.

In addition to beneficial properties, such as antioxidant activity and UV radiation protection, coffee oil has a volatile profile similar

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to that of coffee bean flavor (Arruda et al., 2012). Among the techniques applied to discriminate coffee bean origins using its volatile profile, multivariate analysis with principal components **(PCA)** of the identified substances via headspace-solid phase microextraction-gas chromatography-mass spectrometry (HS-SPME-GC-MS) has gained prominence in recent years (Mondello et al., 2005; Gonzalez-Rios et al., 2007; Arruda et al., 2011).

The search for n-hexane alternatives in vegetal oil extraction aims to reduce the economic dependence on fossil solvents and to reduce the toxic solvents used in food processing (Mejean and Hope, 2010). In Brazil, the use of ethanol (EtOH) to replace n-hexane is possible once EtOH can be obtained from sugarcane at competitive prices (Freitas and Lago, 2000).

In the cosmetics industry, coffee oil is applied in the product formulation to block UV radiation and to moisturize, lubricate and improve skin texture by promoting its hydrolipidic layer regeneration (Grollier and Plessis, 1988; Coiffard et al., 2016; Marto, et al., 2016). In the pharmaceuticalindustry, the main value of coffee oil is the presence of compounds that can stabilize free radicals. These compounds have also been evaluated in spent coffee grounds, which could be a source for the compounds once the grounds are widely available for large-scale processing and reuse (Mussato et al., 2011; Zuorro and Lavecchia, 2012; Petrucci, et al., 2013).

Spentcoffee ground reuse would mitigate waste disposal and create beneficial natural food products. The present study was undertaken to evaluate the volatile profile **(VP)**, antioxidant activity **(AA)** and sun protection factor **(SPF)** of the lipid extract obtained from spent coffee grounds in capsules using ethanol as the solvent.

2. Materials and methods

2.1. Raw materials

Six samples of the commercial coffee in capsules were analyzed. The capsules were blends from coffees with different origins. Information provided by the manufacturer about each sample is provided in Table 1

2.2. Coffee brew processing of espresso capsules

Coffee brews were prepared via hot extraction with the conditions recommended by Caprioli et al. (2012), 92 °C and 9 bars, using a ratio of water to sample of 5:1. After extraction, the capsules containing the spent coffee grounds were kept in freezer at −20 °C.

Table 1
The main features of roasted beans according to the manufacturer's data. Source: Nespresso®.

Sample	Description
A	Coffee grown in higher regions of Colombia with red fruit notes and a touch of wine
B	Blend of arabica coffee from Costa Rica and Colombia with cereal, malt and caramel notes
C	Blend of arabica from Central America plus Brazilian arabica and robusta with woody and roasted notes
D	Blend of red and yellow bourbon coffee plantations at high altitudes in southeastern Brazil with cereal, honey and maple syrup notes
E	Brazilian and Colombian arabica combination with red fruits, dried fruits and cereal notes
F	Blend of arabica from Kenya, South and Central America with lemon notes

2.3. Spentcoffeegroundscharacterization

The spentcoffee ground ether and ethanol extracts were determined using, respectively, petroleum ether and ethanol in a soxhlet apparatus at the solvent boiling point for 6 haccording to the AOCS Ca 6a-40 standard method (AOCS, 1997).

The moisture contentwasdetermined using the AOAC 984.20 method. The sample was maintained in an oven at 105 °C until it had a constant weight (AOAC, 2004).

2.4. Spent coffee grounds processing

Before extraction, the spent coffee grounds were lyophilized for 12 h after they were frozen in liquid nitrogen (−196 °C). The lyophilized samples were incubated at 60 °C with anhydrous ethanol in a ratio of 4:1 (EtOH:dry, spent coffee grounds, w/w) in a thermostatic shaker water bath at 2000 rpm for 30 min. The suspension was filtered under vacuum and separated in two streams: micelle (lipids + ethanol) and cake. Finally, the ethanol was distilled under vacuum in rotating evaporator to obtain the spent coffee ground lipid extract (Freitas et al., 2000). Three process replicates were performed for each of the six samples (A, B, C, D, E and F).

2.5. Chemical properties of the lipid extract

The unsaponifiable matter **(U.M.)** content was determined using the AOCS Ca 6a-40 standard method (Aocs, 1997). The lipids present in the extract weresaponified with 5% KOH solution (m/v). The reaction was conducted on orbital shaker under agitation of 200 rpm at 70 °C for 1 h. Thus, the **U.M.** was recovered in four successive extractions with hexane. The sample, after evaporation of the solvent, was weighed by determining the mass of **U.M.** in the extract.

To evaluate the volatile profile using HS-SPME-GC–MS, 0.20 g of the lipid extract were heated to 60 °C in a 5 mL sealed vial for 20 min. Then, the grey fiber (polydimethylsiloxane/divinylben zene/carboxen) was exposed to the vial's headspace for 10 min to allow substance adsorption. The fiber was inserted for 5 min into the injector of an Agilent 6890 GC chromatograph at 240 °C (splitless mode) for volatile desorption (Caprioli et al., 2012). A chromatographic column (DBwax, J & W Corp.) with a 25 m × 0.2 mm internal diameter and 0.25 μM film thickness was used; the temperature ramping was 45 °C (5 min) to 230 °C at 4 °C min^{-1}, and the final temperature was maintained for 10 min. The mass spectra were obtained using an Agilent5973 selective mass detector model operating in the electronic ionization mode (70 eV) with a transfer line temperature of 280 °C and the ion source at 220 °C.

Linear retention indices **(LRI)** were calculated via a standard n-alkanes (C_7-C_{28}) injection under the same analytical conditions (Viegas and Bassoli, 2007). Compound identification was performed by comparing the mass spectra to the spectra in the NIST 2.0 electronic library. The LRI found were compared to the literature data, and the identification was also conducted using Sigma Chemicals Co. (St. Louis, EUA) external standard, GC grade co-injections, namely, Pyridine, Pyrazine, 2,5-Dimethyl pyrazine, 2,6-Dimethyl-pyrazine, 2,3-Dimethyl pyrazine, 2-Ethyl-6-methyl-pyrazine, 2-Ethyl-5-methyl Pyrazine, Furfural, 5-Methyl-2-furyl carboxaldehyde, Maltol, 2-Methoxy-4-ethyl-phenol, and -Methoxy-4-vinyl-phenol (Arruda et al., 2011).

To ensure a greater SPME reliability, six injections of the same sample were performed, and the average, standard deviation and variation coefficient of each identified peak area were calculated. From this test, 70 compounds among the 182 chromatographic peaks detected were compared to the NIST spectra, and the statistical significance was considered at the $p < 0.1$ level.

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