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Nutritional, chemical and antioxidant/pro-oxidant profiles of silverskin, a coffee roasting by-product

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ABSTRACT

Coffee silverskin (a coffee roasting by-product) contains high amounts of dietary fibre (49% insoluble and 7% soluble) and protein (19%). Potassium (~5 g/100 g), magnesium (2 g/100 g) and calcium (0.6 g/100 g) are the major macrominerals. The vitamin E profile of silverskin comprises α-tocopherol, β-tocopherol, ɣ-tocopherol, δ-tocopherol, β-tocotrienol, ɣ-tocotrienol, and δ-tocotrienol. The fatty acid profile is mainly saturated (C16:0 and C22:0), but the total amount of fat is low (2.4%). Caffeine (1.25 g/100 g), chlorogenic acid (246 mg/100 g), and 5-hydroxymethylfurfural (5.68 mg/100 g) are also present in silverskin. Total phenolics and flavonoids are partially responsible for the *in vitro* antioxidant activity. Silverskin extracts protected erythrocytes from oxidative AAPH- and H_2O_2-induced hemolysis, but at high concentrations a pro-oxidant effect on erythrocyte morphology was observed.

1. Introduction

In recent years (2015/16), the global coffee production reached 145 million of 60 kg bags (ICO, 2016). Along with this production, a great amount of residues (*e.g.* husks, hulls, defective beans, coffee silverskin, and spent coffee grounds) is generated. They constitute a source of contamination and a severe environmental problem, especially due to their richness in phytotoxic and/or *anti*-nutrient compounds (*e.g.* caffeine, tannins, and polyphenols) that can limit their direct use in soil or feed applications. However, they may be a good source of bioactive compounds that can be extracted and further used in food, cosmetics or pharmaceuticals (Mussatto, Machado, Martins, & Teixeira, 2011; Oliveira & Franca, 2015). Thus, the management and re-use of these high added-value residues can contribute to the sustainable development of the coffee chain itself, the global economy and, simultaneously, to a greener environment.

Based on this, it is crucial to make a general effort to valorize the by-products that result from coffee processing. In this context, coffee silverskin (the by-product of coffee roasting) emerges as a particularly interesting product. It is a thin tegument that constitutes the outer layer of raw coffee beans which is detached during the expansion of the beans when subjected to the high temperatures of roasting.

To date, coffee silverskin has been mainly used as direct fuel (*e.g.* firelighters), for composting and soil fertilization but, recently, several innovative approaches have been suggested, essentially based on its richness in dietary fibre, phenolic compounds and other antioxidants, such as melanoidins (Ballesteros, Teixeira, & Mussatto, 2014; Borrelli, Esposito, Napolitano, Ritieni, & Fogliano, 2004; Costa et al., 2014; Mussatto et al., 2011). For instance, Mussatto et al. (2011) suggested the incorporation of coffee silverskin in flakes, breads, biscuits and snacks. Also, Pourfarzad, Mahdavian-Mehr, and Sedaghat (2013) used this by-product to improve quality, shelf life, and sensorial properties of Barbari flat bread, while reducing its caloric density and increasing the dietary fibre content. In turn, Martinez-Saez et al. (2014) used silverskin to prepare a novel antioxidant beverage for body weight control, while Rodrigues, Matias, Ferreira, Amaral, and Oliveira (2016)

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reported the successful use of silverskin as a cosmetic active ingredient with results similar to hyaluronic acid in the improvement of skin hydration and firmness.

Different classical spectrophotometric methods (DPPH·-scavenging ability, ferric-reducing antioxidant power, trolox equivalent antioxidant capacity, among others) have been used to evaluate the antioxidant properties of coffee silverskin (Ballesteros et al., 2014; Borrelli et al., 2004; Costa et al., 2014; Napolitano, Fogliano, Tafuri, & Ritieni, 2007; Narita & Inouye, 2012). In addition, Mesías et al. (2014) found that, in association with its antioxidant activity, silverskin aqueous extracts also have *in vitro* antiglycative properties, protecting against the formation of advanced glycation end-products and trapping of carbonyl-reactive species, such as methylglyoxal.

In this work, we analysed, for the first time, the vitamin E (an antioxidant liposoluble vitamin) profile of coffee silverskin, as well as, the capacity of this by-product to protect human erythrocytes from oxidative damage under oxidative stress conditions. This can suggest the ability of silverskin to protect cells against oxidative injuries in a real biological system. Coffee silverskin was also characterized regarding its nutritional composition, including soluble and insoluble fibre, macromineral content, and fatty acid profile. Caffeine, chlorogenic acid, total phenolics, and total flavonoid contents, as well as *anti*-radical scavenging capacity and ferric-reducing antioxidant power were also assessed.

2. Material and methods

2.1. Reagents and standards

For the macronutrients analysis, all analytical grade reagents were purchased from Panreac (Barcelona, Spain) and Merck (Darmstadt, Germany). The standards, sodium, potassium, calcium, magnesium, iron, chlorogenic acid, caffeine and 5-hydroxymethylfurfural, and the Supelco 37 Component, FAME Mix, were all obtained from Sigma–Aldrich (St. Louis, USA). Tocopherols (α, β, γ and δ) and tocotrienols (α, β, γ and δ) were purchased from Calbiochem (La Jolla, CA, USA) and tocol was obtained from Matreya Inc. (Pennsylvania, USA). HPLC grade solvents were obtained from Sigma–Aldrich (St. Louis, USA) or Merck (Darmstadt, Germany).

For the antioxidant assays, gallic acid, epicatechin, ferrous sulfate heptahydrate and trolox, as well as the Folin-Ciocalteu's reagent, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH·), sodium nitrite, ferric chloride, aluminium chloride, 2,4,6-tripyridyl-s-triazine (TPTZ), 2,2′-azobis(2-amidinopropane dihydrochloride (AAPH), sodium acetate, and sodium azide were all acquired from Sigma-Aldrich (St. Louis, USA). Anhydrous sodium carbonate, sodium hydroxide, absolute ethanol and hydrogen peroxide were purchased from Merck (Darmstadt, Germany). All other reagents were of analytical grade. Ultrapure water was obtained in a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2. Sample and sample preparation

Silverskin (~2.5 kg) representing the major roasting by-product of a national coffee industry, was kindly supplied by BICAFÉ, Torrefação e Comércio de Café, Lda (Portugal). After reception, the sample was stored in a fresh and dry place, protected from light.

2.3. Nutritional analysis

Moisture was determined using an infrared balance (Scaltec model SMO01, Scaltec Instruments, Heiligenstadt, Germany). The remaining nutritional analyses were performed according to AOAC procedures (AOAC, 2012). Briefly, ashes were quantified after incineration at 500 °C. Total lipids and protein were determined by the Soxhlet and the Kjeldahl methods, respectively. Fibre was analysed through enzymatic-gravimetric procedures. Non-fibre carbohydrates were calculated by difference.

2.4. Macromineral composition

The mineral analysis was performed according to Pinto, Almeida, Aguiar, and Ferreira (2014). Briefly, silverskin was digested in an MLS-1200 Mega microwave digestion unit (Milestone, Sorisole, Italy), in the presence of HNO_3 (65%) and H_2O_2 (30%). After digestion, the mixture was diluted to 25 ml with ultrapure water. Macromineral contents were determined using a Perkin Elmer (Überlingen, Germany) 3100 flame (air-acetylene) atomic absorption spectrometer. Calibration standards were prepared from 1000 mg/l single-element standard solutions of Ca, Na, Mg, Fe, and K.

2.5. Fatty acids profile

Silverskin lipids were obtained by Soxhlet extraction during 2.5 h with *n*-hexane, which was subsequently evaporated under a nitrogen stream. The fatty acids were derivatized according to Fernandes et al. (2012) to form the corresponding fatty acid methyl esters (FAMEs). Briefly, the sample was heated at 100 °C for 10 min in the presence of 0.5 M KOH in methanol. Thereafter, 2 ml of boron trifluoride solution (14% in methanol) were added and the mixture was heated at 100 °C for 30 min. After cooling, 2 ml of deionized water and 5 ml of *n*-hexane were also added. The mixture was vortexed and centrifuged. The upper layer was transferred to a 4 ml vial and anhydrous sodium sulfate was used to eliminate any remaining water. This mixture was further vortexed and centrifuged. The supernatant was analysed in a gas chromatograph (GC) Shimadzu GC-2010 Plus (Shimadzu, Tokyo, Japan) coupled with a split/splitless Shimadzu AOC-20i auto-injector (Shimadzu, Tokyo, Japan) and a flame ionization detector (FID) (Shimadzu, Tokyo, Japan). A CP-Sil 88 silica capillary column (50 m × 0.25 mm i.d, 0.20 μm film thickness; Varian, Middelburg, Netherlands) was used to achieve compound separations. The injection was performed in the split mode (1:25), and helium was used as carrier gas. The injection volume was 1.0 μl. The column temperature was programmed as follows: 80 °C, 5 min;, from 80 to 200 °C, at 5 °C/min and then held 5 min and from 200 to 220 °C, at 4 °C/min and held 15 min. Injector and detector temperatures were 250 and 270 °C, respectively. FAMEs were identified by comparison with standards (FAME 37, Supelco). Data were analysed, using the Shimadzu software GC Solution (Shimadzu, Tokyo, Japan). The results were expressed as relative percentage of each fatty acid.

2.6. Chromatographic analyses

2.6.1. HPLC equipment

The chromatographic analyses were conducted in an HPLC integrated system composed of an AS-2057 automated injector, a PU-2089 pump, and a MD-2018 multi-wavelength diode array detector (DAD), and a FP-2020 fluorescence detector (FD), from Jasco, Japan. Data were analysed with JASCO-Chrom NAV Chromatography Software (Jasco, Japan).

2.6.2. Vitamin E profile

Silverskin lipids were obtained by Soxhlet extraction during 2.5 h with *n*-hexane (Pimentel et al., 2014), which was then evaporated under a nitrogen stream. A small amount of lipids (~50 mg) was mixed with the 20 μl of tocol (1 mg/ml) and *n*-hexane. The

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