Food Research International 61 (2014) 196–201

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Phenolic composition, caffeine content and antioxidant capacity of coffee silverskin

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ARTICLE INFO

Article history:
Received 26 August 2013
Received in revised form 25 October 2013
Accepted 27 October 2013
Available online 5 November 2013

Keywords:
Coffee silverskin
Chlorogenic acids
Caffeine
Total antioxidant capacity
Total polyphenol content

ABSTRACT

Coffea arabica silverskin (CSS), the inner fruit layer surrounding coffee beans, was analyzed for its (poly)phenolic and caffeine content by means of liquid chromatography–tandem mass spectrometry and evaluated for its antioxidant properties by means of the Folin–Ciocalteu and FRAP methods. The most abundant quantified phenolics were caffeoylquinic acids, with the 5- and 3-isomers being the most relevant (199 mg/100 g and 148 mg/100 g, respectively). The three caffeoylquinic acid isomers reached a total concentration of 432 mg/100 g, corresponding to 74% of the total chlorogenic acids detected in CSS. The level of the three feruloylquinic acids detected was 143 mg/100 g, corresponding to 23%, and the two identified coumaroylquinic acids plus the two caffeoylquinic acid lactones were only marginally contributing to the final figure (only 3% of total hydroxycinnamates). No unconjugated phenolic acid was detected. Caffeine content in CSS was equal to 10 mg/g of product, 3.5 times lower than most coffee brews. The total antioxidant capacity (TAC) of CSS was 139 mmol Fe^{2+}/kg, a value similar to those of valuable sources of food antioxidants like dark chocolate, herbs and spices. Besides its potential as a food supplement, CSS may represent an innovative functional ingredient exploitable to increase the TAC of a wide range of food products.

1. Introduction

Coffee is one of the most widely consumed beverages (Freedman, Park, Abnet, Hollenbeck, & Sinha, 2012) and with a production of 8 million metric tons per year represents one of the most important food products traded. Since coffee contains caffeine, a stimulant substance, its consumption has not been considered a healthy habit (Freedman et al., 2012) and has been linked to cardiovascular adverse effects and to increased risk of myocardial infarction in the past (O'Keefe et al., 2013). However, more recent and critical epidemiological and intervention studies have attributed many positive effects to moderate daily consumption of coffee (O'Keefe et al., 2013), particularly linked to its polyphenolic content, especially chlorogenic acids (Gómez-Ruiz, Leake, & Ames, 2007). In fact, coffee intake may improve glucose metabolism and insulin sensitivity, thus decreasing the risk of type 2 diabetes, coronary heart disease, ischemic stroke, depression, Alzheimer's and other diseases of the central nervous system, including Parkinson's disease (Huxley et al., 2009; O'Keefe et al., 2013). Moreover, coffee consumption has shown inverse association with death linked to heart disease and respiratory disease, stroke, injuries, accidents, diabetes and infections (Freedman et al., 2012).

Coffee fruit is a drupe with an outer skin or pericarp, usually green in unripe and red-violet or deep red in ripe fruits (even yellow or orange in particular cultivars). The pericarp covers a soft yellowish, fibrous and sweet pulp (outer mesocarp), a highly hydrated layer of mucilage (the pectin layer), and a thin endocarp (the parchment). Finally, the so-called "silverskin" covers each hemisphere of the endosperm, which represents the common coffee seed (Fig. 1) (Belitz, Grosch, & Schieberle, 2009; Berbert et al., 2001). Industrial processing causes the removal of the husks, including the pericarp, outer mesocarp, pectin layer, endocarp and part of the silverskin, from green coffee beans. During the roasting processes the residual coffee silverskin (CSS) is completely removed and the ground roasted coffee beans are finally used for coffee beverage production (Esquivel & Jiménez, 2012). Considering the large consumption of this beverage, and since more than 50% of the coffee fruit is not used for coffee production and is discarded during processing (Esquivel & Jiménez, 2012), characterizing this fraction for its content of typical coffee bioactives could be a promising strategy for future recovery, or in the context of new functional food design, also considering its lower methylxantine level.

Abbreviations: CID, collision induced dissociation; CRM, consecutive reaction monitoring; CSS, coffee silverskin; LITMS, linear ion trap mass spectrometry; $[M-H]^-$, negatively charged molecular ion; $[M+H]^+$, positively charged molecular ion; m/z, mass-to-charge ratio; SIM, single ion monitoring; TAC, total antioxidant capacity; TPC, total polyphenol content.

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http://dx.doi.org/10.1016/j.foodres.2013.10.047

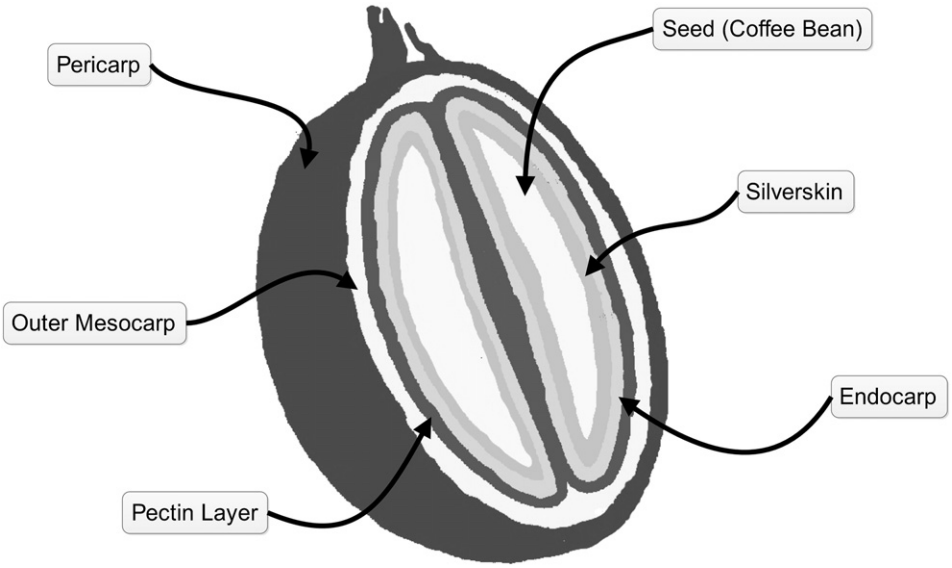

Fig. 1. Coffee fruit structure.

CSS, given the volumes of crude coffee processed at present, is an industrial waste readily available in large amounts and in need for a definition of its potential value-added uses. Nevertheless, it has been poorly investigated in the past and has been almost invariably used only as combustible or fertilizer (Saenger, Hartge, Werther, Ogada, & Siagi, 2001). It is rich in fiber, high in ash, suggesting a relevant mineral content, high in protein and low in lipids (Borrelli, Esposito, Napolitano, Ritieni, & Fogliano, 2004; Pourfarzad, Mahdavian-Mehr, & Sedaghat, 2013). Previously, CSS has been described for its caffeine and 5-caffeoylquinic acid content, but attention was focused only on the extraction yields at different temperatures (Narita & Inouye, 2012). However, CSS being the outer layer of the roasted coffee beans, it is conceivable that some of the properties described for coffee brews could be maintained also in CSS, making it a potentially high value-added by-product if properly used by the food industry (Pourfarzad et al., 2013). Nevertheless, few reports about CSS have been published in the scientific literature (Narita & Inouye, 2012), mainly dealing with its antioxidant and prebiotic properties (Borrelli et al., 2004), and hyaluronidase inhibitory activity (Furusawa, Narita, Iwai, Fukunaga, & Nakagiri, 2011).

To date, a detailed polyphenolic composition of CSS is lacking. Therefore, this study aims to define for the first time a detailed quali-quantitative (poly)phenolic profile of CSS obtained from *Coffea arabica* beans harvested in an area near Santos (Brazil), to better understand if this by-product could harbor the potential to become an innovative functional food ingredient. Moreover, caffeine content, total polyphenol content (TPC) and total antioxidant capacity (TAC) were also evaluated.

2. Materials and methods

2.1. Plant material

CSS, harvested in an area near Santos (Brazil), was obtained from a mix of *C. arabica* beans (kindly provided by Soremartec s.r.l., Alba, Italy), removed during roasting through a cyclone. CSS samples were then stored at room temperature and under vacuum in plastic bags until extraction.

2.2. Chemicals

All chemicals and solvents were of analytical grade. Caffeine, 3-caffeoylquinic acid (98%), 5-caffeoylquinic acid (95%), Folin–Ciocalteu reagent, (+)-catechin and iron(II) sulfate heptahydrate were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). All solvents and reagents were purchased from Carlo Erba Reagents (Milano, Italy). Ultrapure water from MilliQsystem (Millipore, Bedford, MA, USA) was used throughout the experiment.

2.3. Phenolic and caffeine extraction from CSS

CSS was pulverized and then extracted with acidified water (1% formic acid) as previously reported by Del Rio, Calani, Dall'Asta, and Brighenti (2011). The extracts were stored at −20 °C until analysis.

2.4. UHPLC–LITMS analysis

Identification and quantification of phenolic compounds and the quantification of caffeine content of CSS samples were performed using an Accela UHPLC 1250 equipped with linear ion trap-mass spectrometer (LTQ XL, Thermo Fisher Scientific Inc., San Jose, CA, USA) fitted with a heated-electrospray ionization (H-ESI-II) probe (Thermo Fisher Scientific Inc., San Jose, CA, USA). Separations were carried out by means of a C18 BlueOrchid column (50 × 2 mm; 1.8 μm particle size; Knauer, Berlin, Germany). The analytical mass spectrometric conditions were optimized by infusion of pure standards of 5-caffeoylquinic acid and caffeine. The mobile phase, pumped at a flow rate of 0.3 mL/min, was acetonitrile in 0.1% aqueous formic acid and acidified water (0.1% formic acid) for all the applied chromatographic separations. The gradient was a 9-minute linear gradient of 3% to 20% acetonitrile in 0.1% aqueous formic acid. The H-ESI-II interface worked with a capillary temperature of 275 °C and the source heater temperature was 50 °C. The sheath gas flow (N_2) was set at 40 (arbitrary units) and the auxiliary gas flow (N_2) at 5. The H-ESI-II interface worked in negative (for phenolics), or in positive ionization mode (for caffeine). During polyphenol analysis, the source voltage was 4 kV, and the capillary voltage and tube lens were −26 and −77.71 V, respectively. During caffeine analysis, the source voltage was 4 kV, the capillary voltage was set at 40 V and tube lens at 120 V.

Initially, 5 μL of CSS aqueous extracts were analyzed in negative ionization full scan data-dependent MS^3 mode to obtain a preliminary overview about (poly)phenolic compounds, scanning from m/z 100 to m/z 1500. After this preliminary analysis further specific MS^2 and MS^3 experiments were performed to unambiguously identify the CSS phenolics. Molecules were fragmented using pure helium (99.99%), setting a collision-induced dissociation (CID) equal to 30 (arbitrary units) for the production of the first daughter ion and equal to 35 to obtain the subsequent fragmentation. For CSS phenolic quantification, a single ion monitoring (SIM) method was carried out. The analyzed molecules