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Short Communication

Isolation of green coffee chlorogenic acids using activated carbon

Mirna Leonor Suárez-Quiroz [a], Angelina Alonso Campos [a], Gerardo Valerio Alfaro [a], Oscar González-Ríos [a], Pierre Villeneuve [b], Maria Cruz Figueroa-Espinoza [c,*]

[a] Instituto Tecnológico de Veracruz, Unidad de Investigación y Desarrollo en Alimentos, Miguel Angel de Quevedo N° 2779, 91860 Veracruz, Veracruz, Mexico
[b] CIRAD, UMR 1208 IATE, 2 Place Viala, F-34060 Montpellier, France
[c] Montpellier SupAgro, UMR 1208 IATE, 2 Place Viala, F-34060 Montpellier, France

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ABSTRACT

Chlorogenic acids, which are interesting natural antioxidants widespread in the plant kingdom, were extracted and purified from Mexican green coffee beans (*Coffea arabica*) using different methods. The final objective was to find an easy way to extract high-value molecules from a complex mixture, avoiding as much as possible the use of toxic solvents. Three extraction methods (hot water at 80 °C, aqueous methanol 70% (v/v), and aqueous isopropanol 60% (v/v)) were tested in combination with two isolating methods (activated carbon, different solvents). The extracted amounts of chlorogenic acids with the six treatments (4.67–5.87% dry basis) presented no significant differences. The one using hot water for extraction and of activated carbon for isolation, was the simplest and the most environmentally friendly. Thus it can be used as a previous step to obtain from green coffee a mixture rich in chlorogenic acids which can be further fractionated to purify a specific chlorogenic acid (i.e. in this work, 5-*O*-caffeoyl quinic acid using a silica gel column). Chlorogenic acids can be used as natural antioxidants in food or non-food products. To the best of our knowledge, activated carbon has not been used to isolate chlorogenic acids from green coffee.

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1. Introduction

Chlorogenic acids (CGA) (mono- and di-acyl quinic acids, with caffeic, ferulic, and *p*-coumaric acids as the main acylating residues) are natural antioxidants widespread in the plant kingdom (Clifford, 1999), and well represented in coffee beans. Depending on the species, green coffee beans contain some 6–10% (dry basis (db)) of CGA, with levels of CGA higher in *Coffea robusta* beans than in *C. arabica* beans (Clifford, 1999; Debry, 1993; Ky et al., 1997). The most commonly found individual CGA is 5-*O*-caffeoylquinic acid (5-CQA) (Fig. 1; IUPAC numbering (IUPAC, 1976)), often called chlorogenic acid, which is usually the only one commercially available. According to Clifford and Jarvis (1988), a Mexican robusta green coffee contained 5.98, 1.11, and 1.20% (db) of caffeoyl quinic acids (CQAs), feruloyl quinic acids (FQAs), and dicaffeoyl quinic acids (diCQAs), respectively. Ky et al. (1997) quantified CGA on a *C. liberica* var *dewevrei*, and they observed a maximum of 6.5% of 5- and 4-CQA from a total CQAs of 7.3% (db), and 0.76 and 1.43% (db) of total FQAs and diCQAs, respectively.

Different methods have been used to extract and isolate CGA from green coffee. Generally, beans are first frozen by liquid nitrogen to minimize CGA oxidation (Colonna, 1979) and ground. Then most of the CGA extraction methods use polluting organic solvents as aqueous methanol (Andrade et al., 1997; Colonna, 1979; Dibert et al., 1989; Rakotomalala, 1992), aqueous methanol and Carrez reagents (Balyaya and Clifford, 1995; Clifford et al., 2003; Trugo and Macrae, 1984), or aqueous 2-propanol 70% (v/v) (Morishita et al., 1984).

Adsorption can be a more environmental friendly technique allowing the separation of selected compounds from diluted solutions and avoiding the use of toxic solvents. It has been largely used for the recovery of plant phenolic compounds.

Activated carbons (AC) have been used as adsorbents to selectively separate phenolic compounds from foods or by-products (Soto et al., 2011). Concerning the family of cinnamic acid derivatives, AC has been used to isolate ferulic acid from an aqueous sugar-beet pulp enzyme hydrolyzate (Couteau and Mathaly, 1997) and from the cooking water of maize (Creppy, 2002). To the best of our knowledge, AC has not been used to isolate CGA from green coffee beans. Reports on the use of other kind of absorbents to recover CGA can be found in literature, i.e. non polar resin tested on apple juice (Kammerer et al., 2007), hydrophobic styrene-divinylbenzene copolymer used on model solutions (Kubo et al., 2002) or on apple pomace (Schieber et al., 2003), and polyvinylpyrrolidone (Olsson and Samuelson, 1974).

The method proposed in this work could be an environmentally friendly procedure to extract value-added CGA compounds from coffee industry by-products (Murthy and Madhava Naidu, 2012),

* Corresponding author. Tel.: +33 04 99 61 28 42; fax: +33 04 99 61 30 76.
E-mail address: maria.figueroa@supagro.inra.fr (M.C. Figueroa-Espinoza).

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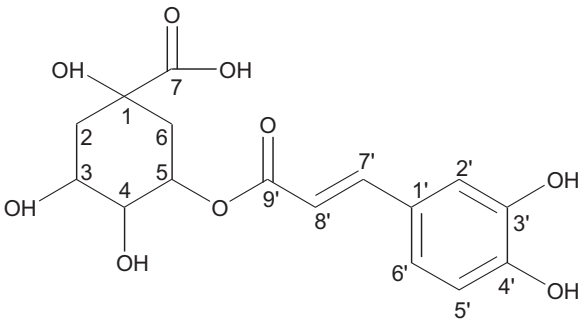

Fig. 1. Chemical structure of 5-*O*-caffeoyl quinic acid.

which are considered as waste materials and are widely available in the world. CGAs are phenolic compounds of interest as they present several biological and functional properties: antimicrobial, antiviral, anti-mycotoxigenic, anti-carcinogenic, antioxidant, chelating, and ultraviolet filter (Morishita and Ohnishi, 2001; Scholz et al., 1994; Suárez-Quiroz et al., 2004, 2013a, 2013b). CGAs could be then used as multifunctional natural antioxidants in food, feed, pharmaceutical, cosmetics or nutraceutical industries. In food and feed formulations, for example, these compounds could be used as natural antioxidant CGA-rich extracts with preservative properties.

The aim of this work was to compare six methods of extraction and isolation of CGA from green coffee beans, in order to find the simplest and the most environmentally friendly to be used as a previous step to simplify CGA fractionation. The example of 5-CQA purification from the CGA mixture is given. To our knowledge, this is the first report indicating the use of AC to isolate CGA from green coffee grains.

2. Materials and methods

2.1. Plant material

Green coffee beans (*Coffea arabica*) came from the Huatusco municipality (Veracruz, Mexico), and were harvested in 2008.

2.2. Chemicals and materials

5-CQA, acetic acid, ammonium sulphate, anhydrous sodium sulphate, butanol, ethanol 96% (v/v), ethyl acetate, formic acid, iodine, isopropanol, methylene chloride, phosphoric acid, toluene, celite (≥95% SiO_2 basis), tetramethylsilane (TMS), and activated carbon (AC) (glassy spherical powder, 2–12 μm, 99.95%) were purchased from Sigma Aldrich (Toluca, Mexico), and all solvents were of analytical grade; HPLC grade methanol from Baeyer (Mexico City, Mexico), aluminium thin layer chromatography (TLC) plates silica gel 60 F_{254} from Merck (Estado de México, Mexico).

2.3. Sample preparation

Green coffee beans were previously frozen by liquid nitrogen in order to minimize CGA degradation (Colonna, 1979), lyophilized, and ground with a coffee grinder (Krups North America, Inc., Mexico City, Mexico) to pass a 0.5 mm sieve.

2.4. Extraction and isolation of CGA

Three extraction and two isolation methods were tested in triplicate. Different extraction times for each method were tested (not shown) in order to obtain a maximum of CGA from green coffee. Only the most efficient time periods were retained for the rest of this work.

Extraction method 1. A mixture of lyophilized green coffee powder (100 g) and distilled water (500 mL) was magnetically stirred for 30 min at 80 °C, in the dark. After cooling, the solution was vacuum filtered through celite (1 cm).

Extraction method 2. A mixture of lyophilized green coffee powder (100 g) and aqueous methanol 70% (v/v) (500 mL) was magnetically stirred for 24 h at room temperature, in the dark. The solution was then vacuum filtered through celite (1 cm), and methanol was evaporated in a rotary evaporator (Bioblock, Mexico City, Mexico).

Extraction method 3. A mixture of lyophilized green coffee powder (100 g) and aqueous isopropanol 60% (v/v) (500 mL) was magnetically stirred for 48 h at room temperature, in the dark. The solution was then vacuum filtered through celite (1 cm), and isopropanol evaporated in a rotary evaporator.

Isolation method 1 (Rakotomalala, 1992). To aqueous extract obtained from each of the three extraction methods was added ammonium sulphate to a final concentration of 20 g/L, in order to precipitate proteins by increasing the ionic strength. To make CGA more soluble in ethyl acetate, 4% phosphoric acid was added. Extracts were then treated three times with methylene chloride (300 mL) to eliminate caffeine in the organic phase. The aqueous phase containing CGA was extracted 4 times using ethyl acetate (300 mL). The four ethyl acetate phases were pooled, dried with anhydrous sodium sulphate (10 g), filtered (N°1 filter paper, Whatman, Mexico City, Mexico), and dried at 40 °C and 120 rpm in a rotary evaporator. The residue was analyzed by TLC and by HPLC.

Isolation method 2 (AC). The aqueous extract obtained from each of the three extraction methods was adjusted to pH 3.0 with phosphoric acid, to which AC at 40 g/L was added, and magnetically stirred for 30 min at 60 °C, under dark. After cooling at room temperature, the mix was vacuum filtered through celite (1 cm). CGA were desorbed from AC using ethanol 96% (v/v), then dried with anhydrous sodium sulphate, and finally dried in a rotary evaporator at 60 °C and 120 rpm. The residue was analyzed by TLC and by HPLC.

2.5. Purification of 5-CQA

The 5-CQA (Fig. 1) was purified from each of the six CGA mixtures with a silica gel 60 column (25 cm long, 1.6 cm diameter) using toluene/ethyl acetate (90:10, v/v) as the eluted solvent. Collected fractions were dried in a rotary evaporator at 60 °C and 120 rpm, followed by a TLC, HPLC, and NMR analysis.

2.6. Thin-layer chromatography (TLC)

TLC was performed using aluminium silica gel 60 F_{254} plates (4 cm × 6.6 cm). Five microliters of each sample or commercial 5-CQA (used as the control) diluted in methanol, were spotted at 0.6 cm from the bottom of the plate. The TLC plate was then placed in a developing chamber containing butanol/water/acetic acid (6:2:2, v/v/v) at room temperature (Lewis et al., 1998; Lu et al., 2004). When the solvent reached 0.4 cm from the top of the plate, the plate was removed, dried for 5 s with a hair-dryer, observed at 254 and 360 nm, and finally revealed using iodine. The retention factor (R_f) was calculated as the distance travelled by the individual compound, divided by the distance travelled by the solvent. Assays were performed in duplicate.

2.7. HPLC analysis

Diluted samples were filtered (Millex-HV, Millipore Co.) (0.45 μm) and injected (10 μL) into an HPLC (Hypersil C_{18};

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