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Mirna Leonor Suarez-Quiroz, Angelina Alonso Campos, Gerardo Valerio Alfaro, Oscar Gonzalez-Rios, Pierre Villeneuve, et al.. Isolation of green coffee chlorogenic acids using activated carbon. *Journal of Food Composition and Analysis*, 2014, 33 (1), pp.55-58. <10.1016/j.jfca.2013.10.005>. <hal-01223544>

HAL Id: hal-01223544

<https://hal.science/hal-01223544v1>

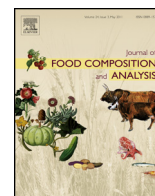
Submitted on 2 Nov 2015

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Short Communication

Isolation of green coffee chlorogenic acids using activated carbon



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ARTICLE INFO

Article history:

Received 1 November 2012

Received in revised form 20 September 2013

Accepted 5 October 2013

Keywords:

Activated carbon

Chlorogenic acids

Green coffee

Extraction

5-O-Caffeoylquinic acid

Isolation

Environmentally friendly

Food analysis

Food composition

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 adsorbents 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),

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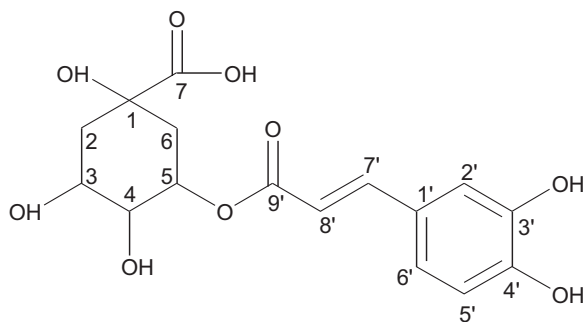


Fig. 1. Chemical structure of 5-*O*-caffeoyl quinic acid.

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 ($\geq 95\%$ SiO₂ 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 F₂₅₄ 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 F₂₅₄ 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 C₁₈;

5 μm ; 250 mm \times 4.6 mm; detection by UV absorbance at 276 nm and room temperature). Elution was performed during 14 min using aqueous methanol (70%, v/v) at 1 mL/min, and 40 °C (Yuan et al., 2006). CGA are expressed as equivalents of 5-CQA. All samples were injected in triplicate.

2.8. ^1H NMR and ^{13}C NMR

30 mg of the sample were analyzed by ^1H and ^{13}C NMR spectra were recorded using a Varian 500 MHz NMR spectrometer in methanol- D_4 solutions (Budryn et al., 2009; Hernandez et al., 2009). Chemical shifts were read relative to the internal standard (TMS).

3. Results and discussion

Methods using chemical reagents or organic solvents to extract and isolate phenolic compounds from plant extracts are not always ecologically friendly. In this research, AC was tested to isolate CGA from green arabica coffee beans as an alternative to limit the use of polluting solvents. Three extraction methods (water at 80 °C, aqueous methanol 70% (v/v) and aqueous isopropanol 60% (v/v)) and two isolation methods (Rakotomalala (1992) and AC) were tested. Results obtained from the six extraction-isolation treatments are presented in Table 1. No significant differences ($\alpha = 0.05$) were observed between results and the CGA content varied from 4.67 to 5.87% (db).

5-CQA was then purified in a silica gel column from the CGA mixtures. The monitoring of 5-CQA purification (97% of purity) was made by TLC ($R_f = 0.6$) and HPLC, and its structure was confirmed by ^1H and ^{13}C NMR spectroscopy (Table 2). The purified 5-CQA was identified by comparison with spectroscopic data reported by Budryn et al. (2009), Hernandez et al. (2009), and Bhatt (2011).

The ^{13}C NMR spectrum showed the presence of sixteen carbon atoms, including two carbonyl groups at δ 175.61 and δ 167.27, corresponding to carbons 7 and 9', respectively; two aromatic carbons bonded to hydroxyl groups at δ 148.11 and δ 145.33 identified as C4' and C3'; two olefinic carbons at δ 145.66 and δ 113.79 corresponding to C7' and C8'; four aromatic carbons assigned to C1', C2', C5', and C6' at δ 126.36, δ 113.86, δ 115.07, and δ 121.58, respectively; three carbons bonded to hydroxyl groups at δ 74.71, δ 70.51, and δ 72.06 identified as C1, C3, and C4; one carbon bonded to an ester group at δ 70.57 attributed to C5; and two methylene identified as C2 and C6 at δ 37.33 and δ 36.76, respectively.

The ^1H NMR spectrum displayed two ortho-coupled doublet each for 1H, at δ 6.94 and δ 6.75, and a broad singlet for 1H at δ 7.027, confirming the presence of a tri-substituted aromatic ring; and two doublets, each for 1H, at δ 7.56 (H-7') and 6.22 (H-8'), indicating the presence of trans-di-substituted ethylene moiety in the molecule. The main spectroscopic data are resumed in Table 2.

Ky et al. (1997) compared different isolation methods on coffee beans previously crushed and frozen in liquid nitrogen. After an aqueous methanol 70% (v/v) extraction at 4 °C overnight, different methods were tested, based either on the aqueous extract (after evaporation of methanol): a solvent extraction with organic solvents (Rakotomalala, 1992); or a filtration through a C18 cartridge (Bicchi et al., 1995); or a treatment by Carrez reagents (Balyaya and Clifford, 1995); or on the methanol extracts (without evaporation of methanol): Carrez reagents (Trugo and Macrae, 1984); or directly analyzed by HPLC (DIN-10767, 1992). When using an aqueous methanol 70% (v/v) extraction combined with the Rakotomalala (1992) isolation method, they obtained 4.1% (db) of total CGA. In our study, treatment T3 (Table 2) is similar to that used by these authors and very close results were obtained (5.87 \pm 1.1% db of total CGA).

Table 1

Green coffee chlorogenic acids extraction and isolation yields.

Treatment (T)	Extraction/isolation method	Total CGA ^a (% db ^b)
T1	Water 80 °C/Rakotomalala (1992)	5.62 \pm 0.8 ^c
T2	Water 80 °C/activated carbon	5.07 \pm 1.0
T3	Methanol 70% (v/v)/Rakotomalala (1992)	5.87 \pm 1.1
T4	Methanol 70% (v/v)/activated carbon	4.67 \pm 1.6
T5	Isopropanol 60% (v/v)/Rakotomalala (1992)	5.87 \pm 1.0
T6	Isopropanol 60% (v/v)/activated carbon	5.28 \pm 1.2

^a Chlorogenic acids.

^b Dry basis.

^c Mean of triplicates (mean values \pm standard deviations).

Table 2

^{13}C NMR and ^1H NMR (500MHz, methanol- D_4) chemical shifts for 5-O-caffeoyl quinic acid.

5-CQA ^a number of carbon (Fig. 1)	^{13}C (δ /ppm)	^1H (δ /ppm)
1	74.71	
2	37.33	2.02 br t ^b 2.22 br d ^b
3	70.51	5.31 t ^b
4	72.06	3.71 d ^b
5	70.57	4.15 br s ^b
6	36.76	2.05 br d 2.14 d
7	175.61	
1'	126.36	
2'	113.86	7.027 br s
3'	145.33	
4'	148.11	
5'	115.07	6.94 d
6'	121.58	6.75 d
7'	145.66	7.56 d
8'	113.79	6.22 d
9'	167.27	

^a 5-O-caffeoyl quinic acid.

^b br t broad triplet, br d broad doublet, t triplet, d doublet, br s broad singlet.

Results are consistent with the CGA coffee content reported in the literature (Clifford and Jarvis, 1988; Ky et al., 1997). Differences in results can be explained by the small variations between methods and by the coffee variety.

The use of water at 80 °C combined with AC (treatment T2 in Table 2) is less polluting than treatments T1 and T3 to T6, gave a good extraction yield (5.07 \pm 1.0% db), and presented no significant differences to alcohol extraction methods combined with AC.

4. Conclusion

In conclusion, the use of AC to isolate CGA presented no significant differences with the Rakotomalala (1992) method. Adsorption with AC proved to be a suitable means to trap CGA from a complex medium like a green coffee extract obtained either by alcohol or by hot water extraction. Adsorption of CGA on AC avoids the use of toxic solvents and is a simple and less time-consuming method, and could be used to replace methods using solvents. This method is a good alternative prior to the purification of 5-CQA or another single (monomer or dimer) CGA, which are not always commercially available, or are very expensive.

Acknowledgments

We thank Dr. Jorge Suárez Medellín from the University of Veracruz (Mexico) for his analytical advices. Angelina Alonso Campos thanks CONACYT for her Master degree scholarship.

References

- Andrade, P.B., Leitao, R., Seabra, R.M., Oliveira, M.B., Ferreira, M.A., 1997. Development of an HPLC/diode-array detector method for simultaneous determination of seven hydroxycinnamic acids in green coffee. *Journal of Liquid Chromatography and Related Technologies* 20 (13) 2023–2030.
- Balyaya, K.J., Clifford, M.N., 1995. Individual chlorogenic acids and caffeine contents in commercial grades of wet and dry processed Indian green Robusta coffee. *Journal of Food Science and Technology-Mysore* 32 (2) 104–108.
- Bhatt, B., 2011. Chemical constituents of *Solanum xanthocarpum*. *Journal of Chemical and Pharmaceutical Research* 3 (3) 176–181.
- Bicchi, C.P., Binello, A.E., Pellegrino, G.M., Vanni, A.C., 1995. Characterization of green and roasted coffees through the chlorogenic acid fraction by HPLC-UV and principal component analysis. *Journal of Agricultural and Food Chemistry* 43 (6) 1549–1555.
- Budryn, G., Nebesny, E., Podsedek, A., Żyżelewicz, D., Materska, M., Jankowski, S., Janda, B., 2009. Effect of different extraction methods on the recovery of chlorogenic acids, caffeine and Maillard reaction products in coffee beans. *European Food Research and Technology* 228 (6) 913–922.
- Clifford, M.N., 1999. Chlorogenic acids and other cinnamates – nature, occurrence and dietary burden. *Journal of the Science of Food and Agriculture* 79 (3) 362–372.
- Clifford, M.N., Jarvis, T., 1988. The chlorogenic acids content of green robusta coffee beans as a possible index of geographic origin. *Food Chemistry* 29 (4) 291–298.
- Clifford, M.N., Johnston, K.L., Knight, S., Kuhnert, N., 2003. Hierarchical scheme for LC-MSn identification of chlorogenic acids. *Journal of Agricultural and Food Chemistry* 51 (10) 2900–2911.
- Colonna, J.P., 1979. L'acide chlorogénique et les depsides de divers caféiers africains et malgaches: leur participation au métabolisme et leur signification biologique. O.R.S.T.O.M., Paris, France.
- Couteau, D., Mathaly, P., 1997. Purification of ferulic acid by adsorption after enzymic release from a sugar-beet pulp extract. *Industrial Crops and Products* 6, 237–252.
- Creppy, E.E., 2002. Update of survey, regulation and toxic effects of mycotoxins in Europe. *Toxicology Letters* 127 (1–3) 19–28.
- Debry, G., 1993. Le café et la santé.
- Dibert, K., Cros, E., Andrieu, J., 1989. Solvent extraction of oil and chlorogenic acid from green coffee. Part I. Equilibrium data. *Journal of Food Engineering* 10 (1) 1–11.
- DIN-10767, 1992. Analysis of coffee and coffee products – determination of chlorogenic acids content – HPLC method.
- Hernandez, C.E., Chen, H.H., Chang, C.I., Huang, T.C., 2009. Direct lipase-catalyzed lipophilization of chlorogenic acid from coffee pulp in supercritical carbon dioxide. *Industrial Crops and Products* 30 (3) 359–365.
- IUPAC, 1976. Nomenclature of cyclitols. *Biochemical Journal* 153, 23–31.
- Kammerer, D.R., Saleh, Z.S., Carle, R., Stanley, R.A., 2007. Adsorptive recovery of phenolic compounds from apple juice. *European Food Research and Technology* 224 (5) 605–613.
- Kubo, I., Fujita, K., Nihei, K., 2002. Anti-Salmonella activity of alkyl gallates. *Journal of Agricultural and Food Chemistry* 50 (23) 6692–6696.
- Ky, C.-L., Noirot, M., Hamon, S., 1997. Comparison of five purification methods for chlorogenic acids in green coffee beans (*Coffea* sp.). *Journal of Agricultural and Food Chemistry* 45 (3) 786–790.
- Lewis, C.E., Walker, J.R.L., Lancaster, J.E., Sutton, K.H., 1998. Determination of anthocyanins, flavonoids and phenolic acids in potatoes. I: Coloured cultivars of *Solanum tuberosum* L. *Journal of the Science of Food and Agriculture* 77 (1) 45–57.
- Lu, H.-T., Jiang, Y., Chen, F., 2004. Application of preparative high-speed counter-current chromatography for separation of chlorogenic acid from *Flos lonicerae*. *Journal of Chromatography A* 1026 (1–2) 185–190.
- Morishita, H., Iwashita, H., Osaka, N., Kido, R., 1984. Chromatographic separation and identification of naturally occurring chlorogenic acids by ¹H nuclear magnetic resonance spectroscopy and mass spectrometry. *Journal of Chromatography A* 315 (0) 253–260.
- Morishita, H., Ohnishi, M., 2001. Absorption, metabolism and biological activities of chlorogenic acids and related compounds. In: Atta ur, R. (Ed.), *Stud. Nat. Prod. Chem. Elsevier*, pp. 919–953.
- Murthy, P.S., Madhava Naidu, M., 2012. Sustainable management of coffee industry by-products and value addition—a review. *Resources, Conservation and Recycling* 66 (0) 45–58.
- Olsson, L., Samuelson, O., 1974. Chromatography of aromatic acids and aldehydes and phenols on cross-linked polyvinylpyrrolidone. *Journal of Chromatography A* 93 (1) 189–199.
- Rakotomalala, J.J.R., 1992. Diversité biochimique des caféiers: analyse des acides hydroxycinnamiques, bases puriques et diterpènes glycosides. Particularités des caféiers sauvages de la région malgache (Mascarochea chev.) Université Sciences et Techniques du Languedoc, Montpellier II, France, Montpellier, France, pp. 219.
- Schieber, A., Hilt, P., Streker, P., Endreß, H.-U., Rentschler, C., Carle, R., 2003. A new process for the combined recovery of pectin and phenolic compounds from apple pomace. *Innovative Food Science and Emerging Technologies* 4 (1) 99–107.
- Scholz, E., Heinrich, M., Hunkler, D., 1994. Caffeoylquinic acids and some biological-activities of *Pluchea-Symphytifolia*. *Planta Medica* 60 (4) 360–364.
- Soto, M.L., Moure, A., Dominguez, H., Parajo, J.C., 2011. Recovery, concentration and purification of phenolic compounds by adsorption: a review. *Journal of Food Engineering* 105 (1) 1–27.
- Suárez-Quiroz, M.L., Alonso Campos, A., Valerio Alfaro, G., González-Ríos, O., Villeneuve, P., Figueroa-Espinoza, M.C., 2013a. Anti-*Aspergillus* activity of green coffee 5-O-caffeoyl quinic acid and its alkyl esters. *Microbial Pathogenesis* 61–62, 51–56.
- Suárez-Quiroz, M.L., González-Ríos, O., Barel, M., Guyot, B., Schorr-Galindo, S., Guiraud, J.P., 2004. Effect of chemical and environmental factors on *Aspergillus ochraceus* growth and toxigenesis in green coffee. *Food Microbiology* 21 (6) 629–634.
- Suárez-Quiroz, M.L., Taillefer, W., López Méndez, E.M., González-Ríos, O., Villeneuve, P., Figueroa-Espinoza, M.C., 2013b. Antibacterial activity and antifungal and anti-mycotoxigenic activities against *Aspergillus flavus* and *A. ochraceus* of green coffee chlorogenic acids and dodecyl chlorogenates. *Journal of Food Safety* 33 (3) 360–368.
- Trugo, L.C., Macrae, R., 1984. Chlorogenic acid composition of instant coffees. *Analyst* 109, 263–266.
- Yuan, B., Qiao, M., Xu, H., Wang, L., Li, F., 2006. Determination of chlorogenic acid in rat plasma by high performance chromatography after peritoneal administration of compound Daqingye injection. *Yakugaku Zasshi Journal of the Pharmaceutical Society of Japan* 126 (9) 811–814.