Available online at www.sciencedirect.com
ScienceDirect
Food Chemistry 101 (2006) 1087–1094
Food Chemistry
www.elsevier.com/locate/foodchem

Extraction of coffee diterpenes and coffee oil using supercritical carbon dioxide

Júlio M.A. Araújo *,[1], Delcio Sandi

DTA/UFV (Department of Food Technology), UFV (Universidade Federal de Viçosa), 36570-000 Viçosa, Minas Gerais, Brazil

Received 2 December 2005; received in revised form 22 February 2006; accepted 4 March 2006

Abstract

Commercial green and roasted coffee beans were used to maximize oil extraction and conditions were studied to obtain the highest and lowest diterpene levels on green and roasted coffee oil, respectively. Thus, operational temperatures (60–90 °C) and pressure (235–380 bar) were optimized for coffee oil extraction. Oil content levels and diterpene oil concentration were compared to the results obtained with the extraction with Soxhlet apparatus, using hexane as solvent. In general, an inverse correlation was observed between the amount of extracted oil and diterpene concentration levels. As a result, different oil contents with different diterpene concentrations could be obtained. The HPLC analysis of cafestol and kahweol in the oil extracted from green coffee beans at 70 °C/253 bar resulted in the highest concentration (453.3 mg 100 g^{-1}), which was 48% lower than in the oil extracted with hexane while in the oil extracted from roasted coffee beans at 70 °C/371 bar, resulted in 71.2% reduction of diterpenes.

Keywords: Supercritical carbon dioxide extraction; Green coffee oil; Roasted coffee oil; Cafestol; Kahweol; HPLC

1. Introduction

The food and pharmaceutical industries have rapidly taken advantage of the possibilities of using carbon dioxide as a nontoxic, environmentally safe, cheap, and selective extraction solvent (Brunner, 1994; McHugh & Krukonis, 1994). Compared to liquid solvents, carbon dioxide has the advantage of displaying adjustable selectivity or solvent power that can be set to values ranging from gas to liquid-like. Carbon dioxide has a lower critical temperature (31.1 °C) and moderate critical pressure (73.8 bar), thus being an ideal solvent for compounds that may suffer thermal degradation (Palmer & Ting, 1995).

Global coffee production comes from two major species, *Coffea arabica* and *Coffea robusta*, with nearly three-quarters coming from the former, which contains cafestol (about 0.6%) and kahweol (0.3%) (Urget & Katan, 1996) (see Fig. 1). The latter, *C. robusta*, contains mostly cafestol (0.2%). Total diterpene content ranges from 1.3% to 1.9% (w/w) in *C. arabica* beans and 0.2–1.5% in *C. robusta* beans (Ratnayake, Hollywood, Ogrady, & Stravic, 1993).

Cafestol and kahweol, naturally occurring diterpenes found only in coffee, are present in the unsaponifiable lipid fraction (Kolling-Speer, Strohschneider, & Speer, 1999). Their content in a coffee drink is influenced by the brewing method (Gross, Jaccaud, & Huggett, 1997); brewing releases oil droplets containing cafestol and kahweol from the ground coffee beans. Boiled coffee, such as Scandinavian-style and Turkish-style, contains the highest concentrations, while instant, drip-filtered, and percolated coffees contain negligible amounts. The amount of cafestol and kahweol can be significantly reduced by roasting the green coffee (Bak & Grobee, 1989; Kolling-Speer et al., 1999).

Green coffee oil has been used in the cosmetics industry because of the emollient property provided by its fatty acids and its capacity to block sunlight harmful to human skin (Alvarez & Rodriguez, 2000; Grollier & Plessis, 1988;

* Corresponding author. Tel.: +55 38 99 18 57; fax: +55 38 99 220 8.
E-mail address: jaraujo@ufv.br (J.M.A. Araújo).
[1] Tel.: +31 31 3899 1857; fax: +31 31 3899 2834.

0308-8146/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2006.03.008

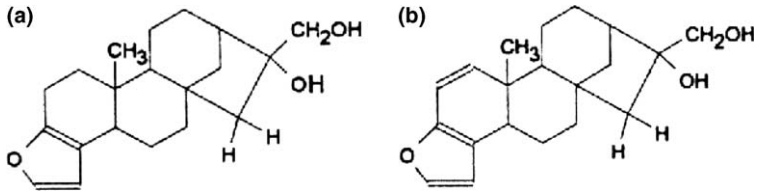

Fig. 1. Chemical structure of cafestol (a) and kahweol (b).

Pelle, 1999). Roasted coffee oil has also been widely used as a flavor source in food and cosmetics. Moreover, a reduction in the diterpene levels of roasted coffee oil significantly increases its stability and sensorial profile, decreasing its hypercholesterolemic effect (Bak & Grobee, 1989; Kolling-Speer et al., 1999).

The anticarcinogenic property of cafestol and kahweol has been hypothesized to be related to their ability to induce glutatione S-transferase (GST). In mice and rats, both substances were found to induce GST activity of the liver and intestinal mucosa. Studies with derivatives of cafestol and kahweol indicate that furan moiety is the active site for induction of enzyme activity (Aro, Kostiainen, Huttunen, & Sepalla, 1985; Cavin, Holzhaeuser, Scharf, Constable, & Hubber, 2002; Lam, Sparnins, & Wattenberg, 1982; Miller, McWhorter, Rivera-Hidalgo, & Wright, 1991; Scharf, Prutomersky, & Huber, 2001; Wattenberg, 1984).

The cholestrol-raising effect of boiled coffee in humans has been linked to these diterpenes (AL Kanhal, 1997; Burr, Limb, Sweetnan, & Fehily, 1995; Heckers, Gobel, & Kleppel, 1994; Mensink, Lebbink, Lobbezoo, & Katan, 1995). Paper-filtered coffee does not elevate cholesterol since the lipid content (including diterpenes) is negligible (Urget & Katan, 1996). Studies have shown that an intake of cafestol and kahweol causes an increase in total cholesterol as well as low-density lipoprotein (LDL) cholesterol, triglycerides, and alanine aminotransferase (ALT) activity in abnormal subjects (Grubben, Boers, & Blom, 2000; Halvorsen, Ranhein, Nenseter, Huggett, & Drevon, 1998; Roos, Caslake, & Stalenhoef, 2001; Terpstra, Katan, & Beynen, 2000; Van Rooij et al., 1995).

Common methods for extracting the oil from coffee beans include organic solvent extraction with hexane using soxhlet over several hours. However, this procedure has an important drawback, long extraction time, consuming large quantities of solvent and requiring additional concentration step. Some research has been published on supercritical extraction of oil from coffee beans as a source of aroma (Gopalakrishnan, 1990; Lopez-Fontal & Castano-Castrilon, 1999; Roselius, Vitzthum, & Hubert, 1982; Sarrazin, Le Quere, Gretsh, & Liardon, 2000). However, none studied the behavior of the diterpenes on extraction of oil in green and roasted coffee beans.

This work aimed to study the feasibility of applying carbon dioxide under supercritical conditions to maximize oil extraction to obtain the highest and lowest diterpenes levels on green and roasted oil, respectively. Operational temperature, carbon dioxide density, moisture content, granulometry and CO_2 flow rate were optimized for coffee oil extraction. A method using high performance liquid chromatography (HPLC) with detection at 220 nm has been used for diterpene identification.

2. Materials and methods

2.1. Materials

The standards used in this work for HPLC analysis were cafestol (LKT Labs. Inc., Saint Paul, MN and kahweol (Sigma, Saint Louis, MO). HPLC grade methanol and hexane (Merck) were used as solvents after filtration through a 0.45 μm pore size filter (Milipore, Bedford, MA). Two different types of carbon dioxide, (supercritical fluid and refrigerant fluid), were supplied by White Martins (Brazil).

2.2. Sample preparation

Commercial green and roasted coffee beans (*C. arabica*) containing 9.98% and 2.40% humidity, respectively, were used for supercritical extraction. The coffee beans were ground in a bench coffee grinder and sieved to obtain particles with diameters ranging from 0.297 to 0.35 mm; 0.35 to 0.42 mm; and 0.42 to 0.50 mm.

2.3. Extraction methods

2.3.1. Soxhlet method

Twenty grams of sample were weighted in filter paper and placed in a 500 ml soxhlet glass timble. The extraction was carried out using hexane as solvent (10 ml g^{-1} of sample) at the solvent boiling point for 16 h. After extraction, the solvent was evaporated by reduced pressure evaporation (30 °C; Fisaton model 802) and the extract was dried at 103 °C to remove residual solvent, cooled for 30 min in a dessicator, and weighted. This procedure was repeated until a constant extract weight was obtained. Table 1 summarizes the average percent extractives obtained by soxhlet extraction.

2.3.2. Supercritical fluid extraction method

The SFE experiments were performed on a Hewlett-Packard model 7680A SFE module. An experimental design of two factors (temperature and pressure) was per-