

https://dx.doi.org/10.21577/0103-5053.20230131

J. Braz. Chem. Soc. **2024**, *35*, 3, e-20230131, 1-8 ©2024 Sociedade Brasileira de Química

Bioactive Diterpenes and Serotonin Amides in Cold-Pressed Green Coffee Oil (Coffea arabica L.)

Rodrigo M. V. Silva,^{a,b} Ana Laura M. Brand,^a Natalia A. B. Tinoco,^a Suely P. Freitas^b and Claudia M. Rezende[®]*,^a

^aInstituto de Química, Universidade Federal do Rio de Janeiro, 21941-909 Rio de Janeiro-RJ, Brazil ^bEscola de Química, Universidade Federal do Rio de Janeiro, 21941-909 Rio de Janeiro-RJ, Brazil

Cold pressing is an environment-friendly mechanical extraction for oils from seeds. In this work, cold-pressed green Arabica coffee oil was investigated related to the influence of the pressing variables (preheating, exit diameter, screw speed, and particle size) on the chemical oil composition, mainly on the diterpenes and, for the first time in the scientific literature, on the content of serotonin amides ($^{\beta}N$ -alkanoyl-5-hydroxytryptamides (C_n -5HT)). The oil yield from screw pressing varied from 2.65 to 6.27%, with major yields obtained as the size of the particle and temperature increased. Soxhlet extraction produced 9.46 ± 0.04% of oil. The fatty acid content of the oils varied from 32.79 to 33.49% and showed no significant difference among the different pressing conditions. The amount of the diterpenes kahweol and cafestol ranged from 13.33 to 16.72 mg g⁻¹ and 37.11 to 47.14 mg g⁻¹ of oil, respectively, summing 50.44 to 63.86 mg g⁻¹ of diterpenes. The total content of C_n -5HTs ranged from 307.92 to 1716.52 µg g⁻¹, being 114.42 to 577.37 µg g⁻¹ for arachidic acid-5-hydroxytryptamide, (C_{20} -5HT) and 193.50 to 1068.08 µg g⁻¹ for behenic acid-5-hydroxytryptamide (C_{22} -5HT) in oil, the most abundant in coffee bean. From the 16 cold press treatments, six conditions showed significant amounts of these compounds. Aspects related to the biological activity and relevance of coffee lipid diterpenes and C_n -5HTs are discussed.

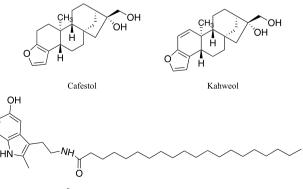
Keywords: crude coffee oil, cold pressing, diterpenes, serotonin amides, Arabica coffee

Introduction

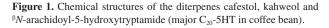
Cold pressing is an environmentally friendly mechanical extraction for obtaining oils from a range of matrices, especially oilseeds, and is usually used when there is interest in maintaining organoleptic properties.^{1,2} Compared to solvent extraction, the process of cold-pressing edible oils has a lower yield. However, advantages in extracting other phytochemicals of interest alongside the lipid fraction, without the use of solvents, are highlighted in sustainable approaches.³

Green Arabica coffee oil (GCO) (unroasted beans or crude beans) contains from 7 to 17% (dry basis) of lipids that are mainly located at the endosperm and are mostly composed of triacylglycerols (TAGs) (75%). Besides TAGs, in which linoleic (C18:2, around 43%) and palmitic (C16:0, around 31%) acids are the major acyl units, there is an expressive unsaponifiable matter up to

*e-mail: claudia.rezendeufrj@gmail.com Editor handled this article: Paulo Cezar Vieira 15%, while most vegetable oils range from 1.0 to 1.5%.^{4,5} This fraction includes subclasses as esterified *ent*-kaurane furan diterpenes (up to 17%), free diterpene alcohols (0.4%), sterols (2.2%), tocopherols (0.04%), phosphatides (0.5%) and ^{β}N-alkanoyl-5-hydroxytryptamides (C_n-5HT) (1.0%) (Figure 1),⁴ these last also found in Brazil nuts and hazelnuts.⁶



 $^{\beta}N$ -arachidoyl-5-hydroxytryptamide (C₂₀-5HT)



Several techniques have been investigated to extract GCO. Mechanical cold pressing,⁷ supercritical fluid extraction,⁸ ultrasound-assisted,⁵ microwave-assisted⁹ and high-speed countercurrent chromatography.¹⁰ Most of them compared their results with the traditional extraction by Soxhlet. While some techniques are labor intensive or time-consuming, others require large quantities of solvents. From all of these, cold pressing is considered the most environmentally friendly, as no solvent is used.

GCO has attracted the attention of the cosmetic industry due to the absorption capacity of solar UVB radiation and to a protective effect on physiological balance of the skin, where the *ent*-kaurane diterpenes cafestol and kahweol were correlated to UV-light protection.¹¹⁻¹⁴ Some papers¹⁴⁻¹⁹ also highlight their antitumor and anti-inflammatory aspects. When absorbed through oral ingestion, these diterpenes have a hypercholesterolemic effect, mainly cafestol.²⁰⁻²² We recently evaluated the addition of GCO defective Arabica beans and its residues (cake and sediments) to carboxymethyl cellulose (CMC) films, showing promising results in sustainable perpectives.⁷

 C_n -5HTs also components of the unsaponifiable fraction of coffee, are present in the wax bean. They consist of a serotonin unit conjugated to acyl moieties through an amide link, mostly represented by C-20 and C-22 units (Figure 1).²³ Some authors correlated C_n -5HTs to stomach irritation,^{24,25} besides interesting biological properties such as anti-inflammatory, antinociceptive, anxiolytic, and others.²⁶⁻²⁸

Continuing our studies on Arabica GCO, we discuss here the influence of the pressing parameters on the chemical oil composition, mainly on the diterpenes and, for the first time in scientific literature, on the content of C_n -5HTs in coffee oil, also focusing on cold pressing oil yields. Some aspects related to the biological activity of these classes of compounds are also discussed showing the relevance of green coffee oil for industrial uses.

Experimental

Solvents and reagents

Petroleum ether, sodium hydroxide, methanol, ammonium chloride, sulfuric acid, potassium carbonate, diethyl ether, ethanol, phenolphthalein, acetonitrile, acetone and formic acid (all in analytical grade) were from Sigma-Aldrich (Saint Louis, USA).

Green coffee beans

Green (unroasted) *Coffea arabica* L. (var. "*Catuaí amarelo*") beans were harvested on a farm located

in São José do Vale do Rio Preto, RJ, Brazil (22°11'35.2"S, 42°59'8.6"W). The harvest occurred in 2018 and the beans were treated by a dry post-harvest process. For further analysis, beans were grounded and sieved (Bertel sieves, 0.85 and 2.00 mm).

Screw pressing

Ground green coffee beans were pressed in an expeller screw press (IBG Monforts, model CA 59 O, Mönchengladbach, Nordrhein-Westfalen, Germany) according to a full factorial design 2^4 (two levels and four factors) as described further. An expeller press is a screw-type machine that presses oil seeds through a perforated steel barrel. One kilogram of ground green coffee beans (particle size between 0.85 and 2 mm) was used in each pressing. Press throughput on this work was 0.67 and 1.2 kg h⁻¹ for 30 and 18 rpm screw speed, respectively.

Full factorial design of experiments (24)

Classical pressing parameters such as preheat, exit diameter (ED), and screw speed (SS) of continuous expeller, as also particle size (PS), were combined as indicated in the Results and Discussion section, resulting in 16 experiments. All parameters were chosen based on previous studies.⁷

Soxhlet extraction

This extraction occurred according to the German Society for Lipid Sciences (DGF) protocol.²⁹ Twenty-five grams of grounded coffee beans were extracted with 400 mL of petroleum ether in a Soxhlet apparatus for 4 h.

Total moisture content

Total water content was determined by the weight loss after 2 g of coffee beans were placed in a drying oven at 105 ± 3 °C and weighed every hour until constant weight, according to American Oil Chemists' Society (AOCS).³⁰

Fatty acid profile by gas chromatography with flame ionization detector (FAMEs)

As described by Antoniassi *et al.*,³¹ 5 mL of 0.5 M methanolic solution of sodium hydroxide (NaOH) were added to 0.5 g of oil and kept in reflux for 5 min. Then, 15 mL of an esterifying solution (2 g of ammonium chloride is added to 60 mL of methanol followed by 3 mL of concentrated sulfuric acid in reflux for 15 min) were added still in reflux

for another 3 min. Then, a liquid-liquid extraction was carried out by adding 50 mL of water and 25 mL of petroleum ether, followed by two washings with 25 mL of water. The petroleum ether layer containing the fatty acid methyl esters (FAMEs) was dried under reduced pressure in a rotary evaporator. A 20 mg mL⁻¹ FAME solution was prepared and an aliquot of 1 µL was injected at 1:20 split in an Agilent 6890N chromatograph equipped with a flame ionization detector (GC-FID, Palo Alto, CA, USA). A SupelcowaxTM $10 \operatorname{column} (15 \mathrm{m} \times 0.1 \mathrm{mm} \times 0.1 \mathrm{\mu m}, \operatorname{Sigma-Aldrich}, USA)$ was used. The oven started at 160 °C for 2 min, 6 °C min⁻¹ until 240 °C for 7 min. Injector and detector temperatures were 230 and 260 °C, respectively. The carrier gas was H₂ at 0.3 mL min⁻¹ and FAMEs were identified by comparing the retention time with a standard FAME mix (n-C14-C22, Supelco, Bellefont, USA), by co-injection and by analysis in an Agilent 5975C GC-MS equipment (Palo Alto, CA, USA).

Quantification of cafestol and kahweol contents by highperformance liquid chromatography (HPLC-UV-Vis)

A microwave-assisted procedure was performed as described by Tsukui et al.9 To a 10 mL flask were added 0.5 g of oil, 3 mL of methanol (MeOH) and 23 mg of potassium carbonate (K_2CO_3). The reaction was carried out on a microwave reactor (Monowave™ 300; Anton Paar GmbH, Graz, Austria) at 100 °C, 800 rpm for 7 min followed by cooling until 55 °C. The methanolized material was then filtered on a Millipore 0.22 µm membrane. An aliquot of 20 µL was injected on a Shimadzu 20A LC System equipped with an SPD-M20A photo diode array detector (Shimadzu, Tokyo, Japan) using a reversed-phase Zorbax Eclipse C18 column (150 mm \times 4.6 mm, 5 μ m, Sigma-Aldrich, USA). The mobile phase was acetonitrile/ water (55:45, v/v) at a flow rate of 0.7 mL min⁻¹. The detection wavelength was set to 220 nm. Quantification was performed through an external analytic curve of cafestol (>98%) (10, 40, 70, 100, 130, and 160 µg mL⁻¹). Cafestol was isolated from green coffee beans employing a method previously developed by our research group and confirmed by ¹H nuclear magnetic resonance (NMR), as also melting point, according to Novaes et al.³² Method validation was performed according to Araujo³³ and Zanella et al.,³⁴ as shown in Table S1 (Supplementary Information (SI) section). NMR data are also shown in SI section.

Quantification of arachidic and behenic acid-5-hydroxy-tryptamides (C_{20} -5HT and C_{22} -5HT) by HPLC-fluorescence

Ten microliters of GCO were diluted in 990 μ L of acetone. An aliquot of 5 μ L was injected in a Waters e2695

chromatograph, equipped with a Waters Alliance 2475 fluorescence detector (Waters, Milford, USA). A Hypersil C18 BDS column (50 mm × 4.6 mm, 2.4 μ m, Thermo, Waltham, MA, USA) was used with a flow of 1.00 mL min⁻¹ and mobile phase composition of methanol/formic acid 1% (70:30) from 0 to 15.50 min, 100% methanol from 15 to 16.50 min, and methanol/formic acid 1% (70:30) again from 16.50 to 20 min. The detector was set to 280 nm (excitation) and 340 nm (emission). Quantification was performed as Tinoco *et al.*³⁵ through an external analytical curve of C₂₂-5HT (0.9, 2.4, 4.6, 7.5, and 12.5 μ g mL⁻¹). The C₂₂-5HT was synthesized and confirmed by ¹H NMR, according to Giorno *et al.*²⁸ Method validation was performed according to Araujo³³ and Zanella *et al.*,³⁴ as shown in Table S1. NMR data are shown in SI section.

Statistical analyses

Statistical analyses were performed using Statistica 12³⁶ (StatSoft, Inc., 2012) and Microsoft Excel.³⁷ The comparison was performed using variance analysis (two-way analysis of variance (ANOVA)), followed by Fisher (LSD) post-test. Differences were considered significant when $p \le 0.05$.

Results and Discussion

The influence of classical pressing parameters, such as press preheating, press ED, and press SS, as well as PS, on crude coffee oil yield and composition, was evaluated.

Yield of coffee oil extraction

Table 1 shows the effect of different conditions on oil extraction process yield. The oil yield from screw pressing varied from 2.65 to 6.27%, while Soxhlet extraction gave 9.46 ± 0.04 and $5.47 \pm 0.05\%$ of oil for particles smaller than 0.85 mm, and greater than 2.00 mm, respectively.

It was observed that the smaller particles partially escape the screw and consequently the pressing, which may be responsible for the lower oil yield observed in entries 1-4 (Table 1).

The Pareto diagram (Figure 2a) shows that all screw pressing parameters investigated in this study had a significant impact (p < 0.05) on crude green Arabica coffee oil yield. It can be observed the main effects of size particle, temperature, exit diameter, screw speed, and their interactions on green Arabica coffee oil yield. Notice that the process yield increased as the size particle and temperature increase. As expected, the heat favors cellular wall rupture and enhanced the permeability and oil recovery as it reduces intermolecular attraction with a consequent

decrease in oil viscosity, and larger particle sizes promote greater friction, also favoring cellular wall rupture. In its turn, the screw speed presented a negative effect on the process yield. This occurs, probably, due to the residence time reduction of coffee beans inside the pressing cage.

Figure 2a shows a significative interaction between the size particle and temperature. Although no maximum point was observed in Figure 2b, the positive interaction between these two parameters introduced a curvature in the response function (yield). Figure 2b also shows that green coffee oil yield is directly influenced by pre-heating and coffee beans particle size, in which higher yields were achieved with preheating turned on and larger particle sizes.

In our study, the maximum yield obtained by screw pressing was 6.27% (entry 8, Table 1), which represents 66.3% of the bean's total lipid content determined by Soxhlet (9.46%). Cornelio-Santiago *et al.*⁸ obtained a maximum yield of 7.60% through supercritical fluid extraction (SFE), representing about 100% of the total lipid content (7.57%) in the coffee beans used in their study. SFE extraction at high pressure usually shows greater yields than cold pressing, but an important point is that cold pressing is a much-simplified technique than SFE.

Tsukui *et al.*⁹ compared Soxhlet and microwave-assisted extractions, both with petroleum ether as the solvent, for green Arabic coffee oil. Microwave-assisted extraction

entry	Preheat ^a	PS/	ED /	SS /	Yield ^b /	Kahweol /	Cafestol /	Total diterpenes /	C/K	C ₂₀ -5HT /	C ₂₂ -5HT /	Total C _n -5HTs /
		mm	mm	rpm	%	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	ratio	(µg g ⁻¹)	(µg g ⁻¹)	(µg g ⁻¹)
1	off	0.85	4	30	2.65	15.09 ± 0.67	44.13 ± 2.08	59.22 ± 2.74	2.61	150.11 ± 4.84	228.30 ± 7.59	378.42 ± 12.42
2	off	0.85	4	18	3.25	14.72 ± 1.36	42.58 ± 4.15	57.30 ± 5.51	2.65	114.42 ± 13.35	193.50 ± 23.29	307.92 ± 36.64
3	off	0.85	5	30	3.13	14.25 ± 1.89	40.46 ± 6.08	54.71 ± 7.97	2.92	225.50 ± 10.30	360.86 ± 16.94	586.36 ± 27.23
4	off	0.85	5	18	4.61	13.88 ± 0.89	38.96 ± 2.96	52.84 ± 3.84	2.89	255.03 ± 35.67	453.07 ± 63.99	708.11 ± 99.65
5	off	2.00	4	30	5.38	14.33 ± 0.66	38.46 ± 1.88	52.80 ± 2.37	2.84	273.00 ± 34.93	588.81 ± 76.40	861.81 ± 111.33
6	off	2.00	4	18	5.48	14.07 ± 1.15	39.60 ± 3.58	53.67 ± 4.72	2.81	368.23 ± 8.97	778.42 ± 18.83	1146.65 ± 27.79
7	off	2.00	5	30	5.33	14.39 ± 1.24	40.55 ± 3.87	54.94 ± 5.11	2.82	439.82 ± 38.00	916.95 ± 81.23	1356.77 ± 119.23
8	off	2.00	5	18	6.27	13.33 ± 0.77	37.11 ± 2.37	50.44 ± 3.14	2.81	124.16 ± 1.63	208.82 ± 2.55	332.98 ± 4.18
9	on	0.85	4	30	4.46	14.53 ± 0.51	39.42 ± 1.82	53.95 ± 2.31	2.82	567.03 ± 94.19	1005.96 ± 167.32	1716.52 ± 114.76
10	on	0.85	4	18	5.28	15.04 ± 1.22	42.08 ± 3.91	57.12 ± 5.14	2.78	358.12 ± 45.72	582.94 ± 75.08	877.24 ± 68.88
11	on	0.85	5	30	4.54	14.91 ± 0.33	41.14 ± 0.71	56.05 ± 1.04	2.63	472.09 ± 19.41	895.96 ± 39.71	1368.05 ± 59.12
12	on	0.85	5	18	5.20	15.73 ± 1.11	44.40 ± 3.46	60.13 ± 4.56	2.60	577.37 ± 8.86	1068.08 ± 15.68	1645.45 ± 24.53
13	on	2.00	4	30	5.05	16.72 ± 1.62	47.14 ± 4.99	63.86 ± 6.61	2.76	283.69 ± 93.05	542.66 ± 179.99	680.67 ± 147.48
14	on	2.00	4	18	6.25	15.76 ± 0.70	43.69 ± 2.15	59.45 ± 2.86	2.72	235.95 ± 48.99	446.41 ± 94.21	600.09 ± 19.97
15	on	2.00	5	30	5.32	15.39 ± 0.57	42.64 ± 1.71	58.03 ± 2.28	2.66	130.07 ± 14.90	230.27 ± 27.29	360.34 ± 42.18
16	on	2.00	5	18	6.14	14.87 ± 1.11	41.02 ± 3.18	55.89 ± 4.29	2.80	176.70 ± 19.72	320.55 ± 36.26	497.25 ± 55.98

^aWhen preheat is on, press temperature reaches 75-80 °C. For preheat off, temperature < 50 °C. ^bData are presented as a mean, the cold pressing was performed in duplicate, and the standard deviation for all samples was \pm < 0.56. The oils obtained from pressing were at a temperature between 35-40 °C. PS: particle size; ED: exit diameter; SS: screw speed; C/K: cafestol/kahweol ratio.

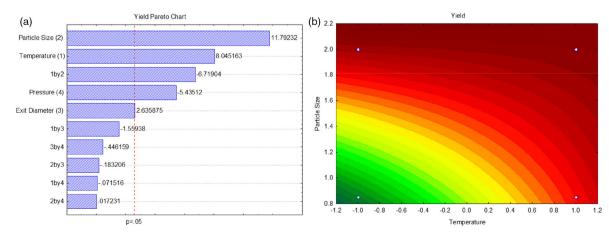


Figure 2. Pareto diagram showing which pressing parameters (preheat, particle size, press exit diameter, and screw speed) impact green coffee oil yield obtained by screw pressing extraction (a). Surface plot of green coffee oil yield in the function of pre-heating/particle size during screw pressing process (b).

proved to be a powerful, fast, and smooth methodology (10 min at 45 $^{\circ}$ C) compared to the traditional Soxhlet extraction method but is not sustainable for large-scale production.

In literature, coffee oil extraction using Soxhlet varies from 4 to 24 h, in different quantities and particle sizes, which makes comparison difficult.^{4,6-10,29} Cold pressing, on the other hand, has the great advantage of being a solventless procedure besides taking place in reduced time, which in this study was around 1 h in total, 20 min in each pressing, with a mass flow rate of around 3 kg h⁻¹.

Fatty acid profile in the crude green coffee oil

The fatty acid profile obtained in different conditions of cold screw pressing showed no significant difference (Table 1). The major fatty acids identified in green Arabic coffee oils were linoleic (44 to 46%) and palmitic acid (32.8 to 33.5%), besides oleic (8.5 to 8.7%), stearic (7.6 to 7.8%), arachidic (2.9 to 3.2%), linolenic (1.4%) and behenic (0.7 to 1.0%) acids (Table S2, SI section), which agree to Speer and Kölling-Speer⁴ and Calligaris *et al.*³⁸ Results obtained by solvent extraction with petroleum ether using Soxhlet apparatus were 42.91 \pm 0.00% for linoleic acid and 35.05 \pm 0.00% for palmitic acid, besides 8.52 \pm 0.00% for oleic acid, 8.05 \pm 0.00% for stearic, 3.23 \pm 0.00% for arachidic, 1.32 \pm 0.00% for linolenic and 0.94 \pm 0.00% for behenic acids, which are also in agreement with Speer and Kölling-Speer⁴ and Calligaris *et al.*³⁸

Our results showed unsaturated fatty acids in 54.47-56.01% and saturated in 43.99-45.53%, with a positive balance for the first group, an interesting aspect of this cold pressing process when looking for antioxidative aspects of this oil.

Amounts of diterpenes and ^β*N*-alkanoyl-5-hydroxytryptamides in the green Arabica coffee oil

Coffee oil is a source of valuable bioactive compounds (fatty acids, diterpenes, sterols, tocopherols, serotonin amides, and phosphatides) and some of them are not found in other seed oils, such as cafestol and kahweol or are not well explored in the literature, as ${}^{\beta}N$ -alkanoyl-5-hydroxytryptamides.^{4,23} This study evaluated the influence of different pressing conditions in the content of the diterpenes kahweol and cafestol and ${}^{\beta}N$ -alkanoyl-5-hydroxytryptamides (arachidic acid-5-hydroxytryptamide, C₂₀-5HT, and behenic acid-5-hydroxytryptamide, C₂₂-5HT), this class of compounds being investigated for the first time in scientific literature in crude green coffee oil (Table 1).

The amount of kahweol ranged from 13.33 to

16.72 mg g⁻¹ and cafestol from 37.11 to 47.14 mg g⁻¹, summing 50.44 to 63.86 mg g⁻¹ for both diterpenes. The total content of C_n -5HTs ranged from 30.79 to 150.04 mg g⁻¹, being 11.44 to 52.65 mg g⁻¹ for C_{20} -5HT and 19.35 to 97.39 mg g⁻¹ for C_{22} -5HT (Table 1). The results of the diterpenes agree with Tsukui *et al.*³⁰ developed under the same experimental conditions used in this work.

From the 16 treatments performed, six conditions stood out, as presented significant amounts of these compounds, when compared with others. Entry 13 (Table 1) shows a significative difference when compared with other conditions, with higher content for kahweol (p < 0.05). The amounts of cafestol also present significative difference between the different conditions, entry 13 showing the higher content and entry 8 shows the lowest content (p < 0.05).

From the content of C_n -5HTs in crude Arabica green coffee oil, entries 9 and 12 present the higher content for total C_n -5HTs (p = 0.33), while entries 2, 8, and 15 (Table 1) showed the lowest content for total C_n -5HTs (p = 0.59). Entry 8 presents the lowest content for diterpenes and total C_n -5HTs.

The extraction of green coffee oil by Soxhlet, with particles of 0.85 and 2.00 mm, showed no significant difference in the content of diterpenes (kahweol and cafestol) and C_n -5HTs.

From the analysis of ANOVA one-way, it was possible to see that the content of diterpenes found in entry 8 (Table 1) (lowest diterpenes content) does not present a significant difference when compared to Soxhlet (p = 0.38). Regarding the content of C_n-5HTs, the entries that presented the lowest content (2, 8, and 15) also did not present significant differences compared to the oils obtained by Soxhlet (p = 0.33).

The chemical composition of green coffee oil is dependent on many factors that encompass the bean's characteristics (species type), edaphoclimatic conditions of coffee cultivation, processing methods of seeds, as well extraction technique.⁶ As can be observed in the Pareto chart (Figures 3a and 3b), the pre-heated (on or off) has a significative effect on the content of diterpenes and C_n -5HTs, respectively. When the pre-heated is on, their amounts are higher in the crude green Arabica coffee oil, as shown in the surface plot (Figures 3c and 3d). This probably occurs due to the positive correlation between temperature and oil permeability. Additionally, the interactions between temperature and particle size present a negative coefficient.

As previously pointed, the cold-pressed green coffee oil has been explored in cosmetics. Going a little deeper into possible applications for this oil, Pereda *et al.*³⁹ showed that

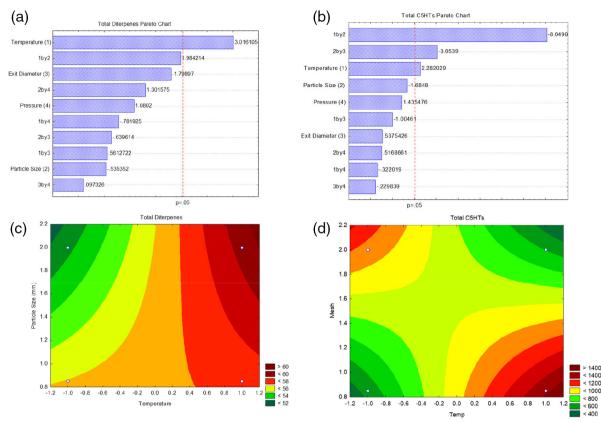


Figure 3. Pareto diagram showing the importance of the variables (preheat, mesh, press exit diameter, and pressure) for diterpenes (a) and C_n -5HTs (b) in crude green coffee oil obtained by cold screw pressing extraction process. Surface plot of the number of diterpenes (c) and C_n -5HTs (d) in crude green coffee oil as a function of temperature and particle size during the cold screw pressing extraction process.

it increases the production of dermal extracellular matrix components (collagen, elastin, glycosaminoglycans) in a dose-dependent manner, also stimulating other important factors involved in skin repair and regulation. The lipid composition, with an expressive contribution of linoleic acid and the sun protection factor of GCO and its diterpenes are important aspects for the valorization of this oil.^{13,40} Furthermore, C_n-5HTs are antagonists of vanilloid 1 transient potential receptor (TRVP1), a capsaicin family receptor involved in processes mediating inflammatory and neuropathic pain. This dual-action TRVP1 receptor can also be found in many skin structures.^{41,42}

Together, all these factors suggest that GCO has the potential to be used in dermocosmetic formulations, or skincare solutions for different skin problems.

Conclusions

In this work, we investigated the influence of pressing variables, such as press preheating, press exit diameter, press screw speed, and particle size in extraction yield and composition of cold pressed crude Arabica coffee oil (GCO). The oil yield varied from 2.65 to 6.27% and all the screw pressing parameters impact (p < 0.05) on GCO

yield. Size particle and temperature have a positive impact on extraction yields.

Regarding the oil composition, the major fatty acids identified in GCO were linoleic (44 to 46%) and palmitic acid (32.8 to 33.5%). Of all the pressing variables studied, temperature had a significant and positive effect on diterpenes and C_n -5HT amounts. The amount of the diterpenes kahweol and cafestol ranged from 13.33 to 16.72 mg g⁻¹ and 37.11 to 47.14 mg g⁻¹ of oil, respectively. For C_n -5HT, 114.42 to 577.37 µg g⁻¹ was found for C_{20} -5HT and 193.50 to 1068.08 µg g⁻¹ for C_{22} -5HT. Also, this work is the first in scientific literature to report C_n -5HT content in GCO.

The cosmetics industry has already been exploring the use of coffee oil as emollients. Knowing its potential against UV radiation and due to the metabolite content of the oil, as well as its biological properties related to skin protection, the data obtained here suggest that this oil can be better exploited in the production of dermocosmetics.

Supplementary Information

Supplementary information of the proposed analytical method is available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

The authors thank Embrapa Café, (Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior), Embrapa Café and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for financial support.

References

- Ramadan, M. F.; Cold Pressed Oils: Green Technology, Bioactive Compounds, Functionality and Applications; Academic Press: London, United Kingdom, 2020.
- Lavenburg, V. M.; Rosentrater, K. A.; Jung, S.; *Processes* 2021, 9, 1839. [Crossref]
- Aydeniz, B.; Güneşer, O.; Yilmaz, E.; J. Am. Oil Chem. Soc. 2014, 91, 99. [Crossref]
- Speer, K.; Kölling-Speer, I.; *Braz. J. Plant Physiol.* 2006, 18, 201. [Crossref]
- Dong, W.; Hong, Q.; Cheng, J.; He, H.; Li, Y.; Hu, R.; Long, Y.; Food Res. Int. 2023, 165, 112470. [Crossref]
- 6. Speer, K.; Zahm, A.; Lipid Technol. 2011, 23, 127. [Crossref]
- Lombo, V. O.; Pereira, S. F.; Bizzo, H. R.; Ferreira, M. S. L.; Rezende, C. M.; *J. Food Process. Preserv.* 2022, *46*, e16361. [Crossref]
- Cornelio-Santiago, H. P.; Gonçalvez, C. B.; Oliveira, N. A.; Oliveira, A. L.; *J. Supercrit. Fluids* 2017, *128*, 386. [Crossref]; Araújo, J. A. M.; Sandi, D.; *Food Chem.* 2007, *101*, 1087 [Crossref]; de Azevedo, A. B. A.; Kieckbush, T. G.; Tashima, A. K.; Mohamed, R. S.; Mazzafera, P.; de Melo, S. A. B. V.; *J. Supercrit. Fluids* 2008, *44*, 186. [Crossref]
- Tsukui, A.; Santos Jr., H. M.; Oigman, S. S.; de Souza, R. O.; Bizzo, H. R.; Rezende, C. M.; *Food Chem.* **2014**, *164*, 266. [Crossref]
- Scharnhop, H.; Winterhalter, P.; J. Food Comp. Anal. 2009, 22, 233. [Crossref]
- Oliveira, N. A.; Sandini, T. M.; Cornelio-Santiago, H. P.; Martinelli, E. C. L.; Raspantini, L. E. R.; Raspantini, P. C.; Momo, C.; Oliveira, A. L.; Fukumasu, H.; *Regul. Toxicol. Pharmacol.* 2020, *110*, 104517. [Crossref]
- Nosari, A. B. F. L.; Lima, J. F.; Serra, O. A.; Freitas, A. P. P.; *Rev. Bras. Farmacogn.* 2015, 25, 307. [Crossref]
- Wagemaker, T. A. L.; Carvalho, C. R. L.; Maia, N. B.; Baggio, S. R.; Guerreiro Filho, O.; *Ind. Crops Prod.* 2011, *33*, 469. [Crossref]
- Chiari, B. G.; Trovatti, E.; Pecoraro, É.; Corrêa, M. A.; Cicarelli, R. M. B.; Ribeiro, S. J. L.; Isaac, V. L. B.; *Ind. Crops Prod.* 2014, *52*, 389. [Crossref]
- Cavin, C.; Holzhäuser, D.; Constable, A.; Huggett, A. C.; Schilter, B.; *Carcinogenesis* 1998, 19, 1369. [Crossref]

- Cavin, C.; Mace, K.; Offord, E. A.; Schilter, B.; *Food Chem. Toxicol.* **2001**, *39*, 549. [Crossref]
- 17. Kim, J. Y.; Kim, D. H.; Jeong, H. G.; *BioFactors* **2006**, *26*, 17. [Crossref]
- Kim, J. Y.; Jung, K. S.; Jeong, H. G.; *FEBS Lett.* 2004, 569, 321. [Crossref]
- Silva, M. A. E.; Brand, A. L. M.; Novaes. F. J. N.; Rezende, C. M.; *Food Rev. Int.* **2022**. [Crossref]
- Thelle, D. S.; Arnesen, E.; Førde, O. H.; *N. Eng. J. Med.* 1983, 308, 1454. [Crossref]
- Urgert, R.; van der Weg, G.; Kosmeijer-Schuil, T. G.; van der Bovenkamp, P.; Hovenier, R.; Katan, M. B.; *J. Agric. Food Chem.* 1995, 43, 2167. [Crossref]
- Weusten-Van der Wouw, M. P.; Katan, M. B.; Viani, R.; Huggett, A. C.; Liardon, R.; Lund-Larsen, P. G.; Thelle, D. S.; Ahola, I.; Aro, A.; *J. Lipid Res.* 1994, *35*, 721. [Crossref]
- Brand, A. L. M; Lima, F.; Tinoco, N. A.; Mota, J. C.; Moreira, I. G. S.; Novaes, F. J. M.; Garrett, R. C.; Giorno, T.; Fernandes, P. D.; Rezende, C. M.; *Food Rev. Int.* 2022. [Crossref]
- Lang, R.; Bardelmeier, I.; Weiss, C.; Rubach, M.; Somoza, V.; Hofmann, T.; *J. Agric. Food Chem.* **2010**, *58*, 1593. [Crossref]
- Rubach, M.; Lang, R.; Skupin, C.; Hofmann, T.; Somoza, V.; J. Agric. Food Chem. 2010, 58, 4153. [Crossref]
- Lee, K. W.; Im, J. Y.; Woo, J. M.; Grosso, H.; Kim, Y. S.; Cristovao, A. C.; Sonsalla, P. K.; Schuster, D. S.; Jalbut, M. M.; Fernandez, J. R.; Voronkov, M.; Junn, E.; Braithwaite, S. P.; Stock, J. B.; Mouradian, M. M.; *Neurotherapeutics* 2013, *10*, 143. [Crossref]
- Basurto-Islas, G.; Blanchard, J.; Tung, Y. C.; Fernandez, J. R.; Voronkov, M.; Stock, M.; Zhang, S.; Stock, J. B.; Iqbal, K.; *Neurobiol. Aging* **2014**, *35*, 2701. [Crossref]
- Giorno, T. B. S.; Lima, F. A.; Brand, A. L. M.; de Oliveira, C. M.; Rezende, C. M.; Fernandes, P. D.; *Molecules* 2021, 26, 3709. [Crossref]
- Folstar, P. In *Coffee Chemistry*; Clarke, R. J.; Macrae, R., eds.; Elsevier: Amsterdam, Netherlands, 1985, ch. 6.
- American Oil Chemists' Society (AOCS); Official Method Ca 2C-25, Official Methods and Recommended Practices of the American Oil Chemists' Society, 5th ed.; Firestone, D., ed.; AOCS: Champaign, USA, 1998.
- 31. Antoniassi, R.; Wilhelm, A. E.; de Faria-Machado, A. F.; Guedes, A. M. M.; Bizzo, H. R.; Otimização do Método Hartman e Lago de Preparação de Ésteres Metílicos de Ácidos Graxos; Embrapa Agroindústria de Alimentos: Rio de Janeiro, Brazil, 2018. [Link] accessed in July 2023
- Novaes, F. J. M.; Lima, F. A.; Calado, V.; Marriott, P. J.; Aquino Neto, F. R.; Rezende, C. M.; *Ind. Crops Prod.* 2020, *152*, 112494. [Crossref]
- 33. Araujo, P.; J. Chromatogr. B 2009, 877, 2224. [Crossref]
- Zanella, R.; Prestes, O. D.; Martins, M. L.; Adaime, M. B. In High Performance Liquid Chromatography in Pesticide Residue

Analysis; Tuzimski, T.; Sherma. J., eds.; CRC Press Taylor & Francis Group: USA, 2015, p. 303.

- Tinoco, N. A. B.; Pacheco, S.; Godoy, R. L. O.; Bizzo, H. R.; de Aguiar, P. F.; Leite, S. G. F.; Rezende, C. M.; *Food Res. Int.* 2019, *115*, 487. [Crossref]
- 36. Statistica, version 12; StatSoft, Tulsa, OK, USA, 2012.
- Microsoft Excel, Microsoft Office 2016; Microsoft, Redmond, WA, USA, 2016.
- Calligaris, S.; Munari, M.; Arriguetti, G.; Barba, L.; *Eur. J. Lipid Sci. Technol.* 2009, 111, 1270. [Crossref]
- Pereda, M. C. V.; Dieamant, G. C.; Eberlin, S.; Nogueira, C.; Colombi, D.; Di Stasi, L. C.; Queiroz, M. L. S.; *J. Cosmet. Dermatol.* 2009, *8*, 56. [Crossref]
- Wagemaker, T. A. L.; Fernandes, A. S.; Maia Campos, P. M.; Rodrigues, L. M.; Rijo, P.; *J. Biomed. Biopharmac. Res.* 2012, 9, 207. [Crossref]
- 41. Caterina, M. J.; ACS Chem. Neurosci. 2014, 5, 1107. [Crossref]
- 42. Bíró, T.; Tóth, B. I.; Haskó, G.; Paus, R.; Pacher, P.; *Tr. Pharmacol. Sci.* **2009**, *30*, 411. [Crossref]

Submitted: April 9, 2023 Published online: August 8, 2023