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Extraction, characterization, and evaluation of the functionality of fixed oil low-quality coffee beans for use as pharmaceutical ingredients

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ABSTRACT

In order to offer a viable destination for green coffee beans classified as non-beverage type, this work aimed to extract and characterize the fixed oil from these beans and perform a preliminary evaluation of its functionality as a pharmaceutical ingredient. The extraction yield obtained was 3.70 ± 1.29% (w/w). The oil present in its composition high levels of fatty acids with emulsifying and emollient properties, palmitic acid (47.76%) and linoleic acid (32.98%); and compounds with antioxidant functional properties, tocopherols (788.71 ± 56.08 mg/kg) and phenolic compounds (3312.40 ± 14.62 mg/kg). This oil showed antioxidant activity against the free radical 2,2-diphenyl-1-picryl hydrazil at all tested concentrations, reaching 50% inhibition at the concentration of 0.59 mg/ml and 90% at 0.96 mg/ml. The preliminary evaluation of the physical stability of the creams showed that, when incorporated into formulations, this oil has the potential to be used as a substitute for the synthetic ingredients liquid petrolatum, decyl oleate, and butylated hydroxytoluene.

1. Introduction

Brazil is the largest producer and exporter of coffee globally, and the species of greatest economic importance are *Coffea arabica* L. and *C. canephora* P., popularly known as arabica and conilon, respectively. In the 2020 harvest, production reached a total harvested volume of 63.08 million benefited bags, equivalent to approximately 3.8 million tons, with 77.3% corresponding to arabica coffee and 22.7% to conilon (Brasil, 2020a).

Regarding the production of Brazilian coffee, problems with the low quality of the beans have been observed. It is estimated that 12 million bags of coffee per year produced in Brazil do not meet the quality standards established by Normative Instruction 08/2003 of the Ministério da Agricultura Pecuária e Abastecimento-MAPA (Brasil, 2003; Brasil, 2020b; Kalschne et al., 2018). Defects and impurities can be due to genetic and physiological causes, problems in nutrition, attacks by pests and diseases, climatic conditions, in addition to external factors such as poor regulation of the processing machine and poor drying and storage structure, among others (Hameed et al., 2018; Poltronieri and Rossi, 2016).

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In order to be marketed, these low-quality coffees must go through the process of grain reclassification, carried out by densimetric separation and electronic sieve shaker, but this process is only carried out in export-type coffees due to the high cost. Or dilution in batches of better-quality coffees, which in turn will generate a product that has low market value, but meets current legislation (de Almeida and Spers, 2020; Kalschne et al., 2018; Santos and Nantes, 2014; Toci and Farah, 2014).

However, these low-quality coffees have the potential to be used for other purposes besides foods, such for example: as fertilizers, fuels, adsorbents, as a source of enzymes, among others (Durán et al., 2017; Esquivel and Jiménez, 2012; Jenkins et al., 2017; Rodrigues and Bragagnolo, 2013; Wei and Tanokura, 2015). They can also be used as a source of raw material to produce fixed oil, rich in polyphenolic compounds, kahweol, cafestol, tocopherols, in addition oleic, linoleic, and palmitic fatty acids (Acevedo et al., 2013; Esquivel Rodríguez et al., 2020; Jham et al., 2007; Oliveira et al., 2020; Ren et al., 2019; Tsukui et al., 2014).

Several applications for green coffee fixed oils in the pharmaceutical and cosmetic industries have been proposed. Wagemaker et al. (2012), Chiari et al. (2014), Nosari et al. (2015), and Acevedo et al. (2013) have demonstrated *in vitro* antioxidant activities of green coffee fixed oil and related it to preventing cellular skin damage. *In vitro* tests performed by Chiari et al. (2014) demonstrated that green coffee fixed oil has a synergistic effect when combined with a conventional synthetic sunscreen (ethyl-hexyl-methoxycinnamate) by increasing 20% the sun protection factor (SPF). *In vivo* tests performed on humans with formulations containing up to 15% (w/w) of green coffee fixed oils showed a significant reduction in transepidermal water loss (TEWL) after application for three days. The same formulations were also applied to the skin on the back of the volunteers using occlusive adhesive for two days, and no adverse reactions were observed (Wagemaker et al., 2013, 2015).

Studies carried out by Pereda et al. (2009) identified a dose-dependent relationship on the stimuli in the synthesis of collagen by green coffee oil; production of elastin and glycosaminoglycans by fibroblasts *in vitro*; greater stimuli to the growth factors (TGF-b1 and GM-CSF), and a positive association with the expression of aquaglyceroporins (AQP3) in keratinocytes, responsible for water transport and hydration in human skin epidermis. Low cytotoxicity of green coffee oil at models tested *in vitro* on human keratinocyte (HaCat) and human hepatoma (HepG2) cultures with a cell density of 1 x 10^6 cells/ml in formulations (10-100 µL green coffee fixed oils/ml, 24 h incubation, 3-4,5-dimethyl-thiazole-2-il-2,5-diphenyltrazzole bromide reduction assay) was reported (Wagemaker et al., 2013; Chiari et al., 2014).

Based on this information, the option of using low-quality coffees to obtain vegetable oil intends to use it as a cosmetic ingredient is visualized, which adds value to the coffee production chain by obtaining a by-product with greater market value and an abundant source of raw, especially in Brazil. In addition, it corroborates with the evidence that vegetable oils have attractive, functional properties for the pharmaceutical and cosmetic sectors, which have great interest in seeking new excipients and active ingredients from natural sources to replace compounds of synthetic origin (Ahmad and Ahsan, 2020; Bera et al., 2006; Blasi and Cossignani, 2020; Cruz et al., 2007; Garg et al., 2021; López-Barrera et al., 2016; Lourenço et al., 2019; Milatovic et al., 2016; Scott et al., 2020; Taghvaei and Jafari, 2015; Xu et al., 2015).

Thus, the objective of this work was to extract and characterize the fixed oil from non-beverage type green coffee beans and perform a preliminary evaluation of its functionality as a pharmaceutical ingredient.

2. Materials and methods

2.1. Raw materials

The fixed oil was obtained from green conilon coffee beans (GCC) classified as non-beverage type, with more than 50 black beans in 300 g of samples and impurity content of 12.6%. The sample was provided by the Cooperative of Coffee Growers of the South of Espírito Santo (CAFESUL), Brazil, and classified in accordance with the Official Brazilian Classification, following Normative Instruction No. 8/2003 of the Identity and Quality Technical Regulations for Processed Coffee Classification (Raw Grains) (Brasil, 2003; Brasil, 2020b). The other excipients of pharmaceutical-grade used to prepare the formulations were: Polawax®, decyl oleate, glyceryl monostearate, isopropyl myristate, and propylene glycol (Mix das Essências), liquid petrolatum (Farmax), methylparaben (Vetec), propylparaben (Êxodo), ethylenediaminetetraacetic acid disodium (Dinâmica) and butylated hydroxytoluene (BHT) (Vetec).

2.2. Obtaining the green conilon coffee fixed oil (CFO)

To obtain the fixed oil, the GCC was dried in an air circulation oven at 55 °C, crushed in a micro-Wiley knife mill (MARCONI, model MA 048), with a sieve of 20 mesh opening and subjected to extraction by Soxhlet (FISATOM, model 22/6, Brazil) with ethyl ether as solvent. The oil was centrifuged at 2.500 rpm (25 ± 2 °C, 5 min) in a centrifuge (HERMLE Labortechik GmbH, model Z206, Germany), filtered in qualitative filter paper, and refrigerated at -20 °C until analysis and preparation of the creams. The oil obtained was named CFO.

2.3. Composition and physicochemical properties of CFO

The physicochemical properties (refraction index-RI, acidity index, peroxide index, density, and the ultraviolet absorption coefficients at 232 nm and 270 nm) were investigated according to standard methods described in the guidelines of the Instituto Adolfo Lutz (2008).

Total tocopherol determination followed the methodology proposed by Durán et al. (2004) and Otemuyiwa and Adewusi (2013) with modifications. The oil samples were diluted in ethanol at a 1:10 ratio. A 1.0 ml aliquot was mixed with a 10^{-3} mol/l ferric chloride solution and stirred for 1 min. Then, 2.0 ml of acetic acid/sodium acetate buffer (pH = 3.3), 2.5 ml of 0.3% orthophenanthroline (m/v), and 0.2 ml of 10^{-3} mol/l phosphoric acid were added. The system was homogenized and kept in the dark for 10 min, followed by an absorbance reading at 534 nm in a UV-Vis spectrophotometer (EDUTEC, model EEQ-9023, Brazil). Quantification was performed by constructing a calibration curve prepared with an α-tocopherol standard (Merck, DL-α-Tocopherol, purity ≥ 98%) in ethanol.

Total phenolic compound content was determined by the Folin-Ciocalteu method according to Singleton et al. (1999). The absorbance was measured at 760 nm on a UV-Vis spectrophotometer (EDUTEC, model EEQ-9023). Quantification was performed by constructing a calibration curve with a gallic acid standard (Dinâmica, AG, purity ≥ 99%) in methanol.

The chromatographic profile was analyzed to determine the oils grease composition. The samples were derivatized and analyzed by gas chromatography coupled to mass spectrometry (GC-MS) in Agilent Technologies gas chromatography (GC 7890A, USA) equipped with a mass detector and DB-23 capillary column, 60 m length x 0.25 mm inner diameter x 0.25 µm film thickness. The identification of the components from fixed oils was performed by comparing the mass spectra of the device database (NIST 2.0) with data from the literature and also with the injection of standard substance solutions. The relative percentage of each compound was calculated by the ratio between the integral area of their respective peaks and the total area of all sample constituents.

2.4. In vitro antioxidant activity

The antioxidant activity of the CFO was determined by an extinction method for 2,2-diphenyl-1-picrylhydrazyl (DPPH) (Brand-Williams et al., 1995; Ndayishimiye and Chun, 2017) with modifications (de Lima Souza et al., 2021). The absorbance was measured at 515 nm using a spectrophotometer (UV-VIS EDUTEC, model EEQ-9023), and the percentage of DPPH sequestration was calculated (Equation 1). The effective concentrations (IC_{50} and IC_{90}) of the oil and the BHT samples were estimated by a predefined tendency curve obtained in Microsoft Excel.

$$DPPH\ scavenging\ (\%) = 100 \times [(A_0-A_n)/(A_0)] \quad (1)$$

Where A_0 = control absorbance (no antioxidant) and A_n = sample absorbance at concentration n.

2.5. Pharmaceutical formulations of the creams

Three formulations using self-emulsifying non-ionic wax were prepared (F1, F2, and F3), with modifications described in the National Formulary from Brazilian Pharmacopeia (Brasil, 2012). A system of conventional synthetic emollients was used in the oil phase in F1: decyl oleate, isopropyl myristate, and liquid petrolatum. In F2, liquid petrolatum was replaced by CFO, and in F3, liquid petrolatum and decyl oleate was replaced by CFO. BHT was used as an antioxidant in F1 and was replaced by CFO in F2 and F3. The composition and denominations of the formulations are listed in Table 1.

Table 1. Formulations designed to evaluate the use of the CFO as pharmaceutical ingredients

Components	Formulation*		
	F1	F2	F3
% Oil phase (w/w)			
Self-emulsifying non-ionic wax (Polawax®)	11.00	11.00	11.00
Glyceryl monostearate	2.00	2.00	2.00
Isopropyl myristate	2.50	2.50	2.50
Decyl oleate	2.50	2.50	-
Liquid petrolatum	2.50	-	-
Butylated hydroxytoluene (BHT)	0.10	-	-
Green conilon coffee fixed oil (CFO)	-	2.50	5.00
% Aqueous phase (w/w)			
Propylene glycol	5.00	5.00	5.00
Methylparaben	0.15	0.15	0.15
Propylparaben	0.05	0.05	0.05
Ethylenediaminetetraacetic acid disodium	0.25	0.25	0.25
Purified water qs to	100	100	100

*Formulations described in the Brazilian Pharmacopeia National Formulary (Brasil, 2012), with adaptations.

The formulations were prepared on a laboratory scale, using a conventional emulsification process according to the National Formulary from Brazilian Pharmacopeia (Brasil, 2012), with modifications. The components of the aqueous and oily phase were heated separately to a temperature of 70-75 °C; the aqueous phase was added to the oily phase and subjected to moderate and continuous stirring in a domestic mixer (BRITANIA, model 200, Brazil) until complete cooling.

2.6. Analysis of the quality and preliminary physical stability of the creams

The description of the aspect and the formation of the emulsified systems were researched by macroscopic and microscopic analysis (Hu et al., 2017). The organoleptic characteristics of the creams (appearance, color, brightness, odor, texture, skin coverage, and residual color after application) were analyzed. The presence of phase separation was also observed. Microscopic evaluation was performed using an optical microscope (LEICA, model DM 500, Germany) with a built-in camera (LEICA, model ICC50 HD) at 40x magnification.

To assess the potential of using fixed oils as excipients, the prepared formulations were subjected to tests provided by ANVISA's cosmetic formulations quality and physical stability guidelines (Brasil, 2004). The pH was measured by direct potentiometry (MS-TECNOPON, model mPA-220, Brazil). To predict physical stability, the creams were subjected to different temperature conditions (40, 45, 50, 55, and 60 °C; during 15 min each cycle) and centrifugation cycles (1.000, 2.500, and 3.500 rpm; during 15 min each cycle).

Another important parameter that influences the acceptance of the formulations is the spreadability related to the sensorial properties of semi-solid formulations. The spreadability was determined by the parallel plate method according to the methodology described by Montenegro et al. (2015). Weighed 0.15 g of each formulation evenly in the center of a glass plate of known dimensions properly positioned on graph paper. Then, another glass plate of the same size and previously weighed was placed carefully above the plate containing the formulation. Then, known weights were added in sequence, and the values of the diameters reached by the sample corresponding to the weights were measured, and the area of the scattered sample was calculated (Equation 2).

The spreadability factor was calculated using the ratio between the maximum spreadability and the limit effort (Equation 3). To evaluate the spreadability behavior of the creams, graphs of spreadability versus strain (weight to which the sample was submitted) its first derivative was constructed.

$E_i = (\pi d^2)/4$ (2)

$Spreadability\ factor\ (mm^2/g) = (E_{max}/m_{max})$ (3)

Where E_i = spreadability of the sample for a given weight (mm^2); d = average diameter (mm), E_{max} = maximum spreadability of the sample, from which the product no longer spreads even when more effort is applied (mm^2) and m_{max} = corresponding weight to obtain maximum spreadability (g).

The method of compression of a sample between parallel plates was used to estimate the behavior of a fluid (Montenegro et al., 2015; Mezger, 2020). For this, the compression and its deformation were calculated from the Equations (4, 5), and the behavior of each cream was evaluated using compression versus volumetric deformation graphs.

$Compression\ (Pa) = (P_n/A)$ (4)

$Volumetric\ Strain = (\Delta V_n/V_0)$ (5)

Where P_n = corresponds to the accumulated weight with each new mass addition multiplied by the acceleration of gravity; A = glass plate area (m^2); ΔV_n = volume variation of cream corresponding to the masse addition; V_0 = initial volume of the cream.

2.7. Potentiality evaluation of CFO oil as an antioxidant in formulations

The potential use of CFO as an antioxidant in creams formulations instead of BHT was investigated by studying *in vitro* antioxidant activity, according to the previously described methodology for the fixed oil (Brand-Williams et al., 1995; Ndayishimiye and Chun, 2017). DPPH was diluted in absolute ethanol at a 1:20 ratio.

2.8. Statistical data analysis

The results obtained for oil extraction yield, physicochemical properties, chemical composition, and antioxidant activity of the oil and creams were subjected to descriptive analysis with a minimum of three experimental repetitions and expressed as mean ± standard deviation, calculated by the packages ExpDes, MASS, and STATS, program R, version 3.5.1 (R: Development Core Team, 2019). The chromatographic profile was carried out by a single repetition. The IC_{50} and IC_{90} values were estimated by the predefined tendency curve obtained in Microsoft Excel, using the best fit model.

3. Results and discussion

In the last few decades, an increase in interest in natural products can be noticed, as well as a growing consumer market worldwide for "green products", which are formulated with natural ingredients. The exclusion of traditional quality control methods based on animal testing and the encouragement to search for natural raw materials from renewable sources ensure the success of the "green cosmetics" market (Fonseca-Santos et al., 2015). The use of non-beverage type green coffee beans in the production of natural ingredients for use in the "green market", satisfies the interest of industries and consumers and adds value to the product regarding the coffee agribusiness. The oil obtained from the green conilon coffee presented, in its composition, high levels of fatty acids with emulsifying and emollient properties (palmitic acid, linoleic acid) and compounds with antioxidant functional properties (tocopherols and phenolic compounds). When incorporated into cream formulations, this oil has proven useful to be used as emollients and antioxidants in place of liquid petroleum jelly, decyl oleate, and BHT, widely used synthetic ingredients.

3.1. Physical classification of GCC

Physical classification is one of the tools responsible for assessing the quality of grains. The physical classification defines the type of coffee, ranked on a scale of two to seven or non-beverage type, the marketing of the latter being prohibited for not meeting the quality standards determined in Normative Instruction 08/2003 of Ministério da Agricultura, Pecuária e Abastecimento-MAPA (Brasil, 2003; Brasil, 2020b). The coffee used in this work presented more than 50 black grains in 300 g of sample, which classifies it as non-beverage type, and content of impurities above 1.0% that disqualifies it for commercialization unless it is processed again.

To be sold in the domestic or foreign market for food purposes, coffees with similar classifications to those analyzed in this work need to go through the re-processing of the beans, carried out by densimetric separation and electronic sieve shaker, at the cost of U$ 2.00 per bag of 60 kg (Cafesul, 2021), however, this process is only carried out in export-type coffees, due to the high cost. If not, then they must be diluted in batches of better-quality coffees, which it will result in a product with low market value, but that meets the current legislation (de Almeida and Spers, 2020; Kalschne et al., 2018; Santos and Nantes, 2014; Toci and Farah, 2014).

Based on this assessment, the search for more viable ways to use these low-quality coffees is suggested. Among the possibilities of use for the grains would be as a source of raw material for the extraction of fixed oil (Acevedo et al., 2013; Chiari et al., 2014; Nosari et al., 2015; Pereda et al., 2009; Tsukui et al., 2014; Wagemaker et al., 2012, 2013, 2015; Xu et al., 2015).

3.2. Obtention and physicochemical characterization of CFO

After drying in an air circulation oven at 55 °C, the GCC sample showed 3.92 ± 0.12% (w/w) moisture content. Extraction of GCC by the Soxhlet device with ethyl ether as solvent produced a yield of 3.70 ± 1.29% (w/w) in fixed oil (CFO). This yield can be considered low when compared to those obtained by other authors for good quality varieties of *C. canephora* (2-12% w/w) (Aguiar et al., 2005; Brige, 2016; Mazzafera et al., 1998; Kemsley et al., 1995), which was already expected because the sample had a high content of impurities (12.60%). However, considering the market value (U$ 100.00/kilogram of fixed coffee oil), the quantity obtained was expressive.

The CFO obtained from GCC was liquid at room temperature, clear to slightly cloudy, brownish-green to amber in color, with a characteristic odor of green coffee beans, density at 20 °C (0.9117 ± 0.0027 g/cm^3), and refractive index at 40 °C (1.4630 ± 0.0015 g/cm^3). Despite the large number of impurities contained in GCC, the density (D) and refractive index (RI) values of CFO did not differ much from those found by other authors in quality coffees (D = 0.9157-0.9418 and IR = 1.4300-1.4810) (Abdullah and Koc, 2013; Al-Hamamre et al., 2012; de Oliveira et al., 2014; Oliveira et al., 2020; Somnuk et al., 2017).

The acidity and peroxide index parameters make it possible to assess the conservation status of fixed vegetable oils since lipid decomposition is almost always accompanied by the formation of free fatty acids and peroxides (Hosseini et al., 2016; Instituto Adolfo Lutz, 2008). According to Anvisa (Brasil, 2005) and Codex Standards for fats and oils from vegetable sources (FAO, 2021), crude or

unrefined oils must have a maximum of 4.0 mg KOH/g acidity index and 15 meq/kg peroxide index. The CFO showed an acidity index (3.61 ± 0.08 mg KOH/g) and a peroxide index (138.31 ± 15.31 meq/kg). These results indicate high levels of lipid decomposition products.

The presence of lipid decomposition products in the CFO was also verified by measuring the extinction coefficient at 232 nm (4.46 ± 0.07) and at 270 nm (19.68 ± 0.08). A high absorption in 232 nm region indicates the presence of conjugated dienes, which are produced from the degradation of polyunsaturated fatty acids, and high absorption in 270 nm indicates the presence of aldehydes and ketones, a result of lipid oxidation (Dantas et al. 2011; Ferrari and Souza, 2009).

3.3. Chemical characterization of CFO

The CFO showed in its saponifiable fraction predominance of palmitic and linoleic acids. The unsaponifiable fraction showed considerable levels of tocopherols and phenolic compounds (Table 2).

Table 2. Chemical composition of green conilon coffee fixed oil (CFO)

Fatty acids	RT (min)	Relative area (%)*	Literature values***
Palmitic (C16:0)	13.346	47.76	27.2-32.1
Linoleic (C18:2 $\Delta^{9,12}$)	16.357	32.98	43.9-49.3
Oleic (C18:1 Δ^{9})	16.509	7.66	9.7-14.2
Stearic (C18:0)	17.009	9.55	5.8-8.0
Arachidic (C20:0)	21.097	2.05	2.1-4.4
Insaponification compounds		**Content (mg/kg)****	
Total tocopherols		788.71 ± 56.08	
Total phenolics		3312.40 ± 14.62	

*Values were determined by using gas chromatography with mass detector (CG-EM) and capillary column DB-23, with single injection of the samples and patterns.
**Values are means ± SD of three determinations (*n*=3). Abbreviations: CFO, green conilon coffee fixed oil obtained by solvent extraction with ethyl ether.
***(D'Amelio et al., 2013; Górnaś et al., 2014; Górnaś et al., 2016; Speer and Kölling-Speer, 2006; Wagemaker et al., 2011)

The presence of saturated and unsaturated fatty acids in the constitution of fixed oils attributes emollient properties when they are incorporated into cosmetic formulations (Pereira et al., 2005). Emollient oils containing these acids are incorporated on the keratinocytes of the epidermis, favoring the maintenance and regeneration of the lipidic barrier and, contributing to the formation of an occlusive layer, preventing the transepidermal water loss (TEWL) (do Rosário et al., 2021; Lu et al., 2011; Sarkar et al., 2017; Zielińska and Nowak, 2017). Additionally, the fatty-acid components of vegetable oils, polyunsaturated fatty acids such as linoleic and linolenic, have a pro-inflammatory effect and can accelerate the healing process (Poljšak et al., 2020). Palmitic and stearic acids are also used by the cosmetic industry to manufacture formulations due to their emulsifying and stabilizing properties (Rosiaux et al., 2015; Sarkar et al., 2017; Zielińska and Nowak, 2017).

In the unsaponifiable fraction of the CFO, the presence of the aforementioned bioactive compounds was identified. Tocopherols, precursors of vitamin E, considered a protective vitamin for the skin due to their powerful antioxidant capacity, act as scavengers of free radicals, protecting the skin from the harmful effects of solar radiation and haves emollient properties, promoting skin hydration (Keen and Hassan, 2016). Phenolic compounds help to improve the immune system, preventing degenerative progressions such as cancer, cataracts, neurological diseases, cardiovascular diseases, and chronic diseases (do Rosário et al., 2021; Lu et al., 2011; Rosiaux et al., 2015; Sarkar et al., 2017; Zielińska and Nowak, 2017).

3.4. Antioxidant activity of CFO

The CFO showed antioxidant activity against the free radical DPPH in all tested concentrations, reaching 50% inhibition (IC_{50}) in the concentration of 0.59 mg/ml and 90% (IC_{90}) in 0.96 mg/ml. The sequestering behavior of the CFO was linear, and at concentrations ≥ 1.0 mg/ml, the antioxidant action was similar to BHT 0.20 mg/ml (Figure 1).

The IC_{50} and IC_{90} values of the CFO were higher than those of the BHT (0.04 and 0.2 mg/ml), which requires a greater amount of CFO to inhibit the free radical DPPH. However, it must be considered that the active antioxidant compounds present in the CFO, tocopherols, and phenolic compounds (Table 2) are from a natural source and offer low risk to human health.

3.5. Preliminary stability studies in creams formulations prepared with CFO

Creams are semi-solid dosage forms obtained from the emulsification of two phases (aqueous and oily) in the presence of one or more emulsifiers, under heating and with stirring (Allen Jr et al., 2013). Therefore, it has peculiar characteristics. Preliminary stability studies can be carried out during the formulation phase of a product to guide the choice between different formulations and evaluate the need for modifications to adapt them (Brasil, 2004). The tests performed to determine the preliminary stability in the present work were the aspect description, pH determination, thermal and mechanical stress, and spreadability.

When analyzed with the naked eye, all proposed formulations were smooth and lump-free with no evidence of creaming, flocculation, or coalescence. The F1 formulation showed milk-white color, and formulations prepared with CFO (F2 and F3) showed a beige-white color. When analyzed macroscopically, no creaming, flocculation, or coalescence was noted. The odor was characteristic of the raw materials used, with no rancid odor or of the solvent used to extract the oil.

Regarding the sensory aspect on the skin, the formulation prepared with the conventional emollient system (F1) presented less dense, with a tackiness touch, high gloss, low coverage, thin layer, and white on the skin after application disappeared within a few seconds. The formulation in which liquid petrolatum, decyl oleate, and BHT were replaced by CFO (F3) presented denser, with a dry touch, the lower gloss, high coverage, and transparency on the skin after application. The formulation in which liquid petrolatum and BHT were replaced by CFO (F2) presented intermediate characteristics.

In the photograph analysis of optical microscopy, individual spherical droplets dispersed in the medium were observed (Figure

2). A reduction in droplet size was observed in formulation with a higher proportion of fixed oil (F3). Such observations suggest that this formulation has a greater tendency to physical stability since the drop size correlates with the physical stability of the emulsion. When emulsified systems do not tend to flocculate, the observed drops are uniformly distributed and small; in emulsions that tend to flocculate, the droplets are larger and are close to each other, without merging into bigger ones (Allen Jr et al., 2013; Hu et al., 2017).

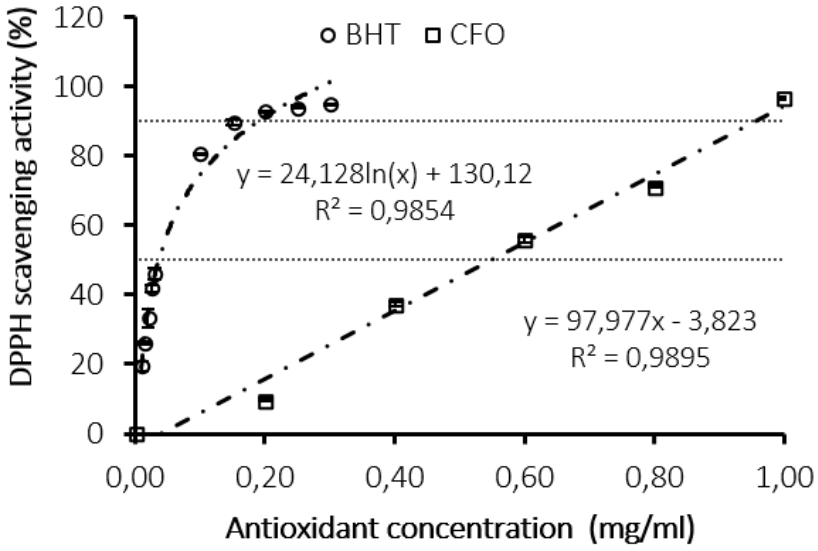

Figure 1. Antioxidant activity of BHT and CFO
Values are means ± SD of three determinations (*n*=3).
Abbreviations: BHT-butylated hydroxytoluene, and CFO-green conilon coffee fixed oil obtained by solvent extraction with ethyl ether

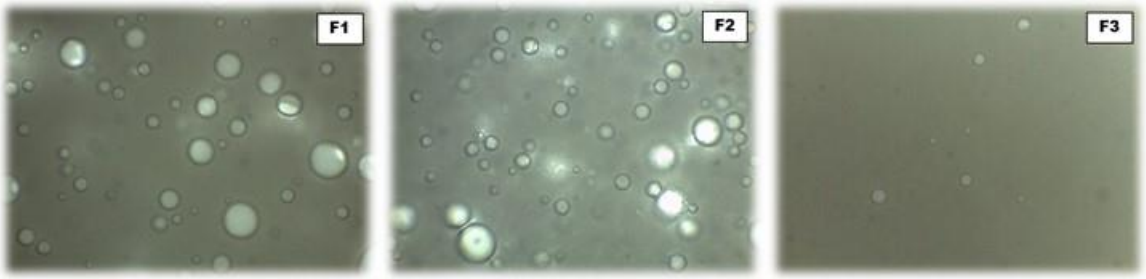

Figure 2. Microphotographs of creams prepared in a single batch each, under 40× magnification
F1: Cream with isopropyl myristate emollient system, liquid petrolatum and decyl oleate
F2: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent to replacing liquid petrolatum
F3: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent, to replace liquid petrolatum, decyl oleate and BHT

A factor of great relevance for the acceptance of cosmetic products by consumers is the sensory aspect, among which is the ease of spreading and removal (Allen Jr et al., 2013; Aulton and Taylor, 2016). The F1 and F2 formulations presented the highest spreadability factors (23.2 ± 0.4 and 26.2 ± 0.5 mm^2/g, respectively), being the easiest to spread. In F3, the lowest value was observed (5.5 ± 0.6 mm^2/g), suggesting it was more difficult to spread. F1 and F2 formulations showed more pronounced variations in spreadability at the beginning of the application of the masses (*f*'1 and *f*'2) and tending to constancy, and F3 formulation practically did not vary the spreadability with the increase in the application of the masses (*f*'3) (Figure 3A).

The replacement of liquid petrolatum by CFO in F2 effectively increased the spreadability of the formulation, while the replacement of decyl oleate and liquid petrolatum by CFO in F3 provided the formulation with a decrease. The first one is indicated for cosmetic products submitted to small compressions, with minimum effort conditions required for application to the skin. The last one is indicated for cosmetic products that are used to cover fine lines, facial sunscreen, and makeup in general, as they can be subject to great tensions, with the high effort required for application to the skin, but providing a more uniform coverage (Aulton and Taylor, 2016; Parente et al., 2005).

When evaluated in relation to the volumetric compression-deformation effect, a similar behavior was observed in formulations F1 and F2; both behaved as non-Newtonian pseudoplastic fluids, becoming more fluid when subjected to high stresses, while F3 showed a characteristic behavior of Newtonian fluid with a proportional increase between the volumetric strain and the compression rate (Figure 3B). This characteristic may be associated with the presence of air droplets in the F1 and F2 creams (Figure 2), which are removed with compression, causing an increase in fluidity, due to structural changes resulting from the applied forces (Attwood et al., 2011; Dak et al., 2007; Shamsudin et al., 2013). Meanwhile, in F3, these changes are less pronounced due to smaller droplet size and greater emulsion homogeneity (Figure 3) with constant cream fluidity, regardless of the applied force (Allen Jr et al., 2013).

Another important quality parameter for topical products is pH determination. The pH values of the creams were in accordance with the normal cutaneous pH, which corresponds to a range of 4 to 6.5 (Proksch, 2018). The incorporation of CFO in the formulation in a 2.5% w/w proportion did not affect the pH of the formulation since F1 and F2 presented similar pH values. In the proportion of 5.0%, there was a significant reduction in the pH of the formulation, observed in F3. This decrease in the pH values of formulations where there was a total replacement of liquid petroleum jelly and decyl oleate emollients is mainly associated with the increase of the CFO content in the formulation and, consequently, of free fatty acids, since part of the carboxylic groups present in fatty acids tend to ionize at the interface of the emulsion droplets (Bruxel et al., 2012; Rabinovich-Guilatt et al., 2005).

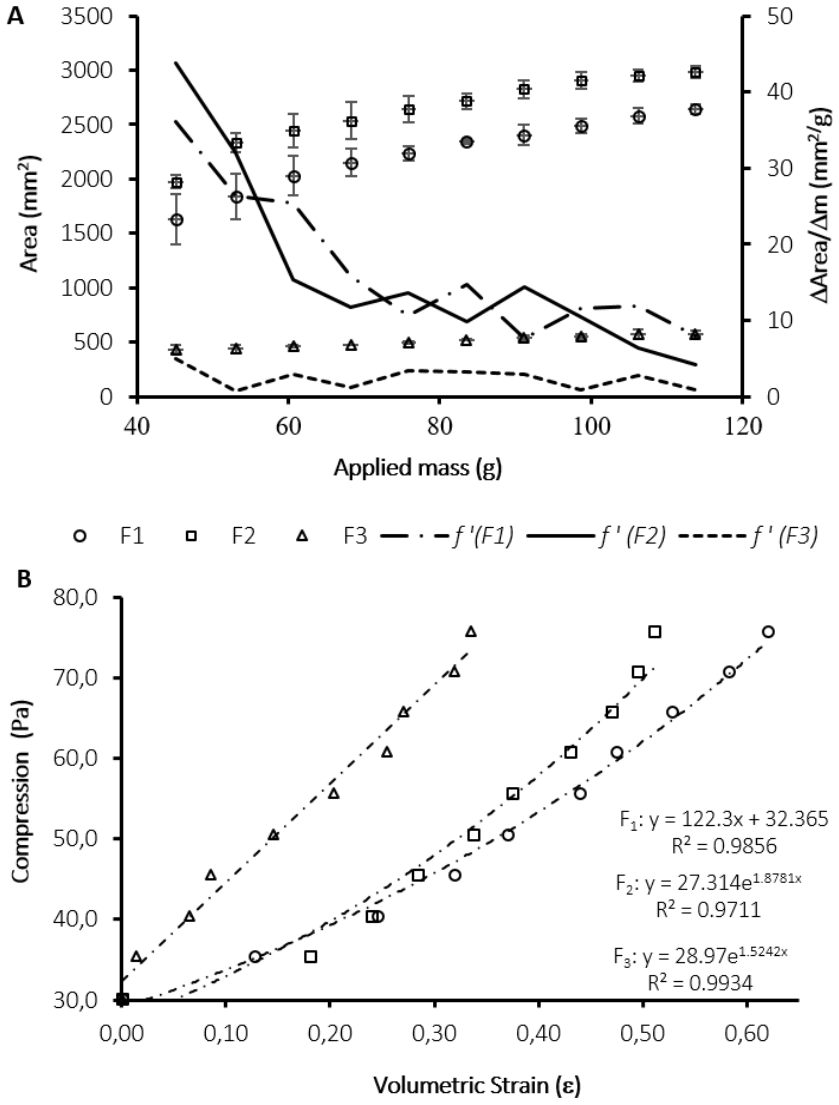

Figure 3. Creams spread profile using the parallel plate method
F1: Cream with isopropyl myristate emollient system, liquid petrolatum and decyl oleate
F2: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent to replacing liquid petrolatum
F3: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent, to replace liquid petrolatum, decyl oleate and BHT

Finally, formulations were submitted to thermal and mechanical stress. None of the formulations showed signs of flocculation, sedimentation, and creaming formation. However, formulations F1 and F2 showed an increase in fluidity from 50 °C, and F2 presented air bubbles at the bottom of the tube when subjected to centrifugation, starting at 1.000 rpm. These changes are probably due to the sedimentation phenomenon because the test is based on separating phases with different densities (Mohsin et al., 2016). Formulation F3 did not show any type of alteration, which may indicate greater physical stability, which is in accordance with the images observed by microscopy (Figure 2).

3.6. Antioxidant activity of CFO in creams

The possibility of replacing BHT by CFO in formulations becomes quite attractive due to the fact of replacing a synthetic component with a natural one, and also due to the concentration limits of BHT recommended by international regulatory authorities for their presence in topical use formulations (0.0075-0.1% w/w) (Rowe et al., 2009).

Figure 4A expresses the CFO antioxidant activity present in the creams in terms of DPPH sequestration: F1 (16.2 ± 0.3%), F2 (44.5 ± 1.1%), and F3 (44.6 ± 0.8%). Greater efficiency was observed in

scavenging the free radical DPPH in formulations containing CFO as an antioxidant (F2 and F3) than in the formulation with BHT (F1).

The effective concentrations for 50% inhibition of the free radicals DPPH were: F1 (0.07 mg/ml of BHT), F2 (0.13 mg/ml of CFO) and F3 (0.26 mg/ml of CFO) (Figure 4B). These results indicate that incorporating CFO in both cream formulations at the concentrations tested is sufficient to replace the use of BHT as an antioxidant. This converges with evidence that natural antioxidants can present antioxidant activity comparable to synthetic antioxidants (Ahmad and Ahsan, 2020; Bera et al., 2006; Blasi and Cossignani, 2020, Cruz et al., 2007; Garg et al., 2021; López-Barrera et al., 2016; Lourenço et al., 2019; Milatovic et al., 2016; Taghvaei and Jafari, 2015; Xu et al., 2015).

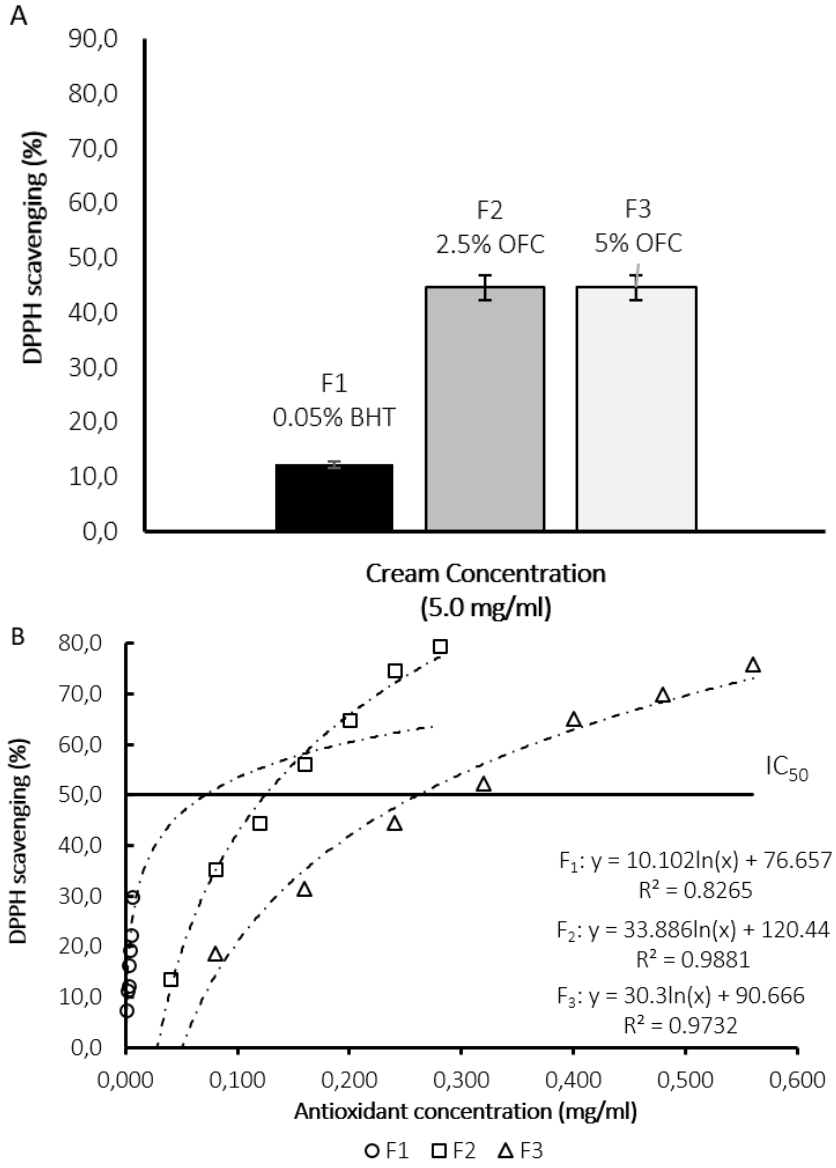

Figure 4. DPPH scavenging by the action of creams, and comparative behavior related of the antioxidant concentration present in each formulation

F1: Cream with isopropyl myristate emollient system, liquid petrolatum and decyl oleate
F2: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent to replacing liquid petrolatum
F3: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent, to replace liquid petrolatum, decyl oleate and BHT
Effective concentrations-IC_{50}

For active antioxidant purposes, the increase in CFO concentration, F2-2.5% (w/w) and F3-5.0% (w/w), provided no difference in DPPH sequestration activity, showing similar behavior (Figure 5). This result shows that the presence of the CFO compounds with antioxidant action in the formulation (F2 and F3) is not only related to their concentration but depends on a variety of physicochemical factors, including pH, the viscosity of the continuous phase, droplet size distribution, oil/water ratio and temperature (Frelichowska et al., 2009; Salmela and Washington, 2014; Spernath et al., 2008).

4. Conclusions

Increasingly, consumers are looking for products or products based on ingredients that have less impact on the environment, including cosmetics. Formulating "eco-friendly" cosmetics is a challenge for formulators who must be able to guarantee stability, safety, and efficiency to the product. Preliminary CFO analysis obtained from non-beverage type green coffee beans showed that the fixed oil was promising in preparing creamy foundations, replacing synthetic

emollients, liquid petroleum jelly, and decyl oleate, and replacing the BHT synthetic antioxidant. Creams with 5% w/w of CFO (F3) showed aspect, droplets size, pH, spreadability, and thermal and mechanical stability profile according to guidelines recommendations.

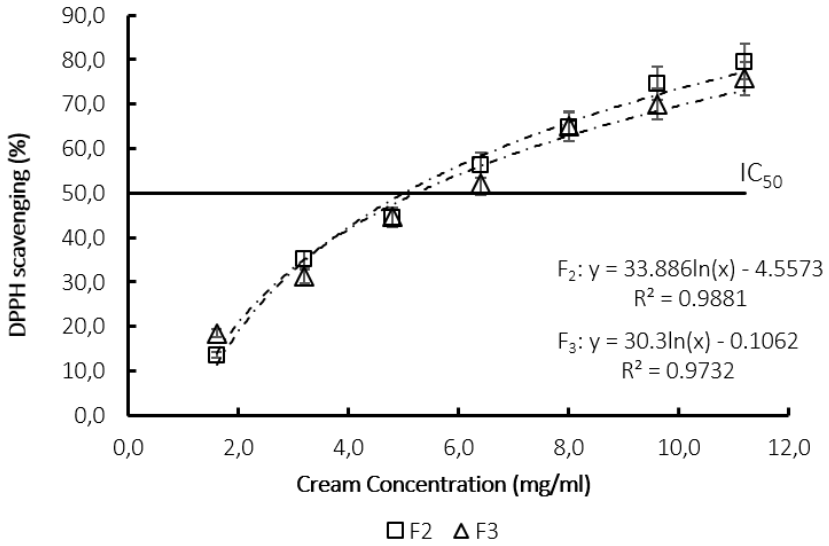

Figure 5. Comparison of DPPH scavenging of the creams
F1: Cream with isopropyl myristate emollient system, liquid petrolatum and decyl oleate
F2: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent to replacing liquid petrolatum
F3: Cream incorporated with green conilon coffee fixed oil obtained by extraction with ethyl ether solvent, to replace liquid petrolatum, decyl oleate and BHT
Effective concentrations-IC_{50}

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Conflict of interest

The authors declare that they have no known competing financial interests or relationships that could have influenced the work reported in this paper.

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Milene Miranda Praça Fontes: Writing-review & editing.
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Supplementary File

None.

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