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Sun protection factor, content and composition of lipid fraction of green coffee beans

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ABSTRACT

Coffee is a much enjoyed beverage because of its unique flavor and taste characteristics. The lipid fraction of coffee beans, composed of wax, oil and unsaponifiable matter, prevents volatilization and loss of flavor during the roasting process. The lipid fraction extracted from green beans is high in linoleic acid and has an ultraviolet absorption. These properties that can be very useful and suitable for cosmetic products such as skin moisturizers and sunscreens. The aim of this study was to characterize the lipid fraction and to determine the sun protection factor of 10 species of *Coffea*. Significant variability was found for all the parameters investigated: the wax content varying between 0.0 and 2.8%, the oil content ranging from 6.9% to 32.4%, unsaponifiable matter from 0.3% to 13.5% and the sun protection factor from 0.0 to 4.1. Fatty acids widely used in the cosmetics industry, such as linoleic and oleic acid were found to be present in excellent proportion.

1. Introduction

According to Davis et al. (2006), there are 103 species within the *Coffea* genus: 41 are native to Africa, 59 come from Madagascar and three from the Macarena Islands. Two of these species – *C. arabica* and *C. canephora* – account for virtually all coffee traded on the world market.

Lipids are among the most important components of coffee beans. The lipid content consists of wax, triglycerides and unsaponifiable matter (Tango, 1971). According to Clifford (1985), the oil content in *C. arabica* is about 16.0%, while *C. canephora* contains about 10.1%.

Wax may be responsible for the unpleasant sick-to-the stomach feeling after drinking some coffees (Wurziger and Harms, 1973). However, this negative characteristic of high wax content has a positive side to it in that this same substance has antioxidant properties, especially in foods that are high in fat and oil (Lehmann et al., 1968).

Green coffee oil has been used in the cosmetics industry for its ability to help maintain natural skin humidity. According to Beveridge et al. (1999), linoleic acid – its main fatty acid – provides relief from eczema and has therapeutic properties in the treatment and cure of dermatitis. Furthermore, there is evidence that coffee oil is able to absorb UV radiation in UVB range, which causes the greatest damage to the human skin (Grollier and Plessis, 1988).

Coffee beans contain significant amounts of unsaponifiable matter. According to Khan and Brown (1953), while the content of unsaponifiable exhibits varies greatly in coffee beans and may reach levels of up to 12%, the content of unsaponifiable matter of most vegetable oils ranges from 1.0% to 1.5%.

The constituents of lipid fraction of coffee have valuable properties for formulating cosmetic products like antioxidants and UVB protection. Furthermore, the composition of coffee oil is rich in unsaturated fatty acids and unsaponifiable matter. However, the content of these constituents is variable between plants and species.

Thus, this study aimed to investigate the genetic variability of each characteristic of the lipid fraction of coffee beans from the Campinas Agronomic Institute *Coffea* Gene bank (São Paulo, Brazil) to allow correlations between these constituents for the purpose of selecting plants for breeding programs and subsequent use in cosmetic products.

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2. Materials and methods

2.1. Plant material

Coffee cherries were harvested at the peak of ripeness and subsequently air dried. Ten species of *Coffea* genus: *C. arabica*, *C. canephora*, *C. congensis*, *C. eugenioides*, *C. heterocalyx*, *C. kapakata*, *C. liberica*, *C. racemosa*, *C. salvatrix* and *C. stenophylla* were evaluated (Table 1).

2.2. Chemicals

Petroleum ether, chloroform, ethyl alcohol, ethyl ether at analytical grade were purchase from Sigma.

2.3. Wax and oil content

The wax content was determined by the Folstar et al. (1976) method using a *Butt* extraction apparatus with chloroform as solvent under reflux for 30 min. The oil content was determined by the AOCS Am 2-93 method with petroleum ether reflux for 16 h in a *Butt* apparatus (Aocs, 1998).

2.4. Oil composition

After oil transesterification according to the method proposed by Hartmann and Lago (1973), fatty acids composition was determined in a Varian gas chromatograph, model 3900, equipped with an automatic sampler, injector split ratio of 75:1; capillary column Chrompack CP-SIL 88 (100 mx 0.25 mm ID, 0.20 ìm film) with flame ionization detector (FID) and controlled by a computer running the STAR Chromatography Workstation software. Column temperature was programmed as follows: initial temperature of 120 °C/5 min, heating from 120 to 220 °C (3 °C min^{-1}) and from 220 to 235 °C (1 °C min^{-1}), hold at a temperature of 235 °C for 12 min. Nitrogen was used as carrier gas at a flow rate of 1 ml min^{-1} and hydrogen, at a flow rate of 30 ml min^{-1}, was used as the make up gas. The injector temperature was set at 270 °C, while the detector was set at 300 °C. An injection volume of 1 μl was used for all samples and standards. Identification of fatty acids was performed by comparing the retention times of the samples with those of known fatty acids. In all, 37 patterns of saturated, monounsaturated and polyunsaturated fatty acids were determined (Supelco 37 Component FAME Mix – 47885-U). The relative amounts of the fatty acids were calculated from the total area of the peaks in the chromatograms and the results expressed in g 100 g^{-1} sample. Unsaponifiable matter was obtained by the AOCS Ca 6B-53 method (Aocs, 1998).

2.5. Sun protection factor determination

The sun protection factor was calculated based on the spectrophotometric method proposed by Mansur et al. (1986).

2.6. Statistical analyses

The characteristics of wax content; oil content and sun protection factor were statistically analyzed as a randomized design with the species as the main effect and plants as secondary effect, three replicates per plant. Each selection of *C. liberica* was considered one treatment.

A mixture of the oil extracted from plants of each specie investigated was analyzed for fatty acid composition and unsaponifiable matter content in a randomized design experiment, with samples in duplicate. Means were compared using the Tukey test at the 1% level of probability.

3. Results and discussion

3.1. Wax content

According to Folstar (1985) *apud* Folstar et al. (1976), *C. arabica* contains between 0.2% and 0.3% coffee wax, which is located in a thin layer forming the outermost part of the bean.

According to Wurziger (1972), coffee wax is responsible for the unpleasant feeling after drinking. For that reason, removal of the wax layer by processing considerably improves drinking quality. Coffee cultivars or plants with less wax covering their beans produce a more easily digested beverage with enhanced flavor and quality characteristics.

The highest wax content was found in *C. congensis* (2.5%) and *C. eugenioides* (2.3%), while *C. canephora* (0.1%) and *C. arabica* (0.2%) had the lowest. These comparatively lower wax content values are probably one of the reasons for their popularity and worldwide consumer preference.

Significant intra- and interspecies variability in wax content was found, as illustrated by *C. liberica* var. *dewevrei* 'Abeokutae' (0.7–2.5%) and *C. stenophylla* (1.0–2.2%), the latter exhibiting the greatest degree of variability among the plants investigated (Table 2).

Coffee wax can not only be used as natural antioxidant in food products (Lehmann et al., 1968), but also as a source of serotonin using special liquid chromatography separation techniques (Kele and Ohmacht, 1996). As high contents are found only in wild species, interspecies hybrids with cultivated species should be developed to obtain coffee plants with high wax content and provide the pharmaceutical industry with a source of high-quality raw material.

Table 1
Genetic material of the *Coffea* species studied.

Species	Variety	Plants
C. arabica	cv.Obatã IAC 1669-20	C 4. C 43. C 47 and C 66
C. canephora	cv. ApoatãIA	IAC 3597-9, IAC 3599-1, IAC 3599-7, IAC 3599-9, IAC 3600-5, IAC 3600-6, IAC 3600-9, IAC 3600-12
C. congensis		IAC 4351
C. eugenioides		IAC 1098
C. heterocalyx		Combination of plants: IAC 2980 and IAC 2981
C. kapakata	IAC4511	C 19, C 20-1 and C 20-2
C. liberica	var. *dewevrei* 'Abeokutae'	Col. 5, col. 6 and col. 15
	var. *dewevrei* 'Excelsa'	Col. 3, col. 10 and col. 11
	var. *liberica*	IAC 747 col. 7, col. 8 and col. 9
	var. *liberica* 'Passipagore'	IAC 4079 col. 1
C. racemosa		IAC 6608-2, IAC 6505-10 and IAC 4913-1
C. salvatrix	IAC 1288	Col. 9 and Combination of plants
C. stenophylla	IAC 1070	Col. 2, col. 3, col. 4 and col. 10

Table 2
Wax and oil content of Coffea species (dry green beans basis).

Species	Plants n°	Wax Content Mean	Wax Content Variation	Oil Content Mean	Oil Content Variation
C. arabica	4	0.24 i	0.07–0.41	13.33 d	11.53–14.95
C. canephora	8	0.08 j	0.01–0.18	8.531	6.25–14.64
C. congensis	1	2.55 a	2.32–2.75	8.511	8.18–8.98
C. eugenioides	1	2.34 b	1.97–2.55	16.79 c	16.14–17.21
C. heterocalyx	1	1.24 f	1.12–1.31	21.29 b	20.92–21.67
C. kapakata	3	0.56 h	0.14–1.15	10.58 i	9.56–11.56
C. liberica var. *dewevrei* 'Abeokutae'	3	1.65 e	0.72–2.45	11.15 g	9.80–12.54
C. liberica var. *dewevrei* 'Excelsa'	3	0.91 g	0.62–1.10	11.21 g	10.75–11.88
C. liberica var. *liberica*	3	1.91c	1.25–3.27	11.09 h	10.17–11.89
'Passipagore'	1	1.17 f	1.04–1.31	10.06 j	9.63–10.56
C. racemosa	3	1.00 g	0.62–1.44	11.60 f	10.12–13.81
C. salvatrix	2	1.58 de	1.18–2.04	28.07 a	23.30–32.40
C. stenophylla	4	1.68 e	1.02–2.22	12.85 e	11.17–14.96

*Means followed by the same character are not statistically different ($P < 0.01$).

3.2. Oil content

Coffee oil extracted from roasted beans is mainly used to flavor instant coffee and prevent granules from fragmenting. It is also used in the food industry to flavor cakes and candies.

Some authors state the significance of species and/or varieties with greater oil content that can be used to produce coffee oil which is a highly valued additive used to preserve the flavor and taste of improved quality coffees (Menchu, 1966; Fonseca et al., 1974; Oliveira et al., 2006).

Oil extracted from unroasted beans is mainly used by the cosmetics industry due to its property to assist in the prevention of skin dehydration.

According to Alvarez and Rodriguez (2000), oil from *C. arabica* is a mixture of substances with excellent properties for the human skin due its fatty acid composition. In addition, its ability to absorb UV radiation in the UVB range enables its use in sunscreens (Grollier and Plessis, 1988).

Although there are many studies on coffee oil content (Tango, 1963; Poisson, 1979; Aguiar et al., 2005), most of these investigations focus on *C. arabica* and *C. canephora.*

Mazzafera et al. (1998) studied the oil content of several coffee species extracted with hexane for 16–18 h. The highest oil content found by these authors was that of *C. salvatrix* (29.2%) and the lowest that of *C. canephora* (8.1%). In the present work, similar results were found using petroleum ether as solvent, for example *C. salvatrix* (28.1%) and *C. canephora* (8.5%).

The data depicted in Table 2 show that the oil content exhibits little variation within the *C. liberica* species: *C. liberica* var. *dewevrei* 'Abeokutae' (9.8–12.5%), *C. liberica* var. *dewevrei* 'Excelsa' (10.8–11.9%), *C. liberica* var. *liberica* (10.1–11.9%) and *C. liberica* var. *liberica* 'Passipagore' (9.6–10.6%).

C. stenophylla (11.2–15.0%), *C. arabica* (11.5–15.0%) and *C. eugenioides* (16.8%) were also found to have high oil contents, though not as high as *C. heterocalyx* (21.3%).

Despite the autogamous nature of the *C. arabica* species and the fact that analysis was performed on only one cultivar, significant intraspecies variability in oil content was found, suggesting that new experiments should be conducted to more accurately evaluate the variability of this characteristic within this species.

3.3. Oil composition

According to Folstar (1985), the main fatty acids of green coffee beans are: linoleic acid (41.2–42.6%), palmitic (35.2–36.7%), oleic (9.5–11.9%), stearic (7.2–9.7%), linolenic (1.3–2.7%), arachidic (0.3–1.5%) and myristic acid (0.2%). Analyses of the oil extracted from 10 species of *Coffea* showed the same main fatty acids in varied proportions (Table 3).

The fatty acid content of *C. arabica* observed in this work was similar to the data reported by Tango (1971). Recently, Oliveira et al. (2006) confirmed the results: the main fatty acids in *C. arabica* found by these authors were linoleic (44%) and palmitic acid (34%), followed by oleic (9%) and stearic acid in moderate quantities (7%) and small quantities of arachidic (3%), linolenic (1.5%), behenic (0.7%) and eicosanoic acid (0.3%). The same authors studied the differences in fatty acid composition between defective and non-defective coffee beans but no significant differences were found.

Dussert et al. (2008), studying the chemotaxonomy of *Coffea* species on the basis of seed fatty acid composition, reported compositional data in line with the results of our study regarding the main fatty acids in coffee beans: linoleic acid (45.2%), palmitic (33.4%), oleic (8.9%), stearic (7.0%), arachidic (2.2%) and linolenic acid (1.7%).

Each fatty acid has unique chemical and physical properties that make it suitable for use in several cosmetics applications. Coffee oil with high levels of linoleic acid is an excellent emollient, while high concentrations of palmitic acid provide good skin protection (Alvarez and Rodriguez, 2000).

Although this study (Table 3) identified *C. liberica* var. Passipagore ($48.5\,g\,100\,g^{-1}$) and *C. kapakata* ($47.7\,g\,100\,g^{-1}$) as the species with the highest linoleic acid content, no significant differences were found when compared to *C. arabica* ($46.3\,g\,100\,g^{-1}$), *C. salvatrix* ($46.4\,g\,100\,g^{-1}$) and *C. heterocalyx* ($47.4\,g\,100\,g^{-1}$), all of which exhibit high oil content values. Differently from the other species, *C. liberica* var. *liberica* was also found to contain trans isomers of linoleic ($0.32\,g\,100\,g^{-1}$) and linolenic ($0.20\,g\,100\,g^{-1}$) acid.

3.4. Unsaponifiable matter content

According to Lago and Antoniassi (2001), a high content of unsaponifiable matter, such as about 14.84%, complicates purification and causes the oil to retain color and odor characteristics that are undesirable for the food industries (Hartmann et al., 1968). Therefore, coffees with low unsaponifiable matter content can contribute to increase oil quality and reduce refining cost.

Lago and Antoniassi (2001) reported sitosterol as the main sterol in the unsaponifiable matter of oil extracted from roasted and green coffee beans.

Unsaponifiable matter would be responsible for moisture binding, skin penetration and adhesion properties. For that reason, the high content of unsaponifiable matter such as that found in *C. arabica*, *C. congensis* and *C. salvatrix* (Table 4) could improve the quality of cosmetic products. On other hand, *C. kapakata* and *C. liberica* var.

Table 3
Composition (g 100 g^{-1}) of the main fatty acids of coffee species (oil samples obtained by combining the oil extracted from all individual plants of each species).

Species	Palmitic	Stearic	Oleic	Linoleic 100 g^{-1}	Linolenic	Arachidic
C. arabica	30.2 c	8.0 b	10.6 b	46.3 a	1.6 a	2.3 a
C. heterocalyx	35.6 a	5.8 c	6.5 ef	47.4 a	1.9 a	1.9 a
C. canephora	31.3 b	5.9 c	12.5 a	44.0 b	1.5 a	2.4 a
C. congensis	34.8 a	7.5 de	7.5 de	44.4 ab	1.2 b	2.8 a
C. eugenioides	35.6 a	7.1 e	7.1 e	45.9 a	2.2 a	2.2 a
C. kapakata	30.7 b	6.4 c	9.6 bc	47.7 a	0.8 c	2.4 a
C. liberica var. *dewevrei* 'Abeokutae'	35.9 a	5.8 c	7.3 de	47.4 a	1.7 a	1.6 b
C. liberica var. *dewevrei* 'Excelsa'	35.0 a	7.1b	9.6 bc	44.2 ab	1.2 b	1.9 a
C. liberica var. *liberica*	35.0 a	7.3 b	9.3 c	44.0 b	1.4 a	1.8 a
C. liberica var. *liberica* 'Passipagore'	24.1 d	9.6 a	8.0 d	48.5 a	1.9 a	2.1a
C. racemosa	36.8 a	9.9 a	8.4 d	39.6 d	2.3 a	2.4 a
C. salvatrix	31.1b	6.0 c	10.2 b	46.4 a	1.8 a	1.6 b
C. stenophylla	38.7 a	6.1c	8.6 cd	41.6 c	2.2 a	2.8 a

*Means followed by the same character are not statistically different ($P < 0.01$).

dewevrei 'Excelsa', which exhibited the lowest unsaponifiable matter content, can be used in blends as suggested by Carvalho et al. (1990).

The characterization of wax, oil and unsaponifiable matter contents in coffee beans of several species as done in this research study may contribute to generate information on genetic variability that will aid research and breeding programs aimed at increasing or decreasing the levels or amounts of target compounds to meet specific needs of the industry.

3.5. Sun protection factor

The efficacy of a substance or product to absorb ultraviolet radiation is measured by the Sun Protection Factor (SPF). This factor indicates how many times longer a person wearing the sunscreen substance can stay in the sun without getting burned as opposed to not wearing any sun protection.

The highest SPF values were found in *C. eugenioides* (2.6), *C. salvatrix* (2.2–3.1) and *C. stenophylla* (0.9–4.1), and the lowest in *C. kapakata* (0.0–0.1), *C. liberica* var. *liberica* 'Passipagore' (0.3), *C. liberica* var. *dewevrei* Abeokutae (0.2–0.6) and *C. canephora* (0.2–0.6).

About 70% of all the coffee grown in the world is *C. arabica*. The high SPF of *C. arabica* shown in Table 5, makes it the species of choice for applications in cosmetics. On the other hand, the probability of using the *C. canephora* species for this same purpose is remote since the SPF calculated for this species (0.35) is much lower than that of *C. arabica* SPF (1.50).

According to Schaefer et al. (2000), sunscreens are products that protect the skin against DNA, cell and tissue damage, cancer, mutations, immunosuppression, dermatitis, photoaging and photodermatoses. For this reason, sunscreen chemicals should have the following characteristics: they should be chemically, photochemically and thermally inert; should not be toxic, sensitizing, irritant nor mutagenic; should have appropriate solubility and no volatility in the final product. Besides this, the product should not be absorbed by the skin, should not change its color or discolor the skin, nor stain clothes; it should be colorless and compatible with the other ingredients of the cosmetic formulation and its packaging; in addition to being chemically stable in the final product (Rosen, 2003).

The skin is formed by several layers of fat-cells. Therefore, the more lipophilic the sunscreen, the greater its substantivity. In other words, the product has the ability to retain its effectiveness for prolonged periods of time, especially when exposed to water (Mansur, 1984).

The coffee oil studied in this work has many of the properties required for sunscreens and may be considered a good ingredient for industrial applications. Moreover, in addition to being a 100% natural product, it contains a series of lipophilic substances with important antioxidant characteristics, such as tocopherols, and is able to protect the skin against UVB radiation.

When high wax and oil contents are combined with a composition rich in unsaturated acids, a high SPF value and high unsaponifiable matter content, the result is a product or ingredient that is ideally suited for formulating high quality cosmetic products able to promote moisture retention and provide sun protection.

Those attributes are found in the lipid fraction of the majority studied species. Two species *C. arabica* and *C. canephora* are responsible for almost 100% of coffee production and their oils are available to use in industry. Wild species like *C. salvatrix* and *C.*

Table 4
Average unsaponifiable matter content of the *Coffea* species investigated (oil samples obtained by combining the oil extracted from all individual plants of each species). Means followed by the same character are not statistically different (dry oil basis).

Species	Unsaponifiable matter content (%)
C. arabica	13.54 a
C. canephora	4.23 b
C. congensis	10.54 a
C. eugenioides	1.93 b
C. heterocalyx	3.90 b
C. kapakata	0.36 c
C. liberica var. *dewevrei* 'Abeokutae'	1.86 b
C. liberica var. *dewevrei* 'Excelsa'	0.28 c
C. liberica var. *liberica*	5.36 b
C. liberica var. *liberica* 'Passipagore'	0.89 bc
C. racemosa	2.19 b
C. salvatrix	10.71 a
C. stenophylla	4.36 b

Table 5
Sun protection factor (SPF) of the *Coffea* species investigated. Means followed by the same character are not statistically different (dry oil basis).

Species	Sun Protection Factor	
	Means	Variation
C. arabica	1.50 e	1.24–1.78
C. canephora	0.35 hi	0.20–0.62
C. congensis	1.08 f	1.02–1.15
C. eugenioides	2.59 a	2.49–2.65
C. heterocalyx	2.37 c	2.06–2.55
C. kapakata	0.06 i	0.00–0.13
C. liberica var. *dewevrei* 'Abeokutae'	0.42 h	0.17–0.64
C. liberica var. *dewevrei* 'Excelsa'	0.88 g	0.24–1.60
C. liberica var. *liberica*	0.48 h	0.29–0.69
C. liberica var. *liberica* 'Passipagore'	0.29 i	0.20–0.40
C. racemosa	1.59 d	1.43–1.74
C. salvatrix	2.54 a	2.14–3.12
C. stenophylla	2.45 b	0.95–4.14

stenophylla are not cultivated and their oils are only used in experimental conditions.

C. arabica, besides its cosmetic properties, is the most cultivated specie around the world and it presented a high intraspecific variability. These facts suggest that this specie should be further studied in depth with regard to its genetic variability.

4. Conclusion

It was found a lot of variability intra and interspecific nevertheless the oil of all the species presents good characteristics that it can be used in cosmetic products.

C. arabica, besides being the most important specie, presented high content of oil and wax, rich composition of unsaturated fatty acids and unsaponifiable matter and high sun protection factor when compared with the other species.

The high degree of variability found in this research study indicates that a properly conducted breeding program will make it possible to obtain specific coffee cultivars capable of producing high added value oil specifically tailored for the cosmetics industry.

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