ISSN 2175-6813

Revista Engenharia na Agricultura

Viçosa, MG, DEA/UFV - DOI: 10.13083/reveng.v30i1.14761 v.31, p.64-75, 2023

INFLUENCE OF MATURITY AND HARVEST REGION ON THE CHEMICAL COMPOSITION AND PHYSICOCHEMICAL PROPERTIES OF OILS DERIVED FROM MACAUBA FRUITS

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Keywords:
Acrocomia aculeata
Carotenoids
Fatty acids
Triacylglycerol
Chemical composition

ABSTRACT

Macauba (*Acrocomia aculeata*) is a good source of vegetable oil in tropical America. Its fruits are highly suitable for biodiesel, cosmetics and food production owing to the high quality of its oil. However, the influence of maturity and harvest region on the quality of oils is not known. Thus, the chemical composition and physicochemical properties oils extracted from the macauba palm fruit at two regions of Minas Gerais and different maturity stage were investigated. C16:0 and C18:1 were the most abundant fatty acids in the mesocarp oil. C12:0, C14:0, C16:0, and C18:1 prevailed in the kernel oil. The High-Resolution Gas Chromatography analysis revealed triacylglycerols (TGs) with equivalent carbon numbers (CN) ranging between 28 and 54. TGs composed of long-chain fatty acids prevailed in the mesocarp oil (CN52 and CN54). On the other hand, the kernel showed a more complex lipid profile, containing TGs with CN between 30 and 54. The lipid content in the oils increased significantly with the ripening of the fruit and the harvest regions. Furthermore, changes in physicochemical properties were observed for both oils depending on the stage of maturity and harvest point. Macauba oils can be used in several industries, such as food and cosmetics. Thus, for its best use, the physicochemical properties of greatest interest should be evaluated in order to identify the ideal cultivation region and maturity stage.

Palavras-chave:
Acrocomia aculeata
Carotenóides
Ácidos graxos
Triacilglicerol
Composição química

INFLUÊNCIA DA MATURIDADE E DA REGIÃO DE COLHEITA NA COMPOSIÇÃO QUÍMICA E PROPRIEDADES FÍSICO-QUÍMICAS DOS ÓLEOS DERIVADOS DO FRUTO MACAUBA

RESUMO

A macaúba (*Acrocomia aculeata*) é uma boa fonte de óleo vegetal na América Tropical. Seus frutos são altamente adequados para a produção de biodiesel, cosméticos e alimentos devido à alta qualidade de seu óleo. No entanto, a influência da maturidade e da região de colheita na qualidade dos óleos não é conhecida. Assim, foram investigadas a composição química e as propriedades físico-químicas dos óleos extraídos do fruto da macaúba em duas regiões de Minas Gerais e em diferentes estágios de maturação. C16:0 e C18:1 foram os ácidos graxos mais abundantes no óleo da polpa. C12:0, C14:0, C16:0 e C18:1 prevaleceram no óleo da amêndoa. A análise de cromatografia gasosa de alta resolução revelou triacilgliceróis (TGs) com números de carbono equivalentes (NC) variando entre 28 e 54. Os TGs compostos por ácidos graxos de cadeia longa prevaleceram no óleo da polpa (CN52 e CN54). Por outro lado, a amêndoa apresentou perfil lipídico mais complexo, contendo TGs com NC entre 30 e 54. O teor de lipídios nos óleos aumentou significativamente com o amadurecimento do fruto e as regiões de colheita. Os óleos de macaúba podem ser utilizados em diversas indústrias, como alimentícia e cosmética. Assim, para seu melhor aproveitamento, devem ser avaliadas as propriedades físico-químicas de maior interesse, a fim de identificar a região ideal de cultivo e o estágio de maturação.

Received 4 Oct, 2022 • Accepted 21 Mar, 2023 • Published 16 May, 2023

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SECTION EDITOR IN CHARGE
Gabriel Henrique Horta de Oliveira

INTRODUCTION

Acrocomia aculeata is a palm tree bearing oleaginous fruits from the Aceraceae family. It is present in tropical and subtropical regions from Mexico to Argentina, although it is more abundant in Brazil (CICONINI *et al.*, 2013). Commonly known as macauba, in natural conditions it generates a bunch with oil fruits that can weigh more than 25kg (PIRES *et al.*, 2013).

The fruit is rounded (25–60 mm in diameter) of the drupe type, in which it has a thin layer (epicarp) surrounding a fibrous part (mesocarp) of various coloration and sweet taste. There is a hard-wooden endocarp that protect the lipid-rich endosperm (SILVA and ANDRADE, 2011). Approximately, the fruits are composed of 20% of epicarp, 40% of mesocarp, 33% of endocarp and 7% of kernel.

The fruits of macauba, more specifically the mesocarp and kernel, have a high potential for oil production. These oils can be used for the food and non-food sector, such as medicines, animal feed, fibers, biodiesel, and the cosmetics industry (SOUZA *et al.*, 2019; TILAHUN *et al.*, 2019) .

The macauba oils can be extracted from mesocarp and kernel, mainly differing in their physicochemical properties and chemical composition (DEL RÍO *et al.*, 2016). Mesocarp oil is predominantly composed of unsaturated fatty acids (74–81%), with oleic acid (63–65%) being the main compound, while lauric acid (38–45%) is predominantly present in the kernel oil (DEL RÍO *et al.*, 2016; VALERIO, FRIAS, CREN, 2020).

In addition, to the high oil productivity, an important characteristic of macauba fruit is the presence of bioactive compounds such as carotenoids, tocopherols and tocotrienols, in its composition (MAGALHÃES *et al.*, 2020). Macauba mesocarp oil content was 49 $mg.g^{-1}$ of β-carotene, representing 82% of the total carotenoids (COIMBRA and JORGE, 2012).

According to Evaristo *et al*. (2016), harvest and postharvest conditions may influence the quality of the extracted oils. The effect of ripening on fruit morphology and accumulation of total carbohydrates and total lipids in the mesocarp has been characterized of *A. aculeata* fruits in Costa Rica by Lieb *et al* (2019) and southern in Brazil by Souza *et al.* (2019). However, changes of fatty acids or triacylglycerols (TAGs) in the mesocarp and kernel depending on the maturity stage and geographic location of Brazilian fruits remain unknown. Most of the papers available in the literature report the composition of the oils from Brazilian macauba mesocarp and kernel focused on the fatty acid profile after saponification of the triglycerides (COIMBRA and JORGE, 2011).

This study can provide a comprehensive characterization of mesocarp and kernel lipids of two regions of Brazil at two defined maturity stages. Understanding changes in macauba oils regarding total lipids, fatty acids, and TAGs during ripening and in different geographical regional should allow the optimization of harvesting time and techniques, in order to achieve higher quality oils for use in various industries.

MATERIAL AND METHODS

Raw Materials

Two regions of the Minas Gerais State (MG, Brazil) were selected to harvest bunches of ripe fruits from a native population of macauba palm. The regions were classified according to the city of macauba harvesting, such as (A) North of Minas, municipality of Mirabela (16° 21’ 26.6”S / 44° 06’ 21.4”W) and (B) Metropolitan Region of Belo Horizonte (19° 52’ 21.7”S / 43° 58’ 23.9” W). The color of the fruit surface was used to classify the maturity stages. Ripe fruits were harvested directly from the bunch and had green to brown exocarp (1). Fruits considered to be fully ripe were harvested manually in the soil shortly after their fall and had brown exocarp (2).

After fruits harvesting, they were selected by discarding the broken and damaged ones and the selected fruits were mixed and homogenized. Mesocarp and kernels of the macauba fruit were manually separated using a knife and subsequently were dried in a vacuum oven at 60ºC for overnight. The oil extraction from the mesocarp and the kernel was performed in a continuous expeller pressing. The oils obtained were stored at −20ºC packed in amber glass vials wrapped with aluminum foil for further analyses.

Physicochemical analysis of oils

Acidity index, peroxide value, saponification index and iodine index were determined by official methods (AOCS, 2017). Lipid extraction was conducted in a Soxhlet extractor, according to the AOAC Official Method 920.39C (AOAC, 2019).

Total carotenoids were measured spectrophotometrically, using the method described by Higby (1962). The reading of the samples was performed in spectrophotometer with a wavelength range of 300–550nm. Carotenoids were expressed as µg/g of oil.

Determination of fatty acids composition

Fatty acid composition was determined using gas chromatography (GC) after the samples were trans-esterified into methyl esters using potassium hydroxide in methanol and hexane, according to the AOCS Ce 2-66 method (AOCS, 2017). The GC fitted with a flame ionization detector and a SPTM-2560 capillary column (100 mm× 0.25 mm× 0.2µm). A mixture of 37 methyl esters was used as a standard (Supelco, Bellefonte, PA, USA). The operating conditions used were: 1 µL injection volume; 1:100 split ratio; detector temperature 260 °C; injector temperature 260 °C; oven temperature program: 60 °C for 1 min, heat to 140 °C at 4 °C/min, hold at 140 °C for 5 min, heat to 240 °C at 4 °C/min, and hold for 30 min. Fatty acids were identified according to retention times and quantification was performed by normalization of areas, based on relative area (%).

Determination of the triglycerides composition

Oil samples were diluted with toluene to the final concentration of 0.7%. High resolution gas chromatography (HRGC) analysis was performed without derivatization on a thermo-stabilized fused silica capillary column of TG-5HT from Thermo (15 meters x 0.25 mm x 0.10 micrometers). The analysis was performed with hydrogen flow of 1.5 mL at 50 ºC under constant pressure. The initial temperature of the column was 50 ºC, with a temperature setting of 15 ºC / minute up to 180 ºC, with a ramp of 7 ºC / minute up to 230 ºC and up to 350 ºC with an increase of 10 ºC / min, staying at this temperature for another 25 minutes. The injector was maintained at 320 ºC, in the 1:50 flow division mode and 1 microliter of solution was injected. The detector was maintained at 380 ºC. To quantify the triacylglycerols, internal normalization was performed. For identification, palmitic, linoleic, monolein, monopalmitin, diolein, dipalmitin, tripalmitin and triolein standards of the SIGMA and NU CHEK were used, which were dissolved in toluene PA.

Statistical analysis

The results of the analytical determinations, in triplicate, were subjected to analysis of variance (ANOVA) and Tukey test for pairwise mean comparisons ($p<0.05$), through the Minitab program, version 19.0.

RESULTS AND DISCUSSIONS

Main constituents of the macauba fruit

The macauba fruit consists of an epicarp with a mesocarp that involves the nut (endocarp + kernel). The mesocarp and kernel are rich in oils, which were extracted with a continuous expeller press as explained above. The percentage of the different parts of the macauba fruit, the moisture and oil content are shown in Table 1. On average, it can be observed that the fruits of the macauba present 25.24% of epicarp, 36.08% of mesocarp, 23.56% of endocarp and 14.28% of kernel, together with 56.73% of mesocarp oil and 42.82% of kernel oil. It can be noted that this composition changes significantly with the maturity stage and harvest region.

The mesocarp and kernel oils are of great interest in food, cosmetic, pharmaceutical and biodiesel industries. Therefore, their compositions and physicochemical properties were analyzed in detail in the present study.

Experimental data obtained from unripe fruits harvesting (1) showed a low oil content and high moisture. Fruits harvested as ripe held high oil content (59.3% A2 and 66.0% B2 for mesocarp oil). There is evidence that macauba is a climacteric fruit with increasing oil contents after its harvesting (TILAHUN *et al.*, 2019). Likewise, a difference in the amount of water and oil was detected in the different regions of the fruit harvesting (A and B). The quality characteristics of some vegetable oils have been vastly associated with their regions of production (JOLAYEMI *et al*., 2018), since it involves prevailing natural factors, such as solar radiation, soil composition and precipitation

characteristics. Thus, for the installation of commercial plantations of the macauba palm it is important to obtain a better understanding of the plant's responses to harvesting conditions, such as fertilization and humidity regime.

High initial moisture contents were measured in fruits mesocarp from all regions, ranging from 34.3% in Mirabela (A1) to 36.8% in Belo Horizonte (B1). Pulp moisture content at ripening stage was reported as 52.99% (RAMOS *et al.*, 2008). Moisture contents of the macauba kernel were more stable, ranging from 9.9% (A2) to 17.7% (B2). Similar value (12.1%) was found by Dessimoni-Pinto *et al.* (2010), while Hiane *et al.* (2005) observed 6.5% moisture for macauba kernel.

High levels of moisture in the fruit, make it difficult to extract oils from the mesocarp and kernel, which consequently increase the costs of the process. In addition, the presence of water in high concentrations favor the growth of microorganisms and physicochemical reactions of deterioration in the fruit. Thus, a fast processing of the fresh fruits, or a fruit drying process must be performed before its storage for late processing.

Physicochemical analysis of oils

The physicochemical characteristics of the oils from mesocarp and kernel of different maturity stage and different regions of Minas Gerais are presented in Table 2.

Cold-pressed unrefined oils must have a

Table 1. Percentage of the main parts of macauba fruit and the respective moisture and oil contents

		A1	***A2***	***B1***	***B2***
Fruit part (%, wt)	*Epicarp*	18.74 ± 1.71c	27.18 ± 0.92a	23.30± 1.56b	30.48± 0.89a
	Mesocarp	29.37± 2.58c	35.52± 2.02b	36.64± 1.98b	43.22± 2.11a
	Endocarp	25.74± 2.33ab	27.10± 1.64a	21.38±1.23bc	18.14± 1.87c
	Kernel	18.70± 1.52a	11.30± 1.00c	15.77±0.95ab	12.80±1.42bc
Moisture (%, wt)	Epicarp	34.30± 4.35a	17.05± 5.14b	36.79± 4.87a	21.57± 3.98b
	Mesocarp	34.84± 2.98a	15.70± 3.77b	38.12± 4.01a	25.19± 3.84b
	Kernel	11.31± 1.86a	9.88± 2.98a	18.26± 2.38b	17.74±2.73b
Oil (%, wt)	Epicarp	30.80± 4.65c	34.50± 3.83bc	41.59±4.21ab	47.10± 2.89a
	Mesocarp	52.36± 5.20b	59.28± 3.42ab	54.18±5.04ab	66.00± 4.78a
	Kernel	37.86± 3.22b	43.41± 2.07b	42.23± 4.51b	49.98± 3.07a

Value represent means ± standard deviations of each maturity stages and regions of Minas Gerais (n=2). Means followed by different letters within a row indicate significant differences ($p \leq 0.05$) by Turkey test. A1= Unripe fruit harvested in the North of Minas; A2= Ripe fruit harvested in the North of Minas; B1=Unripe fruits harvested in Belo Horizonte-MG; B2= Ripe fruit harvested in Belo Horizonte-MG

Table 2. Physicochemical characterization of the mesocarp and kernel oil of macauba

	Acidity Value *[mgKOH.g^{-1}]*	***Peroxide Value*** *[mEq.kg^{-1}]*	***Saponification Value*** *[mg KOH.g^{-1}]*	***Iodine Value*** *[g_{iodine}.100 g^{-1}]*	***Carotenoids*** *[µg.100g^{-1}]*
			Mesocarp		
A1	1.38± 0.82b	6.56± 0.03c	185.84 ± 0.80d	66.42± 1.21b	270.65± 4.90c
A2	0.47± 0.05c	9.03±0.06a	193.57 ± 0.75c	78.46 ± 2.32a	311.95 ± 5.00a
B1	0.93± 0.03a	7.28 ± 0.02b	211.80 ± 1.30a	77.84 ± 2.03a	273.97± 3.30c
B2	0.39± 0.01d	5.43± 0.01d	204.32 ± 1.25b	79.01± 1.63a	296.08± 4.15b
			Kernel		
A1	0.37± 0.01a	0.00 ± 0.01a	225.13 ± 0.60d	31.08 ± 1.01b	1.74 ± 0.01a
A2	0.21±0.03b	0.01 ± 0.01a	229. 25 ± 0.85c	32.76 ± 0.95b	1.81 ± 0.05a
B1	0.36±0.04a	0.07 ± 0.02a	268.00 ± 1.15a	38.68 ± 1.02a	1.04 ± 0.02b
B2	0.20 ± 0.01b	0.03 ± 0.02a	256.45 ± 1.18b	37.47 ± 1.23a	1.01 ± 0.01b

Values represent means ± standard deviations of each maturity stages and regions of Minas Gerais (n=2). Means followed by different letters within a column indicate significant differences ($p \leq 0.05$) by Tukey test. A1= Unripe fruit harvested in the North of Minas; A2= Ripe fruit harvested in the North of Minas; B1=Unripe fruits harvested in Belo Horizonte-MG; B2= Ripe fruit harvested in Belo Horizonte-MG

maximum acidity of 4.0 mg KOH g^{-1} for human consumption according to Resolution 270 – ANVISA (BRAZIL, 2005). Acidity values of macauba mesocarp oil lower than 2 mgKOH.g^{-1} were reported in ripe fruits, while a 0.93 mgKOH.g^{-1} (B1) and 1.38 mgKOH.g^{-1} (A1) acidity was registered in oil obtained from unripe fruits. Similar behavior was observed by Evaristo *et al.* (2016) for fruits harvested in Sete Lagoas, Minas Gerais. The high acidity value is a consequence of oil degradation with production of free fatty acids (FFA) from triglycerides (TG).

Acidity values (<0.37%) found for kernel oil are in accordance to those values observed by Coimbra e Jorge (2011), who analyzed oil from *A. aculeate* kernels and found 0.45% oleic acid in the ripe fruit. Low acidity is desired to maintain sensory attributes of vegetable oils and avoid high costs of the refining and conversion process. Higher acidity demands acid-based catalysis which is more expensive than the alkali one used for biodiesel manufacturing (KNOTHE *et al.*, 2010).

Acidity development in the macauba pulp oil seems to be dependent on the method by which the fruits are harvested stored (EVARISTO *et al*., 2016; DEL RIO *et al*.,2016), and the samples are prepared for analytical procedures (TRENTINI *et al.*, 2016). It is commonly accepted that fruits should be harvested from the bunch and processed as soon as possible to undergo low acidification. Acidity values were higher for the mesocarp than for the kernel (around 3 times higher for unripe fruits). This result can be explained since the mesocarp is more susceptible to degradation for external agents, such as solar light, heat and oxygen, as well as for its larger surface area and the exposure to microorganisms. The kernel, on the other hand, is protected inside the mesocarp. Similarly, Hiane *et al*. (2005) found higher values of acidity for macauba pulp compared to macauba kernel.

Results for peroxide value are also shown in Table 2. Peroxide value is directly related to the oxidative stage of vegetable oil. The oxidation reaction of lipids involves the development of free radicals and thereby, of peroxides. Peroxide values found in this study outweigh the reported value by Bora and Rocha (2004), for macauba pulp oil (2.97 meq kg^{-1}), but present lower values for the kernel's oil (0.07 – 0.00 meq.kg^{-1}). Lower values of peroxide may be associated to the extraction conditions and the fruit storage time until extraction process performed by these authors. Peroxides are generated when the oxidative processes in the fruits are accelerated by the maturity stage, processing and storage conditions.

The mean value obtained for the iodine index for macauba pulp oil was 75.43 $g_{iodine}.100g^{-1}$, while for kernel it was 35.00 $g_{iodine}.100g^{-1}$, as shown in Table 2. The iodine index increases proportionally to the level of unsaturation; accordingly, a higher level of unsaturated fatty acids was found in the pulp compared to the nut. Pulp oil consists mostly of long-chain fatty acids (AMARAL *et al.*, 2011).

These parameters are directly correlated with oil saturation and unsaturation degree. The saponification value is an indicative of fatty acid chain length. The mean value of saponification of the macauba pulp oil was 198.88 ± 1.03 mg KOH g^{-1}. Similar values were reported in the literature: 181 mg KOH g^{-1} and 193.90 mg KOH g^{-1} (COIMBRA and JORGE, 2011; MACHADO *et al.*, 2015).

The reddish yellow color of the macauba mesocarp oil is characteristic of the presence of carotenoids compounds (COIMBRA and JORGE, 2011; RAMOS *et al.*, 2007). Carotenoids can inactivate the singlet oxygen that induces the oxidation decay, making them important antioxidant agents. Total carotene content was measured in the macauba mesocarp oil, and a significant ($P < 0.05$) difference regarding maturity stage and harvest regions was observed. Carotenoids content ranged from 270 mg/g for unripe fruits to 311 mg/g for ripe fruits harvested in Belo Horizonte (A) and from 273 mg/g to 296 mg/g for Mirabela (B), which represents an increase of 15% and 8%, respectively to A and B regions. The synthesis of carotenoids usually takes place with the ripening process and for macauba it does not seem to stop immediately after the abscission. Probably the fruit have water availability and energy sources enough to carry on

with carotenes production during some time after its harvesting.

Total carotenoids content in unripe macauba mesocarp was significantly lower than those determined in ripe fruits harvested from the bunch (Table 2). Thus, it was observed that the concentration of carotenoids is dependent on the maturity stage of the macauba fruit. Alquezar *et al.* (2008) reported an increase in carotenoid concentrations in the mesocarp and exocarp of the orange cultivars during maturity and Marty *et al.* (2005) observed similar behavior for the mesocarp of apricot varieties. No differences were found in the carotenoid content in the kernel oils during the ripening of the fruit. On the other hand, there was a significant difference associated with the harvest region. The fruits harvested in region A had higher levels of carotenoids.

Determination of fatty acid

The fatty acid profiles of the mesocarp and kernel oils are shown in Table 3 and Table 4. The mesocarp oil contain saturated (19.1-21.7%), monounsaturated (70.9 – 75.6%), and polyunsaturated (2.6 – 9.6%) fatty acids. C18:1 (67.1–71.2%) and C16:0 (16.6–18.8%) were the most abundant fatty acids among maturity stages, followed by C18:2 and C16:1. These fatty acid profiles are comparable to those reported for Coimbra and Jorge (2011), Del Rio *et al.* (2016), Lescano *et al.* (2015), Lieb *et al.* (2019) and Trentini *et al.* (2017).

Even though the amount of C18:1 did not present significant difference, for C18:2 a significant difference was observed. On the other hand, an increase in fatty acids C18:0 and C16:1 was identified with the ripening of the fruit. Similarly, Lieb *et al.* (2019) reported that maturity stage of *Acrocomia aculeata* fruits resulted in reduced PUFA and increased MUFA proportions. Proportions of saturated fatty acids (SFAs) changed with harvest regions of the fruit, however, no significant difference was observed after fruits ripeness.

Wannes *et al*. (2010) reported an increase in lauric acid (12: 0) and a decrease in oleic acid (18: 1) in the maturity stage when conducted a study of *Myrtus communis* var. italic. Furthermore, other fatty acids showed random fluctuations in concentration over the time of the experiment. However, in this study, no statistical differences were observed for the composition of oleic and lauric fatty acids with fruit ripening.

Table 3. Composition of fatty acids in the oil from the mesocarp of macauba fruit at different maturity stages and regions of Minas Gerais, Brazil

FFA (%)	*A1*	*A2*	*B1*	*B2*
C8:0	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a
C10:0	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a
C12:0	0.0 ± 0.0b	0.0 ± 0.0b	0.2 ± 0.0a	0.2 ± 0.0a
C14:0	0.0± 0.0b	0.0 ± 0.0b	0.6 ± 0.0a	0.6 ± 0.0a
C16:0	16.5 ±1.0c	17.5 ±1.3b	17.0 ±0.9b	18.4 ± 1.1a
C18:0	2.9 ± 0.4a	1.4 ± 0.2b	2.1 ±0.6a	1.3 ± 0.3b
C20:0	0.0 ± 0.0c	0.0 ± 0.0c	1.2 ± 0.1a	0.8 ± 0.1b
C16:1	2.9 ± 0.8b	6.3 ± 1.2a	3.3 ± 0.5b	5.7 ± 0.8a
C18:1	67.7 ±2.7b	66.7 ±2.0b	70.0 ±2.3a	68.3 ± 2.4a
C18:2	8.8 ± 0.5a	6.7 ± 0.3b	3.4 ± 0.2c	2.2 ± 0.4d
C18:3	0.8 ± 0.1a	0.7 ± 0.0a	0.4 ± 0.1b	0.4 ± 0.1b
SFAs	19.5 ±0.3b	19.1 ± 0.5b	21.5 ± 0.6a	21.7 ± 0.4a
MUFAs	70.9 ±0.4c	73.4 ± 0.5b	74.6±0.7ab	75.6 ± 0.7a
PUFAs	9.6 ± 0.1a	7.4 ± 0.1b	3.9 ± 0.1c	2.6 ± 0.4d

*Values represent means ± standard deviations of each maturity stages and regions of Minas Gerais (n=2). SFAs, saturated fatty acids; MUFAs, monounsaturated fatty acids; PUFAs, polyunsaturated fatty acids. Means followed by different letters within a row indicate significant differences ($p \leq 0.05$) by Tukey test. FFA= Free Fatty Acid; A1= Unripe fruit harvested in the North of Minas; A2= Ripe fruit harvested in the North of Minas; B1=Unripe fruits harvested in Belo Horizonte-MG; B2= Ripe fruit harvested in Belo Horizonte-MG

Table 4. Composition of fatty acids in the oil from the kernel of macauba fruit at different maturity stages and regions of Minas Gerais, Brazil

FFA (%)	*A1*	*A2*	*B1*	*B2*
C8:0	4.1 ± 0.1a	3.9 ± 0.2b	3.9 ± 0.1b	3.6 ± 0.1c
C10:0	4.3 ± 0.1a	3.7 ± 0.2b	3.6 ± 0.1bc	3.3 ± 0.1c
C12:0	41.4±0.4b	41.0 ± 0.3c	43.1 ± 0.5a	42.1 ±0.7b
C14:0	8.0 ± 0.6a	7.7 ± 0.4a	8.0 ± 0.3a	7.4 ± 0.2a
C16:0	6.0 ± 0.2a	6.1 ± 0.2a	5.7 ± 0.2a	5.9 ± 0.2a
C18:0	3.4 ± 0.1b	3.0 ± 0.1c	3.8 ± 0.1a	3.1 ± 0.1bc
C20:0	0.2 ±0.0a	0.1 ± 0.0b	0.2 ± 0.0a	0.1 ± 0.0b
C16:1	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a
C18:1	29.2±0.4bc	30.8 ± 0.7a	28.3 ±0.2c	30.5 ±0.2b
C18:2	3.4 ± 0.1c	3.6 ± 0.1a	3.4 ± 0.1c	3.8 ± 0.2b
C18:3	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a	0.0 ± 0.0a
SFAs	67.4 ±0.4a	65.6 ± 0.5b	68.3 ± 0.2a	65.6 ± 0.4b
MUFAs	29.2±0.4b	30.8 ± 0.7a	28.3 ± 0.2b	30.5 ± 0.2a
PUFAs	3.4 ± 0.0c	3.6 ± 0.1b	3.4 ± 0.1c	3.8 ± 0.2a

FFA= Free Fatty acid (%); A1= Unripe fruit harvested in the North of Minas; A2= Ripe fruit harvested in the North of Minas; B1=Unripe fruits harvested in Belo Horizonte-MG; B2= Ripe fruit harvested in Belo Horizonte-MG

The most abundant kernel fatty acids were C8:0, C10:0, C12:0, C14:0, C16:0, C18:0, C18:1, and C18:2. The oil was mainly composed of SFAs, totaling to 63.0–68.3%. C12:0 represented the major fatty acid (41.0 – 43.1%), followed by C18:1 (28.3 – 30.8%) and C14:0 (7.4–8.0%). Similar fatty acid compositions of kernels were described in literature (COIMBRA and JORGE, 2011; LIEB *et al.*, 2019; MAGALHÃES *et al.*, 2020). A statistical difference was observed in medium chain fatty acids C8:0, C10:0 and C12:0 with fruit ripening. These fatty acids had lower levels when the fruit was ripe compared to the unripe fruit.

The results show that the *A. aculeata* oil has chemical composition comparable with other high-quality commercial vegetable oils. Soybean, olive and canola oil hold high concentrations of MUFA and PUFA. In their composition can be found oleic acid (22.1%, 66.4%, 64.5%, respectively), linoleic acid (55.0%, 16.4%, 23.7%, respectively), and linolenic acid (6.8%, 1.6%, 2.4%, respectively) (CAO; HAN; ZHANG, 2005; ORSAVOVA *et al.*, 2015).

Determination of triglycerides (TG)

The extent of the overall differences in TAG composition of mesocarp and kernel macauba oil at different maturity stages and harvest regions of state of Minas Gerais State is shown in Table 5 and Table 6. TAGs are separated into groups having the same number of carbon atoms (CN), and it was not possible to determine unsaturation because a non-polarized capillary column was used in HRGC. Regarding the TAG from mesocarp oil the highest average percentages correspond to CN = 54 (47.1 – 48.9%), CN=52 (40.5 – 42.1%) and CN=50 (9.76 – 9.96%). The kernel oil presented a more complex profile with TGs ranging from CN=30 to CN=54, compared to TAGs identified in the mesocarp. The most abundant triglycerides for kernel oil were CN=36 (14.5 - 14.8%), CN=38 (11.7 - 12.1%) and CN=32 (10.2%). In addition, it was not possible to detect the correspondence of the CN change of the mesocarp and kernel oil with maturity stage and the harvest region.

According to the results of the fatty acid composition and given the number of carbon (CN) obtained in HRGC for triglycerides molecules, as the CN increases, the chances of that the triglyceride positions be occupied by long-chain fatty acids increase. This effect could explain the reason why the maximum composition of TAG is found between CN 30–54, where the highest values correspond to mesocarp oil at CN = 54 and CN=52, while kernel oil has a maximum CN value < 38.

Table 5. Composition of triglycerides in the oil from the mesocarp of macauba fruit at different maturity stages and regions of State of Minas Gerais State

CN	*A1*	*A2*	*B1*	*B2*
48	0.779 ± 0.000d	0.801 ± 0.000a	0.790 ± 0.001b	0.784 ± 0.000c
50	9.963 ± 0.001a	9.800 ± 0.002c	9.881 ± 0.007b	9.756 ± 0.003d
52	42.180 ± 0.010a	41.928 ± 0.014c	42.054 ± 0.018b	40.540 ± 0.021d
54	47.077 ± 0.013d	47.471 ± 0.012b	47.274 ± 0.020c	48.920 ± 0.017a

Values represent means ± standard deviations (n=2). Means followed by different letters within a row indicate significant differences ($p \leq 0.05$) by Tukey test. CN= Carbon Number; A1= Unripe fruit harvested in the North of Minas; A2= Ripe fruit harvested in the North of Minas; B1=Unripe fruits harvested in Belo Horizonte-MG; B2= Ripe fruit harvested in Belo Horizonte-MG

Table 6. Composition of triglycerides in the oil from the kernel of macauba fruit at different maturity stages and regions of State of Minas Gerais State

CN	*A1*	*A2*	*B1*	*B2*
30	2.427 ± 0.002a	2.380 ± 0.003c	2.403 ± 0.001b	2.422 ± 0.002b
32	10.171 ± 0.011b	10.203 ± 0.009a	10.187 ± 0.002ab	10.200 ± 0.003ab
34	9.207 ± 0.002b	8.995 ± 0.005c	9.101 ± 0.003b	9.188 ± 0.001a
36	14.486 ± 0.015c	14.769 ± 0.010a	14.627 ± 0.012b	14.743 ± 0.018a
38	12.075 ± 0.016a	11.725 ± 0.011c	11.900 ± 0.007b	12.043 ± 0.014a
40	6.385 ± 0.003d	6.621 ± 0.006a	6.503 ± 0.003c	6.599 ± 0.005b
42	9.957 ± 0.004c	10.325 ± 0.009a	10.141 ± 0.007b	10.291 ± 0.010a
44	5.120 ± 0.002d	5.281 ± 0.003a	5.200 ± 0.002c	5.266 ± 0.006b
46	4.067 ± 0.001c	4.188 ± 0.002a	4.127 ± 0.002d	4.177 ± 0.003b
48	9.250 ± 0.002c	9.485 ± 0.005a	9.367 ± 0.003b	9.463 ± 0.004b
50	2.594 ± 0.001a	2.595 ± 0.001a	2.595 ± 0.001c	2.595 ± 0.001b
52	4.379 ± 0.002a	4.280 ± 0.002b	4.330 ± 0.002c	4.370 ± 0.002d
54	9.882 ± 0.003b	9.150 ± 0.002d	9.516 ± 0.004a	9.815 ± 0.004c

Values represent means ± standard deviations (n=2). Means followed by different letters within a row indicate significant differences ($p \leq 0.05$) by Tukey test. CN= Carbon Number; A1= Unripe fruit harvested in the North of Minas; A2= Ripe fruit harvested in the North of Minas; B1=Unripe fruits harvested in Belo Horizonte-MG; B2= Ripe fruit harvested in Belo Horizonte-MG

The identification of triacylglycerols by groups with different numbers of carbon atoms and by different combinations of saturated and unsaturated fatty acids were performed by comparing the percentage data obtained from HRGC with those provided by program developed in Visual Basic. This program was assembled based on equations to calculate the molar percentage of triacylglycerols according to the distribution and molar composition of fatty acids present in the vegetable oil, obtained in the previous item. In Figure 1 and Figure 2 are shown the concentrations of different triacylglycerols (TAG) classified by carbon number, which were found for mesocarp oil and kernel oil of macauba fruit, respectively.

The mesocarp oils had high proportions of unsaturated TAGs, being consistent with data reported by Del Rio *et al.* (2016) and Lieb *et al.* (2019). Triolein (OOO) was the major TAG in all maturity stages assessed (30–50%), followed by TAG with two molecules of oleic acid and one molecule of palmitic acid, OOP (22–26%). It can be seen that the di-unsaturated triglycerides increased during the ripening of the fruits, while the proportions of tri-unsaturated TAGs decreased. As shown for the fatty acid profile (Table 3), TGs composed of C16: 0, C16: 1 and C18: 1 tend to accumulate, while those containing C18: 2, C18: 2 and C18: 3 decreases with maturity, similar to the results reported by Lieb *et al*. (2019). Whereas fatty acids and TAGs remained almost constant during the development of *A. aculeata* mesocarp, significant changes in the moisture, lipid concentration and physicochemical properties were observed.

Thus, it was possible to verify that the TAG of the kernel oil is well distributed in the range of CN from 30 to 54 and they have undergone little change

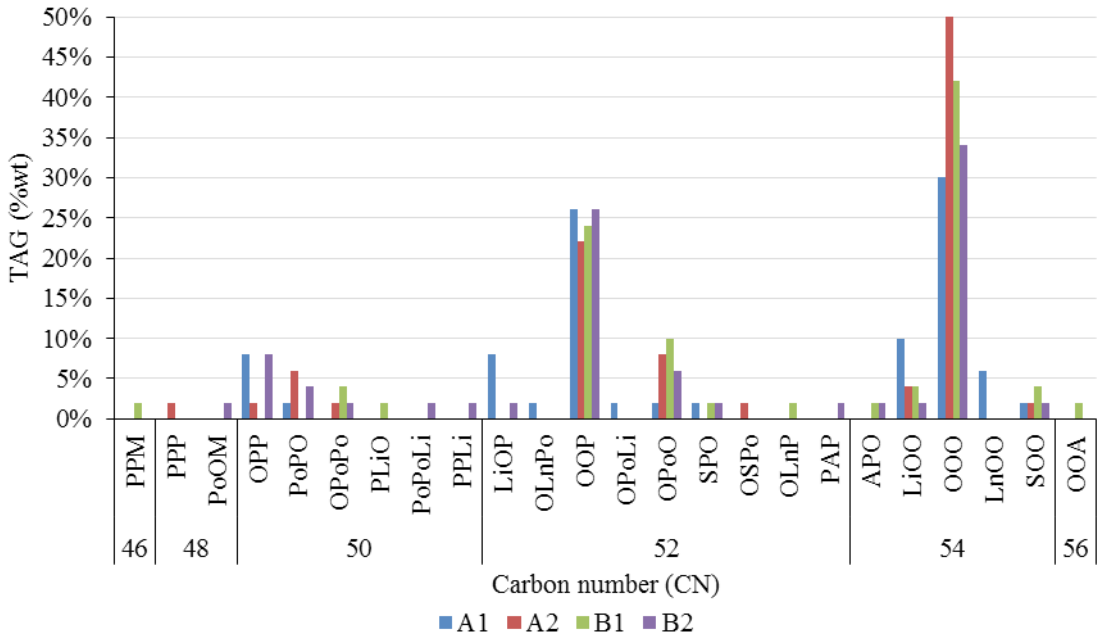

Figure 1. Triglyceride composition (TAG %) in terms of the carbon number (CN) of the lipids extracted from mesocarp oil at different maturity stages and harvest regions

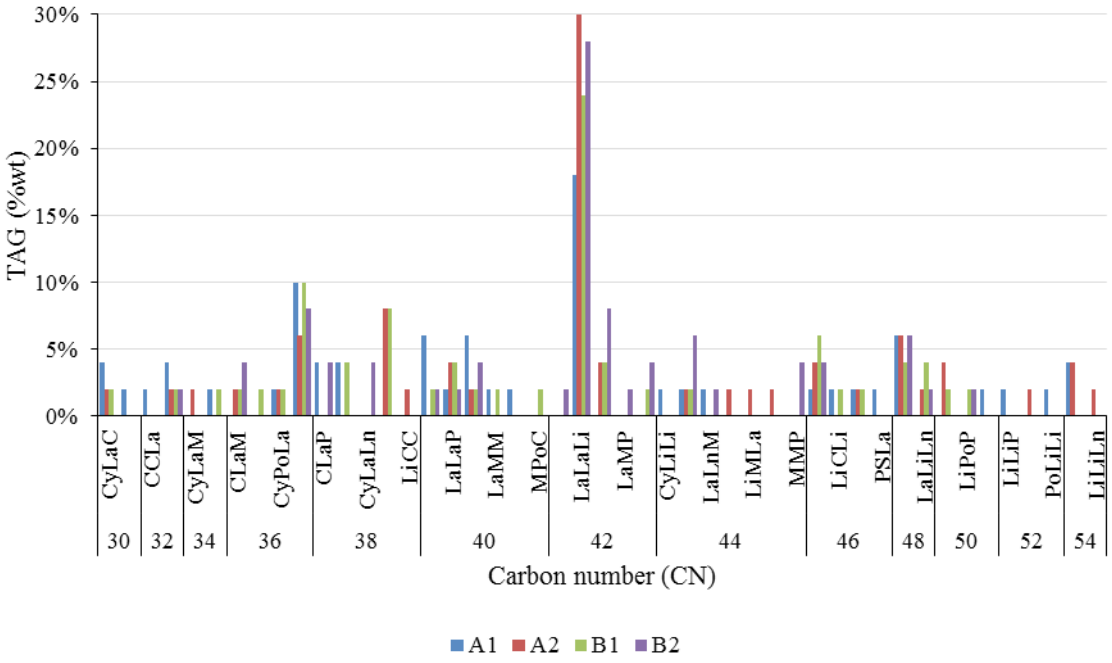

Figure 2. Triglyceride composition (TAG %) in terms of the carbon number (CN) of the lipids extracted from kernel oil at different maturity stages and harvest regions

during the ripening of the fruit. The TAG composed of a sequence of lauric acid, linoleic acid and lauric acid (LaLiLa) had major concentration in all maturity stages and harvest region assessed (18%–30%), followed by TAG with three molecules of Lauric acid (LaLaLa: 6%–10%).

The variability in the fatty acid and triglyceride profile of oils in different harvest regions is related to genetic and climatic factors (MOURTZINIS *et al.*, 2017).

CONCLUSIONS

- The composition of mesocarp and kernel oils extracted from *A. aculeata* fruits have been studied. The analyses of composition and physicochemical properties indicated that macauba oils are very different from each other. Mesocarp oil was predominantly composed of monounsaturated fatty acids C18:1 (66.7%–70.0%), followed by C16:0 (16.5% – 18.4%) and C18:2 (2.2% – 8.8%). In contrast, the kernel oil showed a higher concentration of saturated fatty acids C12:0 (41.0% – 43.1%), proceeded by C18:1 (28.3% – 30.8%) and C14:0 (7.4% – 8.0%). TAGs composed of long-chain fatty acids prevailed in the mesocarp oil (CN52 = 42% and CN54 = 47%). On the other hand, the kernel oil showed a more complex lipid profile, containing TAGs with carbon number between CN=30 and CN=54. In addition, this study evaluated the variability of thermophysical properties and composition of oils obtained from the macauba fruit in relation to its maturity stage and harvest regions. The analyses showed that the profile of fatty acids and TG in the mesocarp and kernel oils remained practically constant in the evaluated stages of maturity. Changes in the chemical composition were observed depending on the different harvest regions. This variation may have been caused by differences in soil and environmental conditions at each site. Fruits harvest as ripe showed a high oil content compared to unripe fruits, which indicates that macauba is a climacteric fruit, which increases the oil content after harvest. Thus, for optimized oil production, it is recommended to harvest the bunch when the fruits are ripe. Considering their similarity with commercial oils, macauba oils can be used in the cosmetic, pharmaceutical and food industries, and in biodiesel production.

ABBREVIATIONS

Cy: Caprylic acid (C8:0); C: capric acid (C10:0); La: lauric acid (C12:0); M: myristic acid (C14:0); P: palmitic acid (C16:0), Po: palmitoleic acid (C16:1); S: stearic acid (C18:0); O: oleic acid (C18:1); Li: linoleic acid (C18:2), Ln: linolenic acid (C18:3); A: arachidic acid (C20:0).

AUTHORSHIP CONTRIBUTION STATEMENT

SILVA, G.C.R.: Conceptualization, Data curation, Formal Analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

DECLARATION OF INTERESTS

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

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