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Sustainable Extraction Methods for the Improvement of the Physicochemical and Nutraceutical Quality of Pequi (*Caryocar brasiliense* Camb.) Pulp Oil

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ABSTRACT: Pequi pulp (*Caryocar brasiliense* Camb.) is an important lipid source among Brazilian Cerrado fruits, with great socioeconomical and environmental relevance for small farmers. However, it is mainly produced on an artisanal scale through high-temperature aqueous extraction (AE), resulting in low-quality oils. Therefore, boosting oil quality and production practices is mandatory. This work evaluated the impact of sustainable and technically viable extraction methods—hydraulic pressing (HP), expeller-type pressing (EP), AE, and ethanol extraction (EE)—on oil quality, physicochemical, and nutritional properties. AE's temperature and time promoted carotenoid losses, harming oil's nutraceutical value. EE provided a high yield (63.96%) and the highest carotenoid extraction (346.39 μg/g), along with other nonlipidic content (>10%), which is a significant bottleneck. HP and EP promoted high yields (64.61%), carotenoids (326.56 μg/g), low acidity, and low oxidation/hydrolysis degree. Lipid profile variations led to small differences in thermal and rheological behavior while preserving oil identity. Mechanical pressing proved to be the most suitable method for small-scale applications, aligning cost, yield, and oil quality, whereas ethanol extraction offers relative advantages for industrial-scale processing, standing out for a higher carotenoid recovery. Results can fill Brazilian legislation gaps on pequi oil quality and identity standards, avoiding low-quality oils and fostering their use in lipid-based products, improving the socio-bioeconomy of the Brazilian Cerrado region.

KEYWORDS: *quality and identity standards, Brazilian Cerrado, food chains, vegetable oils*

1. INTRODUCTION

Brazil is one of the leading global producers of vegetable oils, significantly contributing to the global supply, especially with traditional oils such as soybean, palm, and sunflower.[1] However, the increasing demand concerning food environmental and nutritional aspects has stimulated the exploration of unconventional sources of edible oils,[2,3] such as those derived from fruit pulps and seeds, offering a considerable diversity of fatty acids and phytochemical compounds[4] and representing an opportunity for Brazil to expand its influence in the sector by exploring oilseed sources from its biomes, such as the Brazilian Cerrado region.

The Brazilian Cerrado, which occupies about one-fifth of the national territory, harbors remarkable biodiversity and valuable oleaginous species.[5−7] The promotion of nontimber forest products (NTFPs) has been recognized as a key strategy for conserving this biome and supporting the sustainable use of its resources.[8] Pequi (*Caryocar brasiliense* Camb.) is one of the most prominent Cerrado NTFP species in this context: its commercialization generates approximately 3.5 billion BRL annually, making a significant impact on both local and national economies.[9,10]

Pequi is highly recognized for the high oil content of its pulp, around 30%,[11] with potential benefits for human health,[12] particularly attributed to its high content in carotenoids. These natural pigments, responsible for the oil's red to orange color, exhibit provitamin A activity and potent antioxidant capacity, acting as nutraceutical compounds beneficial to human health and contributing to the oxidative stability of food systems during storage.[13−15]

Despite its economic relevance and nutritional potential, pequi oil is still mostly produced on a small scale and is sold in informal markets, often lacking quality control. The most traditional method for extracting pequi pulp oil is the aqueous extraction also called "cooking", with the use of boiling water to remove the oil from the pulp, separating the phases by density and temperature gradients.[16,17] Although it is a low-cost technique, the artisanal nature of this method, characterized by a high degree of variability and the use of elevated temperatures, can easily lead to lipid degradation,

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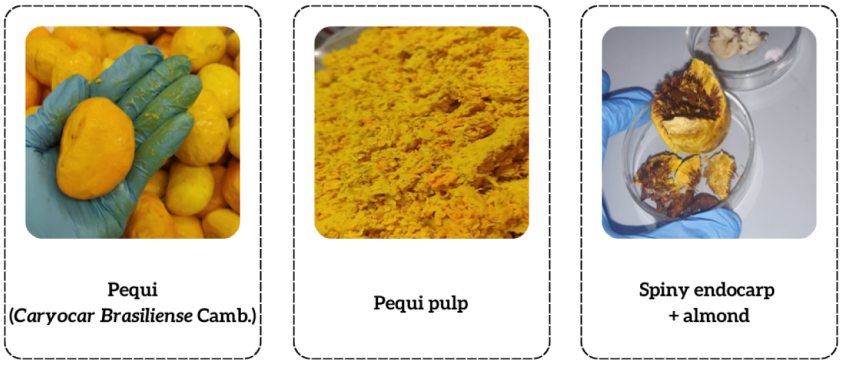

Figure 1. Commercial pequi, pulp, and seed (spiny endocarp + almond). Pequi (*Caryocar brasiliense* Camb.) pulps were obtained from Goiás State (Brazil), where oils were extracted. After depulping, the residue obtained is a spiny endorcarp and an almond.

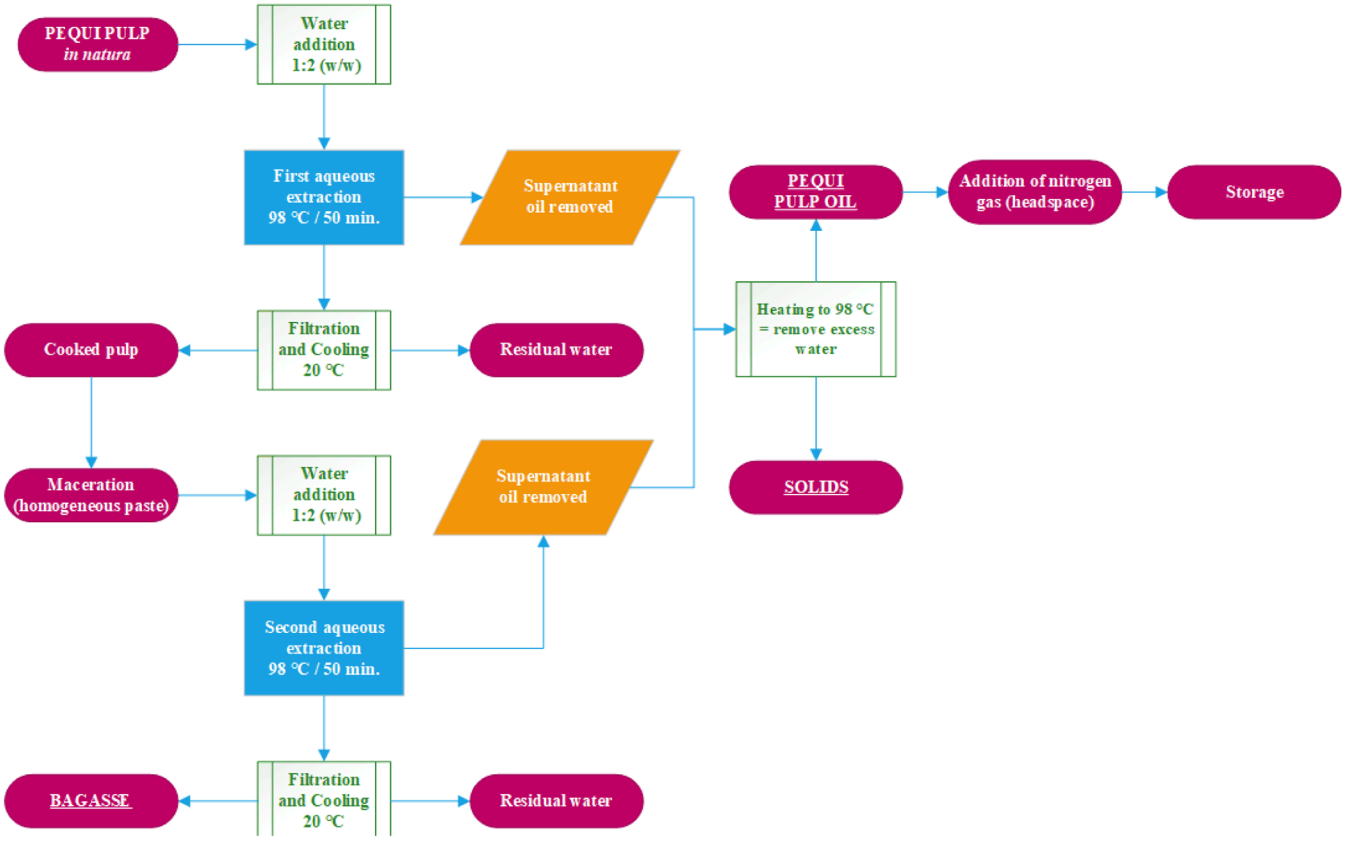

Figure 2. Flow diagram of the aqueous extraction (cooking) method. Flow diagram of the aqueous extraction process for pequi oil. *This method* is mainly used by small farmers in the Brazilian Cerrado region; it *produces moderate oil yields* requiring high temperature and time.

increased acidity, and a reduction in the oil's nutraceutical compounds.[18]

This is probably one of the main reasons of its absence in the Normative Instruction No. 87 of the Brazilian National Health Surveillance Agency (ANVISA),[19] one of the main Regulatory policies for oil production and commercialization, establishing a list of plant species authorized to produce fats and oils in Brazil for consumption, including the Brazilian socio-bioeconomy sources: Brazil nut (*Bertholletia excelsa*), Baru (*Dipteryx alata*), and Babassu (*Attalea speciosa*). The absence of these oils from the list, which regulates attributes such as the fatty acid profile and other quality standards, is a significant bottleneck for the valorization of the pequi oil and strengthening of its production chain, avoiding its resilient insertion in the national and international formal markets.

In this context, the evaluation and standardization of extraction methods is a pivotal demand, focusing on efficient but sustainable technologies that could be applied by local communities/small farmers and economically and technically accessible, allowing the production of high-quality oils. Cold-pressing using screw-type equipment known as *Expeller*-type press or using hydraulic press, solvent extraction, or a combination of them are the main possibilities. In the case of solvent extraction, *n*-hexane is the most widely used solvent in the large-scale vegetable oil industry.[20] Due to its high toxicity, fossil origin, and flammability, more sustainable solvents can be used, especially considering the context of small and family farmers, with bioethanol being the one showing the most interesting cost-benefit for oil extraction, as

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already presented in the literature for other vegetable sources.[21−27]

However, the choice of extraction method can significantly influence not only process yield but also the oil's physicochemical, nutritional, and compositional characteristics. Therefore, considering pequi's socioeconomic importance in the Brazilian Cerrado and the potential to produce high-quality pulp oil with enhanced nutraceutical content for use in food formulations, this study systematically evaluated the influence of extraction methods on the physicochemical, quality, and nutritional aspects of pequi pulp oil, aiming at its standardization and applicability in industrialized lipid-based products such as spreads, fillings, margarines, and ice creams.

2. MATERIALS AND METHODS

For this study, peeled and frozen pequi was used as raw material, commercially acquired in vacuum packaging from Aparecida de Goiânia, Goiás State, Brazil. Additionally, commercial pequi pulp oils from the state of Pará (obtained from the metropolitan region of Belém, Brazil) and from the State of Tocantins (obtained from the mesoregion of Porto Nacional, Brazil) were also used in this work. The study was divided into two parts: (i) the first part evaluated the extraction process yield and main quality aspects of the oils obtained by 4 extraction methods: aqueous extraction, here also referred to as cooking (the conventional method applied on artisanal scale for obtaining pequi oil), mechanical extraction with a hydraulic press, with *expeller*-type press, and solvent extraction using anhydrous ethanol; (ii) in the second part, the oils obtained by the most suitable methods and with the better quality aspects were further assessed by a complete set of physicochemical and rheological properties and antioxidant capacity, focusing on the use of pequi pulp oil on lipid-based food products.

2.1. Pequi Oil Extraction

For the oil extractions, the raw material was previously thawed in a BOD incubator (Tecnal, TE-371/240L, Brazil) at 20 °C for 12 h and subsequently depulped and weighed. Depulping was performed by using a manual grater to preserve the heat-sensitive components present in the raw material. This procedure allowed for more precise control of the process, resulting in thin slices that, for the aqueous extraction process, increased the contact area of the pulp with water, thus increasing the extraction yield. Figure 1 shows commercial pequi, pulp obtained after the depulping process, and residual seed.

The pulp was evaluated for moisture content (Ca 2e-84 method), lipids (Am 5-04 method), proteins (920.152 method), and ashes (Ba 5a-49 method), according to the official methods of the American Oil Chemists' Society[28] and Association of Official Analytical Chemists.[29] Carbohydrate and fiber content were obtained by difference. The results were measured in triplicate, and statistical differences were evaluated through the Tukey test ($p < 0.05$).

The pequi oil extraction methodology by aqueous extraction (conventional artisanal method) was adapted from Viroli et al.[18] and is represented in the flow diagram depicted in Figure 2.

For this extraction method, water at room temperature (≅25 °C) was added to the pulp in a 1:2 (m/m) ratio. Boiling was carried out in an aluminum pot at 98 °C for 50 min. Two consecutive cooking processes were carried out to optimize the oil extraction process by density difference and immiscibility between oil and water. After the first cooking, the pulp was separated, cooled to around 20 °C, and mashed until a homogeneous paste was obtained. The resulting water residue was removed, and the pequi oil (supernatant) was stored. The paste resulting from the first cooking was subjected to a second cooking under the same operational conditions. Then, the residual water was filtered by using a cloth strainer to separate the pulp residue. The oil was transferred to another metal container and heated again to remove the excess water. Finally, the oil was filtered to remove the remaining pulp solids, and the liquid fraction was bottled in amber bottles with added nitrogen gas to fill the headspace and stored in a cool, airy place away from light incidence. Due to the artisanal characteristic of this extraction method and, therefore, high variability, 4 assays were performed, yields calculated, and the oils resulting from the 2 assays that presented the highest lipid contents were those evaluated.

Before mechanical (*expeller*-type press—continuous process—and hydraulic press—batch process) and solvent (ethanol) extractions, a pretreatment described by Aquino et al.[17] was applied. This pretreatment consisted of drying the pulp at 40 °C in a forced-air circulation oven (Marconi, MA03012, Brazil) until a constant weight was achieved. For this, the raw material was arranged on trays to ensure uniformity and to facilitate the process. The time required for hygroscopic equilibrium was 72 h, and the drying process yield was 43.96%. Subsequently, the dried pulp was ground by using a benchtop blender. Due to the high lipid content, pronounced particle aggregation and agglomeration were observed, preventing accurate granulometric analysis. Nevertheless, the maximum particle size was measured in 10 replicates using a digital micrometer (Mitutoyo Co, Kawasaki, precision ± 1 μm) and determined as 641 ± 212 μm. Drying at mild conditions and particle size reduction are crucial for optimizing extraction efficiency while maintaining minor biocompounds, such as carotenoids, and reducing lipid oxidation.

The treated pulp was then packaged and frozen until extraction processes were carried out. Figure 3 shows the pequi pulp after drying for 72 h at 40 °C and after particle size reduction and homogenization.

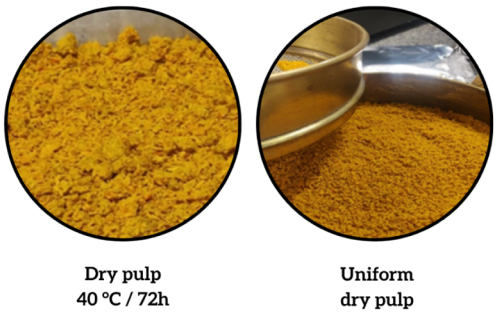

Figure 3. Pequi pulp after drying and particle size reduction prior to extraction. This preprocessing step increases surface area and enhances extraction efficiency.

Extraction in the *Expeller*-type press (Scott Tech, KAF37/DRE80S4, USA) (Figure 4) was carried out at a processing flow rate of 24 kg/h and a screw speed of 45 rpm. The dried pulp was previously heated in a forced-air circulation oven to 70 °C to ensure that the oil was completely melted. The obtained oil was filtered using a vacuum pump system (Büchi, V-855, Switzerland) and a Kitasato apparatus.

Hydraulic press extraction (Charlott, no. 5991, Brazil) (Figure 5a) was conducted by controlling the pressure on an analog pressure gauge, using a piston with hydraulic actuation, with a maximum capacity of 60 tons. The sample was placed in a voile filter bag, properly positioned in the extraction cell (Figure 5b) and placed on an iron block below the piston (Figure 5c). Oil extraction was carried out at 25 °C and low pressure (40 tons).

Solvent extraction using bioethanol was performed according to the studies of Sampaio Neto et al.[21,22] and Gonçalves et al.[25] Figure 6 shows the system assembled to carry out the extraction kinetics. A mixture of dried pequi pulp and anhydrous ethanol (99% m/m) was formulated at a 1:10 pulp:solvent ratio using an analytical balance (Marte, AD5002, São Paulo, Brazil) in an Erlenmeyer flask and was sent to a temperature-controlled orbital shaker system (Novatecnica, NT712, Brazil) at 60 °C and 200 rpm. Oil was separated from deoiled bagasse through filtration using a Kitasato apparatus. Process time was determined through a kinetic study where the lipid content of the extract was measured until no change in the lipid content was observed. Extraction was performed in duplicate, and the extracts

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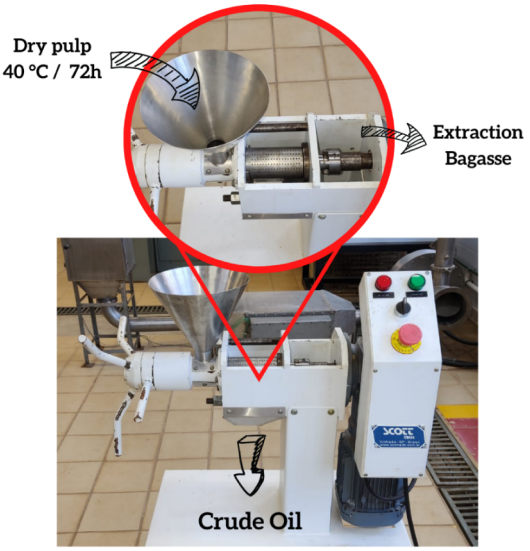

Figure 4. Illustrative diagram of the extraction of oil from pequi pulp in the *expeller*-type press. This continuous mechanical process operates under moderate temperatures, resulting in high oil yield and nutritional value preservation.

were sent for evaporation (under vacuum) in a rotary evaporator (Marconi, Brazil), at 60 °C, for ethanol removal. Total lipid contents for both extracts and raffinates were evaluated according to the AOCS Bc3−49 method,[28] using the Ankom Extractor XT15 equipment (Ankom Technology, Macedon, NY, USA).

The calculation of the yield of the 4 extraction methods employed was given as a mass percentage of extracted oil relative to the amount of oil of the dry pequi pulp used in the extraction (eq 1).

$$\text{Extraction yield}(\%) = \left(\frac{\text{weight}_{\text{oil}}}{\text{weight}_{\text{dry pulp oil}}}\right) \times 100 \quad (1)$$

2.2. Characterization of the Obtained Oils

2.2.1. Main Quality Parameters. The effect of the extraction methods on the quality of the obtained oils was assessed by measuring oils' total lipid, water, acidity (also expressed as free fatty acids), and total carotenoid contents. Results were obtained in triplicate and statistical differences evaluated (Tukey's test, $p < 0.05$). Total lipid content was measured according to the AOCS Bc3-49 method[28] using the Ankom Extractor XT15 equipment (Ankom Technology, Macedon, NY, USA). Water content was analyzed through the AOCS Ca 2e-84 method,[28] using a Karl Fischer equipment (870 KF Titrinoplus, Metrohm, Herisau, Switzerland). Acidity index was determined using method 325/IV from the Adolfo Lutz Institute[30] and calculated according to eq 2

$$\text{Acidity index}(\%) = \frac{V \cdot f \cdot 5.61}{m} \quad (2)$$

where V is the volume of 0.1 N NaOH consumed in the neutralization of the sample, f is the correction factor of the NaOH solution (1.42), and m is the mass of the sample in grams. To express the results in free fatty acids (FFA), the obtained result was divided by 1.99, which is the conversion constant for oleic acid (the major fatty acid). Oils' total carotenoid content was evaluated through a modified method based on Rodriguez-Amaya[31] using a UV−visible spectrophotometer at 446 nm; the absorption coefficient of β-carotene in hexane was used (2590), with values determined as β-carotene equivalents and expressed as μg of β-carotene/g of oil.

2.2.2. Lipid Profile. Additionally, oils obtained were characterized by their fatty acid (FA), TAG profile, and thermal behavior. FA composition was determined by gas chromatography according to the AOCS Ce 1-62 method,[28] using the following equipment conditions: Gas chromatograph (Agilent, 7890B, USA) equipped with a flame ionization detector (FID) and capillary column (Agilent, DB-WAX, USA) with a length of 30 m, internal diameter of 0.25 mm, and film thickness of 0.25 μm. Helium was used as the carrier gas at a flow rate of 38 cm/s, and the column temperature was programmed from 140 to 240 °C, with an increase of 4 °C/min and a 15 min hold. The injector and detector temperatures were set at 250 °C, with an injection volume of 1 μL. The conversion of fatty acids into fatty acid methyl esters (FAME) was based on the methodology developed by Metcalfe et al.,[32] adapted from Hartman and Lago.[33] Peak identification was performed by comparing the retention times of

a) Hydraulic press b) Extraction cell c) Hydraulic piston

Figure 5. System for extracting oil from pequi pulp using a hydraulic press. This batch mechanical extraction method operates at low temperatures, producing cleaner oils with minimal degradation of carotenoids and reduced coextraction of nonlipid compounds, favoring food-grade applications.

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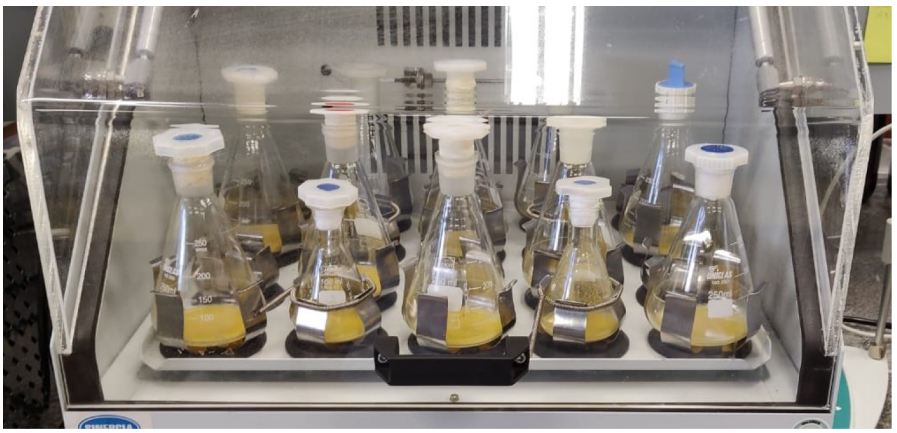

Figure 6. Orbital agitation system used for oil extraction with ethanol. Batch solvent extraction ensured efficient solvent contact and mass transfer between the solid and liquid phases, promoting high extraction yield, maintenance of nutritional value, as well as greater coextraction of polar, nonlipid compounds.

fatty acid methyl ester standards (FAME mix C8−C24; Sigma-Aldrich, USA). Using the experimental FA profile, the TAG profile was determined by the method described by Antoniosi Filho et al.,[34] which uses combinatorial analysis considering a distribution model of FA bound to the glycerol portion. In this method, it is considered that the main TAG represents the component with the highest concentration in the defined isomer with n carbons and double bonds, ignoring the set of TAGs with a composition below 0.5%. As required by the methodology, the content in trisaturated TAGs was obtained from the literature,[35] set as close to 0%. Calculation was performed using an algorithm implemented in the MATLAB software, as described elsewhere.[36]

2.2.3. Thermal Profile. Thermal behavior was analyzed by differential scanning calorimetry, using the DSC 2920 calorimeter equipment (TA Instruments, New Castle, USA) coupled with a cooling system using nitrogen (purity >0.9999% m/m) as the purge gas, following an adapted version of the AOCS method Cj 1−94.[28,37] Samples were weighed in aluminum crucibles (between 3 and 5 mg), with one empty and hermetically sealed crucible used as reference. During analysis, samples were maintained at 70 °C for 10 min, then cooled at a rate of 5 °C/min to −60 °C and held at this temperature for 30 min; after this cycle, the samples underwent a melting process from −60 to 70 °C at a rate of 5 °C/min. The TA Universal Analysis 2000 software was used to obtain the thermal curves and to define the evaluation parameters: *onset* crystallization temperature (T_{onset}), crystallization and melting events (T_{peak}), and final melting process (T_{offset})

2.3. Properties of the Oils Obtained by the Most Suitable Methods

2.3.1. Physicochemical and Compositional Profile. The oils obtained by the most suitable methods (in this work, mechanical extractions, as will be discussed in the Results section), also presenting the best quality parameters, were additionally evaluated by their physicochemical and other composition profile, important for the characterization of the oils for food production: iodine values, acylglycerols content, mineral profile, carboxylic acid profile, and phospholipid content, obtained in triplicate and evaluated by their statistical differences (Tukey's test, $p < 0.05$). Complete Fourier-transform infrared (FTIR) spectra were also provided.

Iodine value (IV), related to unsaturation degree, was determined according to the official AOCS method Cd 1c-85.[28] Total monoglycerides (MAG) and diglycerides (DAG), related to oil quality, were measured by gas chromatography according to method Cd 11-*b*-91,[28] using the equipment. Helium was used as the carrier gas at a flow rate of 5 cm^3/min, and the column temperature was programmed from 80 to 380 °C, with an increase of 10 °C/min and a 1 min hold. The injector and detector temperatures were 320 and 380 °C, respectively, and the injection volume was 1 μL. Acylglycerides were quantified through calibration curves and TAG content obtained by difference with respect to the levels of free fatty acids (FFA), monoglycerides, and diglycerides.

Minerals present in the oils were determined by the official methods 985.35 and 984.27.[29] Quantification of inorganic elements was carried out using inductively coupled plasma optical emission spectrometry (ICP OES 5100 VDV, Agilent Technologies, Japan) equipped with a 27 MHz radiofrequency (RF) source, simultaneous optical detector, peristaltic pump, dual-pass cyclonic nebulization chamber, 1.8 mm quartz torch, and seaspray nebulizer. Liquid argon with 99.996% purity (Air Liquide, Brazil) was used as the plasma gas. The optimized operating conditions for ICP OES were: plasma power, 1.20 kW; argon flow rate, 12.0 L/min; auxiliary argon flow rate, 1.0 L/min; nebulization flow rate, 0.7 L/min; number of replicates, 3; stabilization and reading time, 14 s; and wavelengths, Ca (317.933 nm); Cu (324.754 nm); Fe (259.940 nm); P (213.618 nm); Mg (279.553 nm); Mn (257.610 nm); K (766.491 nm); Na (589.592 nm); and Zn (206.200 nm). Analyses were performed in duplicate, and the concentration data for each mineral were expressed in mg/kg. The phospholipid content was measured by converting phosphorus to phospholipids, calculated by the ratio of the atomic mass of phosphorus (P = 31 u) to the estimated molecular mass of phospholipids (PL), approximately 25 g/mol.[38] The result was obtained by using eq 3

$$\mathrm{PL}(\%) = \frac{25 \cdot P(\mathrm{mg/kg})}{10000} \tag{3}$$

The carboxylic acid profiles of the oils, related to oxidation phenomena, were determined by ion chromatography (IC), according to the method described by Souza et al.,[39] using an ion chromatograph (Metrohm, 940 Professional IC Vario, Switzerland) equipped with a Metrosep organic acid 250−7.8 column (250 × 7.8 mm) and a precolumn with similar internal composition.

FTIR analysis was carried out using an Agilent Cary 630 spectrometer (USA), operated with Microlab software and equipped with an Attenuated Total Reflectance (ATR-MicromATR Czitek, USA) accessory, employing a ZnSe crystal. Liquid and homogeneous samples were obtained by heating at 60 °C, and a small film was deposited on the ZnSe crystal (also at 60 °C). Multiple spectra were obtained over different periods of time. Analysis was performed in the range of 4000−650 cm^{-1}, with resolution of 4 cm^{-1}, in which 8 background scans and 8 sample scans were done for each spectrum. Spectra were acquired through transmittance, and data were subsequently analyzed using the Origin 8.0 software (OriginLab Co., USA).

2.3.2. Rheological Profile. The oils were also evaluated by their rheological behavior using a controlled tension rheometer (Hakke Mars III, Thermo Fisher Scientific, Massachusetts, USA) as

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Table 1. Centesimal composition (% mass) of pequi pulp, dried, and obtained *in natura* in this work and from literature (*in natura*)[a]

Compound	This work		Vera et al.[45]	Alves et al.[46]	Nascimento-Silva et al.[11]
	Dry Pulp	*In natura*			
Moisture	2.50 ± 0.01[b]	52.67 ± 0.48[a]	54.34 ± 4.48; 48.13 ± 2.99	56.21 ± 0.47	50.40 ± 0.04
Lipid	61.30 ± 2.04[a]	27.42 ± 1.82[b]	20.02 ± 1.41; 18.69 ± 1.75	24.27 ± 1.60	28.60 ± 1.00
Protein	6.60 ± 0.27[a]	3.47 ± 0.14[b]	3.89 ± 0.24; 3.18 ± 0.25	3.73 ± 0.00	3.70 ± 0,10
Ash	1.53 ± 0.01[a]	0.81 ± 0.00[b]	–	0.63 ± 0.02	0.7 ± 0.00
Carbohydrate	28.07	15.63	–	15.16	16.60 ± 1.30

[a]Different lowercase letters in the same row indicate significant differences between treatments ($p < 0.05$, Tukey's test).

performed by Pereira et al.[40] In this case, a stainless-steel cone and plate configuration (with a 2 cm diameter, a 2° angle, and a cone truncation of 57 μm) was used, through an up−down−up step procedure. The equipment was equipped with a rough geometry of parallel stainless-steel plates with a diameter of 4 cm. The distance between the plates was 2.0 mm. Measurements were carried out in the shear rate range (γ) from 0 to 300 s^{-1} at temperatures of 35, 60, and 85 °C, with an accuracy of ± 0.1 °C. Shear stress versus shear rate curves, as well as viscosity versus shear rate curves, were obtained.

2.3.3. Antioxidant Capacity. The antioxidant capacity of the oils was also measured by DPPH[41] and FRAP[42] methods, using the following steps: 3 g of each sample was weighed on an analytical digital balance and added to 10 mL of methanol in the absence of light. The mixtures were placed in previously aluminum foil-covered 50 mL Falcon tubes, and then, film-covered caps were added to prevent evaporation. These mixtures were subjected to orbital agitation at 200 rpm in a shaker-type incubator (Novatecnica, Brazil) for 1 h. 250 mL Erlenmeyer flasks were used to accommodate the Falcon tubes containing the samples. After agitation, the solutions were centrifuged at 10,000 rpm for 10 min to separate the phases. The methanolic phase was collected and transferred to 15 mL Falcon tubes previously wrapped in aluminum foil, and film-covered caps were added to prevent evaporation. The samples were stored at −18 °C for use in antioxidant capacity tests. The antioxidant capacities were evaluated using a UV−visible spectrophotometer under different absorbances.

The ability to donate hydrogen to the DPPH free radical was measured at 515 nm. For this, 0.3 mL of each methanolic extract was mixed at room temperature (~25 °C) with 5.97 mL of 0.093 mM DPPH radical, which was homogenized under agitation and left to react in the dark for 1 h before measurement. Measurements were performed in triplicate, their statistical differences evaluated (Tukey's test, $p < 0.05$), and the results were expressed in μmol of Trolox equivalent (TE) per gram of oil. The Trolox standard curve was obtained according to the methodology of Silveira et al.,[43] with modification of the solvent, replacing bioethanol with methanol. The Trolox standard curve was constructed by varying the concentration from 50 μM to 2000 μM. Methanol was used as the blank for the analysis.

For the determination of antioxidant capacity by the ferric reduction method (FRAP), 0.3 mL of each methanolic extract was homogenized with 2 mL of FRAP reagent and 7.7 mL of distilled water. The solutions were kept at 25 °C for 10 min, protected from light. Subsequently, the samples were centrifuged at 10,000 rpm for 10 min, and the absorbance was measured at 593 nm. The blank of the analysis was prepared with 2 mL of the FRAP reagent and 8 mL of distilled water. As for the standard curve, this was prepared with $FeSO_4{\cdot}7H_2O$ solution at different concentrations: 0.00025 to 0.08 mmol of $FeSO_4{\cdot}7H_2O$/L of distilled water, since the reagent is insoluble in methanol and acetone, which are more commonly used. The analysis was performed in triplicate, evaluated according to their statistical differences (Tukey's test, $p < 0.05$), and the results were expressed in μM $FeSO_4$/100 g of oil.

2.4. Evaluation of Commercial Oils

For comparison purposes, some commercial pequi pulp oils were also evaluated, and their results are presented alongside the results for the oils obtained in this work.

3. RESULTS AND DISCUSSION

3.1. Evaluation of the Extraction Methods

Prior to the evaluation of the extraction methods, as mentioned, the commercially acquired pequi fruit was depulped. The depulping yield (pulp mass/core mass) was equivalent to 43.34% (m/m) (core is for pulp + kernel). Despite the mass of pequi pulp varying according to the fruit variety and region, similar yield values have been found in the literature.[11,44] Vera et al.[45] observed a depulping yield (pulp mass/core mass) equivalent to 40.76% for fruits from the State of Goiás (GO). Alves et al.[46] found an average depulping yield (pulp mass/total fruit mass) equivalent to 34.9%, highlighting similarity with fruits from the State of Minas Gerais (average yield 33.4%). Similar values were also found for cultivars in the Mato Grosso Cerrado region, with an average equivalent of 46.71% (pulp mass/core mass), and for a pequi species popularly called "giant pequi," originating from the Federal District, with an average yield (pulp mass/core mass) of 45.62%.[47,48] Obtaining these results for different regions facilitates the selection of fruits with a higher pulp yield to add value and enhance the commercial and industrial utilization of this fruit. Table 1 contains the centesimal composition in mass percentages of both dried and fresh pequi pulp obtained in this study.

The centesimal composition of dried and in natura pequi pulp is presented in Table 1. Statistically significant differences ($p < 0.05$) were observed for all evaluated parameters. The drying process substantially reduced the moisture content from 52.67% to 2.50%, concentrating lipids (from 27.42% to 61.30%), proteins (from 3.47% to 6.59%), and ash (from 0.81% to 1.53%). These differences reflect the removal of water and consequent concentration of solids, typical of dehydration processes. The results align with previous reports for pequi pulp from different Brazilian regions, confirming that drying effectively increases the relative content of lipid compounds on extracted material.[11,44,47]

Observing that pequi pulp is predominantly composed of lipids justifies the interest in its use for oil extraction. Alves et al.[46] found a lipid content of 26.15%, slightly higher for cultivars from the State of Minas Gerais and low lipid content in the State of Tocantins, 8.39%. Lima et al.[49] found higher values in the State of Piauí, at 33.40%, and Cordeiro et al.[47] found levels between 27.06% and 32.40% for fruits originating from the State of Mato Grosso. These results reinforce the

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influence of the region on the characteristics of the raw material.

The centesimal composition values found in this study were consistent with the literature in the region of interest for fresh pulp: since the drying process removes moisture from the pulp, its constituents are concentrated, resulting in higher levels compared to fresh pulp. Medeiros,[50] studying the composition of dried pequi pulp from lots originating from the State of Goiás, reported average values of 2.77%, 6.56%, 52.34%, 1.59%, and 36.74% for moisture, proteins, total lipids, ash, and total carbohydrates, respectively, values consistent with those found for dried pulp obtained in this study. Pequi pulp also presents a relevant protein content when compared to other fruits from the Brazilian Cerrado, with levels similar to those found in baru (5.0%) and lower than those found in jatobá (8.7%).[51]

After depulping and prepreparation, oil extractions were carried out using the 4 methods. Figure 7 presents images of the oils and bagasses obtained by each extraction method, and Table 2 shows the comparative results for parameters obtained in each case.

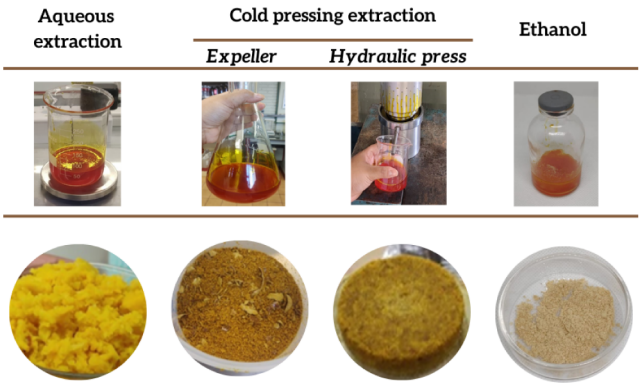

Figure 7. Oils and bagasses were obtained by the four extraction methods. Ethanolic extraction produced darker oils due to the higher content of pigments and polar compounds, while mechanical extraction resulted in lighter and visually cleaner oils, indicating lower levels of nonlipid impurities.

For the cooking extraction, due to its artisanal characteristic, 4 assays were performed. For each assay, the oils obtained had their total lipid contents determined, with values ranging from 92.96% to 96.08%. Residual bagasses presented lipid contents of up to 16.64 ± 0.20% and moisture contents of up to 57.30 ± 0.13%. This high water content of the bagasse is clearly attributed to the use of water in the extraction process: in this case, the low lipid content of the bagasse could be directly related to this effect. The 2 assays that presented the highest lipid contents were those with the highest yield, being 19.52% and 14.59%. When compared with the other extraction routes, the cooking method, conventionally used by local communities for pequi extraction, clearly stands out for its simplicity, including no demand for specialized equipment or operational complexity. However, it could be characterized by some limiting factors such as low yield and process control (due to its artisanal character), justifying the high variability of the values found and contrasting with the higher efficiencies and standardization achieved by mechanical and solvent-based extractions. Cooking extraction is also time-consuming, demanding a higher number of operations. Moreover, they may allow rapid changes in chemical composition due to oxidation reactions, mainly promoted using high temperatures in aqueous medium[52] which will be further explored in this work.

The extraction process performed by the *expeller*-type press, on the other hand, had a mean total yield of 34.32%, and the extraction via the hydraulic press had a total yield of 64.61%. The total lipid content of the oils obtained for both methods was 94.90 ± 1.41% and 96.90 ± 0.63%, respectively, producing bagasses with lipid content of 40.53 ± 0.95% and 35.52 ± 0.08%, respectively. Pighinelli et al.[53] propose that the high lipid levels found for the pequi bagasse indicate the possibility of an additional solvent treatment to increase oil processing yield.

Factors that may be related to the results obtained can be associated with the design of the equipment. The *expeller*-type press is generally recommended for raw materials with high fiber content, i.e., those with greater mechanical resistance, considering the functioning of the screw and its adjustment: in this case, the presence of peels, as in the case of some oilseeds, makes the mechanical process more efficient. Additionally, the extracted oil still contains high levels of particulate matter (bottom solids), requiring an additional filtration step in the process. Hydraulic press extraction, on the other hand, is less dependent on the fiber content of the sample, as the pressure is applied to the sample, which is a determining factor. Furthermore, using a voile-type filter bag, the oil is already removed from the equipment without solid particulate matter, aiding in increasing yield. Overall, while both mechanical extractions provided oils with high lipid contents, the hydraulic press presented almost twice the yield of the expeller press, reinforcing the relevance of applied pressure over friction-based extraction for soft, low-fiber matrices, such as pequi pulp.

Solvent extraction using ethanol could also provide a high yield, as described in the extraction kinetics depicted in Figure 8. The process reached equilibrium after 6 h, where the lipid concentration of the sample becomes constant. The lipid content of the extract (oil + ethanol) was determined to be 13.30%. In this case, the extraction yield was 63.96%, such that the residual bagasse still contains a lipid concentration of 37.15%. Generally, solvent extraction of oily raw materials is carried out using hexane, with extraction yields exceeding 90% in some cases.[20] However, it is a solvent whose handling requires special attention due to its high toxicity and flammability and is not suitable for oils produced in the context of small-scale production and in the production of sociobiodiversity oils. In this case, ethanol presents itself as a very interesting solution in terms of yield, despite the need for solvent evaporation afterward, which would imply a structural difficulty for a small-scale industry (local communities). Studies in the literature found similar yield values for extraction with bioethanol: for babassu, Sampaio et al.[22] found values close to 71.7% for the highest temperature evaluated in the process (45.0 °C) and a mass ratio of approximately 1:4 (m/m) using batch processing (same as this work). The same authors found for Brazil nut, at 60 °C, yields ranging from 97.82% to 35.45%, highlighting better efficiency of the extraction process for solid-solvent ratios close to 1:4 (m/m) and extraction using fixed bed column.[21] Ferreira et al.[23] and Bessa et al.[24] achieved maximum yields of 99.2% and 82% for soybean and rice bran, respectively, using a multiple-stage process, being an interesting solution for improving oil yield by using extraction with ethanol. Despite its promising

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Table 2. Fatty acid profile (% mass), probable TAG profile, and main quality aspects for the oils obtained and other commercial oils

	Aqueous extraction		Mechanical Extraction			Commercial oils	
Parameter	*E*1	*E*2	*Expeller*	Hydraulic press	Ethanol	Pará State	Tocantins State
Extraction yield (%)	14.59	19.52	34.32	64.61	63.96	–	–
Fatty Acids[a]							
C8:0	–	–	–	–	–	–	–
C10:0	–	–	–	–	–	–	–
C12:0	–	–	–	–	–	–	–
C14:0	–	–	–	–	–	–	–
C16:0	40.27	40.54	36.09	34.67	35.07	33.52	35.87
C16:1	–	–	–	–	–	–	–
C18:0	–	–	0.80	1.60	–	1.86	–
C18:1	59.73	59.46	59.64	55.94	60.98	53.96	62.51
C18:2	–	–	1.96	1.82	–	2.04	–
C18:3	–	–	–	–	–	–	–
C20:0	–	–	0.33	–	–	–	–
C22:0	–	–	–	–	–	–	–
Others	–	–	1.17	5.97	3.95	8.63	1.61
SFA[b] **(%)**	40.27	40.54	37.22	36.27	35.07	35.38	35.87
MUFA (%)	59.73	59.46	59.64	55.94	60.98	53.96	62.51
PUFA (%)	–	–	1.96	1.82	–	2.04	–
FFA (%)	$1.12 \pm 0.12^{b,c}$	$1.05 \pm 0.10^{b,c,d}$	1.18 ± 0.01^{b}	$1.11 \pm 0.11^{b,c}$	1.69 ± 0.03^{a}	0.85 ± 0.21^{d}	$0.90 \pm 0.01^{c,d}$
Acidity (mg_{KOH}/g)	$2.23 \pm 0.24^{b,c}$	$2.08 \pm 0.20^{b,c,d}$	2.34 ± 0.02^{b}	$2.21 \pm 0.23^{b,c}$	3.37 ± 0.06^{a}	1.70 ± 0.21^{d}	$1.79 \pm 0.01^{c,d}$
Total lipids (%)	97.28 ± 0.53^{a}	95.40 ± 0.11^{a}	96.38 ± 0.89^{a}	96.90 ± 0.63^{a}	88.42 ± 0.55^{a}	96.15 ± 1.16^{a}	98.92 ± 0.82^{a}
Nonlipid content (%)	2.18	4.19	3.28	2.88	11.24	3.85	0.55
Moisture (%)	0.54 ± 0.04^{c}	0.41 ± 0.07^{c}	0.34 ± 0.04^{c}	0.22 ± 0.01^{c}	0.34 ± 0.06^{b}	0.00 ± 0.00^{c}	0.53 ± 0.04^{a}
Carotenoids ($\mu g/g$)	83.36 ± 0.01^{e}	80.18 ± 0.01^{e}	326.56 ± 0.01^{b}	291.98 ± 0.01^{c}	346.39 ± 0.93^{a}	77.04 ± 0.01^{e}	111.60 ± 0.21^{d}
TAG profile							
OOP	46.35	46.15	43.77	42.80	48.42	41.98	48.44
POP	38.57	39.09	30.80	31.38	31.75	30.91	31.66
OOO	14.13	13.81	15.89	14.92	18.89	14.59	18.95
PPP	0.95	0.95	0.87	0.84	0.94	0.82	0.94
POLi	–	–	2.88	2.80	–	3.18	–
OOLi	–	–	1.61	1.46	–	1.65	–
POS	–	–	1.27	2.70	–	3.20	–
PLiP	–	–	1.02	1.03	–	1.17	–
OOS	–	–	0.92	1.83	–	2.17	–

[a]C8:0—caprylic acid, C10:0—capric acid, C12:0—lauric acid, C14:0—myristic acid, C16:0—palmitic acid (P), C16:1—palmitoleic acid, C18:0—acid stearic (S), C18:1—oleic acid (O), C18:2—linoleic acid (Li), C18:3—linolenic acid (Ln), C20:0—arachidic acid, and C22:0—behenic acid. [b]SFA = saturated fatty acids, MUFA = monounsaturated fatty acids, and PUFA = polyunsaturated fatty acids. Values are expressed as mean ± standard deviation ($n = 3$). Different lowercase letters in the same row indicate significant differences among extraction methods according to Tukey's test ($p < 0.05$).

yield, ethanol extraction requires additional purification and solvent recovery steps, which make it less suitable for small-scale or community-based processing when compared with cooking or mechanical pressing methods.

The four extraction routes, whose parameters are compared in Table 2, reveal distinct trade-offs considering yield, nonlipid components, quality, and operational simplicity. Low water contents were found for all oils, reaching up to 0.5% in the case of the cooking method. The slightly lower water level found on mechanical extraction is relevant as it provides high oxidative stability and improves oil quality during storage or when subjected to high-temperature processes. The obtained crude oils presented low to moderate levels of nonlipid components. While lower nonlipid levels were observed in oils obtained by cooking (up to 4.6%) and mechanical extraction (up to 3.62%), the use of ethanol allowed the coextraction of higher nonlipid content (11.58%). Indeed, Table 1 shows that dried pequi pulp can present a significant content of carbohydrates (28.07%) and proteins (6.06%). The polarity of ethanol can be associated with the extraction of these polar compounds. This effect was also observed by Baümler et al.[27] during sunflower oil extraction with ethanol, by Sawada et al.[26] in soybean oil extraction using this biosolvent, by Sampaio et al.[22] for babassu oil (an important Amazonian oilseed), and by Gonçalves et al.[25] in the extraction of buriti (*Mauritia flexuosa*) oil. These authors reported that ethanol can enhance the extraction of polar compounds from oilseed matrices, emphasizing the need to optimize the extraction time to minimize this effect.

The coextraction of nonlipid components during ethanolic extraction also highlights the demand for subsequent purification/refining processes. Indeed, removal of compounds that may impair oils' quality, improving stability, technological quality, or applications in food industry are recognized strategies during vegetable oil processing:[20,54] physical approaches, such as centrifugation or decantation followed by filtration, can be used for the removal of insoluble

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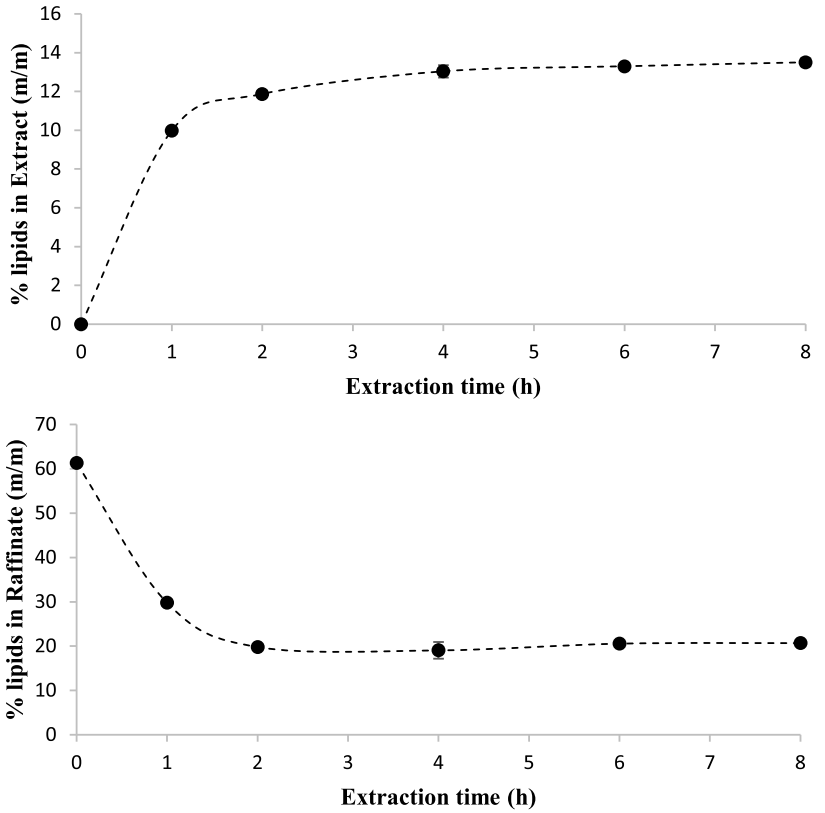

Figure 8. Pequi pulp extraction kinetics were performed with ethanol. Solvent extraction kinetics with ethanol. The kinetic profile shows a rapid initial extraction phase followed by a slower equilibrium stage, typical of solvent−solid extraction systems.

compounds, including carbohydrates; water washing is also effective for the reduction of polar compounds, including proteins.[55−58] Vegetable oil industry also uses other integrated approaches, including chemical deacidification for acidity reduction, enzymatic or chemical routes for phospholipids removal, bleaching with adsorbents, and deodorization for the elimination of pigments and other impurities/volatile components.[20,57] However, these strategies are dependent on oil quality or identity, which will be further discussed in the next section.

The fatty acid profile presented in Table 2 shows that the oils extracted through all methods were predominantly composed of monounsaturated fatty acids (MUFA), mainly oleic acids (C18:1 or ω-9); they also have high levels of palmitic acid (C16:0). Therefore, it can be observed that the application of different extraction methods slightly alters the relative amounts of FA found but not their composition identity. Ethanolic extraction promoted oils with a slightly higher oleic acid content (60.98%), while higher palmitic acid content was found in oils obtained by aqueous extractions (40.27−40.54%). Small fractions of polyunsaturated fatty acids (C18:2 or ω-6) were found in oils extracted via mechanical pressing, corresponding to 1.21% and 1.82% (via *expeller*-type press and a hydraulic press, respectively). Mechanical extraction and ethanolic extraction also provided small fractions of other FA, probably with higher (>C22:0) carbon chains. It is also important to mention that these FA are related to the GC retention peaks, identified by the analysis, that were out of the FA composition range of the standard used. In the case of commercial oils evaluated, slight variations on the FA profile could be seen. Considering that commercial pequi pulp oils here evaluated are from different regions (States) than the pequi pulp processed in this work, one could observe that geographical, climatical, or genetical variations can also be responsible for oils with slightly different FA profiles.

Approximate FA levels were reported by Lima et al.[49] for pequi pulp, equivalent to 55.87%, 35.17%, and 1.53% (C18:1, C16:0, and C18:2, respectively), in addition to other minor acids. A similar fatty acid composition was also found for pequi oil by Garcia et al.[59] with levels equivalent to 54.0%, 41.1%, and 0.9% (C18:1, C16:0, and C18:2, respectively). Similar values were also identified by Facioli and Gonçalves[60] and Figueiredo et al.[61] In the case of TAG profile, Segall et al.[35] (using electrospray and mass spectrometry) experimentally found values close to 6.0% for OOO, 48.0% for OOP, and 47.0% for POP, alongside small amounts of OOS. The same major TAGs were also found in this work for all oils obtained: variations between values found in this work and literature data are probably due to inherent differences among raw materials or processes, as well as the use of a predictive method for calculation of the TAG profile.[34] Among the different extraction routes, mechanically extracted oils and oil from the Para state also presented other TAGs in minor composition, due to their slightly higher content in C18:0 (S) and C18:2 (Li). These small differences in the TAG profiles resulted in different thermal and rheological behavior, as will be further discussed.

Regarding the carotenoid content, according to the literature, their levels in pequi pulp can vary between 155 and 270 μg/g, with these compounds being mainly responsible for the fruit's coloration and consequently the yellow-to-red color of the oil.[47,49,62] Carotenoids can also provide, together with the presence of unsaturated FA, important biological properties for the pequi pulp oil, such as anti-inflammatory or

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cardioprotective effects.[13] However, exposure to heat is the main cause of the degradation of this component.[31] Aquino et al.[17] reported that lower temperatures in preprocessing stages are essential for carotenoids maintenance. Additionally, this work clearly showed that low temperatures during oil extraction were also key to retaining these bioactives. Total carotenoid levels up to 326.56 μg/g were found in mechanically extracted oils via *expeller*-type press and hydraulic press. Otherwise, carotenoids were considerably reduced during cooking extraction, reaching up to 83.36 μg/g, suggesting marked thermal degradation of these compounds. This phenomenon was also reported by Valério et al.[63] for Macauba (*Acrocomia aculeata*) pulp oil, other Brazilian Cerrado's vegetable oil, where faster carotenoids degradation was observed due to the use of high temperatures during processing. On the other hand, among extraction routes, solvent extraction with ethanol was responsible for the oil with the a higher carotenoid level, 346.39 μg/g, which could be mainly attributed to low temperature but also solvent ability (polarity) in extracting this biocompound.[64] These results highlight that pequi pulp oil obtained by mechanical processes or solvent extraction using ethanol represents an important source of carotenoids when compared to other Brazilian Cerrado fruits, known for their carotenoid content, such as Buriti (*Mauritia flexuosa*), Araticum açú (*Annona montana*), or Macauba (*Acrocomia aculeata*).[65−67]

Total carotenoid values for commercial oils were all inferior when compared to those obtained via mechanical or solvent extraction (Table 2), presenting similarity to the values found for the oils obtained via aqueous (cooking) extraction. This suggests that commercial pequi oils were also probably obtained by using processes at high temperatures and/or excessive time, causing degradation of these compounds. Notably, for the commercial pequi oil from Tocantins, carotenoid content was that with a higher value. Despite the possible use of cooking, *in natura* fruits from Brazilian Cerrado present different contents of carotenoids, which could also be the reason for these different values.[46,65−67]

Oils obtained by all extraction methods presented low acidity indices (ranging between 2.08 and 3.37 mg_{KOH}/g in all cases) and therefore low levels of free fatty acids (ranging between 1.05% and 1.69%) (even in the case of aqueous extraction, which used high temperatures). Mechanical extractions (*expeller*-type and hydraulic presses) yielded oils with the lowest acidity and FFA values, indicating a better preservation of triacylglycerols. On the other hand, ethanolic extraction presented a slightly higher acidity, which could also be attributed to the solvent's ability to extract more polar compounds, as previously observed. Therefore, differences in FFA were mainly attributed to the extraction route. However, it is important to note that the vegetable oils' FFA content, in general, is not only related to processing stages but also to the composition and quality of the fruit itself, as well as its handling and storage conditions prior to processing.[20,25] Oil acidity is also largely associated with the high temperatures and humidities found in the oilseeds growing regions, which is the case of Brazilian Cerrado, Amazonia, and Caatinga regions. Pereira et al.[37] found high acidity values of 5.16, 20.98, 10.91, 5.27, and 14.42 mg_{KOH}/g for some exotic Brazilian oilseeds from those regions, respectively: Murumuru (*Astrocaryum murumuru*), Bacuri (*Platonia insignis*), Tucuma kernel (*Astrocaryum vulgare*), Brazil nut (*Bertholletia excelsa*), and Patawa (*Oenocarpus bataua*), whose oils are obtained from kernels/seeds or pulps and present diverse content of both saturated and unsaturated lipids; Rezende et al.[68] also found high FFA content of 43.9% for Macauba (*Acrocomia aculeta*) pulp oil. All of these oils are largely used for the production of cosmetics, but their FFA content is an important bottleneck for their use for food purposes. Otherwise, results found here suggest that pequi is probably a highly stable source when compared to other oilseed matrices with respect to TAG hydrolysis, FFA formation, and increased acidity. This phenomenon will be further discussed in the second part of the study.

Figure 9 shows the thermal curves (from differential scanning calorimetry, DSC) obtained for the oils extracted,

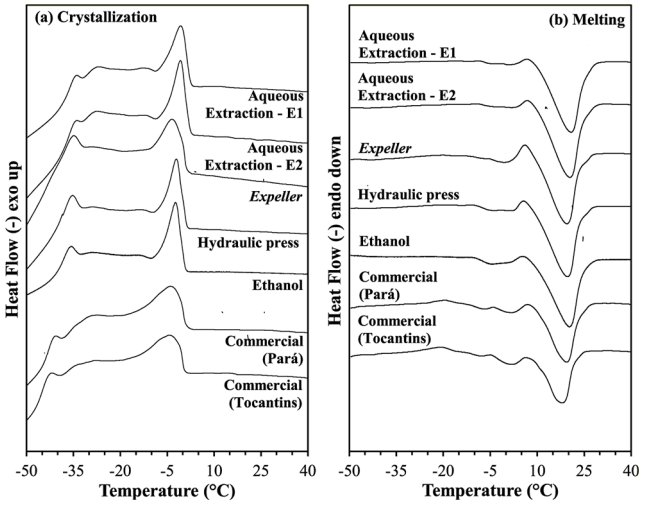

Figure 9. DSC thermal curves for oils' crystallization and melting profiles. Differences in melting and crystallization profiles are mainly related to lipid composition.

where it was possible to evaluate oils' melting and crystallization profiles. The curves exhibited peaks where crystallization and melting processes occurred. Table 3 presents the melting and crystallization temperatures (°C) of the extracted oils.

The peaks depicted in Figure 9 represent the melting or crystallization events of the different TAG fractions present in the oils. As mentioned, according to the TAG profiles (Table 2), the main compounds found are (in order) OOP, POP, and OOO. The main melting peak (peak 3) and crystallization peak (peak 1) are probably due to TAGs with higher concentration in the oil, i.e., OOP and POP, presenting high melting points of 18.5 and 37.2 °C, respectively.[69] The smaller intensity peaks for both melting and crystallization may be related to TAGs of lower concentration and higher unsaturation, such as OOO or others, such as OOLi and POLi. Profiles are quite similar, explained by the similarity in the compositions of fatty acids and TAGs of the obtained oils. Small differences were found for the main crystallization peak: Pequi oil obtained from aqueous extraction presented the highest crystallization peak temperatures (−0.68 and −0.50 °C) when compared to those obtained from mechanical and solvent extraction (crystallization peak temperatures between −3.06 and −1.99 °C), which agrees with the higher content of palmitic acid and disaturated TAG (POP) found for oils obtained by cooking. The lower crystallization peak temperature was found for *expeller*-type press oil, which could also be

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Table 3. Melting and crystallization temperatures (°C) for the extracted oils and commercial oils (Pará and Tocantins States)

	Aqueous extraction		Mechanical extraction			Commercial oils	
T (°C)	*E*1	*E*2	Expeller	Hydraulic press	Ethanol	Pará State	Tocantins State
Crystallization							
T_{onset}	3.48	3.57	3.76	3.72	2.02	2.33	2.06
$T_{peak\ 1}$	−0.50	−0.68	−3.06	−1.99	−2.28	−3.52	−4.08
$T_{peak\ 2}$	−12.46	−11.54	–	−13.22	−13.82	–	–
$T_{peak\ 3}$	−27.35	−27.65	−28.42	−28.47	−28.51	−29.53	−31.11
$T_{peak\ 4}$	−34.09	−34.42	−34.94	−32.21	−35.80	−41.10	−42.41
Melting							
$T_{peak\ 1}$	−5.07	−5.63	−8.09	−5.83	−5.83	−7.77	−8.28
$T_{peak\ 2}$	1.16	2.19	0.89	1.96	−1.32	1.83	1.58
$T_{peak\ 3}$	20.35	19.86	19.03	19.09	19.83	19.01	18.10
T_{offset}	32.92	32.49	30.17	28.54	30.76	30.32	30.16

attributed to its higher PUFA content and MUFA/SFA ratio when compared to other oils. Similar TAG profile justified the similarity between melting and crystallization profiles found for commercial pequi pulp oils from Pará and Tocantins States when compared to that observed for the pequi oils obtained in this work, with a crystallization temperature (T_{onset}) close to 0 °C and final melting process (T_{offset}) close to 30 °C, with the main melting peak at 19 °C, approximately.

As a general observation, when the melting profiles are evaluated, it is noticeable that pequi oils completely melted between 28 and 30 °C: the higher the melting point, the more favorable the formation of crystals at room temperature (or during storage). At room temperature (25 °C), pequi pulp oil is, therefore, not yet completely liquid due to the considerable content of mono- or disaturated TAGs with mild melting temperatures, suggesting an observed tendency to fractionate during storage.

Table 4 presents a comparative summary of the results obtained through characterization of the oils obtained by the 4 different extraction methods evaluated. It presents key points considering oil quality, allowing identification of trade-offs related to costs and feasibility for their use in small-scale facilities, which is a characteristic of the agricultural communities processing this fruit. Considering that mechanical methods (*expeller*-type press and hydraulic press) were that presenting low carotenoid losses, producing oils with a high lipid content (more than 96%), low acidity, water, and FFA; aqueous extraction, although simpler and more accessible, was that resulting in higher carotenoid losses, with the lowest process yield, confirming the influence of temperature and process control on oil quality; ethanolic extraction, despite presenting the highest total carotenoid content, was that resulting in oil with a higher nonlipid content (more than 10%) and FFA, which demands further purification steps, increasing operational costs and limiting its scalability in small-scale contexts; one could conclude that the mechanical extraction processes were that providing the pequi pulp oils with best yield and quality balance to be used for food purposes, also presenting cost and operational feasibility to be used in small-scale facilities.

In this case, the oils obtained by the mechanical extraction processes were additionally characterized regarding a complete set of physicochemical, compositional, and rheological profiles, as well as antioxidant capacity, which are important parameters for the design of food products with this high-quality oil obtained. Commercial oil from the Pará State (Brazil) was also evaluated for comparison purposes. Results are presented in the next section.

3.2. Characterization of the Oils Obtained by Mechanical Methods

Figure 10 shows the results for Fourier-transform infrared spectroscopy (FTIR) for the pequi oils obtained by mechanical extraction, as well for commercial oil; Table 5 lists the general assignment of the bands identified in the spectra of Figure 10. A similarity was observed among the oils evaluated, including a resemblance to spectra provided in the literature, with slight differences in the exact frequency and transmittance intensity of the bands, as presented in Table 4.[70−74] More significant bands were observed close to 1163 cm^{-1}, which is characteristic for bending vibration of the CH_2 groups; 1746 cm^{-1} for the stretching vibration of C═O ester groups; 2924 cm^{-1} for the asymmetrical stretching vibration of CH_2 groups; 2853 cm^{-1} for the symmetrical stretching vibration of CH_2 groups, all of them characteristic of TAG or acylglycerol molecule. Minor peaks were also observed, such as those for 1118 cm^{-1} for stretching vibration of the C−O ester groups and 3010 cm^{-1} for stretching vibration of *cis* olefinic CH double bonds, which are also present in TAG and acylglycerols structures. Results show that, indeed, samples are mostly composed of TAG structures, with no significant fraction of minor compounds or even other substances.

Table 6 presents the results obtained for iodine value (IV), and minor compounds such as acylglycerols content, minerals, including phospholipids, and volatile acid profile for the oils obtained via mechanical extraction and for the commercial oil.

In addition to fatty acids and triacylglycerols, oils may contain other partial acylglycerols (mono- and diacylglycerols, respectively, MAG and DAG), derived from the partial hydrolysis of TAG in the raw material, which are the main components of vegetable oils and fats.[20] It is important to mention that the presence of these partial acylglycerols influences some properties of oils, particularly those responsible for their technological functionality in food formulations such as the melting and crystallization process. The levels of partial acylglycerols found for the oils obtained in this study are very similar to the commercial oil and are also in accordance with values found for other oils from socio-biodiversity in the literature.[37] The low values for partial acylglycerols agree with the low acidity found in the first part of this work. The removal of these compounds, if necessary, can be carried out by industrial deodorization processes,[20,57] which is not a feasible practice in the context of low-scale productions. TAG

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Table 4. Comparative summary of pequi oil obtained by different extraction methods

Parameter	Aqueous (Cooking)	Expeller Press	Hydraulic Press	Ethanol Extraction
Extraction Yield	Lowest efficiency	Mild extraction yield	Best extraction yield	Good extraction yield: can be improved by sequential extraction
Overall oil composition	Slightly higher water content; higher oxidation susceptibility	High lipid composition, low water and nonlipid components content	High lipid composition, low water and nonlipid components content	High nonlipid content: demands further purification steps
Lipid profile	Higher palmitic acid content; higher content of POP	Presence of small contents of stearic and linoleic acid	Presence of small contents of stearic and linoleic acid	Lower palmitic acid; Higher oleic acid contents; Higher content of OOO
Thermal profile	Higher crystallization temperatures and offset melting temperatures	Lower crystallization temperature but regular melting profile like commercial oils	Regular melting profile like commercial oils	Lower onset crystallization temperature but regular melting profile like commercial oils
Bioactive compounds profile	Higher carotenoid losses due to temperature	Good carotenoid retention leading to high antioxidant activity[a]	Good carotenoid retention leading to high antioxidant activity[a]	Solvent ability in carotenoid coextraction; high carotenoid content
Operational trade-offs	No demand for particular apparatus; high yield variability; time-consuming; high number of operations; batch process	Demand specialized equipment (*Expeller* press); good process standardization; continuous process	Demand specialized equipment (hydraulic press); good process standardization; batch process	Demands specialized equipment, solvent handling and recovery steps; good process standardization; continuous or Batch process
Costs and feasability for small/large-scale facilities	Low cost, highly feasible in small-scale facilities	Flexible for small or large-scale facilities; costs largely dependent on equipment scale	Flexible for small or large-scale facilities; cost is also largely dependent on equipment scale	Indicated for large-scale facilities; costly considering solvent use and recovery

[a]Verified in the next section of the manuscript.

hydrolysis can occur by several factors, highlighting harvesting condition, post-harvesting and processing practices, particularly due to the application of high temperature, light, high humidity, considering time, but also fruit injury, favoring enzymatic activity.[57] Usually, artisanal production, as in small farms, is described by low or no good harvesting or postharvesting practices and, consequently, TAG enzymatic hydrolysis. However, fruit morphology (hard shells), in the case of pequi, could prevent pulp oil hydrolysis, despite probable inadequate storage or process conditions. This was already observed previously, when the acidity of oils obtained by all extraction methods was evaluated. Pulp storage, before extraction, otherwise, is still critical, demanding fast processing or thermal treatment for enzymatic inactivation. One should conclude that, considering these factors, pequi's susceptibility to hydrolysis is probably low and acidity/acylglycerols content observed was derived from natural hydrolysis processes, which should be considered in its technical use in food formulations.

The metal contents found in the pequi oils obtained in this study are low when compared to levels found in other oils and fats from Brazilian socio-biodiversity.[37,75] Pereira et al.[37] report values ranging from 0.13 to 36.50 mg/kg for Ca, 0.2 to 59.70 mg/kg for Fe, and 0.68 to 32.5 mg/kg for P in oil and fat samples obtained from pulps and oilseeds in the Amazon region. Cicero et al.,[75] in a study on the characterization of cold-pressed gourmet oils, revealed low levels of Cu for commercially obtained Brazil nut and pequi oils (respectively 0.19 μg/kg and 0.24 μg/kg, $p > 0.05$). They also reported very low levels of other pro-oxidant elements, such as Fe and Mn.

Minerals in oils are primarily related to environmental factors (presence of metals in soil, air, and water) and contamination via application of compounds (fertilizers and others) in regions within or near the plant cultivation, but also in processing, with the influence of stages involving mechanical processes (industrial equipment). This last probably explains the significant differences in the mineral composition of pequi oils evaluated (Table 6), where Ca and K contents were higher in the oil extracted using the *expeller*-type press, characterized by significant friction between equipment material and pulp particles, while hydraulic press extraction produced intermediate mineral levels.

The presence of metallic ions directly influences the quality criteria of vegetable oils, primarily affecting the lipid oxidation processes. Consequently, sensory factors and storage stability are affected. On the other hand, the presence of certain metallic ions is also associated with nutritional benefits, such as Fe, Ca, and K. Despite differences observed on oils' mineral composition among extraction conditions, their low levels revealed that pequi oils here evaluated presented good oxidative stability and nutritional quality.

A highlight, especially for vegetable oils, can be given to the presence of phosphorus, related to the phospholipid content of the sample. It is an industrial practice to remove phosphorus via refining processes, such as degumming, as these substances are surfactants that can affect the technological and application of the oil in food formulations.[20,55−57] This work showed that the *expeller*-type press yielded oils with higher phosphorus content, possibly linked to higher removal of phospholipids during extraction. However, levels are significantly lower than those oils whose high levels of P and phospholipids, such as palm or soybean oil, demands degumming practice.

The volatile carboxylic acid profile of pequi oils showed clear differences among the evaluated samples, reinforcing that the

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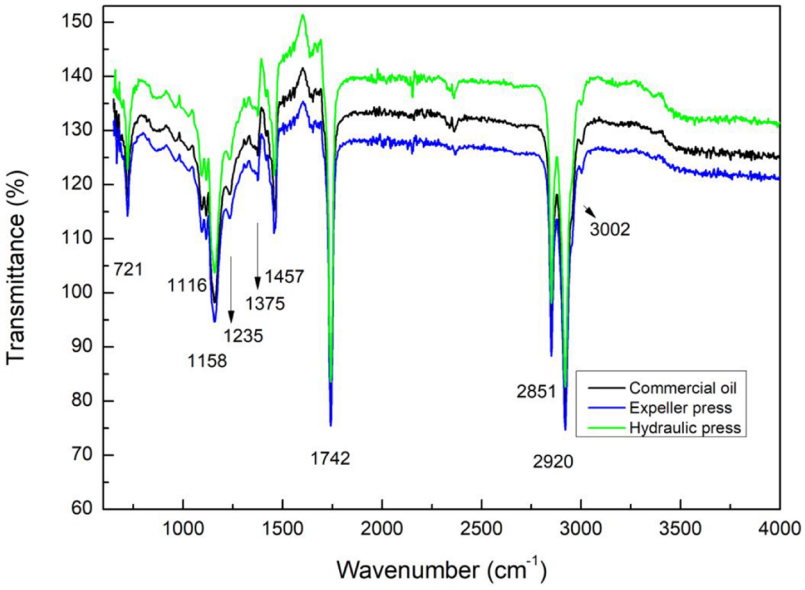

Figure 10. FTIR spectra for the oils obtained from mechanical extractions and for commercial oil (Pará state). The spectra confirm the predominance of triglycerides with characteristic C═O and C−H stretching bands, while minor spectral differences indicate subtle compositional variations among extraction methods.

Table 5. FTIR spectra data for pequi pulp oils[70−74]

Wavenumber ref. (cm^{-1})	Assignment
3010	stretching vibration of *cis* olefinic CH double bonds
2924	asymmetrical stretching vibration of CH_2 groups
2853	symmetrical stretching vibration of CH_2 groups
1746	stretching vibration of C═O ester groups
1465	scissoring vibrations of the CH_2 and CH_3 groups
1377	symmetrical bending vibrations of the CH_3 groups
1238	stretching vibration of the C−O ester groups
1163	bending vibration of the CH_2 groups
1118	stretching vibration of the C−O ester groups
723	overlapping of CH_2 rocking vibration and out-of-plane bending vibration of *cis*-disubstituted olefins

extraction parameters influenced the volatile profile. Formic, acetic, butyric, and hexanoic acids were detected at low concentrations, with hexanoic acid being the most abundant in commercial oil, reaching 79.21 ± 1.34 mg/kg. In contrast, formic acid predominated in the *expeller*-type extracted oil (15.13 ± 0.11 mg/kg), whereas acetic and butyric acids were more representative in the hydraulic press sample (15.85 ± 0.87 mg/kg and 12.98 ± 2.89 mg/kg, respectively). The total levels of volatile carboxylic acids did not exceed 94.4 mg/kg across samples, indicating very limited lipid oxidation. Considering that these values represent only about 3% of the total acidity, approximately, considering samples evaluated (Table 2), the contribution of volatile acids to overall acidity was also minimal. Moreover, the low levels of volatile carboxylic acids detected suggest a reduced formation of primary oxidation products since these acids typically arise from the secondary degradation of peroxides. Previous studies have shown that higher peroxide values are often accompanied by increased concentrations of volatile fatty acids and other low-molecular-weight oxidation markers in vegetable oils.[76−78] Therefore, the minimal volatile acid content observed here is consistent with the overall stability of pequi oil.

Pequi oil extracted by the *expeller*-type press presented the greatest antioxidant capacity according to both methodologies applied, DPPH and FRAP; hydraulic pressing provided an oil with similar antioxidant capacity considering DPPH results and the second greatest antioxidant capacity according to FRAP results. Otherwise, commercial pequi oil presented the lowest antioxidant capacity, according to both methods. Values found in this work were directly correlated with the content of total carotenoids, presented in Table 2, with Pearson correlation values (measured by the linear correlation between both data sets) equal to 0.99 and 0.83, respectively. In other words, total carotenoid content played a fundamental role in determining the antioxidant capacity. This property makes dietary carotenoids from vegetable oils largely associated with the prevention of several metabolic disorders, such as cancer and cardiovascular diseases.[14,15] Moreover, carotenoids are also well recognized as natural antioxidants in food systems. Indeed, oxidation is one of the main factors affecting the quality of oils or lipid-based products such as margarines, spreads, fried foods, puff pastries, and fillings during processing or storage, largely impacting flavor, shelf life, and consumer acceptance.[79] Results therefore showed that the processes involved in pequi oil extraction, particularly in the case of mechanically extracted oils, are significantly relevant for the preservation of thermolabile and oxidation-sensitive compounds, providing an ingredient suitable for the development of high-quality food products.

Figure 11 presents the rheological profile of the oils obtained from mechanical extraction and commercial oil for three different temperatures. Table 6 lists the parameters adjusted for the Newtonian rheological model.

The rheological profile of the oils is characteristic of Newtonian fluids, which are common for vegetable oils and fats. In this case, the behavior is such that the shear stress shows a linear increase with the increase in shear rate without a minimum initial stress for flow. This result was similar for all of the temperatures analyzed. The viscosity has a slight variation with the applied shear rate, decreasing with increasing

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Table 6. Characterization of the oils obtained via mechanical extraction and for commercial oil from the Pará State[1]

Composition	Mechanical Extraction		Commercial oil (Pará State)
	Expeller	Hydraulic press	
MAG (% m/m)	1.75	1.80	1.20
DAG (% m/m)	3.33	4.30	4.75
TAG (% m/m)	93.74	92.79	93.20
TAG IV (g I_2/100 g)	32.96	51.25	49.94
FFA IV (g I_2/100 g)	34.44	53.55	52.18
Mineral profile (mg/kg)			
Calcium (Ca)	0.80 ± 0.01[a]	0.55 ± 0.00[b]	0.251 ± 0.001[c]
Iron (Fe)	0.76 ± 0.07[b]	2.10 ± 0.01[a]	ND*,[c]
Potassium (K)	9.20 ± 0.03[a]	1.94 ± 0.13[b]	ND*,[c]
Magnesium (Mg)	1.50 ± 0.00[a]	0.51 ± 0.01[b]	ND*,[c]
Phosphorus (P)	5.38 ± 0.01[a]	2.90 ± 0.10[b]	1.28 ± 0.11[c]
Total phospholipids (mg/kg)	13.0	7.3	3.2
Volatile carboxylic acids (mg/kg)			
Formic acid	15.13 ± 0.11[a]	ND[c]	6.26 ± 0.01[b]
Acetic acid	ND*,[c]	15.85 ± 0.87[a]	8.91 ±0.14[b]
Butiric acid	ND*,[b]	12.98 ± 2.89[a]	ND*,[b]
Hexanoic acid	30.41 ± 3.02[b]	ND[c]	79.21 ±1.34[a]
Antioxidant activity			
DPPH (μMol Trolox/g)	58.88 ± 5.85[a]	52.77 ± 3.47[a]	7.22 ± 0.96[a]
FRAP (μM $FeSO_4$/100 g)	3.83 ± 0.98[a]	1.28 ± 0.81[b]	ND
Rheology**			
η (Pa.s) at 35 °C	41.70	39.20	34.00
η (Pa.s) at 60 °C	18.40	17.30	15.30
η (Pa.s) at 85 °C	10.10	9.40	8.50

[1]Values are expressed as mean ± standard deviation (n = 3). Different lowercase letters in the same rowindicate significant differences among extraction methods according to Tukey's test ($p < 0.05$). *Not detected (ND). **Newtonian model fitting to experimental data (shear stress versus shear rate curves): $\sigma = \eta \cdot \gamma$, where σ is the shear stress, γ is the shear rate, and η is the viscosity (Pa·s). $R^2 > 0.99$ in all cases.

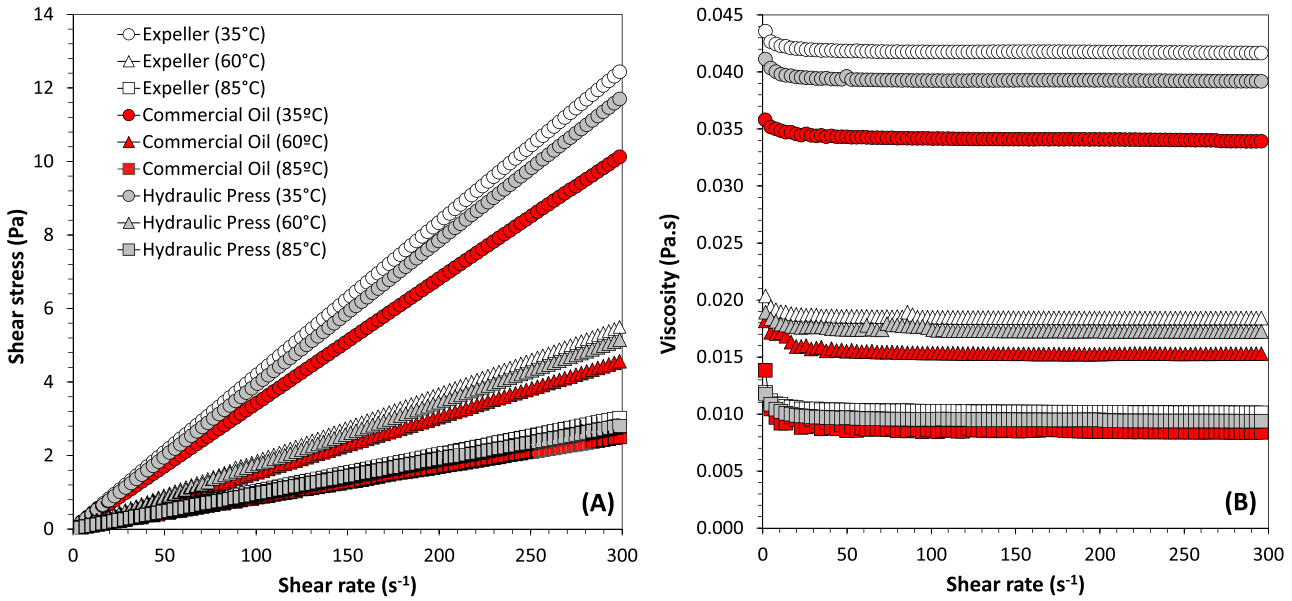

Figure 11. Rheological profile at 35, 60, and 85 °C for oils obtained from mechanical extraction and for commercial oil (Pará State): (A) Stress vs shear rate; (B) viscosity vs shear rate. All samples exhibited Newtonian flow behavior across the tested temperatures, with viscosity decreasing as temperature increased.

temperature. This result is commonly observed considering that the temperature increases the molecular mobility of the compound in the liquid phase. The analysis of rheological behavior in the case of oils and fats is important for designing industrial processes but also for the quality of the final products, related to consistency and flow.[80] It is important to note that the analysis was conducted at temperatures where pequi oil is completely liquid (above 30 °C), considering that the presence of high molecular weight and high melting point saturated TAGs promotes, in pequi oil, a behavior such that a solid phase is observed at room temperature, as mentioned. It can also be mentioned that the viscosity is compatible with

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other vegetable oils with similar levels of saturated and unsaturated compounds.[37,40] In the case of pequi, despite its significant composition in palmitic acid, the TAG profile is predominantly composed of mono-, di-, or triunsaturated compounds, making its viscosity lower when compared to fats with high levels of tri- or disaturated TAGs but slightly higher when compared to oils with more triunsaturated TAG composition.[37,40,81]

Overall, the pequi pulp oils obtained in this work presented a good quality standard for their use in food products formulation. Nevertheless, no specific identity and quality standards, particularly in the case of fatty acid profile and quality aspects, mainly related to its oxidative state, are presented (up to now) for pequi pulp oil in Brazilian legislation (Resolution RDC No. 482/2021[82] and Normative Instruction No. 87/2021[19] of the Brazilian National Health Surveillance Agency, ANVISA). On the other hand, when compared to the established thresholds for cold-pressed and unrefined oils for food purposes, not only in Brazilian law but also those described in document No. CXS 210−1999 of the Codex Alimentarius (Food and Agriculture Organization of the United Nations—FAO)[83] as well as literature,[11,44−48] it is possible to affirm that the pequi pulp oils obtained in this work presented low acidity (<4.0 mg_{KOH}/g established for non-refined/virgin and cold-pressed oils),[19,83] low mineral/metal content (established for refined oils, Fe < 1.5 mg/kg)[83] including low phospholipids composition (when compared to oils requiring degumming),[20,57] very limited lipid oxidation (low volatile acids content), presenting typical fatty acid profile[11,44−48] with characteristic color and flavor.

The alignment with quality requirements reinforces the technological and regulatory feasibility of using pequi oil in food applications, especially in the case of oils obtained by mechanical extraction processes. Indeed, as presented in this work, despite aqueous extraction at boiling temperature being a low-cost and simpler method for artisanal production, its lower yields and higher carotenoid losses were significant drawbacks. Ethanolic extraction, otherwise, despite high efficiency (which could be further improved by applying multiple stages), and high preservation of bioactive compounds, produced oils with high content of nonlipid components (>10%), and demands solvent removal and recuperation, holding greater potential for industrial applications. Therefore, hydraulic and *expeller*-type pressing represents a more balanced and sustainable alternative for pequi oil extraction—combining simplicity, efficiency, and product purity—being also more suitable for community-based production systems.

In terms of food applications, the pequi oil lipid profile, with a predominance of unsaturated fatty acids, particularly oleic acid, highlights its potential as a valuable dietary component. Also, its low acidity and moderate levels of volatile carboxylic acids confirm that pequi oil is a chemically stable matrix, an important advantage for its use as a functional ingredient, as it minimizes the formation of undesirable oxidation products while preserving the sensory and nutritional quality. Also, carotenoid retention allowed by processing steps resulted in oils with high antioxidant capacity—a valuable property for both nutritional and technological applications.

Overall, the results found showed the technological feasibility for producing high-quality pequi oils with socio-economic and environmental sustainability, particularly in the context of small-scale producers, strengthening the value chain and relevance of pequi oil in the context of the Brazilian Cerrado bioeconomy.

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Notes

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