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# Comprehensive analysis of Amazonian oil and fats with different fatty composition: Murumuru fat (*Astrocaryum murumuru*), cupuassu fat (*Theobroma grandiflorum*), and pracaxi oil (*Pentaclethera macroloba*)

Patrícia Tonon de Souza <sup>a</sup>, Gabriel Sthefano Lourenço Pereira <sup>a</sup>, Rafael Fernandes Almeida <sup>a</sup>, Dhayna Oliveira Sobral <sup>a</sup>, Marcelo Antonio Morgano <sup>b</sup>, Antonio José de Almeida Meirelles <sup>a</sup>, Eduardo Augusto Caldas Batista <sup>a</sup>, Klicia Araujo Sampaio <sup>a</sup>, Guilherme José Maximo <sup>a,\*</sup>

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#### ABSTRACT

Amazon is the largest Brazilian biome and has a vast diversity of oilseed species. This work highlighted three of its natural riches, the murumuru (Astrocaryum murumuru) fat, cupuassu (Theobroma grandiflorum) fat, and pracaxi (Pentaclethera macroloba) oil obtained from the seeds of the fruits of these species. It was aimed at a comprehensive evaluation of the chemical and physicochemical properties of these Amazonian products, deepening the knowledge on their quality parameters for products and processes design. The lipid samples showed a mostly yellow color, high total lipid content, with high percentage of triacylglycerols, low water content and low acid value, with insignificant volatile carboxylic acids content, that are end products of lipid oxidation. The FTIR spectra demonstrated a characteristic profile of other vegetable oils, and the lipid samples studied differed among them based on their unsaturation degree. Murumuru fat and pracaxi oil presented high levels of  $\beta/\gamma$ -tocopherols, while cupuassu fat presented high content of polyphenols. Murumuru and cupuassu fats presented high levels of metals (Ca, Fe, Mg, P) responsible for increasing the rate of lipid oxidation, even so they presented higher activation energy values than pracaxi oil and other conventional lipid sources, which were related to the higher saturated fatty acids content in the fatty composition of these fats. For crude murumuru and cupuassu fats, additional refining processes are alternatives for improving fats' oxidative stability by also reducing levels of metals. By demonstrating quality, nutritional value, and physicochemical properties of murumuru fat, cupuassu fat, and pracaxi oil, the results presented in this work highlight these lipids as excellent alternatives to commonly used vegetable fats and oils like palm oil, their fractions, and chemically modified lipids from industrial crops, highly associated to environmental and other impacts, allowing improving industrial sustainability while promoting Amazonian bioeconomy and its socio-biodiversity valorization.

# 1. Introduction

The Brazilian Amazon region is notable for harboring a vast diversity of oilseed species, which play a fundamental role in the local population's diet as a source of lipids, economic and cultural value addition, as well as biodiversity preservation (Pesce, 2009). Among these species, the native murumuru (*Astrocaryum murumuru*), and pracaxi

(*Pentaclethera macroloba*) palm trees, and the native cupuassu tree (*Theobroma grandiflorum*) stand out, providing oils and fats with interesting physicochemical properties and nutraceutical characteristics.

In murumuru palm tree, its fruit is primarily composed of a yellow pulp (53.0 %) (Lima et al., 2017). The almond/seed contains approximately 40.0 % of a white fat rich in fatty acids, such as lauric (45 %) and myristic (31 %) (Fasciotti et al., 2020). Murumuru fat, obtained from the

E-mail addresses: patsouza@unicamp.br (P.T. Souza), g234198@dac.unicamp.br (G.S.L. Pereira), r234206@dac.unicamp.br (R.F. Almeida), d234202@dac.unicamp.br (D.O. Sobral), morgano@ital.sp.gov.br (M.A. Morgano), tomze@unicamp.br (A.J.A. Meirelles), eacbat@unicamp.br (E.A.C. Batista), klicias@unicamp.br (K.A. Sampaio), maximo@unicamp.br (G.J. Maximo).

<sup>&</sup>lt;sup>a</sup> Laboratory of Extraction, Applied Thermodynamics and Equilibrium, Faculty of Food Engineering, Universidade Estadual de Campinas (UNICAMP), 80 Monteiro Lobato St., 13083-970, Campinas, São Paulo, Brazil

<sup>&</sup>lt;sup>b</sup> Institute of Food Technology (ITAL), 2880 Brasil Ave., 13070-178 Campinas, São Paulo, Brazil

 $<sup>^{\</sup>ast}$  Corresponding author.

seed, is used both as a dietary supplement and in the cosmetic industry, in products such as soaps and bases (Pereira et al., 2019).

The fat extracted from cupuassu seeds is gaining interest due to new cosmetic applications, while its fruit is widely used in local cuisine (Barbalho et al., 2022). In addition to use of cupuassu fat in the production of chocolate-like products and cosmetics, cupuassu pulp is rich in vitamin C and pectin, being used in the production of sweets, juices, and ice creams (Santos et al., 2022). The predominant fatty acids in the cupuassu fat are oleic (39 %), stearic (36 %), arachidic (12 %), and palmitic (7 %) acids (Fasciotti et al., 2020).

The fruits of pracaxi palm tree contain between 3 and 8 seeds, providing about 46.5 % of oil rich in oleic (52 %), behenic (17 %), lignoceric (11 %), and linoleic (11 %) acids. This oil is widely used in the cosmetic industry and also demonstrates healing and insect repellent effects (Fasciotti et al., 2020; Teixeira et al., 2020). Despite its primary medicinal and cosmetic use, pracaxi oil is also used as frying oil by riverside populations in the Brazilian Amazon region (Crespi & Guerra, 2013).

One of the most important reactions that can cause deterioration in the quality of edible fats and oils is lipid oxidation, affecting their stability throughout shelf-life, sensorial perception, nutritional quality, but also preventing their use for food formulation and consumption. Several accelerated methods have been developed to test the resistance of edible fats and oils to oxidation. These accelerated methods use elevated temperatures because it is known that the rate of the reaction is exponentially related to temperature. The Rancimat test, due to its ease of use, relatively high speed and very appropriate reproducibility, has become very popular among accelerated methods (Adhvaryu et al., 2000; Aktar & Adal, 2019; Farhoosh et al., 2008; Gharby et al., 2016; Ostrowska-Ligeza et al., 2010; Zaanoun et al., 2014).

Interest in Amazonian matrices has mainly focused on species that produce high edible oil yields, while others are now being more recognized due to changes in dietary consumption patterns and the growing interest in natural oils and fats (Aragão & Maximo, 2024; Bezerra et al., 2017; Fasciotti et al., 2020; Pereira et al., 2019). In this context, this study was aimed at a comprehensive evaluation of the chemical and physicochemical properties of Amazonian oil and fats with different fatty composition: murumuru fat, cupuassu fat and pracaxi oil. This work presents information on their glyceride classes composition, fatty acid profile, triacylglycerol profile, crystallization and melting behavior, rheological characterization, determination of nutraceutical (antioxidant) compounds, antioxidant capacity, kinetic parameters of lipid oxidation, metal traces and levels of volatile carboxylic acids (end products of lipid oxidation), deepening the knowledge on oils' quality parameters for products and processes design.

#### 2. Material and methods

#### 2.1. Samples characterization

The murumuru fat, cupuassu fat, and pracaxi oil used in this study were purchased from the Amazon Oil Industry (Ananindeua – Pará, Brazil), and obtained as cold-pressed and unrefined oil/fats.

# 2.1.1. Fatty acid (FA), glyceride classes, and triacylglycerol (TAG) compositions

The FA profile was determined by gas chromatography according to the AOCS Method Ce 1–62 (AOCS, 2009). The analyses were carry out in a gas chromatograph (model 7890B, Agilent, USA) equipped with a flame ionization detector (FID) and capillary column (model Agilent DB-WAX) with dimensions of 0.25 mm in internal diameter, 30 m in length, and a film thickness of 0.25  $\mu$ m. Before chromatographic analysis, the samples were transesterified in fatty acid methyl esters (FAME), according to Hartman and Lago (1973). The column temperature was programmed from 50 to 250 °C, with an increase rate of 15 °C min 1 until reaching 120 °C and 15 min of hold; then, with an increase rate of

4 °C min<sup>-1</sup> until reaching 200 °C and 3 min of hold; continuing until reaching 250 °C, with an increase rate of 4 °C min<sup>-1</sup>. The injector and detector temperatures were 250 and 300 °C, respectively. The identification of chromatographic peaks was carried out by comparing retention times with the chromatogram of fatty acid methyl ester standards. The iodine value (IV) of the samples was calculated according to the AOCS Method Cd 1c-85 (AOCS, 2009), through the FA composition.

The determination of the classes of monoacylglycerols (MAG) and diacylglycerols (DAG) was carried out by gas chromatography according to the AOCS Method Cd 11-b-91 (AOCS, 2009). On the same gas chromatograph described previously, these analyses were performed using a capillary column (model Agilent DB-5HT) with dimensions of 0.32 mm in internal diameter, 15 m in length, and a film thickness of 0.10 µm. The column temperature was programmed from 60 to 360 °C, starting with an 1 min hold at 60 °C, followed by an increase rate of 10 °C min<sup>-1</sup> until reaching 360 °C and 15 min of hold. The injector and detector temperatures were 50  $^{\circ}\text{C}$  and 380  $^{\circ}\text{C},$  respectively. The MAG and DAG content were determined using calibration curves of external standards and the sum of the areas in the characteristic retention time intervals. The TAG content was determined by the difference to 100 of the values found for the content of MAG, DAG and free fatty acids (FFA), the latter being converted from the acid value according to AOCS Official Method Cd 3d-63 (AOCS, 2009), expressed as oleic acid for pracaxi oil and, stearic acid for cupuassu fat, and lauric acid for murumuru fat.

The determination of the TAGs profile was carried out following the combinatorial analysis approach described by Antoniosi Filho et al. (1995), based on FA profile data, using Matlab version 6.0. This method was based on a random distribution model (without preference for the sn-1,3 and sn-2 position) of fatty acids in glycerol. The levels of trisaturated TAGs considered were: 98.2 % for murumuru fat (Fasciotti et al., 2020), 9.5 % for cupuassu fat (Fasciotti et al., 2020), and 0.75 % for pracaxi oil (Teixeira et al., 2020). Furthermore, the FA composition (%w  $w^{-1}$ ) was required as input data.

#### 2.1.2. Physicochemical analyses

The color of the lipid samples was measured using a Lovibond colorimeter (Lovibond PFX995, Tintometer, United Kingdom) following the AOCS Method Cc13e-92 (AOCS, 2009), measuring color on the Lovibond RYBN scale through visual comparison of lipid samples with Lovibond filters (R the red index, Y for the yellow index, B for the blue index and N for the neutral index).

Water content was determined according to the AOCS Method Ca 2e-84 (AOCS, 2009) using Karl Fisher titrator (model 870 KF Titrino plus, Metrohm, Switzerland) coupled to a temperature-controlled oven at 100  $^{\circ}\mathrm{C}$  (model 860 KF Thermoprep, Metrohm, Switzerland) and nitrogen gas to transport the water vapor to the reaction vessel, with a flow of 50 mL min $^{-1}$ .

The acid value was determined according to the AOCS Method Cd 3d-63 (AOCS, 2009) using an automatic titrator (model 848 Titrino plus, Metrohm, Switzerland) with a LiCl electrode saturated in ethanol for end point detection.

Lipid content was determined using an automatic extractor (model XT15, ANKOM Technology, USA), and dryer (model Dryer HCl Filter, ANKOM Technology, USA), according to the AOCS Official Method Am 5-04 (AOCS, 2009).

Protein and ash content were determined according to the Official Methods from the Association of Official Analytical Chemists (AOAC, 1997). The protein content was determined using the Kjeldahl method (method 988.05), and the ash content was determined by muffle incineration (method 940.26).

The trace of metals was analyzed according to the guidelines described in the American Society for Testing and Materials method D5185-18 (ASTM, 2018). Quantification of inorganic elements was performed in triplicate using axial measurements on a dichroic spectral combiner (model ICP OES 5100 SVDV, Agilent, Japan).

#### 2.1.3. Volatile carboxylic acid profile

The carboxylic acids were determined in their anionic form as carboxylates according to the methodology described by Souza et al. (2017). The equipment used was an ion chromatograph (Metrohm 940 Professional IC Vario), equipped with a Metrosep Organic Acid 250-7.8 column (250  $\times$  7.8 mm) and a pre-column with the same internal composition of the main column. To extract carboxylic acids from the samples, approximately 10.0 g of sample was weighed in a Falcon tube and 20 mL of deionized water was added. The tube was shaken on a vortex shaker (model Genius 3, IKA, Brazil) for 1 min. Next, the tube was placed in a thermostatic bath at 85  $^{\circ}\text{C}$  for 30 min. Afterwards, the tube was transferred to an ultrasonic bath (model USC 2800 A, Unique, Brazil) at 25 °C for 20 min. Then, after phase separation, the aqueous phase was collected with a disposable syringe and needle, filtered through a 0.45 µm hydrophilic filter and transferred to the 11 mL vial of the chromatograph for injection. The determination of the volatile carboxylic acids was performed using analytical curves of external standards.

#### 2.1.4. Melting and crystallization profile

Differential scanning calorimetry (DSC) was used to analyze the melting and crystallization behavior of the samples. The DSC equipment (model 2920 DSC, TA Instruments, USA) was calibrated with pure indium (TA Instruments), naphthalene, cyclohexane and n-decane (purity >99.9 %, Sigma-Aldrich). Nitrogen was used as the purge gas. Samples were weighed in aluminum pans (5.00  $\pm$  0.10 mg), hermetically sealed, and an empty pan was used as a reference. The methodology was based on those presented in previous works (Aragão & Maximo, 2024; Pereira et al., 2019; Tan & Man, 2002) and based on AOCS Method Cj 1-94 (AOCS, 2009). Samples were heated to 70 °C and maintained at this temperature for 10 min for complete sample melting and erase crystalline memory effects. Then, they were cooled to -70 °C at 5 °C min<sup>-1</sup> where crystallization behavior was analyzed. Subsequently, samples were held at  $-70~^{\circ}\text{C}$  for 10 min, followed by heating to 70  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C}$ min<sup>-1</sup> where their melting behavior were analyzed. The thermograms were analyzed with the Universal Analysis 2000 software (TA Instruments, USA).

## 2.1.5. Study of shear stress and shear rate (rheology)

Shear stress and shear rate measurements were conducted using a rheometer (model AR1500ex, TA Instruments, USA). The experiments were conducted across a range of shear rates from 1 to  $300~{\rm s}^{-1}$  at three temperatures, 35 °C, 60 °C, and 85 °C. The calculation of viscosity and regression coefficient (R²) was carried out using Newton's law equation. The shear stress to shear rate data was analyzed using linear regression to fit Newton's model.

#### 2.1.6. Fourier transform infrared (FTIR) spectra

The infrared spectra were recorded with a Fourier transform infrared spectrometer, (model Cary 630 FTIR, Agilent, USA), connected to a computer operating under MicroLab PC software. The instrument has a temperature-controlled Attenuated Total Reflectance (ATR) sample holder accessory with ZnSe crystal (model MicromATR, Czitek, USA).

The samples were previously heated in an oven at 60  $^{\circ}$ C to ensure that they were liquid and homogeneous. A film of a small amount of each sample (approximately 2 drops) was deposited on the ZnSe crystal, which was also heated to 60  $^{\circ}$ C. Multiple spectra (between three and four) were collected from each sample over different periods of time. All spectra were recorded from 4000 to 650 cm $^{-1}$ . For each spectrum, 8 background scans and 8 sample scans with resolution of 4 cm $^{-1}$  were collected.

## 2.1.7. Profile of tocopherols and tocotrienols (tocols)

Tocols analysis was performed according to the methodology of Ansolin et al. (2017), using ultra-high performance liquid chromatography, with electrospray ionization and mass spectrometer detector

(UHPLC/ESI/MS) equipment (model Acquity SQD – Single Quadrupole, Waters, USA). A C18 column (model UPLC Acquity BEH-C18, Waters, USA) was used with a mobile phase, composed of methanol:water: ammonium hydroxide (99:1:0.1 v/v/v) and isopropanol, in gradient mode by pump binary. The equipment was controlled using MassLynx software. The determination of the analytes was carried out using analytical curves of external standards.

#### 2.1.8. Determination of total polyphenols

Total polyphenols content was determined through the Folin-Ciocalteu reagent method adapted from Szydłowska-Czerniak et al. (2008) and Haiyan et al. (2007) Methanol extracts were prepared in 50 mL falcon tubes, mixing 5 g of sample in 15 mL of methanol. The mixture was shaken for 1 h at 200 rpm in a shaker incubator (model, NT 712, Nova Técnica, Brazil) at 35 °C. Then, the tubes were centrifuged (model Rotina 380R, Hettich, Germany) for 10 min at 10,000 rpm and the methanolic phase (extract) was collected. For colorimetric determination, 1 mL of the methanolic extract was mixed with 0.5 mL of Folin-Ciocalteu reagent and waited for 3 min. Then, 1 mL of 10 % saturated Na<sub>2</sub>CO<sub>3</sub> solution was added, concomitantly with the addition of 7.5 mL of deionized water. Finally, after 1 h, the absorbance reading at wavelength 725 nm was recorded using a UV-Vis spectrophotometer (model Orion AquaMate 8000 UV-vis, Thermo Scientific, USA). For the analytical curve, 6 dilutions were prepared from a 1 mg mL<sup>-1</sup> caffeic acid solution (100, 50, 25, 12.5, 6.25, and 3.125  $\mu g \text{ mL}^{-1}$ ). Aliquots of 1 mL of standard caffeic acid solutions were analyzed according to the methanolic extracts. The results were expressed as milligrams of Caffeic Acid Equivalent (CAE) per gram of extract ( $\mu$ g CAE g<sup>-1</sup>).

# 2.1.9. Antioxidant capacity and thermal stability of antioxidants by DPPH $IC_{50}$

The antioxidant capacity of the samples was determined using the DPPH free radical scavenging method using methodology adapted from Valavanidis et al. (2004) and Espin et al. (2000). Stock solution of DPPH  $2\times 10^{-4}$  mol L<sup>-1</sup> in ethyl acetate was prepared. To prepare the samples, 2.4 g of sample was weighed in a 15 mL Falcon tube and 8 mL of ethyl acetate was added. The mixture was shaken on a vortex shaker (model Genius 3, IKA, Brazil) to homogenize. The reaction mixtures were made in a 15 mL Falcon tube, with a total volume of the mixtures of 6 mL and a fixed DPPH concentration of  $1\times 10^{-4}$  mol L<sup>-1</sup>. Sample volumes were variable (0, 100, 200, 400, 600 and 800  $\mu$ L) and the volume was made up to 6 mL with ethyl acetate. The absorbance at 517 nm of reaction mixtures were recorded using a UV–Vis spectrophotometer (model Orion AquaMate 8000 UV–vis, Thermo Scientific, USA) after 30 min. The % DPPH reduction was calculated according to the Eq. (1).

$$\% \textit{ DPPH reduction} = ((\textit{Control Abs} - \textit{Sample Abs}) / \textit{Control Abs}) \times 100$$

(1)

Curves of % DPPH reduction as a function of sample concentration (mg mL $^{-1}$ ) were constructed. The results were expressed as the sample concentration required to reduce the DPPH radical (Control Abs) by 50 %, Inhibitory Capacity (IC $_{50}$ ) – mg mL $^{-1}$ .

For the study of the thermal stability of the antioxidants present, 6 g of samples were weighed in a 50 mL Schott flask and placed in a vacuum oven (model MA 030/12, Marconi, Brazil) without air circulation at 180  $^{\circ}\text{C}$ , with a vacuum of -700 mmHg for 2 h. The samples resulting from this process were analyzed as previously described to determine their IC $_{50}$ .

# 2.2. Kinetic data analysis of lipid oxidation

The oxidative stability of the samples was determined through accelerated lipid oxidation using the Rancimat equipment, according to the AOCS Method Cd 12b-92 (AOCS, 2009). For analysis, tubes containing 5 g of oil samples were placed on an electric heating block. Clean, dry, filtered air was allowed to bubble through the hot oil at 9 L

Table 1
Fatty composition of the murumuru fat, cupuassu fat, and pracaxi oil.

Fatty acid chain	Symbols <sup>a</sup>		$\%  \mathrm{w}  \mathrm{w}^{-1}$		
			Murumuru fat	Cupuassu fat	Pracaxi oil
Caprylic	Ср	C8:0	$1.62 \pm 0.02$ <sup>a</sup>	_	-
Capric	С	C10:0	$1.75\pm0.02$	_	_
Lauric	L	C12:0	$52.83\pm0.01~^{\rm a}$	_	$1.07 \pm 0.01^{\mathrm{b}}$
Myristic	M	C14:0	$26.36\pm0.04~^{a}$	_	$0.50 \pm 0.01^{b}$
Palmitic	P	C16:0	$5.91 \pm 0.01^{b}$	$6.80\pm0.03~^{a}$	$1.32\pm0.03^{\rm c}$
Stearic	S	C18:0	$1.82\pm0.03^{\rm c}$	$38.74\pm0.04~^{a}$	$3.28 \pm 0.01^{\rm b}$
Oleic	O	C18:1	$6.89 \pm 0.01^{\rm c}$	$37.28 \pm 0.01^{\rm b}$	48.11 $\pm$ 0.02 $^{\mathrm{a}}$
Linoleic	Li	C18:2	$0.46 \pm 0.01^{\rm c}$	$3.75 \pm 0.02^{\mathrm{b}}$	$12.55 \pm 0.04$ <sup>a</sup>
Linolenic	Ln	C18:3	_	_	$0.99\pm0.03~^{a}$
Arachidic	A	C20:0	$2.37\pm0.03^{\mathrm{b}}$	11.44 $\pm$ 0.04 $^{\mathrm{a}}$	$1.48\pm0.01^{\rm c}$
Behenic	Be	C22:0	_	$2.00\pm0.01^{\mathrm{b}}$	$16.88\pm0.01~^{a}$
Erucic	Er	C22:1	_	_	$0.92\pm0.02~^{\mathrm{a}}$
Lignoceric	Lg	C24:0	_	_	$12.90\pm0.01~^{a}$
SFA - % w w <sup>-1</sup>	-		$92.65 \pm 0.04^{a}$	$58.97 \pm 0.04^{\mathrm{b}}$	$37.43 \pm 0.03^{c}$
SFA≥C16:0 – % w w <sup>-1</sup>			$10.09 \pm 0.03^{\rm c}$	58.97 $\pm$ 0.04 $^{\mathrm{a}}$	$35.86 \pm 0.03^{\mathrm{b}}$
SFA <c16:0 %="" -="" w="" w<sup="">-1</c16:0>			$82.55 \pm 0.04$ a	_	$1.57\pm0.04^{\rm b}$
$MUFA - \% w w^{-1}$			$6.89 \pm 0.01^{c}$	$37.28 \pm 0.01^{\mathrm{b}}$	$49.03\pm0.02~^{\rm a}$
$PUFA - \% w w^{-1}$			$0.46 \pm 0.01^{c}$	$3.75\pm0.02^{\mathrm{b}}$	$13.54\pm0.04~^{\rm a}$
Iodine value – % w w <sup>-1</sup>			$7.02\pm0.01^{\rm c}$	$40.29 \pm 0.02^{\rm b}$	$69.34 \pm 0.04$ $^{a}$
$TAG - \% w w^{-1}$			$93.98 \pm 0.09^{\rm b}$	$92.22 \pm 0.10^{\rm c}$	95.58 $\pm$ 0.13 $^{\rm a}$
$DAG - \% w w^{-1}$			$3.18\pm0.02^{\mathrm{b}}$	4.48 $\pm$ 0.08 $^{\rm a}$	$3.10\pm0.04^{\rm b}$
$MAG - \% w w^{-1}$			$2.7\pm0.01^{\rm b}$	$3.16\pm0.02$ $^{\mathrm{a}}$	$1.17\pm0.03^{\rm c}$
$FFA - \% w w^{-1}$			$0.14\pm0.01~^{a}$	$0.14\pm0.06~^{a}$	$0.15\pm0.03~^{a}$

<sup>&</sup>lt;sup>a</sup> Cx:y, where x = number of carbon atoms, y = number of double bonds.

 $h^{-1}.$  The effluent air containing volatile organic acids from the oil sample was collected in a measuring vessel containing 50 mL of distilled water. The conductivity of the water was measured automatically as the oxidation proceeded. The oxidation induction time (OIT) is the time taken until there is a sharp increase in conductivity, which is determined by the intersection of the baseline with the tangent to the conductivity curve. The OIT of samples were determined at 110, 120, 130 and 140  $^{\circ}\mathrm{C}.$ 

In this study, the effect of temperature on the rate of lipid oxidation was illustrated by means of the Arrhenius equation (Eq. (2))

$$\ln(k) = \ln A - (E_a/RT) \tag{2}$$

where k is the reaction rate constant or reciprocal OIT, A is the preexponential factor or frequency factor,  $E_a$  is the activation energy (kJ mol<sup>-1</sup>), R is the molar gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), and T is the absolute temperature (K). The activation energy and frequency factors were calculated from the slopes and intercepts of the lines generated by regressing ln (k) vs. 1/T by use of the least squares linear regression, respectively. The kinetic rate constant (k) was taken as the inverse of the OIT ( $h^{-1}$ ).

#### 2.3. Statistical analysis

Results were expressed as mean  $\pm$  standard deviation and the Tukey Test was applied to compare the values obtained at a significance level of 5 % using the R® software version 4.1.1.

## 3. Results and discussion

# 3.1. Samples characterization

Table 1 shows the fatty acid (FA) composition of the samples analyzed by gas chromatography, as well as their iodine value (IV). Pracaxi oil has the higher polyunsaturated fatty acids (PUFA) and murumuru fat has the higher saturate fatty acids (SFA) among the samples studied. Pracaxi oil is rich in oleic (C18:1 – O), behenic (C22:0 – Be), lignoceric (C24:0 – Lg) and linoleic (C18:2 – Li) acids, according to data reported by Fasciotti et al. (2020) and Teixeira et al. (2020). The predominant FAs in cupuassu fat are oleic (C18:1 – O), stearic (C18:0 – S), arachidic (C20:0 – A) and palmitic (C16:0 – P) acids, the same as

demonstrated by Fasciotti et al. (2020). Murumuru fat, in turn, is rich in lauric (C12:0 – L) and myristic (C14:0 – M) acids, as well demonstrated by Fasciotti et al. (2020) and Lima et al. (2017). IV is related to the number of unsaturated FAs (monounsaturated fatty acids – MUFA and PUFA). The highest IV was observed in pracaxi oil, cupuassu fat presented an intermediate IV, and murumuru fat presented the lowest IV.

All the samples demonstrated notable lipid class composition, with TAG comprising most of its constituents. This high proportion of TAG is indicative of the quality of lipid samples, aligning with standards observed in high-quality vegetable oils, which typically contain over 90 % TAG (Table 1). The DAG, MAG, and FFA (minor components) alongside the predominant TAG, contribute to the overall composition and functional properties of the samples (Serra et al., 2019).

Table 2 presents the physicochemical characteristics, the volatile carboxylic acid profile, and trace of metals of the samples under study. The results of the color analysis indicate that all lipid samples studied present the maximum yellow color value (70 on a scale of 0 to 70 in Y), indicating that yellow is the predominant color. The samples also have relatively low red hues, between 3 and 5 (on a scale of 0 to 70 in R). Similar color results for these lipid samples were determined by Serra et al. (2019). The Codex Alimentarius (1999) report the limit for maximum acid value of cold-pressed and unrefined fats and oils as 4.0 mg KOH g<sup>-1</sup>. The lipid samples studied have acid values lower than 0.4 mg KOH  $g^{-1}$ , and water content lower than 0.4 % w  $w^{-1}$ , which are excellent results for their stability and shelf life. Furthermore, the levels of volatile carboxylic acids (end products of lipid oxidation) did not exceed 0.13 mg kg<sup>-1</sup>. This means that within the FFA content determined (approximately 0.15 % w w<sup>-1</sup>) for these lipid samples, the content of volatile carboxylic acids does not amount to more than 0.009 %, proving an insignificant effect of any lipid oxidation process on the quality of these samples. Still regarding non-lipid constituents, the protein and ash content showed insignificant or undetected results. These results supporting that the lipid samples studied in this work are mostly composed by lipids, according to the values presented for lipid content of at least 96 % w w<sup>-1</sup>.

The quality and acceptability of edible oils and fats can be significantly influenced by the presence of metals, responsible for increasing the rate of lipid oxidation and impacting freshness and storage capacity. The iron, calcium and magnesium contents of murumuru and cupuassu

 Table 2

 Physicochemical characteristics, volatile carboxylic acids profile, and trace metals of the murumuru fat, cupuassu fat, and pracaxi oil.

Variables		Results				
		Murumuru fat	Cupuassu fat	Pracaxi oil		
η – Pa·s	35 °C 60 °C 85 °C	0.0301 0.0134 0.0074	0.0396 0.0174 0.0095	0.0345 0.0152 0.0083		
Color	Red Yellow Blue Neutral	$5.2 \pm 0.1^{a}$ $70.5 \pm 0.1^{a}$ $0.5 \pm 0.1^{a}$ $0^{b}$	$\begin{array}{c} 4.0 \pm 0.1^b \\ 70.0 \pm 0.1^b \\ 0^b \\ 0^b \end{array}$	$3.1 \pm 0.1^{c} \ 70.0 \pm 0.1^{b} \ 0^{b} \ 1.2 \pm 0.2^{a}$		
Lipid content – % w w Water content – % w Acid value – mg KOH Protein – % w w <sup>-1</sup> Ash – % w w <sup>-1</sup>	$w^{-1}$	$96.75 \pm 2.12~^{a}$ $0.35 \pm 0.05~^{a}$ $0.39 \pm 0.04~^{a}$ nd nd	$96.14 \pm 2.56~^{a}$ $0.21 \pm 0.07~^{a}$ $0.28 \pm 0.11~^{a}$ $nd$ $0.040 \pm 0.002~^{a}$	$\begin{array}{c} 97.57 \pm 1.48~^{a} \\ 0.29 \pm 0.04~^{a} \\ 0.29 \pm 0.06~^{a} \\ \text{nd} \\ 0.010 \pm 0.001^{b} \end{array}$		
Volatile carboxylic a Formic acid – mg kg Acetic acid – mg kg Propionic acid – mg kg Buttyric acid – mg kg Valeric acid – mg kg Hexanoic acid – mg Octanoic acid – mg	-1 1 1 kg <sup>-1</sup> -1 -1 kg <sup>-1</sup> kg <sup>-1</sup>	$^{nd}$ $^{nd}$ $^{nd}$ $^{nd}$ $^{nd}$ $^{nd}$ $^{nd}$ $^{0.0093} \pm 0.0003 ^{a}$ $^{nd}$ $^{nd}$ $^{nd}$	$\begin{array}{c} nd \\ 0.093 \pm 0.001^b \\ nd \\ 0.0109 \pm 0.0004 \ ^a \\ nd \\ nd \\ nd \\ nd \\ nd \\ nd \end{array}$	$\begin{array}{l} 0.0031 \pm 0.0003 \ ^{a} \\ 0.1169 \pm 0.0003 \ ^{a} \\ \text{nd} \\ 0.0106 \pm 0.0003 \ ^{a} \\ \text{nd} \end{array}$		
Trace of metals Calcium (Ca) – mg kg Iron (Fe) – mg kg <sup>-1</sup> Magnesium (Mg) – m Phosphorus (P) – mg	$ m g~kg^{-1}$	$31.8 \pm 0.2^{\text{ a}} \ 4.83 \pm 0.03^{\text{b}} \ 15.69 \pm 0.04^{\text{b}} \ 55.1 \pm 0.3^{\text{ a}}$	$\begin{aligned} 14.2 &\pm 0.1^b \\ 28.44 &\pm 0.05 \ ^a \\ 26.3 &\pm 0.1 \ ^a \\ 9.30 &\pm 0.05^b \end{aligned}$	$0.251 \pm 0.001^{c}$ nd nd $1.28 \pm 0.11^{c}$		

nd = not detected.

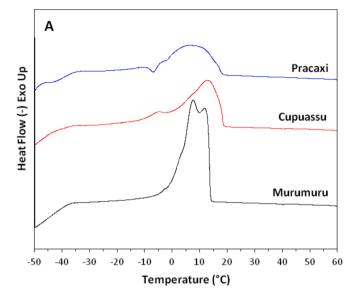
Table 3 Composition of triacylglycerols (TAG) from murumuru fat, cupuassu fat, and pracaxi oil.

TAG Code <sup>1</sup>	Molecular weight	% (mass fraction)			
	$\mathbf{g} \; \mathrm{mol}^{-1}$	Murumuru fat	Cupuassu fat	Pracaxi oil	
LLC	610.96	4.5			
LLL	639.01	22.7			
LLM	667.06	27.1			
MML	695.12	17.0			
LOL	721.16	5.8			
MMM	723.17	7.9			
LLA	751.22	4.5			
POS	861.42		9.1		
OOLi	883.43			10.0	
000	885.44		4.7	12.3	
OOS	887.46		16.1		
SOS	889.48		26.3		
OOA	915.51		6.2		
SOA	917.53		16.2		
OLiBe	941.55			7.9	
OOBe	943.57			14.5	
AOA	945.58		4.7		
OLiLg	969.61			5.2	
OOLg	971.62			10.3	
ВеОВе	1001.7			4.6	
LgOBe	1029.7			5.6	

 $<sup>^1</sup>$  C = capric acid; L = lauric acid; M = myristic acid; P = palmitic acid; S = stearic acid; O = oleic acid; Li = linoleic acid; A = Arachidic acid; Be = Behenic acid; Lg = lignoceric acid.

fats were high compared to olive oil (Benincasa et al., 2007), while pracaxi oil presented lower values. Environmental factors can contribute to metal contamination, with elements in soil, water and air, affecting the composition of oils (Souza et al., 2022). Also, the presence of metals can occur due to contamination during extraction process, from machinery, highlighting demands on good harvesting and manufacturing

practices. The phosphorus content of murumuru and cupuassu fats is above the maximum limit of 5 mg kg $^{-1}$ , described by O'Brien (2009), which is particularly intrinsic of the raw material, due to presence of phospholipids in the lipid matrix. This result proposes that murumuru and cupuassu fats require further degumming or physical refining processes to ensure compliance with the phosphorus standard quality, as



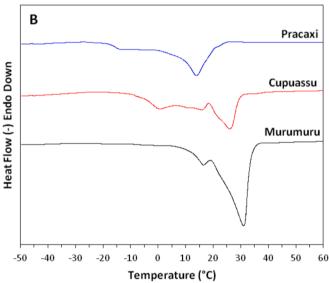


Fig. 1. Crystallization (A) and melting curves (B) of the murumuru fat, cupuassu fat, and pracaxi oil.

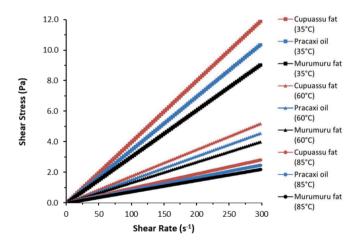


Fig. 2. Shear stress vs. shear rate measurements at different temperatures (35 °C, 60 °C, and 85 °C) for murumuru fat, cupuassu fat, and pracaxi oil.

well as reducing the levels of metals present.

Table 3 presents the TAG composition of the lipid samples, where only TAGs with content greater than 4 % are listed. The majority TAG codes identified for murumuru fat are: LLM, LLL, MML, and MMM, in agreement with reported by Saraiva et al. (2009). For cupuassu fat, the majority TAG codes are: SOS, OOS, SOA, and POS, similar to that indicated by Saraiva et al. (2009). And finally, pracaxi oil presents a greater quantity of the following TAG codes: OOBe, OOO, OOLg, and OOLi, in accordance with that demonstrated by Fasciotti et al. (2020).

Fig. 1 shows crystallization and melting curves of lipid samples. Multiple and overlapping peaks were observed in the crystallization and melting curves. According to the cooling curves (Fig. 1-A), pracaxi oil and cupuassu fat exhibited a large and broad crystallization peak and small crystallization peaks at lower temperatures. This is probably due to the heterogeneity of TAGs in their compositions (Table 3). The first crystallization peak, occurred at a higher temperature (cupuassu fat at 13.0 °C, and pracaxi oil at 10.3 °C), was probably caused by crystallization of mono- and di-saturated TAGs, such as SOS and SOA for cupuassu, and OOBe and OOLg, for pracaxi, all having high melting points. The crystallization peaks that occurred at lower temperatures, around -5.2 °C for cupuassu, and -10.2 °C for pracaxi, were probably caused by fractions rich in unsaturated fatty chains, such as OOO and OOLi, with low melting points (Berčíková et al., 2020). The crystallization curve of murumuru fat exhibited one major event with two minor peaks (at 12.50 °C and 7.7 °C), that was probably due to its homogeneous TAG profile (Table 3), composed of tri-saturated and medium chain TAGs, such as LLL, LLM and MML, with quite similar melting points (Aragão & Maximo, 2024; Pereira et al., 2019). According to the heating curves (Fig. 1-B), cupuassu and pracaxi exhibited multiple endothermic events, with broad and multiple peaks. For cupuassu, the main events were at 0.30 °C and 26.17 °C, with a final melting close to 35 °C. For pracaxi, the main melting events occurred at −13.9 and 13.97  $^{\circ}$ C, with a final melting close to 25  $^{\circ}$ C. The two major causes of this profile are TAG profile heterogeneity, as mentioned, but also the presence of solid-solid transitions during heating, main caused by the polymorphism phenomenon, which is a characteristic of TAG molecules (Berčíková et al., 2020). It is interesting to mention that despite the presence of very long fatty acids, such as behenic and lignoceric acids, pracaxi is liquid close to room temperature (>25 °C), mostly due to the predominance of tri-unstaurated and mono-unsaturated TAGs. Otherwise, cupuassu is mostly composed of di-saturated TAGs, making this lipid almost completely solid at room temperature. The most homogeneous TAG profile for murumuru lead to a single melting event with a main peak at 31.2 °C and a small event at 16.31 °C, resulting from different TAG fractions.

The results of shear stress vs shear rate measurements of the lipid samples at different temperatures (35  $^{\circ}$ C, 60  $^{\circ}$ C and 85  $^{\circ}$ C) are illustrated in Fig. 2. The minimum temperature of 35 °C was chosen to ensure that all samples were melted and homogeneous, avoiding the fractionation of fats. For all lipid samples studied, it is possible to observe that the shear stress increases linearly with the shear rate for all temperatures analyzed, indicating typical Newtonian behavior. It is also possible to observe that, maintaining a constant shear rate, the shear stress decreases as the temperature increases. This phenomenon can be attributed to the increase in the thermal movement of molecules, which reduces intermolecular forces, facilitates the flow and consequently reduces the viscosity (Foster & Ferrier, 1979; Hashempour-Baltork et al., 2018), as illustrated in Fig. 3. The adjusted parameters for the Newtonian rheological model  $\sigma = \eta \gamma$ , where  $\eta$  is the viscosity,  $\sigma$  is the shear stress and  $\gamma$  is the shear rate, are listed in Table 2, all presenting  $R^2 >$ 0.99. Thus, with generally constant viscosity at all temperatures tested, these lipid samples exhibit consistent Newtonian behavior in the shear stress range of 0 to 300 s<sup>-1</sup> (Abedinzadeh et al., 2016). According to literature reports, the length of the fatty chains of oils and fats has a strong influence on their viscosities, with viscosity being directly proportional to the length of the fatty chains in TAGs, where palmitic and

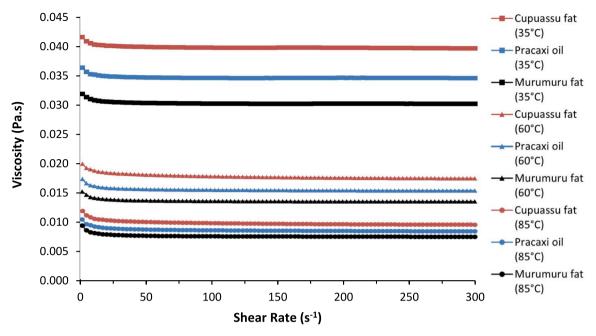


Fig. 3. Viscosity vs. shear rate measurements at different temperatures (35 °C, 60 °C, and 85 °C) for murumuru fat, cupuassu fat, and pracaxi oil.

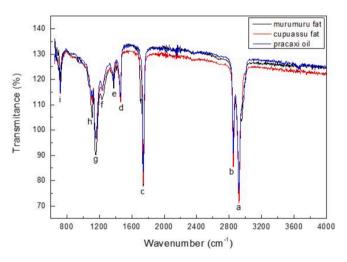


Fig. 4. FTIR spectra of the murumuru fat, cupuassu fat, and pracaxi oil.

oleic acids showed significantly higher viscosities than did the lauric acid (Ceriani et al., 2007; Rodrigues et al., 2006). Furthermore, viscosity is also influenced by the degree of unsaturation of the fatty chains, since

the presence of one double bond (MUFA) increases the viscosity, while the presence of two or three double bonds (PUFA) decreases the viscosity (Demirbas, 2008). As can be seen in the Table 1, the murumuru fat containing 82.55  $\pm$  0.04 % of SFA<C16:0 (lauric and myristic acids) demonstrates lower viscosity than cupuassu fat and pracaxi oil, which have lower than 2 % of SFA<C16:0. Pracaxi oil, in turn, containing 13.54  $\pm$  0.04 % of PUFA presents lower viscosity than cupuassu fat, which has only 3.75  $\pm$  0.02 % of PUFA.

Knowledge about the viscosity of oils and fats is essential to ensure the efficiency of industrial processes (mixing, pumping, frying), the quality of final products and compliance with quality standards and regulations. Rheological measurements can give useful information about the appearance, properties, consistency, and sometimes food product quality (Hashempour-Baltork et al., 2018).

Fig. 4 shows the FTIR spectra of the lipid samples, which were acquired to corroborate with the compositional characterization performed by gas chromatography of the oil/fats studied. These spectra are similar to those of other vegetable oils in the literature, differing slightly in the exact frequency and transmittance intensity of the bands. These variations are due to the different lengths and degree of unsaturation of the constituent acyl groups in the triacylglycerols of each vegetable oil/fat (Aktar & Adal, 2019; Guillen & Cabo, 1997; Guillén et al., 2003; Ioannidi et al., 2023; Quiñones-Islas et al., 2013).

Table 4
Attribution data for the spectra of murumuru fat, cupuassu fat and pracaxi oil, illustrated in Fig. 4 (Aktar & Adal, 2019; Guillen & Cabo, 1997; Guillén et al., 2003; Ioannidi et al., 2023; Quiñones-Islas et al., 2013).

Band	Wavenumber (cm <sup>-1</sup> )				Assignment
	Murumuru fat	Cupuassu fat	Pracaxi oil	Approximate reference	
a	2920	2920	2920	2924	asymmetrical stretching vibration of CH <sub>2</sub> groups
b	2851	2851	2851	2853	symmetrical stretching vibration of CH <sub>2</sub> groups
c	1741	1743	1743	1746	stretching vibration of C=O ester groups
d	1465	1465	1465	1465	scissoring vibrations of the CH <sub>2</sub> and CH <sub>3</sub> groups
e	1375	1375	1375	1377	symmetrical bending vibrations of the CH <sub>3</sub> groups
f	1232	1236	1236	1238	stretching vibration of the C–O ester groups
g	1157	1159	1159	1163	bending vibration of the CH <sub>2</sub> groups
h	1111	1116	1118	1118	stretching vibration of the C–O ester groups
	_	1098	1096	1095	
i	721	721	721	723	overlapping of the ${\rm CH_2}$ rocking vibration and the out-of-plane bending vibration of $\emph{cis}$ disubstituted olefins

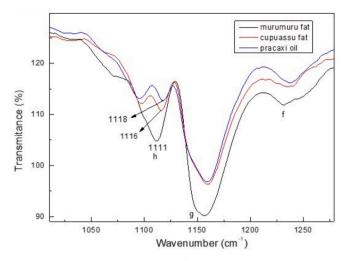


Fig. 5. Spectral region close to  $1118~{\rm cm}^{-1}$  (band h) with greater detail for the murumuru fat, cupuassu fat, and pracaxi oil.

The Table 4 lists the general assignment of the bands identified in spectra of Fig. 4, from a to i. There is a correlation in the literature for the band close to 1118 cm<sup>-1</sup> (band h), whose frequency increases and intensity decreases with the increase in the degree of unsaturation of the lipid sample (Guillén et al., 2003). Fig. 5 illustrates the band h spectral region in greater detail for of the murumuru fat, cupuassu fat and pracaxi oil. It is possible to observe that pracaxi oil has the highest frequency and lowest intensity for the band h, followed by cupuassu fat and finally murumuru fat. This sequence is consistent with the degree of unsaturation of these lipid samples, where pracaxi oil is more unsaturated than cupuassu fat, which is more unsaturated than murumuru fat, as listed in Table 1.

Table 5 presents the tocols profiles for the lipid samples. In general, it is possible to observe that cupuassu fat has much lower amounts of these antioxidants when compared to murumuru fat. Pracaxi oil, in turn, has

significantly higher amounts of these antioxidants when compared to murumuru fat. In a previous work, Serra et al. (2019) found this same order; however, the reported concentration levels were lower than those found in the present work. For murumuru fat, Serra et al. (2019) reported  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ -tocopherol levels of 89.94, 91.52, 10.09, and 5.65 ppm, respectively, and, for pracaxi oil,  $\gamma$  and  $\delta$ -tocopherol levels were 416.13 and 7.78 ppm, respectively. There are previous reports in the literature about variations of tocols levels in lipid samples from tropical plant species from the Amazon region. Among the factors mentioned, the variety of the plant, the climate during growth and maturation, the storage of the raw material after harvest, and the types of processing stand out (Funasaki et al., 2013; Serra et al., 2019; Silva et al., 2009).

The levels of total polyphenols determined showed the following sequence: cupuassu fat > murumuru fat > pracaxi oil (Table 5). The tocols profile and total polyphenols results are important to understand the Inhibitory Capacity (IC<sub>50</sub>) values listed for these lipid samples. Pracaxi oil presented greater antioxidant capacity than cupuassu fat, which presented greater antioxidant capacity than murumuru fat (Table 5). This sequence can be justified by the content of antioxidants present in these lipid samples and, considering that some polyphenols have antioxidant capacity similar to tocopherols, in some cases it can be even greater (Espin et al., 2000; Valavanidis et al., 2004; Yalcin & Schreiner, 2018). After heat treatment (heating samples at 180 °C for 2 h), pracaxi oil presented greater antioxidant capacity than murumuru fat, and both presented much greater antioxidant capacity than cupuassu fat. This sequence can be justified by the fact that pracaxi oil and murumuru fat have higher  $\beta/\gamma$ -tocopherols content than cupuassu fat (Table 5), and considering that  $\beta/\gamma$ -tocopherols have greater thermostability than polyphenols (Valavanidis et al., 2004; Yalcin & Schreiner, 2018).

#### 3.2. Kinetic data analysis of lipid oxidation

The Rancimat measurements for the OIT (time in hours) were made isothermally at four different temperatures (110, 120, 130, and 140  $^{\circ}$  C). The OIT of the lipid samples can be seen in Table 6. The results illustrate

Table 5

Analysis of antioxidants of the murumuru fat, cupuassu fat, and pracaxi oil.

Composition/Analysis		<b>Results</b> <sup>1</sup>		
		Murumuru fat	Cupuassu fat	Pracaxi oil
Tocols profile				
α-Tocopherol – mg kg <sup>-1</sup>		$28.1\pm0.3^{\rm b}$	$7.7\pm0.2^{\rm c}$	$70\pm2^a$
β/γ-Tocopherols – mg kg <sup>-1</sup>		$444\pm10^{\rm b}$	nd	$754\pm23^a$
δ-Tocopherol – mg kg <sup>-1</sup>		$7.1\pm0.2^{\rm b}$	nd	$9.4\pm0.7^{a}$
α-Tocotrienol – mg kg <sup>-1</sup>		$0.36 \pm 0.01^{\mathrm{b}}$	$0.91 \pm 0.05^{a}$	$0.43 \pm 0.01^{b}$
γ-Tocotrienol – mg kg <sup>-1</sup>		$3.7\pm0.1^{\rm c}$	$52\pm1^{a}$	$25.4\pm0.8^{\rm b}$
δ-Tocotrienol – mg kg <sup>-1</sup>		nd	nd	nd
Total polyphenols – $\mu g$ CAE $g^{-1}$		$45.85 \pm 0.82^{b}$	$412.62 \pm 0.73^a$	$38.68\pm0.73^{c}$
Inhibitory Capacity $^2$ (IC <sub>50</sub> ) – mg mL $^{-1}$	before thermal treatment 180 °C (2 h)	$42.3 \pm 0.2^{\rm a} \\ 95.6 \pm 0.3^{\rm b}$	$33.7 \pm 0.7^{\mathrm{b}} \ 177.5 \pm 0.4^{\mathrm{a}}$	$26.3 \pm 0.5^{\rm c} \\ 83.2 \pm 0.3^{\rm c}$

nd = not detected.

Table 6 OIT values and reaction rate constants ( $k_{OIT} = 1/OIT$ ) at four different temperatures (T) for murumuru fat, cupuassu fat, and pracaxi oil.

T (°C)	OIT – h			$k_{OIT} - \times 10^{-3} \ h^{-1}$		
	Murumuru fat	Cupuassu fat	Pracaxi oil	Murumuru fat	Cupuassu fat	Pracaxi oil
110	$89.55 \pm 0.38$ <sup>a</sup>	$48.85 \pm 0.09^{b}$	$31.12 \pm 0.26^{c}$	11.17	20.47	32.14
120	$34.24\pm1.04~^{a}$	$20.20 \pm 0.04^{\rm b}$	$14.24\pm0.11^{\rm c}$	29.21	49.50	70.25
130	$13.04\pm0.23~^{a}$	$8.60 \pm 0.03^{\mathrm{b}}$	$6.81 \pm 0.09^{c}$	76.72	116.28	146.95
140	$5.79\pm0.06~^{a}$	$3.54\pm0.01^{\mathrm{b}}$	$3.33\pm0.04^{\rm c}$	172.71	282.49	300.30

<sup>&</sup>lt;sup>2</sup> DPPH solution was  $1 \times 10^{-4}$  mol L<sup>-1</sup>. Note that the higher the inhibition potential, the smaller the amount (mg mL<sup>-1</sup>) needed to scavenge the DPPH stable free radical.

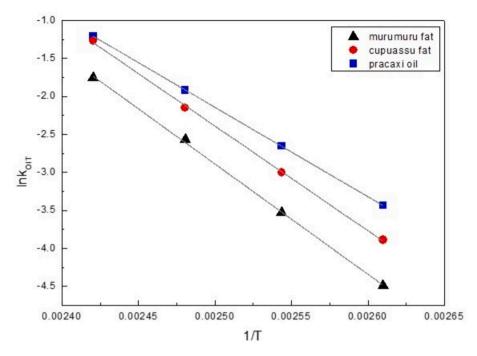


Fig. 6. Linear curves of ln (k) vs. 1/T for murumuru fat, cupuassu fat, and pracaxi oil.

 $\begin{tabular}{ll} \textbf{Table 7} \\ \textbf{Regression parameters, $E_a$ (activation energy) and $A$ (frequency factor) values calculated for murumuru fat, cupuassu fat, and pracaxi oil. \\ \end{tabular}$ 

Parameter	Murumuru fat	Cupuassu fat	Pracaxi oil
Intercept	$33.461\pm0.582~^a$	$32.135 \pm 0.605^{b}$	$27.311 \pm 0.067^{c}$
Slope R <sup>2</sup>	$-14541\pm232~^a$	$-13810 \pm 241^{\rm b}$	$-11782\pm27^{\rm c}$
$R^2$	0.99924	0.99909	0.99998
E <sub>a</sub> /kJ mol <sup>-1</sup>	$120.8\pm0.2~^{a}$	$114.8\pm0.2^{\rm b}$	$98.0\pm0.1^{\rm c}$
$A_{OIT}-\times 10^{12}\ h^{-1}$	340.35	90.38	0.726

that the OIT values are decreasing with increasing temperature. Indeed, as mentioned earlier, the reaction rate constant (k) value represents lipid oxidation of samples, and it was determined by the reciprocal OIT for each temperature, which can be seen for different temperatures in Table 6. As expected, the results indicate that k increases with increasing temperature, corroborating to the known effect of high temperature in the improvement of lipid oxidation.

By using the k value rate of lipid oxidation as a function of temperature, a direct relationship can be observed. As shown in Fig. 6,  $\ln(k)$  vs. 1/T curves were obtained for each lipid sample from the measurements. The slope values were used to calculate the activation energy (E<sub>a</sub>) and the intercept values were used to calculate the frequency factor (A), which are listed in the Table 7. The linear curves of  $\ln(k)$  vs. 1/T (Fig. 6) present excellent coefficient of determination (R<sup>2</sup> > 0.99) for all lipid samples (Table 7).

Lipid oxidation is a very complex process leading to numerous oxidation products involving various intermediates. These intermediate compounds have their own rate constant. The overall  $E_a$  is the cumulative effect of all the activation energies available in the system during the process of oxidation (Adhvaryu et al., 2000).

The lipid oxidation at low and high temperatures can go through different steps or reaction pathways, depending on the reactivity of prooxidants such as metal ions and antioxidants at different temperatures. Lipid oxidation results in the loss of important nutrients in oils and fats, in addition to producing compounds such as free radicals that are harmful to health. In the food industry, through understanding the kinetics of lipid oxidation and the associated activation energy, it is possible to adjust parameters, develop and control the production

processes that preserve the nutritional quality of foods (Adhvaryu et al., 2000; Aktar & Adal, 2019; Farhoosh et al., 2008; Gharby et al., 2016; Ostrowska-Ligeza et al., 2010; Zaanoun et al., 2014). Moreover, the oil temperature affects the degree of oxygen solubility in vegetable oils which decreases by almost 25 % for each 10 °C rise in temperature (Robertson, 2000). Therefore, the results of such predictions can lead to uncertainties and errors, and should be considered as approximate values.

The activation energy (Ea) calculated through Arrhenius equation of the lipid samples are listed in Table 7. Murumuru fat presented the higher  $E_a$  (120.8  $\pm$  0.2 kJ mol<sup>-1</sup>), followed by cupuassu fat (114.8  $\pm$  0.2 kJ mol $^{-1}$ ), and finally by pracaxi oil (98.0  $\pm$  0.1 kJ mol $^{-1}$ ), with the lower Ea among the samples studied. The literature reports that a high content of PUFA decreases Ea, while a high content of MUFA and/or SFA increases Ea for lipid oxidation of oils or fats (Adhvaryu et al., 2000; Farhoosh et al., 2008). These observations from the literature and the data in Table 1 explain the Ea sequence found in this study, where murumuru fat, containing 92.65  $\pm$  0.04 % of SFA content (highest level of SFA among the samples studied), presented higher Ea than cupuassu fat, which in turn has higher Ea than pracaxi oil, this latter containing 13.54  $\pm$  0.04 % of PUFA content (highest level of PUFA among the samples studied). Cupuassu fat contains lower MUFA content (37.28  $\pm$ 0.01 %) than pracaxi oil (49.03  $\pm$  0.02 %), however the cupuassu fat still has higher SFA content (58.97  $\pm$  0.04 %) and lower PUFA content (3.75  $\pm$  0.02 %) than pracaxi oil. Even though pracaxi oil presented better antioxidant capacity and lower trace of metals content, murumuru and cupuassu fats showed higher Ea, indicating that, for the samples studied in this work, the fatty composition was the predominant factor that influences the lipid oxidative stability. Despite being a predominant factor, lipid oxidation could be also altered by the presence of minor compounds. For example, Farhoosh et al. (2008), showed that soybean oil (92.42 kJ mol<sup>-1</sup>) presented higher E<sub>a</sub> than olive oil (86.86 kJ mol<sup>-1</sup>), even though olive oil containing higher levels of SFA and MUFA and lower PUFA content than soybean oil. The authors justified this difference due to several other factors that affect oxidative stability fatty, such as total polyphenols and the addition of synthetic antioxidants in the oils, for which olive oil presented the lowest levels.

Comparatively, previous studies of lipid oxidation kinetics for refined oils presented  $E_a$  values calculated for canola (88.45–89.94 kJ

 $\rm mol^{-1}$ ), soybean (79.66–92.42 kJ mol $^{-1}$ ), sunflower (63.81–90.74 kJ mol $^{-1}$ ) and corn (77.78–88.14 kJ mol $^{-1}$ ) oils (Adhvaryu et al., 2000; Farhoosh et al.,2008). An investigation into the kinetics of four different commercial olive oils showed  $\rm E_a$  values between 97.5 kJ mol $^{-1}$  and 101.9 kJ mol $^{-1}$  (Ostrowska-Ligeza et al., 2010). In another study, Gharby et al. (2016) presented the lipid oxidation kinetics for four olive oils with  $\rm E_a$  between 89.5 kJ mol $^{-1}$  and 101.8 kJ mol $^{-1}$ . Aktar and Adal (2019) calculated  $\rm E_a$  of 99.6 kJ mol $^{-1}$  for avocado oil. Therefore, according to  $\rm E_a$  of pracaxi oil (98.0  $\pm$  0.1 kJ mol $^{-1}$ ), it is stable compared to other oil sources as well as the olive oil from different origins. Murumuru and cupuassu fats, in turn, have higher  $\rm E_a$  values and are even more stable to lipid oxidation than pracaxi oil and the other lipid sources previously described.

All the results presented for murumuru fat, cupuassu fat and pracaxi oil demonstrate that the quality, nutritional value and physical properties of these lipid sources give them greater chances of being considered good alternatives to other vegetable lipid sources. In this sense, it is possible to make some assessments considering different perspectives. Soybean oil is the most produced and sold vegetable oil in Brazil and several other countries, being widely used in the formulation of mixtures for margarines, vegetable creams, confectionery fats, fillings and other products. To achieve this, this oil is usually mixed with highly saturated fats like palm oil fractions or palm kernel oil, as well as with hydrogenated and interesterified oils. However, the production of these lipids, particularly palm oil, has been linked to significant environmental impacts (Meijaard et al., 2020). Additionally, both palm oils and chemically modified oils are associated with the presence of carcinogenic contaminants (Goh et al., 2022) and the generation of potentially toxic chemicals, by-products, and residues (Lee & Wang, 2022). These issues have led to a global trend toward producing and consuming palm oilfree products with clean labels (Savarese et al., 2022; Siddiqui et al., 2022). In this context, using Amazonian oils and fats as alternatives for these industrial fats and palm oil would enhance the sustainability of the food industry while promoting the value of Amazonian sociobiodiversity, and reduction of monoculture.

Another example is the cocoa butter market, which due to the high price, high demand, limited supply and other difficulties, has led to an increase in the incentive to explore alternatives to replace or improve it (Mokbul & Siow, 2022). The potential of fat systems obtained from tropical butters or their mixtures with vegetable oils as cocoa butter equivalents has been deeply investigated and their physicochemical properties have been compared (Ramos et al., 2023). In this context, murumuru fat, cupuassu fat, and pracaxi oil can be studied for similar applications to those of cocoa butter, which is widely used in moisturizing skin and hair, in the production of chocolates and confectionery, and in various cosmetic and medicinal products.

#### 4. Conclusions

Overall, Amazonian oil and fats here evaluated presented adequate quality parameters, responding for the results obtained in the comprehensive characterization that they were subjected. Particularly regarding the antioxidants analyzed, murumuru fat and pracaxi oil presented high levels of  $\beta/\gamma$ -tocopherols, while cupuassu fat presented high content of polyphenols, which give them a greater chance to be considered good alternatives to other vegetable lipid sources. The activation energy values calculated from lipid oxidation kinetics data were understood based on the fatty composition and minority compounds of the analyzed samples. Murumuru and cupuassu fats presented higher Ea values than pracaxi oil and other lipid sources mentioned (olive, avocado, soybean, sunflower, corn and canola oils), and these results were related to the higher SFA content in the fatty composition of these fats, presence of tocopherols, and polyphenols, the latter providing antioxidant activity to the lipid samples. On the other hand, murumuru and cupuassu fats presented phosphorus content above the maximum limit of 5 mg kg<sup>-1</sup> and also presented high levels of iron, calcium and

magnesium, responsible for increasing the rate of lipid oxidation. Therefore, the refining process of murumuru and cupuassu fats, to reduce the levels of these metals, should also contribute to improving oxidative stability and further increasing the activation energy of these fats.

#### CRediT authorship contribution statement

Patrícia Tonon de Souza: Writing - review & editing, Writing original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Gabriel Sthefano Lourenço Pereira: Writing – original draft, Software, Methodology, Investigation, Formal analysis. Rafael Fernandes Almeida: Writing original draft, Software, Methodology, Formal analysis, Conceptualization. Dhayna Oliveira Sobral: Software, Methodology. Marcelo Antonio Morgano: Software, Methodology. Antonio José de Almeida Meirelles: Resources, Funding acquisition. Eduardo Augusto Caldas Batista: Supervision, Resources, Funding acquisition. Klicia Araujo Sampaio: Supervision, Resources, Funding acquisition, Guilherme José Maximo: Writing – review & editing, Visualization, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

#### Declaration of competing interest

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.

#### Data availability

No data was used for the research described in the article.

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