

Accepted Manuscript

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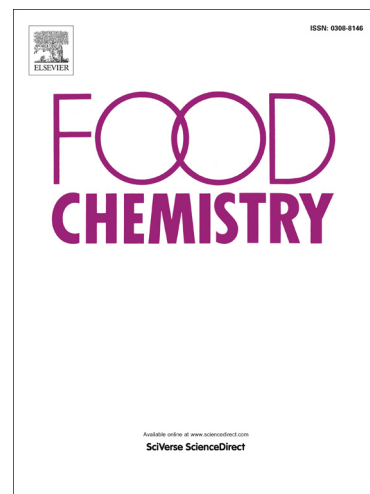
PII: S0308-8146(18)31949-6
DOI: <https://doi.org/10.1016/j.foodchem.2018.11.016>
Reference: FOCH 23824

To appear in: *Food Chemistry*

Received Date: 4 June 2018
Revised Date: 8 October 2018
Accepted Date: 2 November 2018

Please cite this article as: Pereira, E., Ferreira, M.C., Sampaio, K.A., Grimaldi, R., de Almeida Meirelles, A.J., José Maximo, G., Physical Properties of Amazon Fats and Oils and their Blends, *Food Chemistry* (2018), doi: <https://doi.org/10.1016/j.foodchem.2018.11.016>

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Title: Physical Properties of Amazon Fats and Oils and their Blends

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Abstract

Considering their diversity, this work evaluated physical properties of Amazon fats/ oils (murumuru, tucuma kernel, bacuri, pracaxi, patawa, and Brazil nut). Solid fat content (SFC) curves and crystallization/melting profiles were determined. We also explored the possibilities of combining these lipids into blends for improving their nutritional and technological aspects. Patawa, pracaxi, and Brazil nut oils presented high levels of mono- and polyunsaturated fatty acids, displaying low atherogenicity and thrombogenicity indexes (0.10 and 0.18; 0.23 and 0.70; 0.20 and 0.42), respectively. The SFC curves showed that murumuru fat could be used as a cocoa butter replacer, whereas bacuri fat was found to be a promising alternative to hydrogenated oils in shortenings and spreads formulations. The blends expanded fats' melting ranges and enriched their fatty acid compositions from a nutritional standpoint. This work shows that these fats, oils and their blends may be suitable for developing new products in the food industry.

Key-words: fat blends; crystallization; melting; DSC; viscosity; quality parameters.

1. Introduction

The Brazilian Amazon region is rich in oleaginous plant species. Vegetable oils and fats produced by these species have unique compositions, as well as physicochemical and nutraceutical properties (Bezerra, Rodrigues, de Oliveira, da Silva, & da Silva, 2017). In fact, species such as the palm tree (*Elaeis guineensis*) are economically important for the region since they are widely used in the food and pharmaceutical industries (Edem, 2002). However, the great demand for natural oils and fats has brought attention to other matrices.

Among these new matrices, oleaginous species such as Brazil nut tree (*Bertholletia excelsa*), pracaxi (*Pentaclethra macroloba*), and patawa (*Oenocarpus bataua*) are notorious for providing oils with interesting nutritional characteristics, presenting high content of unsaturated fatty acids, specially $\omega 6$ and $\omega 9$ fatty acids (FA). For instance, the oil extracted from patawa pulp has a healthy FA content, presenting a ratio of 18.5/81.5 (w/w) saturated/unsaturated FA (Rodrigues, Darnet, & Silva, 2010), while the pracaxi oil is considered a natural source of behenic acid (Pereira Lima et al., 2017). Moreover, the Brazil nut is regarded as one of the most economically and industrially relevant Amazonian seeds (Chunhieng, Hafidi, Pioch, Brochier, & Didier, 2008).

On the other hand, plant tree species such as murumuru (*Astrocaryum murumuru*), tucuma (*Astrocaryum vulgare*), and bacuri (*Platonia insignis*), provide solid fats rich in lauric and myristic fatty acids. Tucuma and bacuri trees are specific instances of plants which produce fruits consisting of two main oleaginous fractions. While the tucuma fruit pulp provides an orange oil rich in polyunsaturated FA, the kernel produces a lauric fat (Bora, Narain, Rocha, De Oliveira Monteiro, & De Azevedo

Moreira, 2001). Similarly, bacuri tree produces fruits composed of pulp and seed. While the composition of bacuri fruit pulp oil has already been evaluated in the literature (Hiane, Bogo, Ramos, & Ramos Filho, 2003), a study of the composition and physical properties of the fat extracted from their seeds has not been the subject of any previous report. Murumuru, in turn, produces nuts which present an exceptionally high oil content, around 40%, with a beneficial fatty acids (FA) ratio of $\omega 3:\omega 6$, attracting the interest of the fats and oils industry (Pereira Lima et al., 2017).

Characterization of the physical properties of these fats and oils is essential in order to promote their industrial application. These properties are in general directly related to the lipids' triacylglycerol (TAG) composition. Furthermore, determining technological aspects, such as melting and crystallization profiles, are also quite important to develop fat-based food products (Walstra, Klok, & van Vliet, 2001). In this context, blends of fats and oils are interesting alternatives for broadening industrial applications of Amazon fats and oils, building specific physicochemical characteristics and thermal behaviors.

Given the demand for new fats and oils, and the scarce amount of research on physical properties of Amazon oils, this study was aimed at the characterization of physical and physicochemical properties of six vegetable fats and oils: murumuru fat, bacuri fat, tucuma kernel fat, patawa oil, pracaxi oil, and Brazil nut oil, correlating them with their triacylglycerol (TAG) profiles. Melting and crystallization behavior of multiple blends was also investigated in order to identify potential applications.

2. Materials and methods

2.1. Fats, oils, and blend preparations

The murumuru fat, bacuri fat, pracaxi oil, tucuma kernel fat, patawa oil, and Brazil nut oil used in this study were kindly supplied by Amazon Oil Industry (Ananindeua, Brazil). The developed blends were based on the study described by Bezerra, Rodrigues, de Oliveira, da Silva, and da Silva (2017). Thus, binary blends (fat + oil) of murumuru fat + pracaxi oil, tucuma kernel fat + patawa oil and bacuri fat + Brazil nut oil were prepared at 50:50, 60:40, 70:30, 80:20 and 90:10 (w/w) ratios, using an analytical balance (XT220A, Precisa, Switzerland, precision of 2×10^{-4} g). Experimental measurements were performed in triplicates and presented alongside their standard deviations.

2.2. Fatty acid (FA) and triacylglycerol (TAG) compositions

The FA compositions were determined by gas chromatography (GC) using the AOCS official method Ce 1-62 (AOCS, 2009). Conversion of FA to fatty acid methyl esters (FAME) was based on the method described by Hartman and Lago (1973). Analysis was performed in a Clarus 600 gas chromatograph (PerkinElmer, USA) equipped with a flame ionization detector (FID) and a DB-WAX capillary column (length 30 m, internal diameter 0.25 mm, film thickness 0.25 μ m; Agilent Technologies, USA), in the following operating conditions: Helium (carrier gas) at a flow rate of 1.78 mL/min, FID temperature of 250°C, injector at 250°C, injection volume of 1 μ L, column temperature ramp from 50°C to 250°C at 10°C/min. Individual FA peaks were

identified by comparing retention times to an external standard (FAME mix C8-C24; Sigma-Aldrich, USA). Retention times and peak areas were evaluated via Total Chrom software (version 6.3.2, PerkinElmer, USA). Results were expressed as relative percentages of mass of total FA.

TAG compositions were calculated from FA data via combinatorial analysis using the method described by Antoniosi Filho, Mendes, and Lanças (1995). In this method, a model of random distribution (no preference to position sn-1,3 and sn-2) of FA in glycerol was used, hence only bulk FA composition was necessary as input data.

2.2.1. Atherogenicity and thrombogenicity indexes

FA compositions were used for calculation of the lipids' nutritional quality through atherogenicity (AI) and thrombogenicity indexes (TI) (Ulbricht & Southgate, 1991), according to Equations 1 and 2, respectively

$$AI = \frac{C12:0 + 4 \times C14:0 + C16:0}{\sum MUFA + \sum FA\omega6 + \sum FA\omega3} \quad (1)$$

$$TI = \frac{C14:0 + C16:0 + C18:0}{(0.5 \times \sum MUFA) + (0.5 \times \sum FA\omega6) + (3 \times \sum FA\omega3)} \quad (2)$$

where C12:0, C14:0, C16:0, and C18:0 are relative percentage masses of lauric, myristic, palmitic, and stearic acids, respectively; MUFA is the relative percentage mass of monounsaturated fatty acids; FA ω 6 and FA ω 3 are the relative percentage mass of omega-3 fatty acids and omega-6 fatty acids, respectively.

2.3. *Acidity, peroxide, iodine and saponification values, unsaponifiable matter, Oil Stability Index (OSI), water content and trace metals*

Physicochemical characteristics were determined according to the Official Methods and Recommended Practices of the AOCS (AOCS, 2009): Cd 3d-63, Cd 8b-90, Cd 1c-85, Cd 3b-76, Ca 6b-53, Ca 2e-84, Cd 12b-92, for acidity value, peroxide value, iodine value, saponification value, unsaponifiable matter, water content, and Oil Stability Index (OSI), respectively. OSI was determined at 130 °C, air flow rate at 20 L/h using an OSI analysis system (893 Professional Biodiesel Rancimat, Metrohm, Switzerland). Induction time was determined by the OSI inflection point at a maximum of the second derivative of the conductivity curve. Acidity was determined by using an automatic titrator (848 Titrino plus, Mettler, Switzerland). Water content was determined by using an automatic Karl Fisher titrator (870 KF Titrino plus, Metrohm, Switzerland).

Trace metals were determined according to ASTM method D5185 – 13 (ASTM, 2013). Inorganic elements were quantified by axial measurements in a dichroic spectral combiner (ICP OES 5100 SVDV, Agilent Technologies, Japan). Operating conditions were: 1.5 kW plasma power; argon flow at 15 L/min; auxiliary argon flow 0.4 L/min; nebulization flow at 0.45 L/min; stabilization time set at 15 s. Wavelengths of 317.93 nm, 259.94 nm, 280.27 nm, and 213.62 nm were employed for calcium, iron, magnesium, and phosphorus, respectively.

2.4. Viscosity and Density

Viscosities and densities were determined according to the method described by Ceriani, Paiva, Goncalves, Batista, and Meirelles (2008). Density and viscosities were measured at a temperature in which all samples were liquid (40°C), except for bacuri fat, completely melted after 55°C. Thus, an automated micro viscometer (AMVn, AntonPaar, Austria) and a density meter (DMA 4500M, Anton Paar, Austria), were used to measure viscosity and density, respectively. Viscosity measures were based on the efflux time of a ball immersed in the sample, inside a glass capillary (inclination angle of 70°). Each record was replicated four times. Apparatus calibration was made using a standardized mineral oil (according to equipment procedure).

2.5. Solid fat content (SFC)

Solid fat content (SFC) was determined by nuclear magnetic resonance (NMR) according to AOCS official method Cd 16b-93 (AOCS, 2009) using a magnetic NMR (Minispec mq-one, Bruker, USA). Measures were performed in triplicates at 10 °C, 20 °C, 25 °C, 30 °C, 35 °C, 40 °C, 45 °C, 50 °C, and 55 °C.

2.6. Melting and crystallization profile

Differential scanning calorimetry (DSC) was performed for describing the melting and crystallization profiles of the fats, oils and their blends. The equipment (2920 DSC, TA Instruments, USA) was calibrated with pure indium (TA Instruments), naphthalene, cyclohexane and decane (purities > 99.9%, Sigma-Aldrich). Samples of

fats, oils, and prepared blends were weighted (4.93 ± 0.80 mg) using aluminum pans, and hermetically sealed with aluminum covers. An empty hermetically sealed aluminum pan was used as reference. In order to insure a quasi-equilibrium state along the experimental run, and based on previous works on fat and oils, scanning rates of 5 °C/min were employed (Tan & Che Man, 2002). To erase the thermal history and induce crystallization of the most stable polymorphic forms of the samples, they were heated to 70 °C and maintained at this temperature for 10 min. They were then cooled to -70 °C at 5 °C/min to generate the crystallization curve. Samples were maintained at -70 °C for 10 min and then heated to 70 °C at 5 °C/min to generate the melting curve. The thermograms were analyzed with the Universal Analysis 2000 software (TA Instruments, New Castle, USA) according to onset (T_{on}), offset (T_{off}), peak temperatures (T_{peak}) and enthalpy (ΔH) for both crystallization and melting curves.

3. Results and discussion

3.1. FA composition, TAG profile, and nutritional quality indexes

Table 1 shows the FA composition of the fats and oils analyzed by gas chromatography, as well as their atherogenicity and thrombogenicity indexes. While pracaxi, patawa, and Brazil nut oils presented high contents of monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids, tucuma kernel fat, murumuru fat and bacuri fat presented a high content of saturated fatty acids (SFA). Due to their high SFA contents, these last three products are solid at room temperature, whereas pracaxi, patawa, and Brazil nut oils are liquid.

The particular FA composition of Amazon oils opens up possibilities for application in the food industry. For instance, the high concentration of oleic acid found

in patawa oil (74.18%) is in the same range as that found in high oleic sunflower and buriti oil (Silva et al., 2009; Smith, King, & Min, 2007). Furthermore, high concentrations of this fatty acid have a beneficial effect on thermal stability, suggesting that patawa oil could be useful to the food industry as a frying oil. In addition, the high oleic and linoleic ratio ($> 12:1$) of patawa oil could increase shelf life and nutritional value of foods.

While oleic acid is the primary FA in the composition of pracaxi oil and Brazil nut oil, pracaxi oil also showed a high content of behenic acid (17.88%) and Brazil nut oil had a high content of linoleic acid (31.73%). Behenic acid has a neutral impact on serum lipid concentration because of its low bioavailability and very long chain length (Cater & Denke, 2001), suggesting that pracaxi oil can be useful in the preparation of low-calorie products. Since Brazil nut oil has a higher content of linoleic acid when compared to conventional edible nut oils, such as almond or macadamia oils (Maguire, O'Sullivan, Galvin, O'Connor, & O'Brien, 2004), it can be nutritionally beneficial as an ingredient in food products.

Tucuma kernel fat, murumuru and bacuri fats were found to be rich in SFA. Murumuru fat and tucuma kernel fat had a high content of lauric acid, meanwhile bacuri fat had a high content of palmitic acid. Tucuma kernel fat has a FA composition rather similar to coconut oil's (Marina, Che Man, Nazimah, & Amin, 2009). Therefore, like coconut oil, it can be used in cooking and in the pharmaceutical and cosmetic industries. Lastly, the high content of palmitic acid in bacuri fat makes it a potential source of tripalmitin (PPP), a TAG used for formulating lipid nanoparticles and alternative drug delivery systems (Reddy, Sharma, Chuttani, Mishra, & Murthy, 2004). Furthermore, bacuri fat had a relatively high content of palmitoleic acid, a beneficial FA which improves insulin sensitivity (Yang, Miyahara, & Hatanaka, 2011).

Atherogenicity index (AI) and thrombogenicity index (TI) are health lipid indexes, which take into account the effects of saturated and unsaturated FA in the development of coronary heart diseases (Ulbricht & Southgate, 1991). According to Table 1, nutritional quality indicators AI and TI ranged from 0.1 to 14.6 and 0.18 to 6.69, respectively. Tucuma kernel fat and murumuru fat presented the highest values for both indicators due to their SFA contents. Thus, to improve the nutritional quality of fatty products, these lipids could be blended with healthier oils, such as patawa or pracaxi oils.

Table 1

Fatty acid compositions, atherogenicity and thrombogenicity indexes of fats and oils

FA (%)	Patawa oil	Pracaxi oil	Brazil nut oil	Tucuma kernel fat	Murumuru fat	Bacuri fat
C8:0	-	-	-	1.94 ± 0.03	1.19 ± 0.01	-
C10:0	-	-	-	1.95 ± 0.04	1.31 ± 0.02	-
C12:0	1.37 ± 0.03	1.20 ± 0.07	0.59 ± 0.04	50.89 ± 0.19	47.15 ± 0.3	0.88 ± 0.03
C14:0	0.94 ± 0.01	0.71 ± 0.05	0.41 ± 0.01	25.2 ± 0.16	28.75 ± 0.17	0.91 ± 0.02
C16:0	11.04 ± 0.03	1.95 ± 0.09	14.84 ± 0.01	6.23 ± 0.06	7.09 ± 0.07	61.26 ± 0.07
C16:1	0.41 ± 0.01	-	0.35 ± 0.01	-	-	7.12 ± 0.09
C18:0	5.09 ± 0.06	2.92 ± 0.18	10.48 ± 0.06	2.74 ± 0.09	2.92 ± 0.03	1.33 ± 0.03
C18:1	74.18 ± 0.08	47.57 ± 3.27	41.62 ± 0.01	8.1 ± 0.01	7.97 ± 0.06	26.41 ± 0.04
C18:2	5.97 ± 0.07	12.08 ± 0.4	31.73 ± 0.01	2.94 ± 0.05	3.62 ± 0.02	2.09 ± 0.1
C18:3	0.51 ± 0.01	1.07 ± 0.01	-	-	-	-
C20:0	0.5 ± 0.02	1.34 ± 0.12	-	-	-	-
C22:0	-	17.88 ± 2.14	-	-	-	-
C22:1	-	0.82 ± 0.11	-	-	-	-
C24:0	-	12.49 ± 1.92	-	-	-	-
SFA	18.94 ± 0.05	38.47 ± 3.54	26.32 ± 0.01	88.97 ± 0.02	88.41 ± 0.07	64.39 ± 0.05
MUFA	74.59 ± 0.09	48.39 ± 3.15	41.96 ± 0.01	8.1 ± 0.01	7.97 ± 0.06	33.53 ± 0.11
PUFA	6.48 ± 0.08	13.15 ± 0.39	31.73 ± 0.01	2.94 ± 0.01	3.62 ± 0.02	2.09 ± 0.1
AI	0.10	0.23	0.20	14.31	14.60	1.85
TI	0.18	0.70	0.42	6.20	6.69	3.57

Values shown as mean ± SD of replicates.

Table 2 shows the results for TAG composition calculated via the method proposed by Antoniosi Filho et al. (1995). The reported values were related to TAGs that represent more than 5 % of the composition. Tables S3 to S8 (Supplementary Material) show the whole TAG compositions of all fats and oils use in this study. While Brazil nut oil and patawa oil presented TAG mainly derived from oleic and linoleic acids, murumuru fat and tucuma kernel fat contained TAGs composed mainly of lauric and myristic acids. Compositions obtained by this study for Brazil nut oil and murumuru fat were in agreement with those reported by Saraiva, Cabral, Eberlin, and Catharino (2009), who characterized the TAG profile of Amazon vegetable oils and fats by mass spectrometry. The theoretical TAG profile of tucuma kernel fat described here was also in agreement with the one reported by Santos, Morgavi, and Le Roux (2018). These authors also applied a computational tool for estimating TAG profiles of Amazon fatty products. Pracaxi oil was characterized by TAGs containing oleic acid, its main FA, as well as behenic and lignoceric acids, both representative of this oil's TAG composition. Concerning bacuri fat, TAGs derived from palmitic, palmitoleic and oleic acids were found to be the main TAG species. Also, contents of tripalmitin (PPP) were found to be significant; bacuri fat indeed seems to be a natural source of this useful TAG.

289 **Table 2**

290 Triacylglycerol composition of Amazon fats and oils

Molecular formula	MM (g/mol)	TAG code ^a	Patawa oil ^b	Pracaxi oil ^b	Brazil nut oil ^b	Tucuma kernel fat ^b	Murumuru fat ^b	Bacuri fat ^b
C ₃₉ H ₇₄ O ₆	639.01	LLL				19.52	13.73	
C ₄₁ H ₇₈ O ₆	667.06	LLM				22.87	14.69	
C ₄₁ H ₇₈ O ₆	667.06	LML					7.34	
C ₄₅ H ₈₄ O ₆	667.06	LLO				5.91		
C ₄₃ H ₈₂ O ₆	695.12	MML				14.62	7.85	
C ₄₃ H ₈₂ O ₆	695.12	LLP					7.15	
C ₄₅ H ₈₆ O ₆	723.17	PLM				7.50	7.28	
C ₅₁ H ₉₆ O ₆	805.32	PPoP						9.99
C ₅₁ H ₉₈ O ₆	807.33	PPP						23.92
C ₅₃ H ₉₈ O ₆	831.35	PPoO						9.34
C ₅₃ H ₁₀₀ O ₆	833.37	POP						30.31
C ₅₅ H ₁₀₆ O ₆	857.39	POLi			11.59			
C ₅₅ H ₁₀₂ O ₆	859.41	OOP	19.27		7.55			11.49
C ₅₇ H ₁₀₀ O ₆	881.41	LiLiO			7.71			
C ₅₇ H ₁₀₂ O ₆	883.43	OOLi	9.53	8.96	10.04			
C ₅₇ H ₁₀₂ O ₆	883.43	OLiO			5.02			
C ₅₇ H ₁₀₄ O ₆	885.45	OOO	39.83	12.63	6.53			
C ₅₇ H ₁₀₄ O ₆	885.45	SOLi			7.38			
C ₅₇ H ₁₀₆ O ₆	887.46	OOS	7.95					
C ₆₁ H ₁₁₂ O ₆	941.55	BeOLi		7.10				
C ₆₁ H ₁₁₄ O ₆	943.57	OObE		13.45				
C ₆₃ H ₁₁₈ O ₆	971.62	OOLg		8.70				
C ₆₇ H ₁₂₈ O ₆	1029.74	LgOBe		5.11				

291 ^a FA abbreviations: Be, behenic acid; L, lauric acid; Li, linoleic acid; Lg, lignoceric acid; M,
 292 myristic acid; O, oleic acid; P, palmitic acid; Po, palmitoleic acid; S, stearic acid. ^b Relative
 293 molar percentage.

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3.2. Physical and physicochemical properties

Table 3 shows the results for acidity, peroxide, iodine, and saponification values, unsaponifiable matter, OSI and water contents of the samples. The acidity and peroxide values are reference parameters to determine the conservation quality of fats and oils. The *Codex Alimentarius* (1999) report set the limits for maximum acid and peroxide values of cold-pressed and unrefined fats and oils as 4.0 mg KOH/g and 15 meq/kg, respectively. Considering the *Codex* requirements for acidity and peroxide index, only pracaxi oil was in agreement with both specifications, while all of the others samples were in agreement only with the peroxide index specification. The adopted methodology (AOCS Cd 8b-90) did not allow the peroxide value for bacuri fat and Brazil nut oil to be determined, due to the strong color of these oils. It is important to highlight the fact that the fats and oils studied here are not explicitly included in the *Codex Alimentarius* report. As reported by Rodrigues, Silva, Marsaioli, and Meirelles(2005), high temperature and high humidity, characteristics of the Amazon region climate, can affect quality and increase the free acidity of the oils. Thus, high values for acidity and peroxide index of the samples are directly related to the handling, processing and storage of the nuts and seeds. In general, to avoid losses of neutral oil, fats and oils with high acidity values should be submitted to the physical refining, while those with low acidity can follow the chemical refining.

Iodine values are related to the number of FA presenting unsaturation and high carbon chains, therefore the greater the amount of unsaturated FA, the higher these values. The highest values were observed in Brazil nut and patawa oils (91.1 and 75.9, respectively), since they are the samples with the highest PUFA contents.

Saponification is a measure of the average chain length of all FA present in the lipid. Since it is inversely proportional to the fatty acids average molecular weight, glycerides containing short-chain FA have higher saponification values than those with long chain FA (Walia, Rawat, Bhushan, Padwad, & Singh, 2014). This index ranged from 246.4 mg KOH/g (tucuma kernel fat) to 164.4 mg KOH/g (pracaxi oil). Brazil nut oil and bacuri fat reached intermediate saponification values (187.5 and 189.1 mgKOH/g, respectively) close to those of olive oil and buriti oil (O'Brien, 2009; Silva et al., 2009).

Unsaponifiable matter includes substances dissolved in fats and oils that cannot be saponified, such as higher aliphatic alcohols, tocopherols, sterols, phenols and pigments. The unsaponifiable matter found in bacuri fat (2.8%) is comparable to corn oil's, while all of the other samples have values close to those of palm, peanut and other refined oils (O'Brien, 2009; Pereira Lima et al., 2017).

OSI depends on the number and positions of double bonds (Knothe & Dunn, 2003). Even though bacuri fat had a significant MUFA content (Table 1), this fat presented the highest induction time (49.60 h). Such high stability is, probably, related to bacuri fat's high unsaponifiable matter (2.8%) and its saturated/unsaturated ratio (Table 1). Pracaxi and patawa oils had oxidative stabilities of 4.73 and 4.97 h OSI, respectively; these values are comparable to palm oil's. Murumuru had an oxidative stability of 18.0 h OSI, comparable to that of olive and buriti oils (Anwar, Bhanger, & Kazi, 2003; Silva et al., 2009). Brazil nut oil, the sample with the highest PUFA contents, had the lowest OSI.

Moisture can induce hydrolysis, increase free FA content and generate off-flavors, causing problems during the extraction and refining process (O'Brien, 2009).

Water contents in the assayed samples were lower than 0.2%, a low value, especially for crude oils.

Table 3

Psychochemical properties of the fats and oils.

Properties	Murumuru	Bacuri	Tucuma kernel	Brazil nut	Pracaxi	Patawa
Acid value (mg KOH/g)	5.16 ± 0.01	20.98 ± 0.18	10.91 ± 0.01	5.27 ± 0.01	2.63 ± 0.01	14.52 ± 0.10
Peroxide value (meq/kg)	2.26 ± 0.12	ND	2.14 ± 0.16	ND	12.42 ± 2.95	15.94 ± 3.17
Iodine value	13.12 ± 0.07	33.09 ± 0.08	12.05 ± 0.07	91.07 ± 0.01	65.21 ± 3.40	75.85 ± 0.08
Saponification value (mg KOH/g)	226.77 ± 23.29	189.10 ± 12.74	246.43 ± 3.45	187.48 ± 3.37	164.44 ± 0.81	174.12 ± 5.95
Unsaponifiable matter (%)	0.16 ± 0.10	2.83 ± 0.13	0.47 ± 0.02	0.45 ± 0.02	0.64 ± 0.07	0.81 ± 0.08
OSI (h) at 130 °C	18.01 ± 0.49	49.60 ± 0.65	3.87 ± 0.13	0.08 ± 0.01	4.73 ± 0.01	4.97 ± 0.01
Water content (%)	0.09 ± 0.01	0.16 ± 0.00	0.12 ± 0.01	0.14 ± 0.01	0.08 ± 0.01	0.17 ± 0.03

Values shown as mean ± SD of the replicates. ND: Not determined.

Table 4 shows kinematic viscosity, density, and trace metals contents of the tested samples. Kinematic viscosities and densities were evaluated at 40 °C (except in the case of bacuri fat, where viscosity was measured at 55 °C, above its melting point). Viscosity is a measure of resistance to flow of a liquid. It is also related to spreadability and sensorial perception of the fat. Bacuri fat had the lowest kinematic viscosity (28.28mm²/s). Since viscosity is directly proportional to the chain length of FA in the triglycerides (Roberta Ceriani et al., 2007; Hoekman, Broch, Robbins, Ceniceros, & Natarajan, 2012) and inversely proportional to temperature, the high short chain length FA contents of bacuri fat (70.17% of FA ≤ C16) and the higher temperature in which its viscosity was measured (55 °C) might explain the low viscosity values of this sample. Pracaxi oil (32.53% of FA ≥ C20) exhibited the highest viscosity (48.85 mm²/s), which is in agreement with the value reported by Pereira Lima et al (2017).

The density of vegetable oils and fats has been reported to be directly proportional to the degree of unsaturation and inversely proportional to the chain length of the FA in its composition (Hoekman et al., 2012). Values obtained for the samples ranged from 904.17 g/cm³ to 894.13 g/cm³. Notably, the range of densities was small, in agreement with results reported by Ceriani et al (2008) for pure fatty compounds and other oils.

Metals cause deterioration of the product's quality and can be encountered throughout the processing of edible fats and oils (O'Brien, 2009). Notable among these metals are iron, calcium, and magnesium. Contents of these three trace metals in all of the samples, except for bacuri fat, were low, comparable to olive oil (Benincasa, Lewis, Perri, Sindona, & Tagarelli, 2007). Brazil nut oil and patawa oil samples presented phosphorus contents lower than 1 mg/kg, while the other fats and oils presented levels between 20 and 32 mg/kg. Since a phosphorus content lower than 5 mg/kg is one of the requirements for physical refining (O'Brien, 2009), all of the samples, except for Brazil nut and patawa oils, would demand industrial degumming processes, such as water degumming, in order to control phosphorus contents (Dijkstra & Segers, 2007).

Table 4

Trace metals contents, kinematic viscosity, and density of the fats and oils

Samples	Ca (mg/kg)	Fe (mg/kg)	Ma (mg/kg)	P (mg/kg)	KV, 40 °C (mm ² /s)	Density, 40 °C (kg/m ³)
Murumuru	5.79 ± 0.05	4.71 ± 0.05	6.13 ± 0.05	32.5 ± 0.46	29.0 ± 1.65	904.17 ± 0.01
Bacuri	36.50 ± 5.69	59.70 ± 0.65	95.00 ± 1.89	20.50 ± 0.29	28.28 ± 1.68*	894.19 ± 0.01*
Tucuma kernel	5.71 ± 0.69	7.45 ± 0.56	4.35 ± 0.32	20.1 ± 1.70	30.5 ± 1.77	904.15 ± 0.01
Brazil nut	0.15 ± 0.00	0.20 ± 0.01	0.26 ± 0.02	< 0.1	40.80 ± 2.13	904.05 ± 0.01
Pracaxi	8.96 ± 0.19	1.67 ± 0.05	5.60 ± 0.21	18.1 ± 0.48	48.85 ± 2.69	894.13 ± 0.01
Patawa	0.13 ± 0.01	0.90 ± 0.01	0.71 ± 0.07	0.68 ± 0.03	38.96 ± 2.15	900.03 ± 0.02

Values shown as mean ± SD of the replicates. Ca: Calcium; Fe: Iron; Ma: Magnesium; P: Phosphorus; KV: Kinematic viscosity. * Kinematic viscosity and density of bacuri fat measured at 55 °C.

3.3. Solid fat content (SFC)

Solid fat content (SFC) is a measure of the crystalline fat in a sample. Figure 1 shows the solid fat contents of murumuru fat, tucuma kernel fat and bacuri fat analyzed by NMR. The others oils were not evaluated because they are liquid at room temperature.

Increasing temperature caused large reductions in SFC of all samples. However, the slope of the SFC curves suggested that are differences in TAGs solubilities. At 10 °C, SFC of murumuru fat and tucuma kernel fat were quite close (80 % SFC, approximately), and SFC of bacuri fat was slightly lower (70% SFC, approximately). However, when the temperature was raised from 10 °C to 30 °C bacuri fat exhibited the

smoothest decay in solid content through temperature increase. In fact, at 35 °C, murumuru fat and tucuma kernel fat were completely liquid, while bacuri fat still presented 22.19 % SFC. The high SFC value at 35 °C of bacuri fat means incomplete melting at body temperature. On the other hand, this low plasticity could be useful for room temperature storage. SFC content at 35 °C of bacuri fat is comparable to those required for dairy analog shortenings, for example, used for industrial cakes or cookies (O'Brien, 2009). This suggests that bacuri fat might substitute partially hydrogenated oils, known for their high trans fat content, in shortening formulations.

Tucuma kernel fat and murumuru fat presented SFC between 2.0 % and 4.0 % at 33.3 °C, comparable to SFC values required for margarine oils formulation (O'Brien, 2009). Murumuru fat, particularly, presented SFC curve rather similar to those of cocoa butter (Torbica, Jovanovic, & Pajin, 2006), indicating that this product might be also applied as a cocoa butter equivalent.

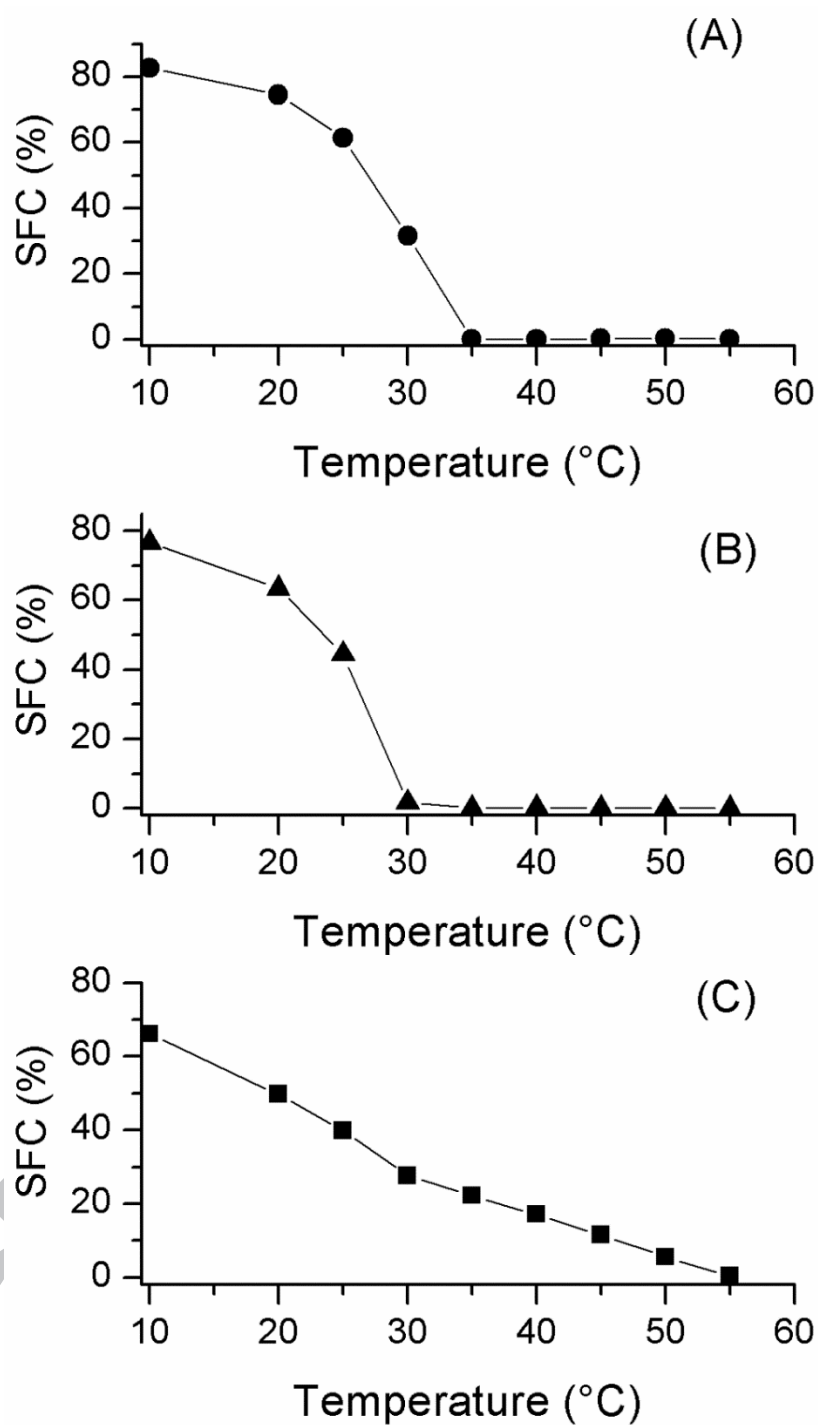


Figure 1: Solid fat contents of murumuru fat (A), tucuma kernel fat (B) and bacuri fat (C).

3.4. Differential Scanning Calorimetry (DSC)

3.4.1. Pure fats and oils

Figure 2 shows crystallization and melting curves, while Table S1 in Supplementary material shows a complete table for melting and crystallization peaks of pure fats and oils. Multiple and overlapped peaks were observed in crystallization and melting curves of Brazil nut oil, pracaxi oil, and bacuri fat. This behavior is probably due to the variety of TAGs present in the composition of these lipids, including differences in the carbon length and saturation grade. Multiple endothermic events were also reported in the publication of Pardaul et al.(2017), where the authors studied thermal profiles of vegetable oils from Amazon region.

In fact, the crystallization curve of these three lipids exhibited two distinct exothermic peaks. The first probably occurred due to presence of TAGs composed of SFA, and the second due to crystallization of TAGs containing MUFA and PUFA. For pracaxi oil these two fractions might correspond to a fraction rich in behenic and lignoceric acids (crystallization at 5.55 °C), and other rich in tri-unsaturated TAGs with oleic and linoleic acids (crystallization at -43.22 °C). For Bacuri oil, these two fractions might correspond to a fraction rich in palmitic acid (crystallization at 25.80 °C) (PPP/PPoP/POP), and another fraction rich in oleic acid (crystallization at 1.23 °C) (PPoO/OOP). In case of Brazil nut oil, one fraction is probably rich in TAGs with palmitic and stearic acids (crystallization at -0.38 °C) (POLi/SOLi) and the other fraction might correspond to tri-unsaturated TAGs with oleic and linoleic acids (crystallization at -60.78 °C). Such fractions might present particular physical

properties that should be investigated more carefully in order to improve the use of these fats and oils in technological applications.

According to the heating curves obtained, pracaxi and Brazil nut oils were fully melted close to 25 °C. This value is close to the melting point of OOBe and OOP (Wesdorp et al., 2005), TAGs with the highest melting temperature in these oils.

Concerning bacuri fat, the melting curve presented a clear recrystallization event (exothermic transition) between the melting of the two main TAG factions. The presence of both endo- and exothermic peaks in the DSC melting indicates that TAG molecules have transitioned from one crystal form into another (Tolstorebrov, Eikevik, & Bantle, 2014). Bacuri fat's last solid fraction melted at 56.79 °C, which is consistent to the melting point of the β' -modification of PPP (Wesdorp et al., 2005).

On the other hand, patawa oil, tucuma kernel fat and murumuru fat presented sharper and more defined crystallization and melting events. This is probably due to their more homogeneous FA content. Patawa has a high content of oleic acid, while tucuma kernel fat and murumuru fat are rich in lauric and myristic acids.

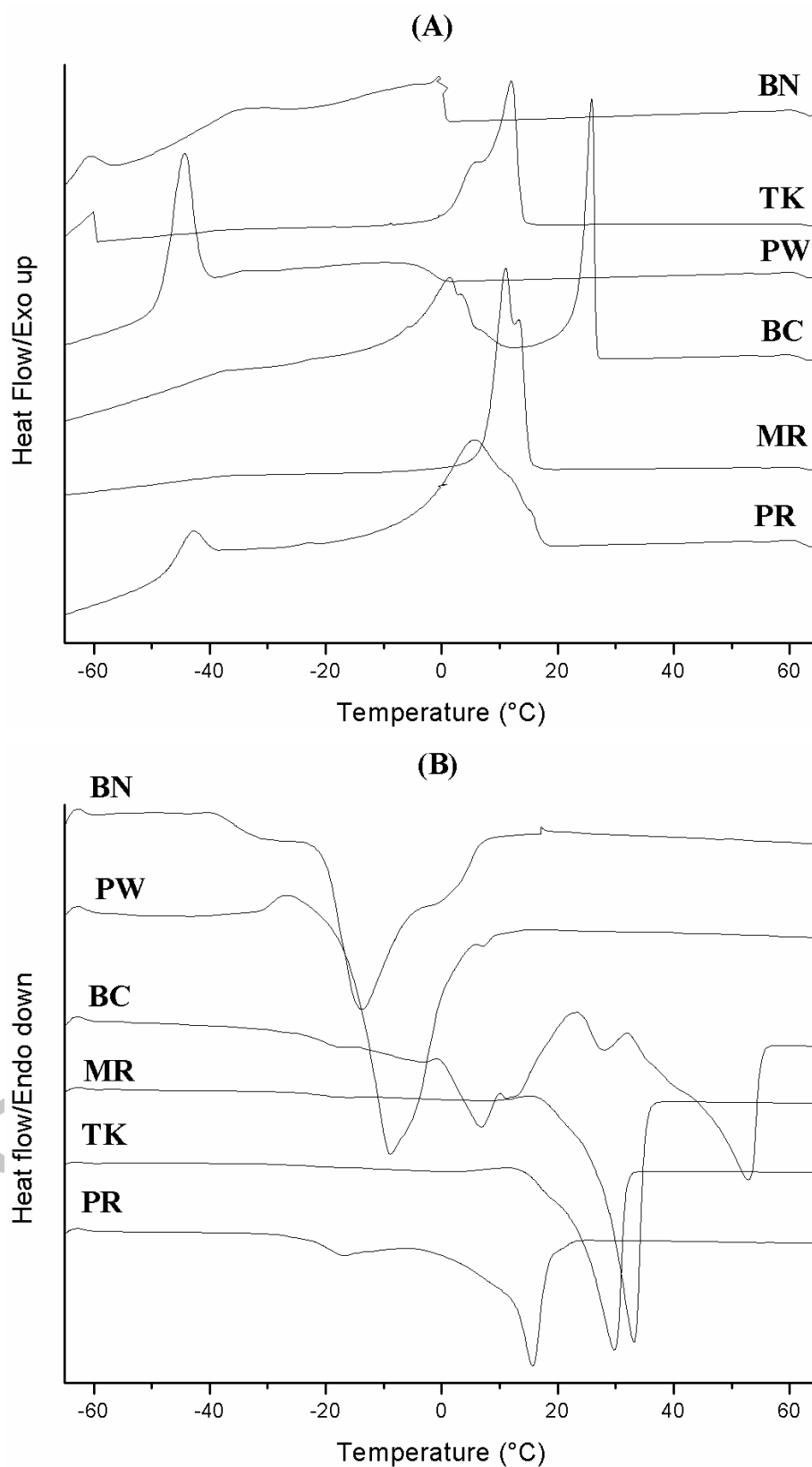


Figure 2: Crystallization (A) and melting curves (B) of pure fats and oils. BN: Brazil nut oil; PW: patawa oil; BC: bacuri fat; MR: murumuru fat; TK: tucuma kernel fat; PR: pracaxi oil.

3.4.2. Blends of fats and oils

In order to match the more adequate melting profile for product formulation, such as for margarine, modified butter, and cocoa replacers, fats with a high melting point can be blended with oils (Oliveira, Rodrigues, Bezerra, & Silva, 2017). Taking into account that MUFA, PUFA, and SFA are present in different ratios in Amazon crude fats and oils, particular FA profiles can be obtained with their blends.

Table S2 (Supplementary Material) shows the calculated FA compositions, atherogenicity, and thrombogenicity indexes for the blends prepared during the course of this study. As expected, addition of oils to the solid fats reduced AI and TI. Tucuma kernel fat, for instance, had its AI reduced from 14.31 to 7.97 with the addition of 10% patawa oil and to 1.89 at 50:50 ratio. Similar results were obtained for murumuru fat and pracaxi oil blends, in which AI/TI were reduced from 14.60/6.69 to 2.40/1.21 at 50:50 ratio blend. These results are quite important since the use of these blends in replacement of partially hydrogenated oils in formulations of spreads, shortenings or margarines, for example, might present not only technological advantages but also improved nutrition values.

Figures S1 to S3 (Supplementary Material) show the melting curves of the blends. All blends showed multiple endothermic peaks related to the variety of TAGs in their compositions. The melting curve of tucuma kernel fat/patawa oil blend presented two main endothermic peaks in all ratios. The first probably corresponded to the melting of OOO and OOP fractions from patawa oil, and the second was probably related to the melting points of LLL, LLM, and MML fractions, the main saturated TAGs of tucuma kernel fat. As expected, the enthalpy of the first peak decreased as the content of patawa oil decreased. The murumuru fat/pracaxi oil blends at the ratios of

50:50 and 60:40 exhibited two main peaks. The first was related to the melting of OOBe fractions, found in pracaxi oil, and the second (around 30 °C) probably corresponded to the melting of TAG fractions rich in lauric and myristic acids from murumuru fat. Notably, at ratios from 70:30 to 90:10 only one main peak was found. This is probably due to the fact that the decreasing in pracaxi oil content decreased the melting enthalpy of fractions rich in unsaturated TAGs, promoting an overlapping of the two main peaks. This could be interesting if one desires a blend without phase separation considering storage conditions.

The melting behavior of Bacuri fat/Brazil nut oil blend was very close to the Bacuri fat melting profile. Indeed, one of the TAG fractions of bacuri fat is rich in oleic acid and presented melting temperatures very close those of Brazil nut oil fractions. However, when compared to Bacuri fat, the last melting peak of the blend was slightly decreased, especially at ratio of 50:50. This means that the fraction which melted around 53 °C in the pure bacuri fat sample, when blended with Brazil nut oil tended to melt around 46 °C. These results showed that one might decrease the melting temperature of bacuri fat and alter its melting profile by blending it to low melting TAGs, such as those observed in Brazil nut oil, broadening its range of industrial application.

4. Conclusion

Patawa, pracaxi and Brazil nut oils are natural sources of unsaturated fatty acids. While patawa oil stood out for its high oleic content, and the Brazil nut oil for its PUFA content, pracaxi oil proved to be a natural source of behenic acid, especially interesting due its neutral impact in serum lipid content. On the other hand, murumuru fat and

tucuma kernel fat are interesting lauric lipids, whereas bacuri fat presented a high content of tripalmitin, quite interesting for applications such as production of lipid nanoparticles. Concerning physiochemical properties, the high acidity and phosphorous values of some of the samples showed that optimal parameters for extraction of these fats and oils is an important demand, as well as, the evaluation of refining steps, such as neutralization, and degumming, in order to improve their quality indexes.

Solid fat content evaluation showed that murumuru fat and tucuma kernel fat could be interesting ingredients for applications which demand low solid content at body temperature, such as margarines, or used as cocoa butter replacers. On the other hand, bacuri fat exhibited a smooth SFC decay similar to shortenings SFC profiles.

The crystallization/melting patterns of the samples are quite particular. Pracaxi and Brazil nut oils, and bacuri fat presented fractions with separated crystallization/melting behavior. Meanwhile, patawa oil, tucuma kernel and murumuru fats presented sharper and low-range melting profiles. In this context, blends improved the spectrum of alternative melting profiles. The increasing presence of unsaturated TAGs in the solid fats expanded the melting range of the blends. Since melting range influences the texture of a fat, the blends developed here can be utilized in the creation of products with good mouth feel. For this purpose, it is essential to know the ratios of high and low melting TAGs of the blends. Overall, our findings provide new information, showing that the studied Amazon fats and oils may be suitable for developing new fatty products in the food industry.

Conflict of interest statement

The authors declare that they have no conflict of interest.

Acknowledgements

Ericsem Pereira thanks the São Paulo Research Foundation (FAPESP) (2017/16979-7) for the scholarship and financial support. The authors thank the national funding agencies FAPESP (2014/2152-0, 2016/08566-1 and 2017/16979-7), the National Council for Scientific and Technological Development (CNPq) (305870/2014-9 and 406963/2016-9), and FAEPEX-UNICAMP (3272/17) for their financial support and scholarships. The authors thank Espaço da Escrita – Pró-Reitoria de Pesquisa – UNICAMP – for the language services provided.

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