Physical Properties of Amazon Fats and Oils and their Blends

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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.

The seed of Brazil nut tree (*Bertholletiaexcelsa*) is considered one of the major economically and industrially relevant Amazonian seeds, presenting a high content of unsaturated fatty acids, which provides its oil with interesting nutritional characteristics (Chunhieng, Hafidi, Pioch, Brochier, & Didier, 2008).

Murumuru (*Astrocaryum murumuru*) is a native plant from the Amazon forest; its nuts present an exceptionally high oil content, around 40%, with a beneficial fatty acids (FA) ratio of ω3:ω6,attracting the interest of the fats and oils industry (Pereira Lima et al., 2017).

Tucuma (*Astrocaryum vulgare*) is also a native species, from north and northeast of Brazil, with fruits consisting of two main oleaginous fractions, the pulp and the kernel. While the pulp produces an orange oil rich in polyunsaturated FA, the kernel produces a fat rich in lauric and myristic acid (Bora, Narain, Rocha, De Oliveira Monteiro, & De Azevedo Moreira, 2001).

Bacuri (*Platonia insignis*), another Amazonian vegetable matrix, produces fruits composed of three main fractions: pulp, shell, and seed. The pulp can be consumed with either raw or processed foods such as juices, ice cream and jams. 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 subject of any previous report.

Pracaxi (*Pentaclethramacroloba*) is a northern Brazilian oil seed plant. Its fruits contain 4 to 8 seeds from which oil is extracted. This oil has a high content of ω6 and ω9 FA, and is considered a natural source of behenic acid (Pereira Lima et al., 2017).

Patawa (*Oenocarpusbataua*) is a lesser known palm tree from the Amazon region. The oil extracted from its pulp has a healthy FA content, presenting a ratio of 18.5/81.5 (w/w) saturated/unsaturated FA (A. M. da C. Rodrigues, Darnet, & Silva, 2010).

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, Kloek, & 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 oil, 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 oil, 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 oil + 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 μm; Agilent Technologies, USA), in the following operating conditions: Helium (carrier gas) at a flow rate of 1.78 mL/min, FID temperature of250°C, injector at 250°C, injection volume of 1 μL, 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

$$\mathrm{AI} = \frac{C12{:}0+4\times C14{:}0+C16{:}0}{\sum \mathrm{M\Upsilon\Phi A}+\sum \Phi\mathrm{A}\omega6+\sum \Phi\mathrm{A}\omega3} \quad (1)$$

$$\mathrm{TI} = \frac{C14{:}0+C16{:}0+C18{:}0}{(0.5\times\sum \mathrm{M\Upsilon\Phi A})+(0.5\times\sum \Phi\mathrm{A}\omega6)+(3\times\sum \Phi\mathrm{A}\omega3)} \quad (2)$$

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; *ΦAω6* and *ΦAω3* 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, Metrhom, 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). 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), using an automated micro viscometer (AMVn, AntonPaar, Austria) and a density meter (DMA 4500M, Anton Paar, Austria), 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 oil, 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 oil, murumuru and bacuri fats were found to be rich in SFA. Murumuru fat and tucuma kernel oil had a high content of lauric acid, meanwhile bacuri fat had a high content of palmitic acid. Tucuma kernel oil 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 oil 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

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 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 oil 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 oil 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.

Table 2

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 oil[b]	Murumuru fat[b]	Bacuri
$C_{39}H_{74}O_6$	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				

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

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 longe chain FA (Walia, Rawat, Bhushan, Padwad, & Singh, 2014). This index ranged from 246.4 mg KOH/g (tucuma kernel oil) 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.

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

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)
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. ND: Not determined.

Table 4 shows kinematic viscosity, density, and trace metals contents of the tested samples. Density and viscosities were measured at a temperature in with all samples were liquid (40°C), except for bacuri fat, completely melted after 55°C. 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 (28.28 mm^2/s). Since viscosity is directly proportional to the chain length of FA in the triglycerides (Hoekman, Broch, Robbins, Ceniceros, & Natarajan, 2012), the high short chain length FA contents of bacuri fat (70.17% of FA [?] C16) explains the low viscosity values of this sample. Pracaxi oil (32.53% of FA [?] C20) exhibited the highest viscosity (48.85 mm^2/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/cm^3 to 894.13 g/cm^3. 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
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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 oil 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 oil 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 oil were completely liquid, while bacuri fat still presented 22.19 % SFC. Considering this fat, the high SFC value at 35 °C 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 oil 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.

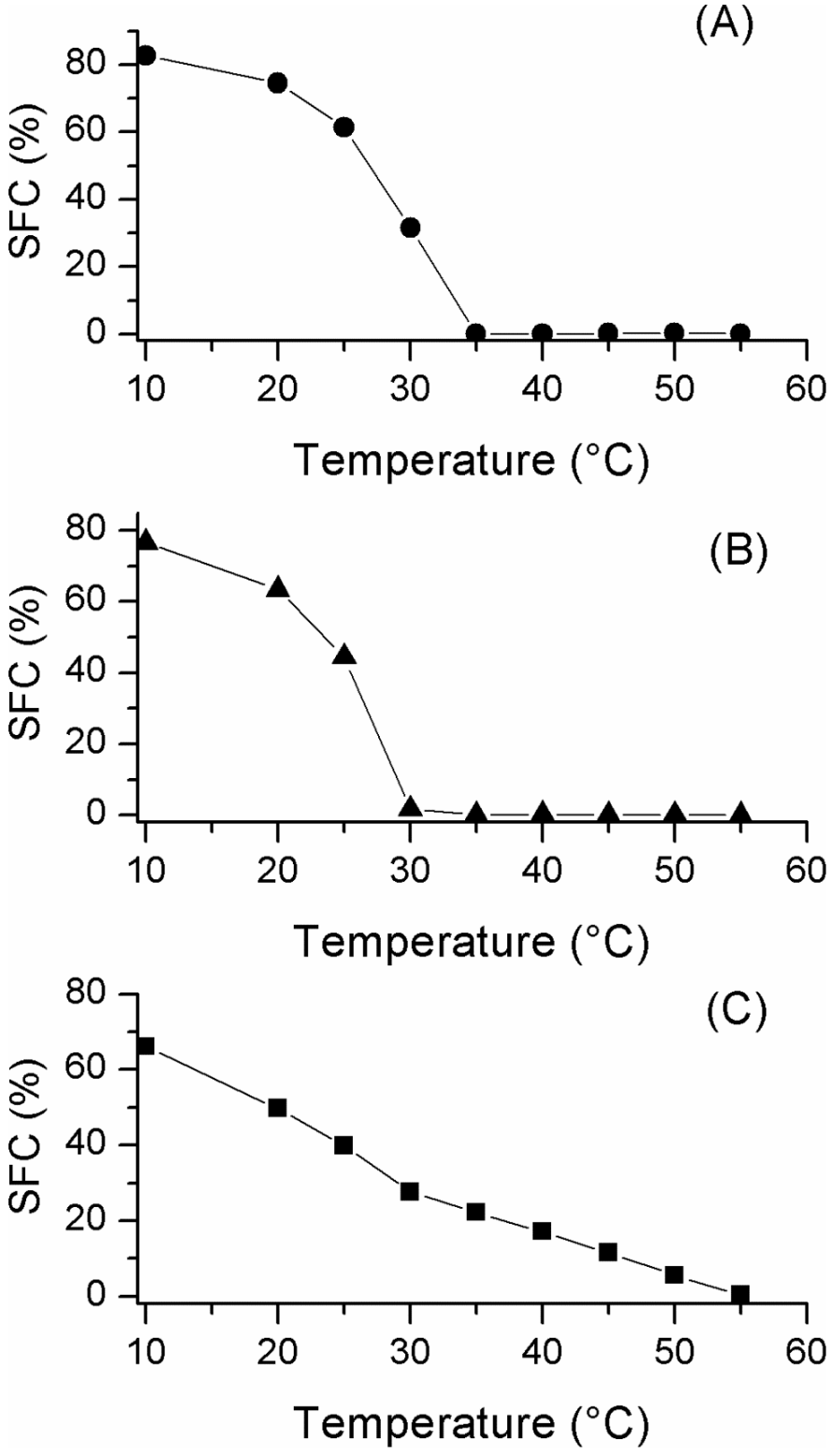

Figure 1 : Solid fat contents of murumuru fat (A), tucuma kernel oil (B) and bacuri fat (C).

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 by Pardauil et al.(2017), who 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 ^{o}C), and other rich in tri-unsaturated TAGs with oleic and linoleic acids (crystallization at -43.22 ^{o}C). For Bacuri oil, these two fractions might correspond to a fraction rich in palmitic acid (crystallization at 25.80 ^{o}C) (PPP/PPoP/POP), and another fraction rich in oleic acid (crystallization at 1.23 ^{o}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 ^{o}C) (POLi/SOLi) and the other fraction might correspond to tri-unsaturated TAGs with oleic and linoleic acids (crystallization at -60.78 ^{o}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 oil 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 oil and murumuru fat are rich in lauric and myristic acids.

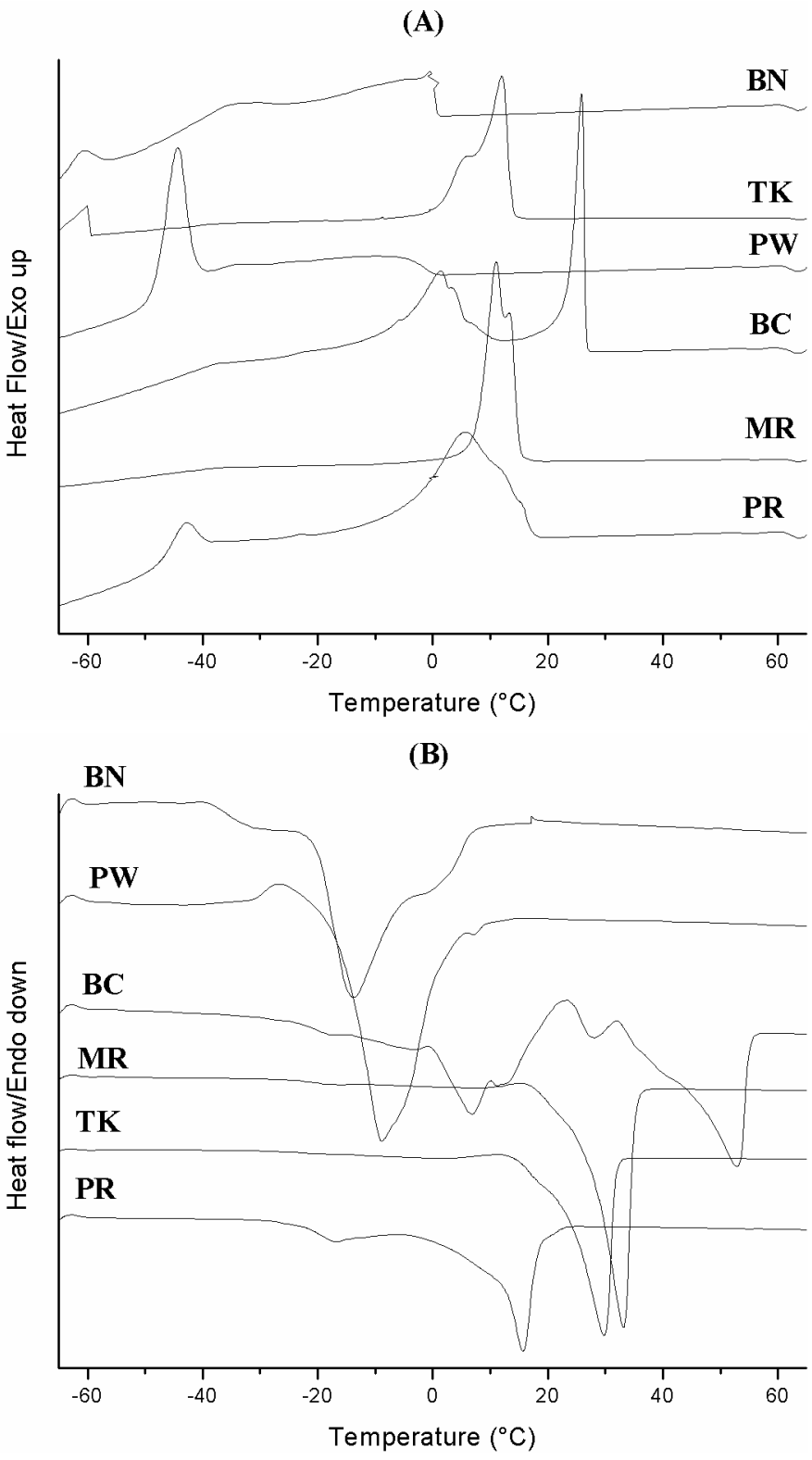

Figure 2: Crystallization (A) and melting curves (B) of pure fats and oils. BN: Brazil nut oil; PW: patawa

oil; BC: bacuri fat; MR: murumuru fat; TK: tucuma kernel oil; 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 oil, 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 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 oil/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 oil. 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 50:50 ratio. 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 oil 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 oil 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. While pracaxi and Brazil nut oils, and bacuri fat presented fractions with separated crystallization/melting behavior, patawa and tucuma kernel oils, and murumuru fat 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 mouthfeel. 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.

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References

Antoniosi Filho, N. R., Mendes, O. L., & Lanças, F. M. (1995). Computer prediction of triacylglycerol composition of vegetable oils by HRGC. *Chromatographia* , *40* (9–10), 557–562. https://doi.org/10.1007/BF02290268

Anwar, F., Bhanger, M. I., & Kazi, T. G. (2003). Relationship between rancimat and active oxygen method values at varying temperatures for several oils and fats. *Journal of the American Oil Chemists' Society* , *80* (2), 151–155. https://doi.org/10.1007/s11746-003-0668-2

AOCS. (2009). *Official Methods and Recommended Practices of the AOCS* . (D. Firestone, Ed.) (6th ed.). Urbana: American Oil Chemists' Society.

ASTM. (2013). *ASTM D5185-13, Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) .Annual Book of Standards* . West Conshohocken: ASTM International. https://doi.org/10.1520/D5185

Benincasa, C., Lewis, J., Perri, E., Sindona, G., & Tagarelli, A. (2007). Determination of trace element in Italian virgin olive oils and their characterization according to geographical origin by statistical analysis. *Analytica Chimica Acta* , *585* (2), 366–370. https://doi.org/10.1016/j.aca.2006.12.040

Bezerra, C. V., Rodrigues, A. M. da C., de Oliveira, P. D., da Silva, D. A., & da Silva, L. H. M. (2017). Technological properties of amazonian oils and fats and their applications in the food industry. *Food Chemistry* , *221* , 1466–1473. https://doi.org/10.1016/j.foodchem.2016.11.004

Bora, P. S., Narain, N., Rocha, R. V. M., De Oliveira Monteiro, A. C., & De Azevedo Moreira, R. (2001). Characterisation of the Oil and Protein Fractions of Tucuma (Astrocaryum Vulgare Mart.) Fruit Pulp and Seed Kernel. *Ciencia y Tecnologia Alimentaria* , *3* (2), 111–116. https://doi.org/10.1080/11358120109487654

Cater, N. B., & Denke, M. A. (2001). Behenic acid is a cholesterol-raising saturated fatty acid in humans. *The American Journal of Clinical Nutrition* , *73* (1), 41–44. https://doi.org/10.1093/ajcn/73.1.41

Ceriani, R., Paiva, F. R., Goncalves, C. B., Batista, E. A. C., & Meirelles, A. J. A. (2008). Densities and Viscosities of vegetable oils of nutritional value. *Journal of Chemical and Engineering Data* ,*53* (8), 1846–1853.

Chunhieng, T., Hafidi, A., Pioch, D., Brochier, J., & Didier, M. (2008). Detailed study of Brazil nut (Bertholletia excelsa) oil micro-compounds: phospholipids, tocopherols and sterols. *Journal of the Brazilian Chemical Society* , *19* (7), 1374–1380. https://doi.org/10.1590/S0103-50532008000700021

Codex Alimentarius. (1999). *Standard for Named Vegetabel Oils .Codex Stan 210* . Retrieved from http://www.fao.org/fao-who-codexalimentarius/sh-proxy/it/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FStandards%252FCODEX%1999%252FCXS_210e.pdf

Dijkstra, A. J., & Segers, J. C. (2007). Production and Refining of Oils and Fats. In F. D. Gunstone, J. L. Harwood, & A. J. Dijkstra (Eds.), *The Lipid Handbook* (Third, pp. 143–251). Boca Raton: CRC Press.

Edem, D. O. (2002). Palm oil: Biochemical, physiological, nutritional, hematological and toxicological aspects: A review. *Plant Foods for Human Nutrition* , *57* (3/4), 319–341. https://doi.org/10.1023/A:1021828132707

Hartman, L., & Lago, R. C. A. (1973). Rapid Preparation of Fatty Acid Methyl Esters from Lipids. *Laboratory Practices* ,*22* (January), 475–476.

Hiane, P. A., Bogo, D., Ramos, M. I. L., & Ramos Filho, M. M. (2003). Carotenóides pró-vitamínicos A e composição em ácidos graxos do fruto e da farinha do bacuri (Scheelea phalerata Mart.). *Ciência e Tecnologia de Alimentos* , *23* (2), 206–209. https://doi.org/10.1590/S0101-20612003000200018

Hoekman, S. K., Broch, A., Robbins, C., Ceniceros, E., & Natarajan, M. (2012). Review of biodiesel composition, properties, and specifications.*Renewable and Sustainable Energy Reviews* , *16* (1), 143–169. https://doi.org/10.1016/j.rser.2011.07.143

Knothe, G., & Dunn, R. O. (2003). Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals. *Journal of the American Oil Chemists' Society* ,*80* (10), 1021–1026. https://doi.org/10.1007/s11746-003-0814-x

Maguire, L. S., O'Sullivan, S. M., Galvin, K., O'Connor, T. P., & O'Brien, N. M. (2004). Fatty acid profile, tocopherol, squalene and phytosterol content of walnuts, almonds, peanuts, hazelnuts and the macadamia nut. *International Journal of Food Sciences and Nutrition* , *55* (3), 171–178. https://doi.org/10.1080/09637480410001725175

Marina, A. M., Che Man, Y. B., Nazimah, S. A. H., & Amin, I. (2009). Chemical Properties of Virgin Coconut Oil. *Journal of the American Oil Chemists' Society* , *86* (4), 301–307. https://doi.org/10.1007/s11746-009-1351-1

O'Brien, R. D. (2009). *Fats and Oils: Formulating and Processing for Applications* (Third). Boca Raton: CRC Press.

Oliveira, P. D., Rodrigues, A. M. C., Bezerra, C. V., & Silva, L. H. M. (2017). Chemical interesterification of blends with palm stearin and patawa oil. *Food Chemistry* , *215* , 369–376. https://doi.org/10.1016/j.foodchem.2016.07.165

Pardauil, J. J. R., de Molfetta, F. A., Braga, M., de Souza, L. K. C., Filho, G. N. R., Zamian, J. R., & da Costa, C. E. F. (2017). Characterization, thermal properties and phase transitions of amazonian vegetable oils. *Journal of Thermal Analysis and Calorimetry* ,*127* (2), 1221–1229. https://doi.org/10.1007/s10973-016-5605-5

Pereira Lima, R., Souza da Luz, P. T., Braga, M., dos Santos Batista, P. R., Ferreira da Costa, C. E., Zamian, J. R., ... da Rocha Filho, G. N. (2017). Murumuru (Astrocaryum murumuru Mart.) butter and oils of buriti (Mauritia flexuosa Mart.) and pracaxi (Pentaclethra macroloba (Willd.) Kuntze) can be used for biodiesel production: Physico-chemical properties and thermal and kinetic studies. *Industrial Crops and Products* , *97* , 536–544. https://doi.org/10.1016/J.INDCROP.2016.12.052

Reddy, L. H., Sharma, R. K., Chuttani, K., Mishra, A. K., & Murthy, R. R. (2004). Etoposide-incorporated tripalmitin nanoparticles with different surface charge: Formulation, characterization, radiolabeling, and biodistribution studies. *The AAPS Journal* , *6* (3), 55–64. https://doi.org/10.1208/aapsj060323

Rodrigues, A. M. da C., Darnet, S., & Silva, L. H. M. da. (2010). Fatty acid profiles and tocopherol contents of buriti (Mauritia flexuosa), patawa (Oenocarpus bataua), tucuma (Astrocaryum vulgare), mari (Poraqueiba paraensis) and inaja (Maximiliana maripa) fruits. *Journal of the Brazilian Chemical Society* , *21* (10), 2000–2004. https://doi.org/10.1590/S0103-50532010001000028

Rodrigues, C. E. C., Silva, F. A., Marsaioli, A., & Meirelles, A. J. A. (2005). Deacidification of Brazil Nut and Macadamia Nut Oils by Solvent Extraction: Liquid-Liquid Equilibrium Data at 298.2 K. *Journal of Chemical & Engineering Data* , *50* (2), 517–523. https://doi.org/10.1021/je049687j

Santos, M. T. dos, Morgavi, P., & Le Roux, G. A. C. (2018). Exploring amazonian fats and oils blends by computational predictions of solid fat content. *OCL* , *25* (1), D107. https://doi.org/10.1051/ocl/2017055

Saraiva, S. A., Cabral, E. C., Eberlin, M. N., & Catharino, R. R. (2009). Amazonian vegetable oils and fats: Fast typification and quality control via triacylglycerol (TAG) profiles from dry matrix-assisted laser desorption/lonization time-of-flight (MALDI-TOF) mass spectrometry fingerprinting. *Journal of Agricultural and Food Chemistry* ,*57* (10), 4030–4034. https://doi.org/10.1021/jf900043u

Silva, S. M., Sampaio, K. A., Taham, T., Rocco, S. A., Ceriani, R., & Meirelles, A. J. A. (2009). Characterization of oil extracted from buriti fruit (Mauritia flexuosa) grown in the Brazilian Amazon Region. *JAOCS, Journal of the American Oil Chemists' Society* ,*86* (7), 611–616. https://doi.org/10.1007/s11746-009-1400-9

Smith, S. A., King, R. E., & Min, D. B. (2007). Oxidative and thermal stabilities of genetically modified high oleic sunflower oil. *Food Chemistry* , *102* (4), 1208–1213. https://doi.org/10.1016/j.foodchem.2006.06.058

Tan, C. ., & Che Man, Y. . (2002). Differential scanning calorimetric analysis of palm oil, palm oil based products and coconut oil: effects of scanning rate variation. *Food Chemistry* , *76* (1), 89–102. https://doi.org/10.1016/S0308-8146(01)00241-2

Tolstorebrov, I., Eikevik, T. M., & Bantle, M. (2014). A DSC determination of phase transitions and liquid fraction in fish oils and mixtures of triacylglycerides. *Food Research International* ,*58* , 132–140. https://doi.org/10.1016/j.foodres.2014.01.064

Torbica, A., Jovanovic, O., & Pajin, B. (2006). The advantages of solid fat content determination in cocoa butter and cocoa butter equivalents by the Karlshamns method. *European Food Research and Technology* ,*222* (3–4), 385–391. https://doi.org/10.1007/s00217-005-0118-7

Ulbricht, T. L. V., & Southgate, D. A. T. (1991). Coronary heart disease: seven dietary factors. *The Lancet* , *338* (8773), 985–992. https://doi.org/10.1016/0140-6736(91)91846-M

Walia, M., Rawat, K., Bhushan, S., Padwad, Y. S., & Singh, B. (2014). Fatty acid composition, physicochemical properties, antioxidant and cytotoxic activity of apple seed oil obtained from apple pomace. *Journal of the Science of Food and Agriculture* , *94* (5), 929–934. https://doi.org/10.1002/jsfa.6337

Walstra, P., Kloek, W., & van Vliet, T. (2001). Fat Crystal Network. In N. Garti & K. Sato (Eds.), *Crystallization Processes in Fats and Lipid Systems* (pp. 289–328). New York: Marcel Dekker Inc.

Wesdorp, L. H., Van Meeteren, J. A., De Jong, S., Giessen, R. V. D., Overbosch, P., Grootscholten, P. A. M., ... Don, A. (2005). Liquid-Multiple Solid Phase Equilibria in Fats: Theory and Experiments. In A. G. Marangoni (Ed.), *Fat Crystal Networks* (pp. 481–709). Boca Raton: Marcel Dekker Inc. Retrieved from http://www.crcnetbase.com/doi/abs/10.1201/9781420030549.ch15

Yang, Z.-H., Miyahara, H., & Hatanaka, A. (2011). Chronic administration of palmitoleic acid reduces insulin resistance and hepatic lipid accumulation in KK-Ay Mice with genetic type 2 diabetes. *Lipids in Health and Disease* , *10* (1), 120. https://doi.org/10.1186/1476-511X-10-120