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Chemical interesterification of blends with palm stearin and patawa oil

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ABSTRACT

The present study sought to develop lipid bases from blends between patawa oil and palm stearin. These blends were analyzed before and after the chemical interesterification process for their fatty acid and triacylglycerol composition, free fatty acid (FFA) content, peroxide index, thermal properties, melting point, consistency, and solid fat content (SFC). Blends with unsaturated fatty acid contents between 60 and 70% were obtained, with a good ratio between saturated and unsaturated fatty acids, which indicates a healthy content of fatty acids. Variations in the triacylglycerol contents and melting and crystallization thermograms evidenced the reaction. The blend with 50% stearin and 50% patawa oil showed the best results after the chemical interesterification reaction regarding the possible application in fatty products for its appropriate melting point, SFC similar to that of soft table margarines, plastic and spreadable consistency at refrigeration temperature, thus combining physical and nutritional properties desirable for the food industry.

1. Introduction

Recently, the interesterification of edible oils and fats and their blends has been researched and considered by several studies as a great alternative to produce commercial fats free of trans fatty acids and to improve the physical properties of fats and oils. (Dinç, Javidipour, Ozbaz, & Tekin, 2011; Fauzi, Rashid, & Omar, 2013). This process involves the redistribution of fatty acids among the triacylglycerols, which can take place within the same molecule or among different molecules (Osborn & Akoh, 2002).

Those studies often employ palm stearin. Stearin is the high-melting-point solid fraction obtained by fractioning palm oil at controlled temperature and has a broad range of triacylglycerols with different melting profiles. Due to its versatile composition in fatty acids and triacylglycerols, it is an excellent raw material for interesterification, producing a host of products such as margarines, vegetable fats, cookies, ice cream, chocolates, and cakes (Adhikari et al., 2010). However, stearin's high melting point (44–56 °C) causes problems in the manufacture of problems by resulting in products with low plasticity and incomplete melting at body temperature. In order to improve its melting properties, several studies have been carried involving the blend and/or interesterification of stearin with other oils whose melting profiles are more appropriate to those products (Da Silva et al., 2010; Fauzi et al., 2013; Zhu et al., 2012, among others).

The literature on crude oils typical of the Amazon and their structural changes is relatively scarce. The Amazon forest is very rich in oily fruits, which represents a great economic potential for the region. Patawa oil is extracted by boiling the fruits followed by collection of the lipid supernatant and is rich in monounsaturated fatty acids (MUFAs), particularly oleic acid (C18:1). The ratio of saturated to unsaturated fatty acids in patawa oil is similar to that of olive oil, which represents a more healthful fatty acid ratio (Darnet, Meller, Rodrigues, & Lins, 2011; Ferreira et al., 2011; Montufar et al., 2010; Rodrigues, Darnet, & Silva, 2010). The fatty acid composition also enables assessing the nutritional quality index of the lipid fraction through the atherogenicity (AI) and thrombogenicity (TI) indices. Those indices indicate the potential for platelet aggregation stimulation, that is, the lower the AI and TI values, the higher the content of antiatherogenic fatty acids in a given oil/fat (Tonial et al., 2011). AI and TI values greatly vary according to the raw material studied and particularly the fatty acid profile (Barros et al., 2013; Filho, Ramos, Hiane, & Souza, 2008).

In face of that, the present study sought to develop lipid bases from blends between patawa oil and palm stearin at different ratios aiming to obtain a product with better physical and chemical properties and desirable functionality to be applied in the food, cosmetic, and pharmaceutical industries.

2. Materials and methods

2.1. Material

The raw materials used were crude patawa oil, obtained from cooperatives in the cities of Salvaterra (PA, Brazil) and Cametá (PA, Brazil), and refined palm stearin provided by the *Companhia*

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Refinadora da Amazônia (Refining Company of the Amazon – CRA) AGROPALMA (PA, Brazil). The raw materials were kept in 500 mL amber flasks and stored at −10 °C for later use.

2.2. Methods

All analyses were performed in triplicate and the chemical interesterification reaction was performed in duplicate.

2.2.1. Blend preparation

The samples were prepared as binary blends between palm stearin and patawa oil (w/w) at different ratios (palm stearin/patawa oil: 30:70, 40:60, 50:50, and 60:40). This step was carried out after the samples were fully melted at 70 °C ± 1 °C and homogenized for 10 min. The blends were stored under refrigeration (5 °C ± 1 °C).

2.2.2. Chemical interesterification

For the interesterification reaction, 100 g of the blend were previously dried in a 250 mL three-necked flask with magnetic stirring under reduced pressure in a water bath at 80–85 °C for 30 min. After drying, 1% (m/m) of powdered sodium methoxide (Sigma-Aldrich/95% purity) catalyzer was added to the blend. The interesterification reaction was carried out under constant magnetic stirring at 400 rpm and reduced pressure (20–30 mmHg) in the three-necked flask immersed in a water bath at 70 °C for 1 h. The reaction was interrupted by adding 5 mL distilled water at 60 °C. Finally, the blend underwent hot filtration under vacuum using filter paper and 5 g anhydrous sodium sulfate to retain moisture. After filtration, the blend was dried under the same initial conditions.

2.2.3. Free fatty acid (FFA)

Determined according to the official AOCS method Ca 5a-40 (1997).

2.2.4. Peroxide index

Determined according to the official AOCS method Ca 8-53 (1997).

2.2.5. Fatty acid composition

Fatty acid composition was determined by converting the fatty acids into methyl esters (FAMEs) based on the method proposed by Rodrigues et al. (2010) and detected using a gas chromatograph (CG) (Varian model CP-3380) equipped with a flame ionization detector (FID) and a CP-Sil 88 capillary column (length 60 m, internal diameter 0.25 mm, film thickness 0.25 μm; Varian Inc., USA). The process conditions were: helium as carrier gas with 0.9 mL/min flow, FID at 250 °C, injector (1:100 split ratio) at 245 °C, and injection volume of 1 μL. The column's temperature was programmed to 4 min at 80 °C followed by an increase to 220 °C at 4 °C/min. The peaks of individual fatty acids were identified by comparing the retention times of known mixtures of fatty acid standards (74X, Nu-check-prep, Inc., EUA) injected under the same operational conditions. The results were expressed as percentages relative to the total fatty acids.

2.2.6. Atherogenicity and thrombogenicity indices

The samples' atherogenicity index (AI) and thrombogenicity index (TI) were calculated according to Eqs. (1) and (2), respectively, as described by Ulbricht and Southgate (2001).

$$AI = \frac{C12{:}0 + 4xC14{:}0 + C16{:}0}{\sum MUFA + \sum \omega 6FA + \sum \omega 3FA} \tag{1}$$

$$TI = \frac{C14:0 + C16:0 + C18:0}{(0.5x\sum MUFA) + (0.5x\sum \omega 6FA) + (3x\omega 3FA)} \tag{2}$$

Parameters: C12:0 (lauric acid), C14:0 (myristic acid), C16:0 (palmitic acid), C18:0 (stearic acid), MUFA (monounsaturated fatty acids), ώ3FA (omega-3 fatty acids), and ώ6FA (omega-6 fatty acids).

2.2.7. Triacylglycerol composition

The triacylglycerol composition was determined by gas chromatography according to the official AOCS method (2009) using a capillary gas chromatograph (CGC Agilent 6850 Series Gc System). Capillary column: DB-17 HT Agilent Catalog: 122–1811 (50% phenyl – ethylpolysiloxane), length: 10 m, internal diameter: 0.25 mm, and film thickness: 0.15 μm. The operation conditions were: column flow = 1.0 mL/min; linear velocity = 40 cm/s; detector temperature: 375 °C; injector temperature: 360 °C; oven temperature: 250–350 °C (5 °C/min), 250 °C for 20 min; carrier gas: helium; injected volume: 1.0 μL at 1:100 split ratio; sample concentration: 10 mg/mL tetrahydrofuran.

2.2.8. Thermal analysis

The samples underwent thermal analysis through differential scanning calorimetry (DSC) according to the official AOCS method Cj1-94 (2004) using a DSC 8500 (Perkin Elmer) thermal analyzer. The DSC was calibrated with indium, lead, and tin as the reference standards provided by the supplier. A sample (5 mg) was hermetically sealed in an aluminium pan with an empty pan serving as reference. Briefly, the sample was rapidly heated from room temperature to 80 °C and held at that temperature for 10 min to erase the crystal memory; cooled to −60 °C at 10 °C/min and held for 10 min; then heated to 80 °C at 5 °C/min to find the crystallization and melting profiles. Heating and cooling thermograms were recorded and used for the determination of temperature for the onset, completion, melting, and crystallization range and also for the melting and crystallization enthalpies. The peak areas were obtained using the software Pyris version 10.1.

2.2.9. Melting point

The blends' melting points were determined by the open capillary tube method, which was immersed in water under stirring and heating, according to AOCS method Cc 3-25 (2004).

2.2.10. Solid fat content

The solid fat content was analyzed using nuclear magnetic resonance (NMR) according to the official AOCS method 23 Cd 16b-93 (2004). The direct method was used with samples read in series at 10, 20, 25, 30, 35, and 40 °C.

2.2.11. Consistency

The blends' consistency was determined using a QTS-25 automated microprocessor-controlled texture analyzer (BROOKFIELD, USA) connected to a computer running the software Texture Pro® version 2.1. The blends were heated in a controlled-temperature water bath (60–70 °C) for the complete melting of the crystals and then stored in acrylic containers (internal diameter = 35 mm, height = 50 mm). The containers were stored for 24 h in a bacteriological incubator (5 °C) for sample stabilization and then stored for further 24 h in a bacteriological incubator at the temperatures for the analyses (5 °C, 10 °C, and 25 °C).

Consistency was analyzed through a penetration test using a 45° acrylic cone probe. The tests were carried out in triplicate under conditions of compression force determination, distance: 10.0 mm, speed: 2.0 mm/s, time: 5 s (D'agostini, Ferraz, & Gioielli, 2000)

Eq. (3), proposed by Haighton (1959), was used to convert the penetration data into a parameter independent on weight or cone type, which provided the yield value:

$$\mathrm{C} = \mathrm{K} \times \mathrm{W}/\mathrm{p}^{1.6} \tag{3}$$