Evaluation of oxidative stability, fatty acid profile and quality physico-chemical parameters of Brazil nut, coconut and Palm oils

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ABSTRACT

The aim of this study was to assess the oxidative stability (OS) of oils Brazil nuts, coconut and palm, as well as determine the quality parameters: acid value (AV), humidity, ash content, and fatty acid profile (FA). According to the results the oils of Brazil nuts, coconut and palm oil showed AV of 2.02, 2.49 and 5.92 mg KOH g⁻¹, humidity of 0.060, 0.101 and 0.040% and ash of 0.010, 0.005 and 0.009%, respectively. Considering FA, the Brazil nut oil showed greater amount of linoleic acid (38.61%) and oleic acid (31.95%) in its composition. While in coconut oil the major amounts were lauric acid (35.22%) and myristic (17.43%) and in the palm oil, oleic acid (48.30%) and palmitic (28.67%). The OS analysis showed that there is a relationship between the FA chemical composition of each oil and oxidative stability index (OSI) that relates to the resilience capacity to lipid degradation.

Keywords: Chromatography; Fatty acids; Industry
1 INTRODUCTION

Vegetable oils occupy large space in the consumer market with potential for the food, cosmetic and pharmaceutical areas. In addition to being used for energetic purposes, which provides new studies about extraction, production and evaluation of quality (FREITAS et al., 2007).

In Brazil, there is a wide range of oilseeds (RIPKE et al. 2016) with potential in the food industry. Among the wide variety of oils that can be found in the different Brazilian biomes, there are the oils of Brazil nuts, coconut and palm oil from the plants Bertholletia excelsa, Cocos nucifera, Elaeis guineenses, respectively. These oils have high nutritional value (CORREIA et al., 2014) and beneficial health properties, such as carotenoids, tocopherols and vitamins (FOOD INGREDIENTS BRASIL, 2014).

Vegetable oils consist mainly of condensing products between glycerol and fatty acids called triglycerides and may contain small amounts of phospholipids and free fatty acids (ANVISA, 2005). The oxidation processes in fatty foods are responsible for the reduction of shelf life in industrialized products, causing changes in quality parameters such as color, smell and taste. These oxidative processes can be accelerated by environmental factors (light, air and temperature) and the chemical components of each product (THODE et al., 2014).

Fatty acids are constituents of fats and oils in the form of mono, di and triglycerides. A large amount of free fatty acids indicates that the product is in accelerated degree of deterioration. In oils in which this process occurs there is an increase in acidity and viscosity, as well as darkening, foaming and flavor changes and undesirable smells (RIOS et al., 2013). Therefore, the acidity index is an important indication of quality, regulated by ANVISA (ANVISA, 2005).

The oxidative stability is also a parameter used in the assessment of quality of edible oils (TAN et al., 2002) and the stability difference between the different types of oils is related mainly with the presence of polyunsaturated fatty acids and the amount of tocopherols. The Rancimat method is an accelerated oxidation test that allows to characterize the conservation state of oils and fats with ease and repeatability of...
results (FARHOOSH; MOOSAVI, 2007), and consists in exposing the sample to an airflow and temperature set (METROHM, 2017). Throughout the analysis, these factors promote the deterioration of the material analyzed forming peroxides and hydroperoxides, which in turn originate from volatile compounds, such as aldehydes, ketones and carboxylic acids with low molecular weight.

To the best of our knowledge, there are not studies of OSI determination by Rancimat method for extra virgin coconut and palm oils produced by the food industry to be destined for human consumption. Since the quality of vegetable oils is directly related to their nutritional value, the aim of this study was to assess the oxidative stability by the accelerated oxidation Rancimat method of commercial oils of Brazil nuts, coconut and palm oil, as well as the quality parameters: acid value, humidity, ash content and fatty acid profile.

2 MATERIAL AND METHODS

2.1 Raw material

Extra virgin oils of Brazil nut, coconut and palm oil, from the Amazon and Northeast region of Brazil, were acquired commercially, stored in a dry, airy place, at room temperature, and protected from light.

2.2 Physico-chemical analysis

The oils were characterized according to the acid value (AV), ash content, humidity and acidity in oleic acid.

The AV was performed based on the potassium hydroxide (KOH) mass in milligrams, spent on the neutralization of the free acids present in 1 g of oil (ESTEVES et al., 1995; MORETTO; FETT, 1986). The ash content was determined by the percentage of minerals that remain after combustion and incineration of the oil (ESTEVES et al., 1995). The humidity analysis was determined according to EN ISO 8534 by the Karl Fischer method (METROHM, 2017).
2.3 Oxidative stability

Oxidative stability measures were performed according to the AOCS Cd 12b-92 method (metroHM, 2017). For this analysis, an oxidative stability Analyzer RANCIMAT 893 (METROHM, Switzerland) was employed. Samples were analyzed under constant airflow of 9 L h\(^{-1}\) at 110 °C and their respective volatile products were collected in a tube containing 50 mL of distilled water. Volatile oxidation products (mainly formaldehyde and short-chain acids) were absorbed by water, resulting in increased conductivity. Water conductivity was monitored in order to determine the Oxidative Stability Index (OSI), acquired for the time of maximum value of the 2nd derivative of conductivity curve in function of time by the software StabNet.

2.4 Fatty acids profile of vegetable oils

The fatty acid profile was determined by transesterification of 10 mg of biomass with 0.2 mL of chloroform: methanol (2:1 v/v) and 0.3 mL hydrochloric acid 0.6 mol L\(^{-1}\) in methanol heated at 85 °C in Dri-Block for 1 hour (WYCHEN et al., 2015), subsequently there was extraction of fatty acids methyl esters in 1 mL hexane and analysis by gas chromatography (AOAC, 2015). The methyl esters were identified by gas chromatography, GC-MS (Agilent Technologies, California, USA), coupled with a flame ionization detector (FID) and fused silica capillary column (100 m x 250 μm x 0.2 μm, Supelco SP). The operating parameters were: detector temperature of 260 °C, injector temperature of 260 °C, oven temperature of 140 °C for 5 minutes, programmed to increase 4 °C/min until 240 °C, with final time of 48 minutes, Helium was used as carrier gas at 1.2 mL min\(^{-1}\) and injection of 10 μL of sample. For identification, the retention times of the fatty acids were compared to those of the standard methyl esters (Sigma-Aldrich, St. Louis, MO, USA). The retention times and percentages of the peak area were calculated automatically by the ChemStation Software.
3 RESULTS AND DISCUSSION

3.1 Physico-chemical analysis

The composition and physico-chemical characteristics of vegetable oils determine their quality and employability. Table 1 shows the results expressed by mean and standard deviation (n = 3) of the physico-chemical analyses of oils of Brazil nuts, coconut and palm oil.

Table 1 - Physical and chemical characteristics of Brazil nut, coconut and palm oil

<table>
<thead>
<tr>
<th>Properties</th>
<th>Edible Vegetable Oils</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brazil nut</td>
</tr>
<tr>
<td>Acid value (mg KOH g-1)</td>
<td>2.02 ± 0.02</td>
</tr>
<tr>
<td>*Acid value (g of oleic acid 100g-1)</td>
<td>1.01 ± 0.01</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>0.060 ± 0.001</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>0.010 ± 0.002</td>
</tr>
</tbody>
</table>

* For conversion of Acid value to acidity in oleic acid, the acid value was divided by 1.99. Results expressed as mean ± S.D. of the three replicates.

According to the results, Brazil nut, coconut and palm oil showed AV of 2.02, 2.49 and 5.92 mg KOH g-1, humidity index of 0.060, 0.101 and 0.040% and ash content of 0.010, 0.005 and 0.009%, respectively. According to Muniz et al. (2015), the AV is one of the important parameters that demonstrate the quality of an oil. In this study the values found for acidity for the oils analyzed are below those established as maximum values by ANVISA (ANVISA, 2005) and by the Codex Alimentarius (Food and Agriculture Organization of the United Nations, 1981), which determine maximum values of 4.00 mg KOH g-1 for chestnut and coconut oil and 10.00 mg KOH g-1 for palm oil, which indicates the good qualities of these oils.

Muniz et al. (2015) obtained acidity value of 2.14 mg KOH g-1 for Brazil nut oil, similar to that found in this study of 2.02 ± 0.020 mg KOH g-1 for the same oil. Still regarding Brazil nut oil, Correia et al. (2016) obtained ash content of 0%, corroborating the results of this study, which showed 0.010%.
Regarding coconut oil, studies by Correia et al. (2014) showed values of acidity index of 4.48 mg KOH g⁻¹, higher than that obtained in the present study. According to Vieira et al. (2018), the high AV of an in natura oil is indicative of low-value-added seeds and improper storage or unsatisfactory processing. Martins and Santos (2015) and Silva Neto et al. (2013) in their studies with this same type of vegetable oil obtained humidity content of 0.26 and 0.38%, respectively, similar values to that found in this study, and ash content of 0.005%, equal to this study.

Regarding palm oil, the AV (expressed as mass of oleic acid) and humidity were analyzed in the study by Hayyan et al. (2014), who reported values of 8.8% and 1.4%, respectively, higher values than those found in this study, 2.97% and 0.040% respectively, indicating that the oil evaluated in this study has higher quality, and ash of 0.015%, a value similar to this study.

3.2 Analyses of oxidative stability

Figure 1 shows results of the oxidative stability index (OSI) for the three oil samples analyzed.

Figure 1 - Graphs of electrical conductivity versus time for determination of oxidative stability of oil samples of Brazil nut, coconut and palm oil
The thermal stability that forms the oil composition depends on the amount of saturations and unsaturations (GENNARO et al., 1998), so that unsaturated fatty acids are more sensitive to oxidation than those saturated (CURVELO et al., 2011). Free fatty acids and other substances, such as carotenoids, sterols, phospholipids, phenolic substances and tocopherol, were also pointed as responsible for the thermal stability (GENNARO et al., 1998). Brazil nut oil has in its composition a high level of unsaturation, 75.60% (CHUNHIENG et al., 2008) and showed OSI of 6.91 ± 0.28 h at 110 ºC (n = 3) in the present study. According to Metrohm (2017) in the Rancimat method the OSI values vary according to the temperature previously determined at the beginning of each analysis, and at each increase of 10 ºC at the analysis temperature the OSI values are reduced by approximately half. In similar studies of determination of OSI at 100 ºC, Santos et al. (2015) found values ranging from 12.73 to 14.85 h (equivalent approximately to 6.36 and 7.42 h, respectively, at 110 ºC) for the mentioned oil, values consistent with the present study. According to Queiroga Neto et al. (2009), this factor indicates a high resistance to oxidative degradation by this product due to the presence of high content of β-tocopherol, 88.30% (CURVELO et al., 2011), an important natural antioxidant.

Regarding the coconut oil the OSI was 49.13 ± 0.39 h, this value demonstrates a high stability to the temperature increase. Santos et al. (2013) in their studies confirmed the high content of saturated fatty acids of coconut oil, mainly due to the high content of lauric acid 34.16% (Table 2), which increases the oxidizing stability, since it is resistant to oxidation (LAWSON, 1999). The same happens with the result of OSI of palm oil, with 11.17 ± 0.19 h, which is composed mainly of palmitic acid (28.67%) and oleic acid (47.56%) (Table 2), rich in carotene and vitamin E, considered highly stable during heating, especially due to the synergistic activity of β-carotene and tocotrienol (MBA et al. 2015).

3.3 Fatty acids profile of vegetable oils

The data of fatty acids composition of the Brazil nut, coconut and palm oils are shown in Table 2.
Table 2 - Fatty acid composition (%) in the vegetable oils of Brazil nut, coconut and palm oil

<table>
<thead>
<tr>
<th>Fatty acids</th>
<th>Edible Vegetable Oils</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brazil nut (%)</td>
</tr>
<tr>
<td>Capric acid C10:0</td>
<td>nd</td>
</tr>
<tr>
<td>Lauric acid C12:0</td>
<td>nd</td>
</tr>
<tr>
<td>Myristic acid C14:0</td>
<td>0.08±0.01</td>
</tr>
<tr>
<td>Palmitic acid C16:0</td>
<td>17.11±1.97</td>
</tr>
<tr>
<td>Margaric acid C17:0</td>
<td>0.10±0.02</td>
</tr>
<tr>
<td>Steraric acid C18:0</td>
<td>11.91±2.28</td>
</tr>
<tr>
<td>Oleic acid C18:1</td>
<td>31.95±1.27</td>
</tr>
<tr>
<td>Linoleic acid C18:2</td>
<td>38.61±1.64</td>
</tr>
<tr>
<td>Linolenic acid C18:3</td>
<td>3.70±0.00</td>
</tr>
<tr>
<td>Beenic acid C22:0</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>Erucic acid C22:1</td>
<td>0.05±0.00</td>
</tr>
<tr>
<td>(\Sigma)SFA</td>
<td>29.24±4.29</td>
</tr>
<tr>
<td>(\Sigma)MUFA</td>
<td>31.95±1.27</td>
</tr>
<tr>
<td>(\Sigma)PUFA</td>
<td>42.31±1.64</td>
</tr>
<tr>
<td>(\Sigma)PUFA/(\Sigma)SFA</td>
<td>1.44</td>
</tr>
</tbody>
</table>

nd: not detected; \(\Sigma\)SFA: sum of saturated fatty acids; \(\Sigma\)MUFA: sum of monounsaturated fatty acids; \(\Sigma\)PUFA: sum of polyunsaturated fatty acids. \(\omega\)-6: Linoleic acid; \(\omega\)-3: Linolenic acid. Results expressed as mean ± S.D. of the three replicates.

Brazil nut oil showed greater amount of linoleic acid and oleic acid in its fatty acids composition, 38.61 ± 1.64 and 31.95 ± 1.27%, respectively. Whereas for coconut oil the main ones were lauric acid (35.22 ± 0.60%) and myristic acid (17.43 ± 0.37%). Finally, for palm oil, oleic acid (48.30 ± 0.99%) and palmitic acid (28.67 ± 1.00) were the main fatty acids, evidencing the differences between these oils.
Regarding the proportions between polyunsaturated and saturated fatty acids (PUFA/SFA), the values observed were 1.44 for Brazil nut, 0.04 for coconut and 0.44 for palm oil. The proportions between polyunsaturated and saturated fatty acids (PUFA/SFA) greater than 0.45 are recommended for daily human ingestion (Wood et al., 2004), although coconut oil has presented PUFA/SFA proportion much lower than 0.45, this oil presents in its composition mainly lauric acid, rich in antioxidants and with antimicrobial properties (NITBANI et al., 2016; SRIVASTAVA et al., 2018).

According to Bodoira et al., (2017) there is a relationship between oxidative stability and the fatty acids profile that compose each oil. Figure 2 shows the correlation between the OSI values and the fatty acids profile in terms of the percentage of SFA, determined by gas chromatography for the samples of Brazil nut, coconut and palm oil. Linear regression using the OSI and SFA values determined for the oils resulted in a straight-line graph of good linear correlation with value of R² = 0.99956 and equation y = -15.977 + 0.772x that confirm the empirical correlation between oxidative stability and SFA.

Figure 2 - Linear regression between OSI in function of the percentage of saturated fatty acids (SFA) for oil samples of Brazil nut (■), coconut (■) and palm oil (■)
Comparing the content of SFA (29.24; 84.27 and 35.82%), MUFA (31.95; 12.23 and 48.30%), PUFA (42.31; 3.46 and 16.06%) and PUFA/SFA (1.44; 0.04 and 0.44%), showed previously in Table 2, with the OSI values (6.91; 49.13 and 11.17 h) of the Brazil nut, coconut and palm oil samples, respectively, it is possible to observe that the higher the content of SFAs the higher the value of OSI, that is, a lower content of MUFAs, PUFA and PUFA/SFA, results in greater oxidative stability and longer shelf life of the oil (Bodoira et al., 2017). This is because the greater the amount of unsaturation, the more susceptible to degradation the oil will be (Farhoosh et al., 2009; Bodoira et al., 2017).

4 CONCLUSIONS

The results obtained by physico-chemical analyses performed in Brazil nut, coconut and palm extra virgin oils are within the parameters established by the Brazilian legislation and the Codex Alimentarius. The oxidative stability analyses showed that there is a relationship between the chemical composition of the fatty acids of each oil and the ability to resist the increase in temperature. The techniques, by which the tests were performed, are useful for quality control of the oils assessed allowing satisfactory results that confirm their use as raw material for the food industry sector.

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