Baru (Dipteryx alata Vogel), known also as cumbaru, cumaru, barujo, coco-feijão, cumarurana, emburena-brava, feijão-coco, and pau-cumaru [1], is a native tree of the Brazilian savanna. The pulp from its fruit is used to make jams and jellies, and the nut is also edible, with good food value, and rich in oil with medicinal properties. Baru seeds were collected in central-western Brazil, and the oil was obtained by pressing the seeds. The Baru oil was heated at 110°C for 24 h, and its oxidative stability was investigated by using fluorescence and absorption spectroscopy. The data showed that both absorption and fluorescence were able to precisely monitor the oil degradation induced by the thermo-oxidative process. The results revealed a rapid growth of the primary compounds generation in the first 16 hours of degradation. Significant amounts of secondary compounds began to be generated after 14 hours.

1. Introduction

Baru (Dipteryx alata Vogel), known also as cumbaru, cumaru, barujo, coco-feijão, cumarurana, emburena-brava, feijão-coco, and pau-cumaru [1], is a native tree of the Brazilian savanna. The pulp from its fruit is used to make jams and jellies, and the nut is also edible, with good food value, and rich in oil with medicinal properties. Previous studies showed that the high nutritional value of Baru nuts stems from their high content of lipids, protein, fiber, and some essential minerals such as potassium, phosphorus, magnesium, calcium, iron, and zinc [3, 4]. Takemoto and collaborators found that Baru seed oil is highly unsaturated due to the predominance of oleic and linoleic acids and its α-tocopherol content [3, 5]. Based on these chemical properties, Baru oil can be used not only for food, but also in the cosmetics and oleochemical industries.

Recently, Baru oil was also proposed for use as an alternative source to produce biofuels, due to its physical and chemical characteristics [6]. Batista and coworkers, by analyzing the peroxide number, iodine number, kinematic viscosity, water content, relative density, saponification number, and refractive index, confirmed the high quality of Baru oil for use as a raw material for biodiesel production [6].

The chemical and physical characteristics of the raw material used in the preparation of biofuel are important, as biodiesel quality is totally dependent on the physical and chemical properties of the oil. For instance, the oxidative stability of the vegetable oil is one of the most important parameters governing the final quality of the biodiesel [7, 8]. The oxidative stability of biodiesel can be affected by many factors such as exposure to UV light, heavy-metal contamination, and temperature changes [9–11]. Although a recent study analyzed the thermal stability of the Baru oil by thermogravimetry [5], to the best of our knowledge, the thermo-oxidative stability of this oil has not yet been evaluated by using optical techniques.

In recent years, optical methods have been used as analytical tools for characterizing and monitoring the stability and quality of vegetable oils, biodiesels, and biofuel blends [12–15]. Dantas and colleagues demonstrated that
the UV-Vis absorption technique can be used to precisely determine the oxidative stability of vegetable oils [9]. They showed that thermodegradation of the oil can be monitored by means of the absorption peaks at around 232 and 270 nm, because light absorption in this wavelength region is strongly affected by the primary and secondary oxidation products generated during the thermooxidation process [9]. Additionally, Cheikhousman and coworkers have shown that fluorescence spectroscopy can be used to investigate the quality of vegetable oil [12]. Fluorescence spectroscopy was successfully used to monitor the deterioration of extra virgin olive oil during heating [12].

As Baru oil has good potential for use in the food, pharmaceutical, cosmetic, and biodiesel industries, where thermal stability is an essential parameter for the final product quality, the present study analyzed the thermooxidative stability of this oil by using UV-Vis absorption and fluorescence spectroscopy measurements.

2. Material and Methods

Baru fruits were collected in central-western Brazil (16°42′50″S 49°00′07″W), and the seeds were extracted from the fruits. Baru oil was obtained by pressing the seeds in a minipress compression machine (Ecrtec). After extraction, the oil was stored in an airtight container, in a freezer at -10°C.

The analysis of the composition of fatty acids was performed by gas chromatography according to the AOCS method [16], using a gas chromatographer (Agilent 6890 series GC system), equipped with capillary column DB-23 (50% cyanopropyl-methylpolysiloxane 60 m × 0.25 mm i.d., 0.25 μm of film) and flame ionization detector (FID). The chromatographic conditions were as follows: initial temperature at 110°C/5 min; heating at 110–215°C on a scale of 5°C/5 min and at 215°C for 24 min; carrier gas, helium (flow of 1 μL/min); injector's temperature, 250°C; detector's temperature, 280°C; and injection volume, 1 μL. The identification of the fatty acids was conducted by comparing the retention time of the fatty acids from the sample and the standards. The quantification was conducted by area normalization, and the results were expressed in g/100 g of the sample.

For the thermodegradation process, the oil sample, divided into 9 aliquots of 5 mL, was placed in an oven with air circulation (Sterilifer SXR42) and heated at 110°C. The oil aliquots were removed after 2, 4, 6, 8, 10, 12, 14, 16, and 24 h.

The UV-Vis absorption was characterized with the use of a bench spectrophotometer (Varian Cary-50) and a quartz cell with 10 mm path length at 22°C. The oil was diluted in hexane (Vetec > 99%) and the absorption was measured between 225 and 750 nm. The absorption bands with maximum absorption at around 475 and 270 and 232 nm were analyzed from diluted samples at concentrations of 50% (w/v) for the absorption at 475 nm and 0.15% (w/v) in the case of the absorptions at 270 and 232 nm.

Fluorescence spectra were collected from diluted samples at a concentration of 50% (w/v) in the 450–750 nm range when excited at 405 nm. The fluorescence signal was obtained by using a portable fluorimeter (MM Optics) containing a laser as excitation source, a monochromator for emission collection, a Y-type optical fiber to collect the light, and a laptop to process the data. The spectra were collected by using front-face geometry and all measurements were carried out using a quartz cell with 10 mm path length, with four polished faces, at 22°C.

3. Results and Discussion

Table 1 presents the composition of fatty acids of Baru oil. As expected, a high degree of unsaturation was determined in which oleic (C18:1) and linoleic (C18:2) acids were the most predominant fatty acids, representing approximately 77% of the total composition.

Table 1: Composition of fatty acids in the oil from Diptereyx alata Vogel oil. Values are expressed as a percentage in relation to total fatty acids quantified.

<table>
<thead>
<tr>
<th>Fatty acids (%)</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic</td>
<td>C14:0</td>
</tr>
<tr>
<td>Palmitic</td>
<td>C16:0</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>C16:1</td>
</tr>
<tr>
<td>Margaric</td>
<td>C17:0</td>
</tr>
<tr>
<td>Heptadecenoic</td>
<td>C17:1</td>
</tr>
<tr>
<td>Searic</td>
<td>C18:0</td>
</tr>
<tr>
<td>Oleic</td>
<td>C18:1</td>
</tr>
<tr>
<td>Linoleic</td>
<td>C18:2</td>
</tr>
<tr>
<td>Linolenic</td>
<td>C18:3</td>
</tr>
<tr>
<td>Arachidic</td>
<td>C20:0</td>
</tr>
<tr>
<td>Eicosenoic</td>
<td>C20:1</td>
</tr>
<tr>
<td>Behenic</td>
<td>C22:0</td>
</tr>
<tr>
<td>Erucic</td>
<td>C22:1</td>
</tr>
<tr>
<td>Lignoceric</td>
<td>C24:0</td>
</tr>
</tbody>
</table>

Equal letters on the column represent values which do not differ significantly (P < 0.05). To compare the means, ANOVA followed by Tukey test was used. The values are mean ± standard deviations of duplicate analysis.
by carotenoids is due to the presence of conjugated carbon-
carbon double bonds and that a typical absorbance spectrum 
of a carotenoid contains three bands in the blue region of the 
optical spectrum (400–500 nm) where the maxima of which 
are functions of the chromophore lengths [18] as carotenoids 
consist of a sequence of alternating carbon double and 
single bonds (C=C and C–C bonds, resp.), with the outer 
electron free to move along the chain [19]. Additionally, it 
is well established that these absorption bands, which give 
carotenoids their color, are due to the \(1\pi_e^- \rightarrow 1\pi_a^+\) transition [20].

As previously mentioned, the thermodegradation of veg-
table oils can be monitored by analyzing the absorption 
peaks at around 232 and 270 nm, because the absorptions in 
these wavelength regions are strongly affected by the primary 
and secondary oxidation products generated during the 
thermooxidation process [9]. Figure 3 shows the absorption 
at 232 and 270 nm as a function of the degradation time.

The observed increase in absorption at 232 nm is due 
to compounds generated during the primary degradation 
of the oil, conjugated dienes, which show \(\pi-\pi^*\) transitions 
[9]. The changes in absorption at 270 nm are related to 
the formation of secondary compounds of the degradation, 
such as diketones and unsaturated ketones, the absorption 
of which is also due to the \(\pi-\pi^*\) transitions [9, 11]. The results 
clearly show that the generation of primary compounds 
increased rapidly in the first 16 hours. In contrast, the 
generation of secondary compounds began to be significant 
after 14 hours of thermodegradation. The relation between 
the primary and secondary compounds during the degradation 
as a function of the heating time can be better visualized from 
the absorption ratio at 232 to 270 nm, as shown in Figure 4.

Although several studies have shown that the increase 
in absorption at 232 and 270 nm can be used to mon-
tor oil degradation induced by thermooxidation, as was 
also demonstrated here, the present data indicate that oil 
absorption at around 475 nm can also be effectively used to 
monitor oil degradation. As shown in Figure 5, the absor-
ption bands between 350 and 550 nm decrease as a function 
of the degradation time. A linear decrease in absorption at 
475 nm was observed during the first 8 hours, with a slope 
of \(-0.069\) and a correlation coefficient of 0.989, and almost 
no absorption was detected after that. This suggests that 
carotenoids are almost totally degraded in the first hours of 
thermal treatment. This is possible because carotenoids are 
highly unsaturated molecules with many conjugated double 
bonds, making them susceptible to degradation [21, 22]. 
Henry and coworkers have demonstrated rapid thermo-
degradation (thermooxidation) of all-trans \(\beta\)-carotene, 9-cis 
\(\beta\)-carotene, lycopene, and lutein in safflower seed oil heated 
at 75, 85, and 95°C [21]. They also found that only trace amounts 
of carotenoids remained after 5, 12, and 24 h when the oil was 
heated at 95, 85, and 75°C, respectively.

In addition to the absorption analyses, fluorescence 
spectroscopy was applied to characterize the emissions from 
the Baru oil, as well as to investigate the potential of the 
fluorescence technique as an alternative method to evaluate 
the oil degradation. Figure 6(a) shows the typical emission 
spectrum of Baru oil when excited at 405 nm. The fluo-
rescence data revealed that \(\beta\)-carotene and chlorophyll are 
the main fluorophores responsible for the emission between 
450 and 750 nm, when excited at 405 nm, as presented in 
Figure 6(b) [17, 18]. In fact, it is well known that different oil 
constituents such as \(\beta\)-carotene, \(\alpha\)-tocopherol, oleic acid, and 
chlorophyll may fluoresce in this range when excited by blue 
radiation (at around 450 nm) [18, 21].

Our results also revealed that the overall fluorescence 
signal between 350 and 750 nm was reduced in response 
to the thermodegradation. As presented in Figure 7, the 
observed decreases in fluorescence at 568 and 675 nm over 
the degradation period are mainly attributed to thermod-
egradation of the carotenoids and chlorophylls, respectively.
However, a fluorescence increase at around 500 nm during the first 8 hours was detected, as also shown in Figure 7, in which this emission is a contribution of the oxidation products [23]. As recently demonstrated by Magalhães et al., conjugated tetraenes were identified in the degraded samples, presenting a fluorescent emission in the 350–500 nm range, in which the conjugated tetraenes molecules were formed from the degradation of unsaturated molecules [24].

In summary, our results indicate that carotenoid and chlorophyll degradation in the oil can be used as an indicator to monitor the overall oil degradation, by both fluorescence and absorption analyses. Therefore, the results showed that fluorescence spectroscopy has great potential to be accurately applied for monitoring the oxidative stability of vegetable oils by using a low cost and portable device.

4. Conclusion

In conclusion, we investigated the thermal stability of Baru oil by analyzing the optical features of the samples. The results strongly suggest that carotenoids and chlorophylls were almost completely degraded during the thermal treatment and that primary (conjugated dienes) and secondary (diketones and unsaturated ketones) oxidation products were generated during the thermooxidation process. In summary, our data showed that fluorescence as well as absorption can be potentially used to detect oxidative degradation of this oil, by monitoring the carotenoid and chlorophyll degradation. In general, as it is possible to obtain a rapid, precise, and noninvasive analysis using a portable device by optical methods, our results indicate that fluorescence and
absorption spectroscopy can be applied to develop alternative methods for assessing oil quality. However, aiming to develop a robust method for oil analysis, it is needed to evaluate different oils produced from different raw materials as well as characterize the oil degradation when exposed to the different environments (e.g., light, heat, metal-containing).

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.
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