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Research Article

Oxidative Stability of Baru (*Dipteryx alata* Vogel) Oil Monitored by Fluorescence and Absorption Spectroscopy

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Baru (*Dipteryx alata* Vogel) is a native fruit of the Brazilian savanna that provides a nutritive oil, which also has medicinal properties. Baru fruits 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 thermooxidative 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, specially used as antirheumatic agent [2]. 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 thermooxidative 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 (Ecirtec). 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 68650 series GC system), equipped with capillary column DB-23 (50% cyanopropil-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 SXCR42) 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.

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

Fatty acids (%)		Values
Myristic	C 14:0	0.06 ± 0.01[a]
Palmitic	C 16:0	6.37 ± 0.01
Palmitoleic	C 16:1	0.07 ± 0.01[a]
Margaric	C 17:0	0.08 ± 0.01[a]
Heptadecenoic	C 17:1	0.06 ± 0.02[a]
Stearic	C 18:0	4.95 ± 0.01
Oleic	C 18:1	47.86 ± 0.05
Linoleic	C 18:2	28.91 ± 0.00
Linolenic	C 18:3	0.18 ± 0.00
Arachidic	C 20:0	1.29 ± 0.00
Eicosenoic	C 20:1	2.46 ± 0.01
Behenic	C 22:0	3.19 ± 0.02
Erucic	C 22:1	0.26 ± 0.04
Lignoceric	C 24:0	4.26 ± 0.04
∑ Saturated		20.20 ± 0.10
∑ Monounsaturated		50.71 ± 0.13
∑ Polyunsaturated		29.09 ± 0.00

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.

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 (C 18:1) and linoleic (C 18:2) acids were the most predominant fatty acids, representing approximately 77% of the total composition.

Figure 1 shows the absorption spectrum of the Baru oil between 225 and 550 nm when diluted in hexane. To better observe the absorption bands, appropriate dilutions were chosen in the ranges of 225–350 nm (0.15% w/v) and 350–550 nm (50% w/v). In general, the molecular absorption of vegetable oils between 225 and 350 nm is mainly attributed to tocopherols, although the contribution of some fatty acids should not be ruled out [17]. Chlorophylls as well as carotenoids may be absorbed in the 350–550 range [17]; however, in analyzing the diluted sample, our data revealed that carotenoids are the main compounds responsible for the observed absorption between 350 and 550 nm, as demonstrated in Figure 2 where β-carotene absorption spectrum is shown. In fact, it is well known that the absorption of light

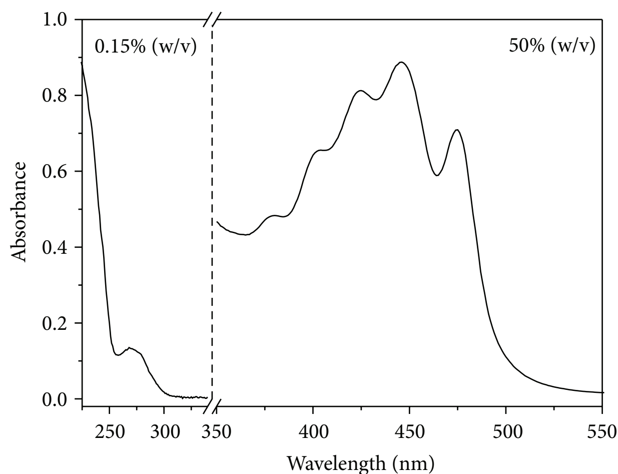

Figure 1: Baru oil absorbance spectrum collected from a diluted sample. The oil was diluted in hexane, and a more concentrated sample was used to better determine the absorption bands in the 350–550 nm range (see text).

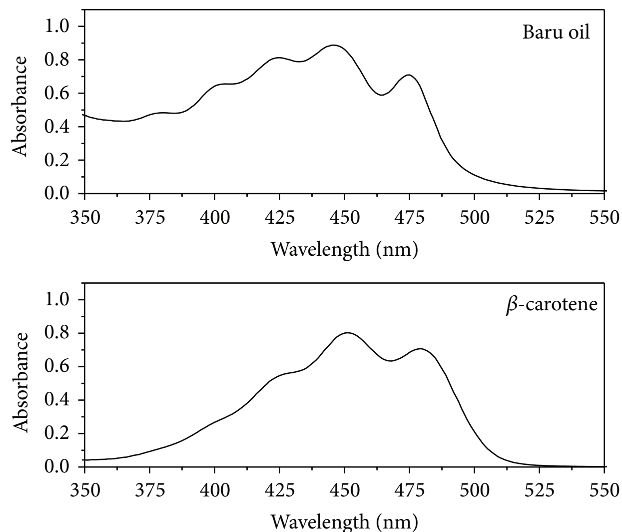

Figure 2: Baru oil and β-carotene absorbance between 350 and 550 nm. All samples were diluted in hexane.

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 $1A_g^- \rightarrow 1B_u^+$ transition [20].

As previously mentioned, the thermodegradation of vegetable 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 π-π^* 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 π-π^* 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 monitor 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 absorption 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 thermodegradation (thermooxidation) of all-*trans* β-carotene, 9-*cis* β-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 fluorescence data revealed that β-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 know that different oil constituents such as β-carotene, α-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 550 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 thermodegradation of the carotenoids and chlorophylls, respectively.

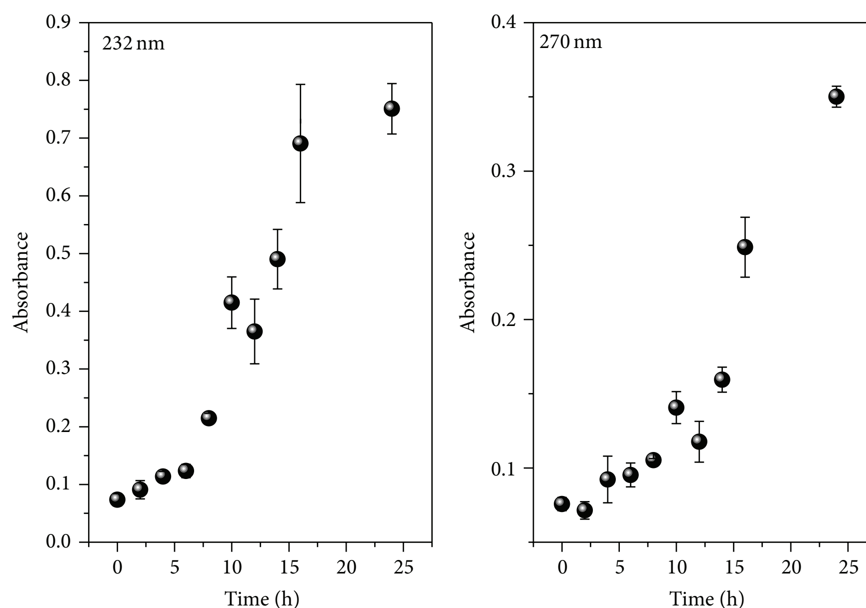

Figure 3: Baru oil absorbance at 232 and 270 nm as a function of the heating time. The oil samples were heated at 110°C.

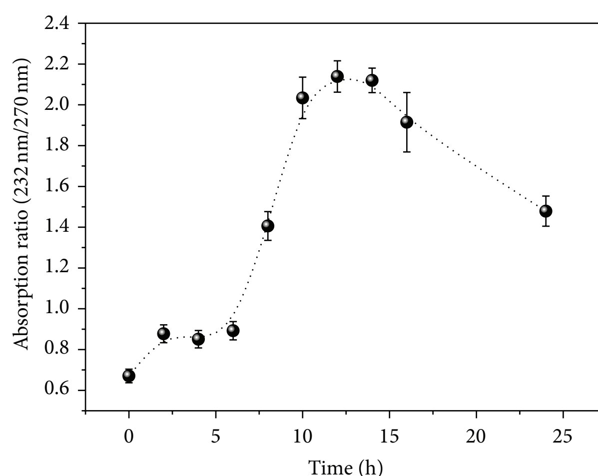

Figure 4: Baru oil absorption ratio at 232 to 270 nm as a function of the heating time.

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

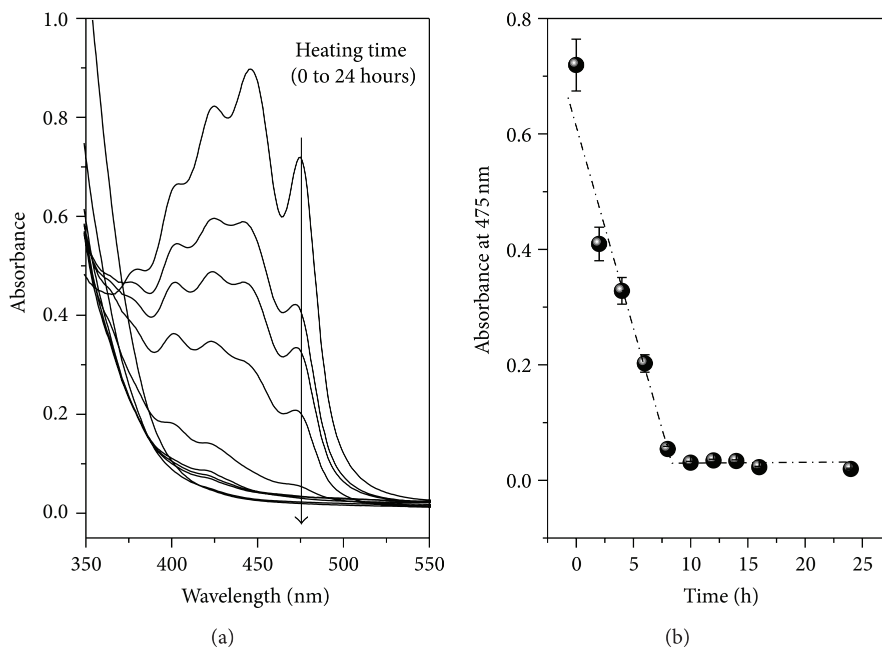

FIGURE 5: (a) Decrease in absorption over the degradation period. (b) Absorbance at 475 nm as a function of the heating time.

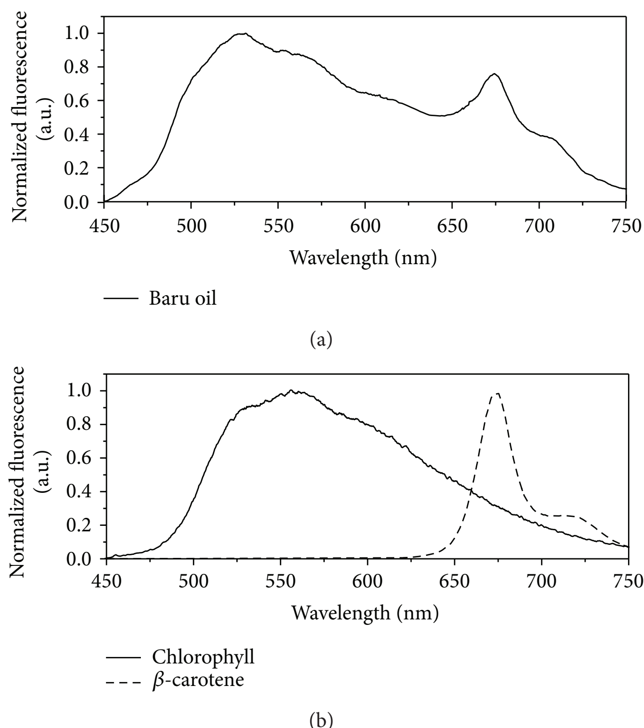

FIGURE 6: Fluorescence spectrum of (a) Baru oil and (b) β-carotene and chlorophyll.

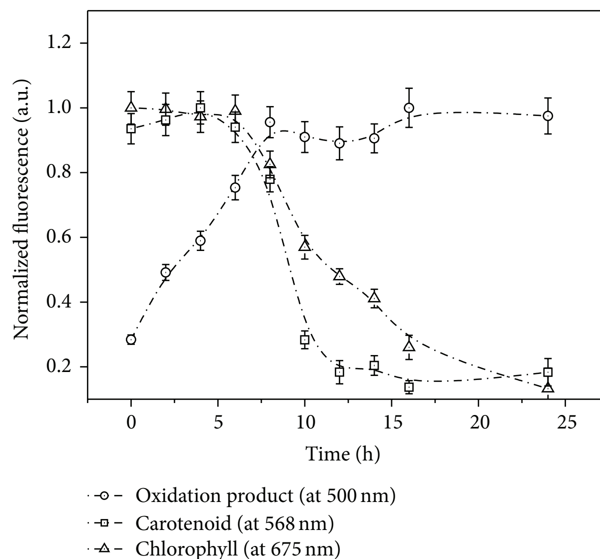

FIGURE 7: Fluorescence intensity at 500, 568, and 675 nm, when excited at 405 nm, as a function of the heating time.

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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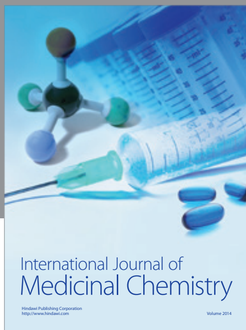
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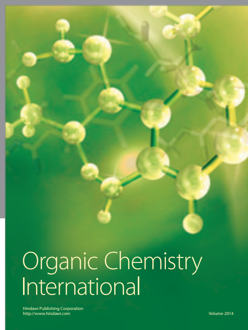
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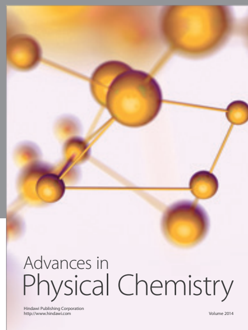
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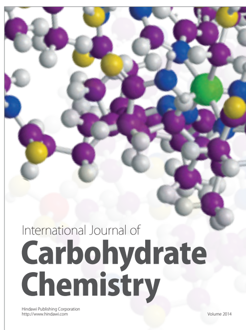
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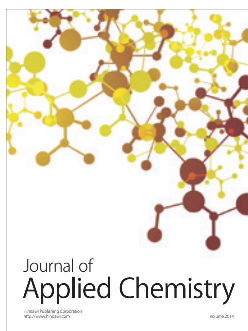
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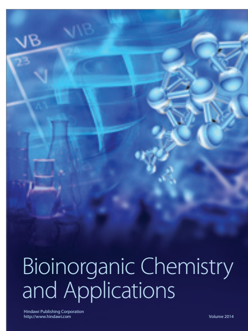
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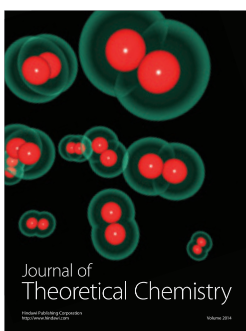
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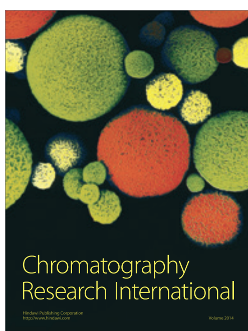
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