J. of Supercritical Fluids 165 (2020) 104932

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Supercritical CO_2 extraction of uxi (*Endopleura uchi*) oil: Global yield isotherms, fatty acid profile, functional quality and thermal stability

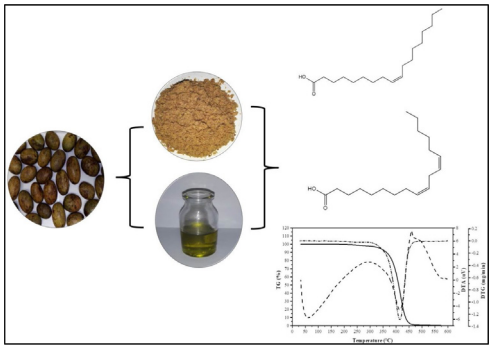
Rafael Henrique Holanda Pinto[a], Eduardo Gama Ortiz Menezes[a], Lucas Cantão Freitas[a], Eloísa Helena de Aguiar Andrade[b], Roseane Maria Ribeiro-Costa[c], José Otávio Carréra Silva Júnior[d], Raul Nunes Carvalho Junior[a,*]

[a] Extraction Laboratory, Post-graduate program in Food Science and Technology, Institute of Technology, Federal University of Pará, Rua Augusto Corrêa S/N, Guamá 66075-900, Belém, Pará, Brazil
[b] Adolpho Ducke Laboratory, Post-graduate Program in Biotechnology and Biodiversity, Museu Paraense Emílio Goeldi, Av. Perimetral, 1900, 66077-530, Belém, Pará, Brazil
[c] Laboratoy of Pharmaceutical Nanotechnology, Federal University of Pará, Rua Augusto Corrêa S/N, Guamá 66075-900, Belém, Pará, Brazil
[d] Laboratory R&D Pharmaceutical and Cosmetic, Federal University of Pará, Rua Augusto Corrêa S/N, Guamá 66075-900, Belém, Pará, Brazil

HIGHLIGHTS

- Uxi (Endopleura uchi) is a native species from the Amazon region.
- The fruits have potential for edible vegetable oil production, due to their chemical composition.
- Uxi oil was obtained with high yields at temperatures of 40 and 60 °C and pressures of 300 and 400 bar.
- The functional quality indices express that uxi oil can be consumed in the human diet as table oil, similarly to olive oil.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 February 2020
Received in revised form 16 May 2020
Accepted 9 June 2020
Available online 13 June 2020

Keywords:
Amazon
Functional food
Supercritical CO_2
Bioactive compounds
Uxi

ABSTRACT

In this research, uxi (Endopleura uchi) oil was obtained via supercritical CO_2 extraction in order to promote the valorization of the species in the industrial scenario, showing the potential of its oil as a functional food. The oil was extracted at temperatures of 40 and 60 °C and pressures of 200–400 bar. The highest yield was obtained at 60 °C / 400 bar (24.48 ± 0.20 %) in db. The oil showed a composition with predominance of oleic acid (n-9), as well as a stable thermal behavior up to 300 °C. The uxi oil obtained via supercritical CO_2 is presented as a potential product for the food industry due to its good functional quality.

1. Introduction

Uxi (Endopleura uchi) is a native species from the Amazon region, and its fruits are widely consumed by the local population

* Corresponding author.
E-mail address: raulncj@ufpa.br (R.N. Carvalho Junior).

https://doi.org/10.1016/j.supflu.2020.104932
0896-8446/

[1–3]. Uxi wood is commercially desirable by the civil construction industry (manufacture of posts and beams), which contributes to the indiscriminate extraction of its species' trees, causing deforestation in the Amazon region [4]. The fruits have potential for edible vegetable oil production, due to their chemical composition [5]. The study by Berto et al. [6] showed that the lipid fraction of the uxi fruit contains a predominance of unsaturated fatty acids. Other characteristic compounds in the uxi oil include phytosterols, tocopherols and carotenoids [7–9]. The phytochemical profile of the species also indicates the presence of bergenin in the bark of its trunk [10].

Unsaturated fatty acids are structural components of cell membranes, incorporated into phospholipids, which regulate the fluidity and function of the membrane, in addition to having the role of metabolites precursors with biological properties of interest. A major effect attributed to linoleic acid (n-6) is the decrease in cholesterol levels in the blood, due to the reduction in the levels of low-density plasma lipoproteins, contributing to the prevention of cardiovascular diseases [11]. The benefits of linoleic acid (n-6) include the reduction of atherosclerosis, carcinogenesis, obesity, diabetes and inflammatory processes [12].

Obtaining high quality lipid products depends on factors related to the extraction process, such as temperature, nature of the solvent, solvent/raw material ratio, extraction period, atmospheric composition and preparation of the raw material. The compounds degradation can be accelerated by the mechanical pressing system, while the use of organic solvents can increase the oils toxicity. Conventional methods, although allowing high yields, are lengthy, exposing raw materials to hydrolytic and oxidative rancidity processes, contributing to the loss of the quality of the final product [13,14].

Considering this scenario, the application of supercritical fluid turn out to be an alternative to obtain high quality vegetable oil, preserving the nature of the characteristic compounds, as in the case of unsaturated fatty acids and other substances of interest (bioactive compounds). Extraction with supercritical CO_2 is considered to be a green technique, environmentally friendly, due to the characteristics of the used solvent, especially because it is non-corrosive, non-toxic, non-flammable, presents low cost and easy removal of the extracted product, besides allowing high profitability in mass and shorter process time [15,16].

In this context, extraction with supercritical CO_2 represents an important tool to replace conventional methods, and it can be applied for the production of uxi oil. This proposal allows the development of a new product and the valorization of the species, especially in terms of environmental preservation. In this research, uxi (Endopleura uchi) oil was obtained via supercritical CO_2 extraction in order to promote the valorization of the species in the industrial scenario, showing the potential of its oil as a functional food.

2. Material and methods

2.1. Uxi samples

The uxi fruits were collected in the municipality of Bujaru, Pará, Brazil (-01°64′09″S, -48°02′73″W), in March 2018. After 48 h of ripening, the material was transported to the Extraction Laboratory of the Federal University of Pará, where manual pulping was performed. The pulp was frozen in an ultra-freezer at −80 °C for 24 h. Dehydration was carried out in a freeze dryer (Alpha, 2–4 LD Plus, Germany) for 72 h. The dehydrated pulp was crushed in a processor (Croydon, LR03, Brazil) and stored in a polyethylene package, kept under vacuum, at a temperature of 5 °C, for five months, until the analysis and extraction of the oil. The real density was determined using the Hélio (He) automatic gas pycnometer Quantachrome Ultrapyc 1200e. The apparent density was determined by the mathematical ratio between the mass and volume of the pulp, according to Eq. 1. The bed porosity was determined through Eq. 2. The average diameter of the particles was determined from granulometric analysis using Tyler sieves 14–32, according to ASAE [17].

$$\rho_a = \frac{m_s}{V_s} \tag{1}$$

$$\varepsilon = 1 - \frac{\rho_a}{\rho_t} \tag{2}$$

Where: ρ_a is the apparent density, ρ_t is the real density, m_s is the sample mass, V_s is the sample volume, and ε is the bed porosity.

2.2. Centesimal composition

The centesimal composition of the dehydrated uxi pulp was determined by analyzing the moisture, ash, lipids, proteins and carbohydrate contents, according to the methods described by Instituto Adolpho Lutz [18]. The moisture content was determined by drying the sample in an oven at 105 °C, until constant weight. The percentage of ash was determined by incinerating the samples in muffle heated to 550 °C. The lipid content was determined by the Soxhlet method, using petroleum ether as a solvent. Protein content was quantified using the Kjeldhal method, using factor 6.25 for nitrogen conversion. Total carbohydrates were calculated from the difference between 100 and the sum of moisture, ash, lipids and proteins.

2.3. Oil extraction with supercritical CO_2

The experiments were carried out in the extraction unit Speed^{TM} SFE (Model 7071, Applied Separations, USA) equipped with 100 mL cell (0.0317 m internal diameter and 0.1244 m high) and cylinder containing CO_2 (99 % purity, White Martins, Brazil). The global yield isotherms were determined through tests with 20 g of uxi pulp (5.05 cm of bed height inside the cell). The extractions occurred at temperatures of 40 and 60 °C and pressures of 200, 300 and 400 bar. The extraction period was divided into two stages: static period of 1800s and dynamic period of 10,800 s. The CO_2 mass flow was $8.85 \times 10^{-5} \pm 2.95 \times 10^{-6}$ kg.s^{-1}. The CO_2 density was determined using the platform from National Institute of Standards and Technology (NIST), which uses the state equation developed by Span and Wagner [19]. The global oil yield (on a dry basis) was determined using Eq. 3. Each condition was performed in duplicate.

$$Y_{(\%db)} = \left(\frac{m_o}{m_s \left(1 - \frac{U_s}{100}\right)} \right) 100 \tag{3}$$

Where: $Y_{(\%db)}$ is the oil global yield in dry basis, m_o is the oil mass, and U_s is the percentage moisture of the pulp.

2.4. Solubility prediction of uxi oil in supercritical CO_2

The solubility of uxi oil in supercritical carbon dioxide was determined according to the methodology described by Cunha et al. [20]. The solubility of uxi oil in CO_2 in a pressurized system was calculated using the Peng-Robinson [21] cubic equation of state (Eq. 4) combined with the quadratic Van der Waals mixing rule. For mixtures, parameters a and b were obtained through the physical properties of pure substances and the use of a mixing rule, with the interactions between the components of the mixture represented by the parameters of binary interaction. In this work it was used the Van der Waals mixing rule with two parameters of binary interaction, represented by Eqs. 5–8. The symbols k_{ij} and λ_{ij} are the parameters of binary interaction. In order to estimate

the parameters of binary interaction, it was used the computer software EDEFLASH as in the research conducted by Araújo and Meireles [22]. This software used the PT flash procedure and the modified Simplex mathematical method by Nelder and Mead [23] to minimize the objective function (OF). The symbols x^e_i, x^c_i, y^e_i, y^c_i represent the fraction of experimental liquid in the system, fraction of calculated liquid, fraction of experimental gas in the system and fraction of calculated gas, respectively.

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{4}$$

$$a_m = \sum\sum x_i x_j a_{ij} \tag{5}$$

$$b_m = \sum\sum x_i x_j b_{ij} \tag{6}$$

$$a_{ij} = \left(a_{ii}a_{jj}\right)\frac{1}{2}\left(1-K_{ij}\right) \tag{7}$$

$$b_{ij} = \frac{(b_{ii}+b_{jj})}{2}\left(1-\lambda_{ij}\right) \tag{8}$$

$$OF = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{x_i^e - x_i^c}{x_i^e}\right)^2 + \left(\frac{y_i^e - y_i^c}{y_i^e}\right)^2} \tag{9}$$

The use of a cubic equation of state to estimate solubility requires specific information about each constituent of the oil, such as critical temperature (Tc), critical pressure (Pc) and acentric factor (ω). For the calculation of critical properties (Tc, Pc), it was used the method of Ashour and Wennensten [24] and Constantinou and Gani [25], while the calculation of the acentric factor was done by using the method of Wagner [26] and Tu [27].

The objective function correlates the difference between the theoretical and the experimental value. Experimental fatty acid balance data were obtained from the literature Maheshwari; Zou; Yau [28–30]. Solubility (S) was calculated according to Eq. 10, and the results were expressed in mg oil/g CO_2.

$$S = \frac{\Sigma M_i z_i}{M_{CO_2} z_{CO_2}} x1000 \tag{10}$$

Where: z_i is the molar fraction of component *i* in the gas phase; *M* is the molar mass of each component.

2.5. Gas chromatography coupled to mass spectrometry (GC–MS)

The fatty acid composition of the uxi oil was determined using fatty acid methyl esters (FAMEs) according to the methodology suggested by Khan and Scheinmann [31] with modifications. The FAMEs were identified by Gas Chromatography coupled to Mass Spectrometry (GC–MS), using the equipment QP-2010-Plus (Shimadzu) by means of silica capillary column (Rtx-5 ms, 30 m × 0.25 mm × 0.25 μm) with the aid of the software MS Solution and literature data [32–34]. The analysis conditions were: oven temperature programmed at 100 °C (5 min) with a gradient from 4 °C/min up to 260 °C (20 min); helium (1.2 mL/min) as carrier gas; splitless injection of 1 μL of sample; ionization by electron impact at 70 eV. The compounds were identified by comparing their retention indices and mass spectra with those from the standard fatty acids available in the literature.

2.6. Functional quality of uxi oil

The functional quality of uxi oil was determined based on the proportions of fatty acids, according to the respective lipid profiles, evaluated in three composition indices: Atherogenicity Index (AI), represented in Eq. 11; Thrombogenicity Index (TI), Eq. 12, following the methodology proposed by Ulbricht and Southgate [35]; and the ratio of hypocholesterolemic / hypercholesterolemic (H/H), Eq. 13, suggested by Santos-Silva et al. [36].

$$AI = \frac{(12:0)+4(14:0)+(16:0)}{(\sum MUFA)+(\sum n-6)+(\sum n-3)} \tag{11}$$

$$TI = \frac{(14:0)+(16:0)+(18:0)}{0,5(\sum MUFA)+0,5(\sum n-6)+3(\sum n-3)+\left(\frac{\sum n-3}{\sum n-6}\right)} \tag{12}$$

$$H/H = \frac{(18:1n-9)+(18:2n-6)+(20:4n-6)+(18:3n-3)+(20:5n-3)+(22:5n-3)+(22:6n-3)}{(14:0)+(16:0)} \tag{13}$$

Where: 12:0 lauric acid, 14:0 myristic acid, 16:0 palmitic acid, 18:0 stearic acid, 18:1 oleic acid, 18:2 linoleic acid, 18:3 linolenic acid, 20:5 eicosapentaenoic acid, 22:5 docosapentaenoic acid, and 22:6 docosahexaenoic acid.

2.7. Prediction of the triglyceride composition of uxi oil

The identification of possible triglycerides was carried out using the methodology developed by Norris and Mattil [37]. This theory addresses the random distribution of fatty acids that make up triglyceride molecules (TAGs), and in this aspect, it is possible to verify that N^3 TAG molecules are possible, considering the identification of N fatty acids present in the uxi oil and the presence of all isomers of the triglyceride molecules. In this context, an alternative to this determination was to develop an Excel spreadsheet, applying knowledge of combinatorial analysis to determine all possible combinations between the fatty acids that constitute a triglyceride molecule. This methodology results in a large number of TAGs, and the results were described by groups of TAGs (NC:NDB), where NC is the number of carbons, discounting three carbon atoms of the glycerol, and NDB is the number of double bonds. Groups with less than 1 % (w / w) of the total concentration were ignored and all isomers were considered. Combinatorial analysis was applied and developed in the Visual Basic for Application (VBA) programming language.

2.8. Thermal analysis

2.8.1. Thermogravimetric (TG-DTG)

The TG-DTG analysis was carried out in a Shimadzu thermobalance (DTG-60 H) according to the following parameters: air flow of 50 mL/min, heating ramp rate of 10 °C/minute and temperature range of 30–600 °C. It was used aluminum crucibles and sample mass of 7 ± 0.5 mg. This analysis was performed for the best condition of global mass yield of uxi oil.

2.8.2. Differential scanning calorimetry (DSC)

DSC analysis was performed on Shimadzu DSC-60A equipment (induced oxidation) according to the following parameters: nitrogen flow of 50 mL / min, heating ramp rate of 10 °C and temperature from 20 to 600 °C. It was used aluminum crucibles and sample mass of 5 ± 0.5 mg. The DSC analysis was performed for the best condition of global mass yield of uxi oil.

2.9. Statistical analysis

The experimental essays of oil extraction were carried out in duplicate. In order to verify the existence of a significant difference between the SFE conditions, the results averages were submitted to

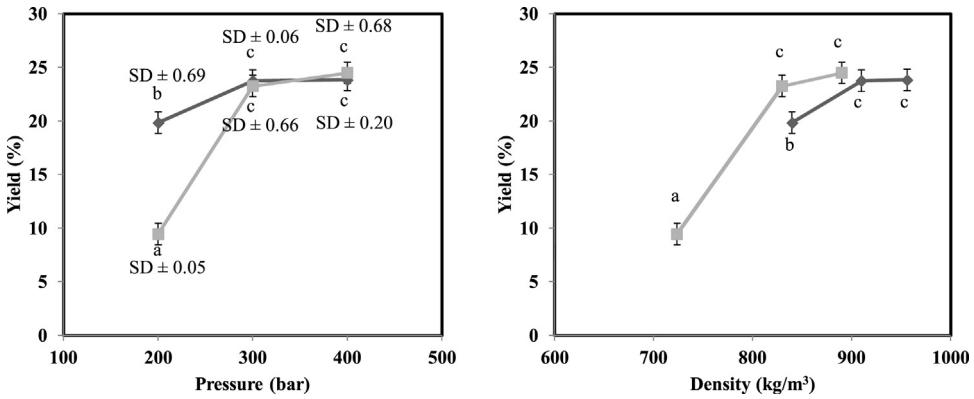


Fig. 1. Global yield isotherms of uxi oil extracted with supercritical CO_2. Fig. 1.1. Yield versus pressure and Fig. 1.2. Yield versus density. Diamond dots represent the isotherm of 40 °C; square dots represent the isotherm of 60 °C. Repeating letters represent conditions statistically equal, with 95 % confidence. SD: Standard Deviation.

analysis of variance and, when significant, compared by the Tukey test with 95 % confidence level, using the STATISTIC®7.1 software (Statsof, Inc., Tulsa, USA).

3. Results and discussion

3.1. Freeze-dried uxi pulp characteristics

The real density of the uxi pulp was 1200 ± 10 kg/m^3, while the apparent density was equal to 504.48 ± 9.36 kg/m^3. The bed porosity was 0.58 ± 0.01. The average diameter of the pulp particles was 0.82 ± 0.02 mm. The centesimal composition of the dehydrated uxi pulp showed moisture equal to 6.96 ± 0.02 %; ash content of 1.49 ± 0.01 %; lipid content equal to 25.61 ± 0.02 %; protein content of 3.87 ± 0.05 % and total carbohydrates of 62.07 %.

3.2. Global yield

The extraction performance and global yields of uxi oil are shown in Fig. 1. The highest yield, 24.48 ± 0.20 % (db), was obtained in the condition of 60 °C and 400 bar, while the lowest yield, 9.44 ± 0.05 % (db), was observed in the condition of 60 °C and 200 bar. The results obtained in the uxi oil + CO_2 system showed a direct relationship between CO_2 yield, pressure and density. At 60 °C/400 bar the density of CO_2 presented a value of 890.14 kg/m^3, causing greater CO_2 solubility power, contributing to greater efficiency of the extraction process, contrary to the condition of 60 °C/200 bar, with CO_2 density equal to 723.68 kg/m^3. This behavior was observed in the research carried out by Pinto et al. [13] and Batista et al. [38]. High yields were also observed at 40 °C/ 300 bar (23.75 ± 0.06 %), 40 °C/400 bar (23.83 ± 0.68 %) and 60 °C/300 bar (23.25 ± 0.66 %) in dry basis. These results are statistically equal to that found at 60 °C/400 bar. Considering these results, the best condition observed in this study was 40 °C/300 bar, as it allows oil to be extracted with lower energy consumption and less work done by the pump.

3.3. Oil solubility in supercritical CO_2

The calculated solubility values are in accordance with the extraction yields obtained experimentally, as it is found that the solubility between the uxi oil and the supercritical solvent is higher at a temperature of 60 °C and 400 bar. However, the operational extraction conditions of 40 °C/300 bar, 40 °C/400 bar and 60 °C/300 bar also showed high solubility values. The parameters of binary interaction are shown in Table 1. The Table 2 shows the calculated values for the physical properties, as well as indicates the methods used for the calculations. Fig. 2 shows the prediction of solubility expressed in mg oil/g CO_2. In this aspect, it is possible to observe that both isotherms showed the dominant effect on the solvent density during the oil extraction/separation process, since an increase in solubility was verified as the pressure increased.

Table 1
Binary interaction parameters.

	Parameters	
FattyAcids	Kij	
16:0 Palmitic	−0.017277716	−0.02322057
18:0 Stearic	0.084396659	−0.00171055
18:1 Oleic	0.090523308	−0.00181091

The values of the binary interaction parameters of the phase equilibrium were calculated using the Peng-Robinson cubic equation of state [21]. The calculated phase balance data are close to the experimental values found in the literature.

The solubility or solvation power of a fluid is determined through its density, and this property increases in isothermal systems by increasing the pressure, whereas in isobaric systems, density increases with decreasing temperature Silva et al. [39]. Fig. 2 shows that the solubility power of CO_2 increased with a pressure increase from 200 to 400 bar, in the isotherm of 60 °C. The behavior of the CO_2 solvation power in the 40 °C isotherm increased from 200 to 300 bar. However, it remained almost unchanged from 300 to 400 bar. These data confirm the extraction performance observed through the results regarding the global yields, considering that the values were statistically equal. The solubility prediction data show the crossing point between the isotherms. Above the crossing point, the vapor pressure of the uxi oil compounds is predominant. The high yields obtained at 40 °C/300 bar and 40 °C/400 bar were due to the high density of CO_2, while the yields observed at 60 °C/300 bar and 60 °C/400 bar are explained through the increased vapor pressure of the lipid compounds in the uxi pulp. Before the crossing point, the density of CO_2 was predominant, and after this point, the vapor pressure turned predominant.

3.4. Fatty acid profile

The fatty acid profile of uxi oil under different temperature and pressure conditions did not change in qualitative terms. The chemical composition of uxi oil showed a predominance of unsaturated fatty acids (UFA) with a concentration of 58.09–59.86 g/100 g oil, with an emphasis on oleic (n-9) and linoleic acid (n-6). Among saturated fatty acids (SFA), palmitic acid and stearic acid were the majority. The results can be seen in Table 3. The concentration of oleic acid (n-9) ranged from 52.32–54.59 g/100 g oil, while for linoleic acid (n-6) the content was between 2.27 and 5.59 g/100

Table 2
Thermophysical properties calculated by group contribution methodology.

FattyAcids	MM (g/mol)	Tb (K)	Tc (K)	Pc (bar)	ω
16:0 Palmitic	256.42	608.4731*	780.3814**	14.1765**	1.0104***
18:0 Stearic	284.48	626.8235**	796.6483**	12.4403**	1.0861***
18:1 Oleic	282.46	626.8074**	797.5042**	12.6837**	0.9245****

Where MM: molar mass, Tb: boiling temperature, Tc: critical temperature, Pc: critical pressure, ω: acentric factor. *Ashour and Wennesten [24], **Constantinou and Gani [25], ***Wagner [26], ****Tu [27].

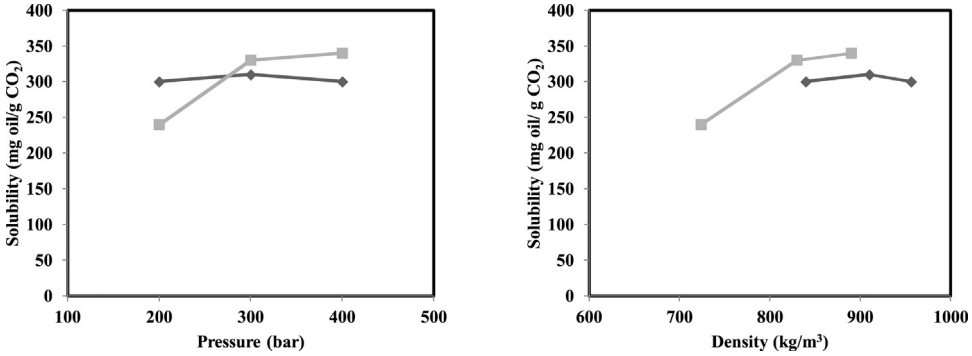


Fig. 2. Solubility of uxi oil in supercritical CO_2. Fig.2.1. Solubility *versus* pressure; Fig. 2.2. Solubility *versus* density. Diamond dots represent the temperature of 40 °C; square dots represent the temperature of 60 °C.

Table 3
Fatty acid composition of uxi oil.

g fatty acid/100 g oil						
Fatty Acid	40 °C 200 bar	40 °C 300 bar	40 °C 400 bar	60 °C 200 bar	60 °C 300 bar	60 °C 400 bar
14:0 Miristic	0.24	0.12	0.06	0.36	0.18	0.05
16:0 Palmitic	23.90	22.84	24.19	24.30	23.21	22.07
16:1 Palmitoleic	0.76	0.42	0.23	0.97	0.64	0.16
17:0 Margaric	0.65	0.38	0.23	0.77	0.59	0.16
18:0 Stearic	14.70	14.36	14.71	13.21	14.49	14.04
18:1 Oleic (n-9)	54.59	52.67	53.69	52.32	53.35	53.69
18:2 Linoleic (n-6)	2.27	4.69	5.59	3.72	3.77	5.16
20:1 Gondoic	1.04	0.64	0.35	1.08	0.92	0.27
24:0 Lignoceric	0.12	0.15	0.12	0.24	0.37	–
∑FA	98.27	96.27	99.17	96.97	97.52	95.60
∑SFA	39.61	37.85	39.31	38.88	38.84	36.32
∑UFA	58.66	58.42	59.86	58.09	58.68	59.28
∑MUFA	56.39	53.73	54.27	54.37	54.91	54.12
∑PUFA	2.27	4.69	5.59	3.72	3.77	5.16
AI	0.42	0.40	0.41	0.44	0.41	0.38
TI	1.32	1.28	1.30	1.30	1.29	1.22
H/H	2.36	2.50	2.44	2.27	2.44	2.66

Where ∑: summative, FA: fatty acids, SFA: saturated fatty acids, UFA: unsaturated fatty acids, MUFA: monounsaturated fatty acids, PUFA: polyunsaturated fatty acids, AI: Atherogenicity Index, TI: Thrombogenicity Index and H/H: Hypo/Hypercholesterolemics. The standard deviations for all fatty acids were lower than 1.8 %.

g oil. The concentration of palmitic acid ranged from 22.07–24.30 g/100 g oil, while stearic acid had a content of 13.21–14.49 g/100 g oil. The sum of unsaturated fatty acids in this research reached a value close to that found by Berto et al. [6] for lipid extract of uxi pulp.

The effects of oleic acid (n-9) include its activity on the hypothalamus, a region that controls energy homeostasis. The hypothalamus combines energy intake with energy expenditure in order to prevent obesity through signs of satiety (leptin) and hormones (insulin). Upon detecting unsaturated fatty acid, the hypothalamus reduces food intake and, consequently, glucose intake [40].

Polyunsaturated fatty acids (PUFA) are considered essential fatty acids, as humans do not have the ability to desaturate bonds of the type n-3 and n-6, and for this reason, they must be obtained through food. Fatty acids n-6 are widely consumed in the form of linoleic acid, mainly from vegetable oils. PUFAs are precursors to eicosanoids, which are potent lipid mediators, playing an important role in inflammatory regulation [41]. According to the Food and Nutrient Database for Dietary Studies (FNDDS), PUFAs have high concentrations in nuts, seeds and oils of vegetable origin, such as flaxseed, soy and sunflower. According to US Institute of Medicine (IOM) the consumption of linoleic acid (n-6) should be 11.1–22.2 g/day, considering a diet of 2000 kcal/day, equivalent to 5–10 % of age-specific dietary macronutrients [42].

Epidemiological investigations demonstrate that an adequate diet with linoleic acid (n-6) is associated with lower levels of low plasma density lipoproteins (LDL-C), and dietary intervention research indicates that replacing 5 % of the energy in the SFA-derived diet with PUFA n-6 decreases LDL-C up to 10 %, significantly reducing the risk of developing cardiovascular disorders [11]. A higher consumption of PUFA, specifically, linoleic acid (n-6), is associated with improved glycemic levels [43].

Table 4
Triglycerides composition of uxi oil.

g Triglycerides/100 g oil								
TAG	X:Y	MM	40 °C 200 bar	40 °C 300 bar	40 °C 400 bar	60 °C 200 bar	60 °C 300 bar	60 °C 400 bar
PPP	48:0	806	1.44	1.34	1.45	1.57	1.35	1.23
PPS	50:0	834	2.65	2.52	2.65	2.57	2.52	2.35
PPO	50:1	832	9.86	9.24	9.66	10.16	9.30	8.98
PPLi	50:2	830	–	–	1.01	–	–	–
PSS	52:0	862	1.63	1.58	1.61	1.40	1.58	1.49
PSO	52:1	860	12.13	11.62	11.75	11.05	11.61	11.42
PSLi	52:2	858	–	1.03	1.22	–	–	1.10
POO	52:2	858	22.52	21.30	21.45	21.89	21.37	21.84
POLi	52:3	856	1.87	3.79	4.47	3.11	3.02	4.20
SSO	54:1	888	3.73	3.65	3.57	3.00	3.62	3.63
SOO	54:2	886	13.85	13.39	13.04	11,9	13.34	13.90
SOLi	54:3	884	1.15	2.39	2.72	1.69	1.89	2.67
OOO	54:3	884	17.14	16.38	15.87	15.71	16.37	17.71
OOLi	54:4	882	2.14	4.37	4.96	3.35	3.47	5.11

Where X: number of carbons, Y: Double Bond, MM: Molar Mass, P: Palmitic acid, S: Stearic acid, O: Oleic acid and Li: Linoleic acid.

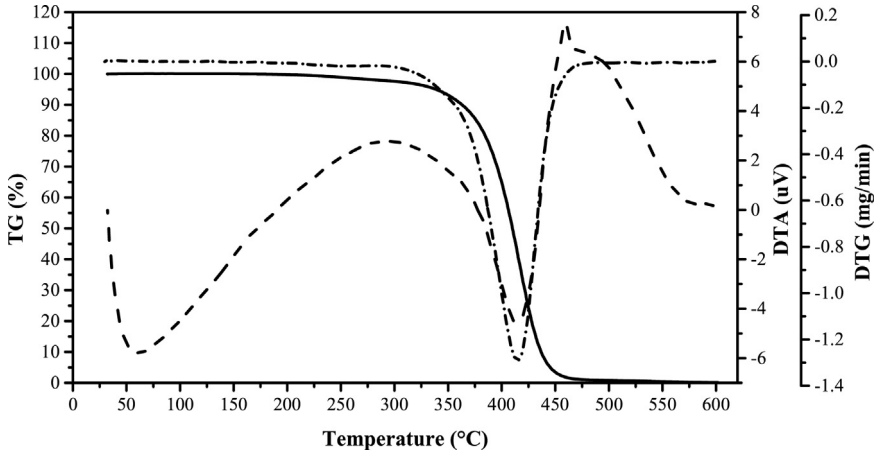


Fig. 3. Thermogravimetric behavior of uxi oil obtained by SC–CO_2.
Where TG: Thermogravimetric, DTA: Differential Thermal Analysis and DTG: Derivative Thermogravimetric.

3.5. Functional quality

Considering the majority composition of unsaturated fatty acids and their functional properties, uxi oil extracted with supercritical CO_2 can be characterized as a functional food due to the atherogenicity index (AI) and thrombogenicity index (TI), as well as the correlation between hypo and hypercholesterolemic compounds (H/H). The results showed that AI varied from 0.38 to 0.44, while TI varied from 1.22 to 1.32, and H/H from 2.36 to 2.66. The AI results were similar to those found by Cunha et al. [20] who evaluated the functional quality of bacaba-de-leque oil (*Oenocarpusdistichus* Mart.) and Silva et al. [39] who evaluated açaí oil (*Euterpe oleracea*), both products extracted with supercritical CO_2. The AI and TI information in lower values in the diets are desirable parameters for revealing a better nutritional and functional composition of the oils, especially for acting in the prevention of cardiovascular disorders. Conversely, H/H values should be analyzed inversely proportional to AI and TI, because H/H is related to the benefits of high-density lipoproteins (HDL) in metabolism. Thus, higher H/H values are desirable in lipid products for human consumption [35,36].

3.6. Triglycerides

In order to determine the composition of triglycerides (TAG), only those that would be present in the oil in an amount greater than 1 % of the total molecules were considered. The predictions were carried out using a computer application in Excel/VBA developed by the research group from the Extraction Laboratory - UFPA. The most representative triglycerides in the composition of uxi oil were OOO, POO, SOO and PSO, whose quantities add up to more than 70 % of the composition. The TAG profile of uxi oil is shown in Table 4. Other oils that also have a proven amount of fatty acids similarly had a high amount of triolein and other triglyceride molecules found in this study [44,45].

3.7. Thermogravimetric study

The degree of unsaturation from the constituent fatty acids represents the main parameter for determining the nutritional and functional qualities of uxi oil. The majority presence of unsaturated fatty acids indicates less stability in the presence of certain extrinsic factors that can contribute to oxidative processes, such as temperature and atmosphere, which represent deleterious elements of oils, as can be seen in Fig. 3. The thermogravimetric profile of uxi oil elucidates its behavior in relation to the gradual rise in temperature and inert atmosphere. Thermogravimetric and derived thermogravimetric analyzes (TG/DTG) show stability up to 300 °C for uxi oil extracted with supercritical CO_2 at 40 °C/300 bar, with pronounced loss of mass at 380 °C. The loss of mass of the uxi oil increases with increasing temperature. The observed temperature levels represent values above the usual for food preparation. Above 380 °C, the sample degrades successively, with loss of mass until complete decomposition at 600 °C.

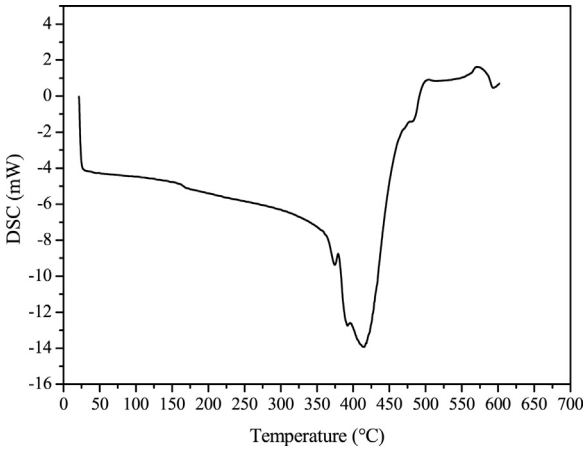


Fig. 4. Differential scanning calorimetry (DSC) of uxi oil extracted at 40 °C/300 bar.

The DTG curve confirms the more pronounced decomposition of the oil at temperature levels close to 380 °C, maintaining a linear pattern of behavioral changes, resisting the action of an oxidative factor, such as temperature, which kept inert the atmosphere applied in this investigation. The dynamics exhibited by the TG and DTG curves indicate changes in the uxi oil extracted via supercritical CO_2 when subjected to temperature increase, in a nitrogen atmosphere. The results of this investigation demonstrate the effects of vegetable oil oxidation on exothermic reactions, similarly to the results obtained by Santos et al. [46] in research carried out with sapucaia oil (*Lecythispisonis*Camb.) obtained via supercritical CO_2. Santos et al. [47] also found similar results in a study carried out for Brazil nut oil (*Bertholletia excelsa*).

The DSC curve (Fig. 4) shows the mass loss behavior of characteristic compounds of uxi oil, with a large oxidation peak at a temperature level close to 400 °C. This dynamics confirms the results observed for the TG and DTG curves, because in this temperature value there is a large release of energy resulting from the large decomposition of the oil's lipid compounds.

4. Conclusion

The process parameters analyzed in this study showed that the density of supercritical CO_2 was the main factor to obtain high mass yield of uxi oil, with the use of temperature close to the CO_2 critical point, which contributed to the quality of the obtained product. The fatty acids and triglycerides profiles (by prediction) and the thermogravimetric study showed that uxi oil has interesting functional quality due to the majority composition of unsaturated fatty acids that can be used to prevent the development of chronic-degenerative disorders. The functional quality indices: atherogenicity (AI), thrombogenicity (TI) and hypo / hypercholesterolemic ratio (H/H) express that uxi oil can be consumed in the human diet as table oil, similarly to olive oil. It also can be applied in the synthesis of functional foods or as phytotherapeutic product in the treatment of coronary and cardiovascular diseases based on n-9 and n-6.

Declaration of Competing Interests

The authors declared that they have no conflicts of interest to this work. We declared that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Finance Code 001.

References

[1] L.V.D. Freitas, A.C.R. Montes, E.I.A. Campos, E.C. Conceição, L.A. Tacon, A.D. Lanchote, L.A.P. Freitas, Rice spouted bed for manufacturing inclusion complexes of *Endopleura uchi* L extracts in β-cyclodextrin, Particuology. 42 (2019) 208–215, http://dx.doi.org/10.1016/j.partic.2018.03.014.
[2] J.F. Bento, G.R. Noleto, C. Lúcia, D.O. Petkowicz, Isolation of an arabinogalactan from *Endopleura uchi* bark decoction and its effect on HeLa cells, Carbohydr. Polym. 101 (2014) 871–877, http://dx.doi.org/10.1016/j.carbpol.2013.10.014.
[3] B.M. de S Hyacienth, B.L. Sánchez-Ortiz, K.R.T. Picanço, A.C.M. Pereira, D.C. de Sá Hyacienth, G.C. de Souza, Rdo S.F.Rodrigues Sarquis, G.M.G. Aduanga, A. Navarrete, J.C.T. Carvalho, *Endopleura uchi* (Huber) Cuatrec.: a medicinal plant for gynecological treatments – a reproductive toxicity assessment in zebrafish (*Danio rerio*), J. Ethnopharmacol. 250 (2020), 112457, http://dx.doi.org/10.1016/j.jep.2019.112457.
[4] P. Shanley, S. Silva, T. Melo, R. Carmenta, R. Nasi, From conflict of use to multiple use: forest management innovations by small holders in Amazonian logging frontiers, For. Ecol. Manage. 268 (2012) 70–80, http://dx.doi.org/10.1016/j.foreco.2011.05.041.
[5] F. Marx, E. Helena, G.B. Zoghbi, J.G.S. Maia, Studies of edible Amazonian plants. Part 5: chemical characterisation of Amazonian *Endopleura uchi* fruits, Eur. Food Res. Technol. 214 (2002) 331–334, http://dx.doi.org/10.1007/s00217-001-0477-7.
[6] A. Berto, A. Fiori, J. Vergilio, M. Matsushita, N. Evelázio, D. Souza, Proximate compositions, mineral contents and fatty acid compositions of native Amazonian fruits, Food Res. Int. 77 (2015) 441–449, http://dx.doi.org/10.1016/j.foodres.2015.08.018.
[7] P.A. Da Costa, C.A. Ballus, J. Teixeira-Filho, H.T. Godoy, Phytosterols and tocopherols content of pulps and nuts of Brazilian fruits, Food Res. Int. 43 (2010) 1603–1606, http://dx.doi.org/10.1016/j.foodres.2010.04.025.
[8] L.R. Silva, R. Teixeira, Phenolic profile and biological potential of *Endopleura uchi* extracts, Asian Pac. J. Trop. Med. 8 (2015) 889–897, http://dx.doi.org/10.1016/j.apjtm.2015.10.013.
[9] L.A.M. Magalhães, P. Lima, H.A. Marinho, A.G. Ferreira, Identificação de bergenina e carotenóides no fruto de uchi (*Endopleura uchi*, Humiriaceae), Acta Amaz. 37 (2007) 447–450.
[10] L.A. Tacon, L.A.P. Freitas, Box-Behnken design to study the bergenin content and antioxidant activity of *Endopleura uchi* bark extracts obtained by dynamic maceration, Brazilian J. Pharmacogn. 23 (2013) 65–71, http://dx.doi.org/10.1590/S0102-695X2012005000134.
[11] F. Marangoni, C. Agostoni, C. Borghi, A.L. Catapano, H. Cena, A. Ghiselli, C. La Vecchia, G. Lercker, E. Manzato, A. Pirillo, G. Riccardi, P. Risé, F. Visioli, A. Poli, Dietary linoleic acid and human health: focus on cardiovascular and cardiometabolic effects, Atherosclerosis. 292 (2020) 90–98, http://dx.doi.org/10.1016/j.atherosclerosis.2019.11.018.
[12] B. Yang, H. Chen, C. Stanton, R.P. Ross, H. Zhang, Y.Q. Chen, W. Chen, Review of the roles of conjugated linoleic acid in health and disease, J. Funct. Foods 15 (2015) 314–325, http://dx.doi.org/10.1016/j.jff.2015.03.050.
[13] R.H.H. Pinto, C. Sena, O.V. Santos, W.A. Da Costa, A.M.C. Rodrigues, R.N. Carvalho Jr., Extraction of bacaba (*Oenocarpus bacaba*) oil with supercritical CO_2: global yield isotherms, fatty acid composition, functional quality, oxidative stability, spectroscopic profile and antioxidant activity, Grasas Y Aceites 69 (2018) 246, http://dx.doi.org/10.3989/gya.0883171.
[14] A. Molino, S. Mehariya, G. Di Sanzo, V. Larocca, M. Martino, G.P. Leone, T. Marino, S. Chianese, R. Balducchi, D. Musmarra, Recent developments in supercritical fluid extraction of bioactive compounds from microalgae: role of key parameters, technological achievements and challenges, J. CO2 Util. 36 (2020) 196–209, http://dx.doi.org/10.1016/j.jcou.2019.11.014.
[15] F.C.S. Pires, A.P.S. Silva, M.A.R. Salazar, W.A. Costa, H.S.C. Costa, A.S. Lopes, H. Rogez, R.N. Carvalho Jr., Determination of process parameters and bioactive properties of the murici pulp (*Byrsonima crassifolia*) extracts obtained by supercritical extraction, J. Supercrit. Fluids 146 (2019) 128–135, http://dx.doi.org/10.1016/j.supflu.2019.01.014.
[16] O.V. Santos, N.C.F. Correa, R. Carvalho Jr., C.E.F. da Costa, J. de F.C. Moraes, S.Cda S. Lannes, Quality parameters and thermogravimetric and oxidative profile of muruci oil (*Byrsonima crassifolia* L.) obtained by supercritical CO_2, Food Sci. Technol. 38 (2018) 172–179, http://dx.doi.org/10.1590/1678-457x.30616.
[17] American Society of Agriculptural Engineers (ASAE), Method of Determining and Expressing Particle Size of Chopped Forage Materials by Screening - Standards S424.1, St. Joseph. MI: ASAE, 1998.
[18] IAL, Instituto Adolfo Lutz - Métodos Físico-químicos Para Análise De Alimentos, 4th ed., 2008, São Paulo.
[19] R. Span, W. Wagner, A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa, J. Phys. Chem. Ref. Data 25 (1996) 1509–1596, http://dx.doi.org/10.1063/1.555991.
[20] V.M.B. Cunha, M.P. da Silva, S.H.B. de Sousa, P.N. Bezerra, E.G.O. Menezes, N.J.N. da Silva, D.A.D.S. Banna, M.E. Araújo, R.N. de Carvalho Jr.,

Bacaba-de-leque (*Oenocarpus distichus* Mart.) oil extraction using supercritical CO_2 and bioactive compounds determination in the residual pulp, J. Supercrit. Fluids 144 (2019) 81–90, http://dx.doi.org/10.1016/j.supflu.2018.10.010.
[21] D. Peng, D.B. Robinson, A new two-constant equation of state, Ind. Eng. Chem. Fundam. 15 (1976) 59–64.
[22] M.E. Araújo, M.A.A. Meireles, Improving phase equilibrium calculation with the Peng-Robinson EOS for fats and oils related compounds/supercritical CO_2 systems, Fluid Phase Equilib. 169 (2000) 49–64, http://dx.doi.org/10.1016/S0378-3812(00)00307-1.
[23] J.A. Nelder, R. Mead, A simplex method for function minimization, Comput. J. 7 (1965) 308–313, http://dx.doi.org/10.1093/comjnl/7.4.308.
[24] I. Ashour, R. Wennersten, Modified carnahan-starling-soave equation for the calculation of vapor pressures for saturated fatty acids, J. Supercrit. Fluids 2 (1989) 73–79, http://dx.doi.org/10.1016/0896-8446(89)90013-2.
[25] L. Constantinou, R. Gani, New group contribution method for estimating properties of pure compounds, AIChE J. 40 (1994) 1697–1710, http://dx.doi.org/10.1002/aic.690401011.
[26] W. Wagner, New vapour pressure measurements for argon and nitrogen and a new method for establishing rational vapour pressure equations, Cryogenics (Guildf). 13 (1973) 470–482, http://dx.doi.org/10.1016/0011-2275(73)90003-9.
[27] C.H. Tu, Group-contribution method for the estimation of vapor pressures, Fluid Phase Equilib. 99 (1994) 105–120, http://dx.doi.org/10.1016/0378-3812(94)80025-1.
[28] P. Maheshwari, Z.L. Nikolov, T.M. White, R. Hartel, Solubility of fatty acids in supercritical carbon dioxide, J. Am. Oil Chem. Soc. 69 (1992) 1069–1076, http://dx.doi.org/10.1007/BF02541039.
[29] M. Zou, Z.R. Yu, P. Kashulines, S.S.H. Rizvi, J.A. Zollweg, Fluid-Liquid phase equilibria of fatty acids and fatty acid methyl esters in supercritical carbon dioxide, J. Supercrit. Fluids 3 (1990) 23–28, http://dx.doi.org/10.1016/0896-8446(90)90046-O.
[30] J.S. Yau, Y.Y. Chiang, D.S. Shy, F.N. Tsai, Solubilities of carbon dioxide in carboxylic acids under high pressures, J. Chem. Eng. Japan. 25 (1992) 544–548, http://dx.doi.org/10.1252/jcej.25.544.
[31] G.R. Khan, F. Scheinmann, Some recent advances in physical methods for analysis and characterization of polyunsaturated fatty acids, Prog. Chem. Fats Other Lipids 15 (1978) 343–367, http://dx.doi.org/10.1016/0079-6832(77)90012-X.
[32] L. Mondello, FFNSC 2: Flavors and Fragrances of Natural and Synthetic Compounds, Mass Spectral Database, 2011, http://dx.doi.org/10.16194/j.cnki.31-1059/g4.2011.07.016.
[33] NIST, Mass Spectral Database, in, 2011.
[34] R. Adams, O. Sparkman, Review of identification of essential oil components by gas Chromatography/Mass spectrometry, J. Am. Soc. Mass Spectrom. 18 (2007) 803–806, http://dx.doi.org/10.1021/jasms.8b02916.
[35] T.L.V. Ulbricht, D.A.T. Southgate, Coronary heart disease: seven dietary factors, Lancet. 338 (1991) 985–992, http://dx.doi.org/10.1016/0140-6736(91)91846-M.
[36] J. Santos-Silva, R.J.B. Bessa, F. Santos-Silva, Effect of genotype, feeding system and slaughter weight on the quality of light lambs. II. Fatty acid composition of meat, Livest. Prod. Sci. 77 (2002) 187–194, http://dx.doi.org/10.1016/S0301-6226(02)00059-3.
[37] F.A. Norris, K.F. Mattil, A new approach to the glyceride structure of natural fats, J. Am. Oil Chem. Soc. 24 (1947) 274–275, http://dx.doi.org/10.1007/BF02643335.
[38] C.C.R. Batista, M.S. Oliveira, M.E. Araújo, A.M.C. Rodrigues, J.R.S. Botelho Filho, A. Souza Filho, N. Machado, R.N. Carvalho Jr., Supercritical CO_2 extraction of açaí (*Euterpe oleracea*) berry oil: global yield, fatty acids, allelopathic activities, and determination of phenolic and anthocyanins total compounds in the residual pulp, J. Supercrit. Fluids 107 (2016) 364–369, http://dx.doi.org/10.1016/j.supflu.2015.10.006.
[39] M.P. Silva, V.M.B. Cunha, S.H.B. Sousa, E.G.O. Menezes, P.D.N. Bezerra, J.T. De Farias Neto, G.N.R. Filho, M.E. Araújo, R.N. De Carvalho, Supercritical CO_2 extraction of lyophilized Açaí (*Euterpe oleracea* Mart.) pulp oil from three municipalities in the state of Pará, Brazil, J. CO2 Util. 31 (2019) 226–234, http://dx.doi.org/10.1016/j.jcou.2019.03.019.
[40] X. Palomer, J. Pizarro-Delgado, E. Barroso, M. Vázquez-Carrera, Palmitic and Oleic Acid: The Yin and Yang of Fatty Acids in Type 2 Diabetes Mellitus, Trends Endocrinol. Metab. 29 (2018) 178–190, http://dx.doi.org/10.1016/j.tem.2017.11.009.
[41] M. Jóźwiak, A. Filipowska, F. Fiorino, M. Struga, Anticancer activities of fatty acids and their heterocyclic derivatives, Eur. J. Pharmacol. 871 (2020), http://dx.doi.org/10.1016/j.ejphar.2020.172937.
[42] K.H. Zirnheld, D.R. Warner, J.B. Warner, J.E. Hardesty, C.J. McClain, I.A. Kirpich, Dietary fatty acids and bioactive fatty acid metabolites in alcoholic liver disease, Liver Res. 3 (2019) 206–217, http://dx.doi.org/10.1016/j.livres.2019.10.001.
[43] M.A. Belury, R.M. Cole, D.B. Snoke, T. Banh, A. Angelotti, Linoleic acid, glycemic control and Type 2 diabetes, Prostaglandins Leukot, Essent. Fat. Acids. 132 (2018) 30–33, http://dx.doi.org/10.1016/j.plefa.2018.03.001.
[44] D. Ollivier, J. Artaud, C. Pinatel, J.P. Durbec, M. Guérère, Differentiation of French virgin olive oil RDOs by sensory characteristics, fatty acid and triacylglycerol compositions and chemometrics, Food Chem. 97 (2006) 382–393, http://dx.doi.org/10.1016/j.foodchem.2005.04.024.
[45] J.S. Amaral, I. Mafra, M.B.P.P. Oliveira, Characterization of three portuguese varietal olive oils based on fatty acids, triacylglycerols, phytosterols and vitamin e profiles: application of chemometrics, olives olive oil heal, Dis. Prev. (2010) 581–589, http://dx.doi.org/10.1016/B978-0-12-374420-3.00063-2.
[46] O.V. dos Santos, R.N. Carvalho, C.E.F. da Costa, S.Cda S. Lannes, Chemical, chromatographic-functional, thermogravimetric-differential and spectroscopic parameters of the sapucaia oil obtained by different extraction methods, Ind. Crops Prod. 132 (2019) 487–496, http://dx.doi.org/10.1016/j.indcrop.2019.02.043.
[47] O.V. Santos, N.C.F. Correa, R.N. Carvalho, C.E.F. Costa, L.F.F. França, S.C.S. Lannes, Comparative parameters of the nutritional contribution and functional claims of Brazil nut kernels, oil and defatted cake, Food Res. Int. 51 (2013) 841–847.