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Influence of toasting and the seed variety on the physico-chemical and thermo-oxidative characteristics of the flaxseed oil

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Abstract Physico-chemical properties, spectroscopy, and thermal analyses were used aiming at evaluating the influence of toasting and of the flaxseed variety on thermo-oxidative behavior of flaxseed oils. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were associated to gas chromatography, infrared spectroscopy and UV–Vis spectroscopy, as well as to physico-chemical analyses to characterize the oils obtained from raw and toasted flaxseeds. No meaningful differences in the thermal and oxidative stabilities were noticed comparing oils obtained from the brown and the golden flaxseeds. Nevertheless, the UV–Vis spectra indicated that both flaxseed oils were at the beginning of the oxidation process. The previous toasting of the seeds led to a higher oxidation for both varieties being harmful to the flaxseed oil quality.

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Introduction

The privileged lipid profile of flaxseed oil, associated to the presence of phytochemicals, such as lignins, flavonoids and phytosterols, and also of fibers, makes this seed into a functional food of high interest for food industry. Flaxseed contains approximately 40% lipids being most of them represented by two important essential fatty acids (EFAs). About 57% of the lipids correspond to the EFA omega-3 (n-3) alpha-linolenic acid and around 16% is composed of EFA omega-6 (n-6) linoleic acid. The monounsaturated fatty acids represent about 18% of the lipids and only 9% of them are found as saturated acids. The high content of alpha-linolenic acid contributes to a balanced dietetic proportion of n-3:n-6 fatty acids of around 1:0.3 [1, 2].

The eicosapentaenoic and the docosahexaenoic fatty acids resultants from the metabolism of alpha-linolenic acid compete with the arachidonic acid derived from gamma-linolenic acid in the enzymatic reactions, reducing the formation of pro-inflammatory mediators and favoring the production of mediators with scarce or none biological activity. These mechanisms bring cardioprotector effects and reduce the risk of cancer, psoriasis, and articular diseases [1–4].

On the other hand, the high content of poly-unsaturated fatty acids present in the flaxseed oils makes it more susceptible to oxidation. Such vulnerability is enhanced when flaxseed in heat treated as in toasting processes used to inhibit anti-nutritional factors [1, 4–6].

Therefore, this study aims at evaluating the influence of toasting and of the flaxseed variety on the thermo-oxidative

properties and characteristics of flaxseed oils, using chromatography, spectroscopy, physico-chemical properties, and thermal analysis.

Experimental

Golden and brown flaxseeds were obtained from Paraoara Alimentos Naturais (Jaboatão dos Guararapes, PE, Brazil), with commercial degree. Each variety was divided in two approximately equal parts. One of these parts was heat treated at 160 °C for 15 min (toasted seed), while the other one was used as received (raw seed). Oil extraction was done by mechanical pressing. Thus, four groups of samples were obtained, being denoted as raw golden flaxseed oil (RGFO), raw brown flaxseed oil (RBFO), toasted golden flaxseed oil (TGFO), and toasted brown flaxseed oil (TBFO). Later, all samples were characterized in triplicate and thermally evaluated as described below.

The thermogravimetric (TG) and the calorimetric (DSC) curves were recorded using a SDT 2960 thermal analyzer (TA Instruments) and a DSC 2920 calorimeter (TA Instruments), respectively. The non-isothermal method was applied using 10 mg of sample heated at 10 °C min^{-1} up to 600 °C. The analyses were performed using platinum pans and synthetic air at a flow rate of 50 mL min^{-1}. The isothermal curves were obtained at 110 °C using the same experimental conditions previously described.

The lipid profile of the oils was determined by gas chromatography, according to the method described by Maia and Rodriguez-Amaya [7]. The methyl esters obtained from the oils were injected into a gas chromatograph coupled to a mass spectrometer GCMS-QP 2010 (Shimadzu). A Durabond DB-23 column from J & W Scientific was used (30-m long, 0.25 mm of internal diameter, and 0.25 μm of film thickness). 1 μL of sample diluted with hexane in the proportion 1:20 was injected into the column with a split ratio of 1:50 and using helium as the carrier gas with a flow rate of 3 mL min^{-1}. Column temperature was raised from 130 up to 200 °C with a heating rate of 10 °C/min with a soaking time of 1 min, followed by a heating up to 218 °C (rate of 3 °C/min) and 230 °C (rate of 20 °C/min), both with soaking times of 1 min too. The injector and the detector temperatures were 230 and 220 °C, respectively. The fatty acids were identified by comparison with the detector library, being quantified by the area of each peak, as a function of the overall peak area.

The physico-chemical properties were measured according to the methods described by AOCS [8]. The oil samples were also characterized by UV–Vis spectroscopy using a Shimadzu UV-2550 spectrophotometer at the 200–400 nm range after dilution in dichloromethane (1:10000). The oil samples were also characterized by infrared spectroscopy using KBr pellets in a BOMEM MB 102 spectrophotometer at the 4000–400 cm^{-1} range.

The results were analyzed on the statistical standpoint. The averages and standard deviations were calculated using comparative tests (*t* test *of* Student and Tukey) for evaluate the presence of meaningful differences ($P < 0.05$) between the treatments, utilizing the *Statistical Package for the Social Sciences* (SPSS), version 13.1 and the Assistat 7.5 beta.

Results and discussion

Results obtained from chromatography are presented in Table 1.

The contents of unsaturated and saturated fatty acids were similar for the two flaxseed oils (Table 1). These

Table 1 Fatty acid profile of the flaxseed oils

Fatty acids	Raw flaxseed oils/%		Toasted flaxseed oils/%	
	Golden	Brown	Golden	Brown
Total saturated	14.61^{a}	14.27^{c}	14.34^{b}	13.65^{d}
Palmitoleic acid (C16:1) n-7	$0.07^{a} \pm 0.00$	n.d.	$0.07^{a} \pm 0.00$	n.d.
Oleic acid (C18:1) n-9	$23.70^{b} \pm 0.00$	$27.36^{a} \pm 0.02$	$24.04^{b} \pm 0.14$	$27.40^{a} \pm 0.31$
Gadoleic acid (C20:1) n-9	$0.36^{a} \pm 0.01$	$0.33^{a} \pm 0.02$	$0.35^{a} \pm 0.01$	$0.30^{a} \pm 0.04$
Total monounsaturated	24.13^{c}	27.69^{a}	24.46^{b}	27.7^{a}
Linoleic acid (C18:2) n-6	$18.48^{a} \pm 0.03$	$15.24^{b} \pm 0.03$	$18.23^{a} \pm 0.05$	$14.85^{b} \pm 0.19$
Alpha-linolenic acid (C18:3) n-3	$43.27^{a} \pm 0.20$	$43.64^{a} \pm 1.03$	$42.88^{a} \pm 0.11$	$43.81^{a} \pm 0.36$
Total polyunsaturated	61.75^{a}	58.88^{c}	61.11^{b}	58.66^{d}
n-3:n-6 ratio	2.34^{c}	2.86^{b}	2.35^{c}	2.95^{a}
Total unsaturated	85.88^{c}	86.57^{a}	85.57^{d}	86.36^{b}

Different letters, in the same line, point out meaningful differences among the samples at the 95% confidence level in the Tukey's test

n.d. not detected

values were quite different than data reported in literature [1, 9, 10]. Morris [1] found lower amounts of saturated fatty acids (9.0%) and higher amounts of unsaturated ones (91.0%) than this study. Moreover, the amount of the n-3 alpha-linolenic acid did not vary with processing or with flaxseed variety. The amount of alpha linolenic acid obtained in this study was also smaller the amounts obtained by Firestone [9] (52.0 and 54.0%) and by Choo et al. [10] (51.8 and 60.4%). Such variations may be related to differences from one variety to another, origin of the seeds, environmental changes, and cultivation methods.

The oil sample from the raw brown flaxseeds (RBFO) presented a smaller content of omega-6 (n-6) linoleic acid than the oil from the golden variety (RGFO). On the other hand, a higher content of oleic acid was found in the RBFO (Table 1).

The fatty acid contents different from data reported in literature associated to physico-chemical properties near the lower standard limit or slightly outside the standard limits reported for flaxseed oils (Table 2) suggest that oxidative processes may have occurred. Inappropriate storage conditions or long storage times may be related to these changes. Other possibility is the degradation due to pressing time and also due to heating released during pressing [10].

The results indicated that toasting increased the oxidative process of the oils from both flaxseed varieties causing meaningful changes in their physico-chemical properties (Table 2), as the increase of acid value, free fatty acids, saponification index, peroxide index and viscosity, and also the reduction of the refractive index.

According to Araújo et al. [4] and to the AOCS [8], exposition to heat and oxidation process associated with the hydrolytic rancidity affect the refraction index and contribute to the increase of the oil acidity. As stated by Benedikt [11], high saponification indexes point out fatty acids of low molecular weight. The viscosity raise in oils submitted to thermal treatments can take place due to the rearrangement of the fatty acid molecules, which are prone to oxidation and polymerization induced by heat [12, 13].

The infrared and the UV–Vis spectra of the flaxseed oils as well the deconvoluted UV–Vis spectra are illustrated in Fig. 1.

Typical triacylglycerol absorptions were noticed in the infrared spectra, such as the strong peak ascribed to the C=O carbonyl stretching vibration at 1744 cm^{-1} and the strong peak at 1165 cm^{-1}, characteristic of the C–O–C ester stretching. Bands at 3009 and 1651 cm^{-1} were also noticed, being assigned to the =C–H and to the alkene C=C stretching, respectively [16–18]. No meaningful differences were noticed among the different samples.

Comparing the UV–Vis spectra of oils from raw and toasted flaxseeds, a reduction in the absorption of the bands at 230 and 270 nm was noticed due to the toasting process. This behavior was attributed to the reduction in conjugated dienes and trienes. The highest reduction observed for the oil obtained from the brown variety indicated that this flaxseed oil was more susceptible to heating. This observation is consistent with a more advanced oxidative process. Moreover, the absorption bands at 230 and 270 nm indicated that both oils were already oxidized, even before seed toasting, being accelerated by this process. These results are in agreement with physico-chemical properties.

The TG, DTG, and DSC curves of the oils obtained from raw and toasted flaxseeds are displayed in Fig. 2. The data obtained from these curves are summarized in Table 3.

It is noticed in Fig. 2a and b that the samples RGFO and RBFO displayed similar thermogravimetric profiles with three mass loss steps and almost the same thermal stability (mass loss starts at 208 and 209 °C, respectively, as presented in Table 3). The oils obtained from both raw flaxseeds also displayed similar oxidative stabilities, with OIT_{onset} values of 55 and 51 min for RGFO and RBFO, respectively (Fig. 2c, d; Table 3). These results are in

Table 2 Physico-chemical data of the flaxseed oils

Parameters	Raw flaxseed oils		Toasted flaxseed oils		Standard [9, 12, 14, 15]
	Golden	Brown	Golden	Brown	
Iodine value/g I_2 100 g^{-1}	$173.44^{a} \pm 0.61$	$171.79^{a} \pm 2.72$	$172.25^{a} \pm 0.07$	$171.55^{a} \pm 0.87$	170–203
Acid value/g oleic acid 100 g^{-1}	$1.11^{b} \pm 0.02$	$0.80^{c} \pm 0.05$	$1.68^{a} \pm 0.01$	$1.08^{b} \pm 0.08$	<3
Free fatty acids/%	$0.95^{c} \pm 0.01$	$0.78^{d} \pm 0.01$	$1.72^{a} \pm 0.00$	$1.04^{b} \pm 0.03$	0.1–2
Saponification index/mg KOH g^{-1}	$182.62^{b} \pm 0.54$	$184.01^{b} \pm 1.07$	$202.49^{a} \pm 0.40$	$201.46^{a} \pm 0.87$	187–195
Peroxide index/meq 1000 g^{-1}	$0.00^{b} \pm 0.00$	$0.00^{b} \pm 0.00$	$0.77^{a} \pm 0.00$	$0.77^{a} \pm 0.00$	Up to 15
Density at 25 °C/g cm^{-3}	$0.926^{a} \pm 0.000$	$0.925^{a} \pm 0.001$	$0.924^{a} \pm 0.000$	$0.924^{a} \pm 0.001$	–
Viscosity/cP	$45.23^{b} \pm 0.15$	$47.83^{a} \pm 0.42$	$47.90^{a} \pm 0.79$	$48.67^{a} \pm 0.76$	42 and 45
Refraction index at 40 °C	$1.4751^{a} \pm 0.0000$	$1.4736^{b} \pm 0.0000$	$1.4731^{c} \pm 0.0000$	$1.4731^{c} \pm 0.0000$	–

Different letters, in the same line, point out meaningful differences among the samples at the 95% confidence level in the Tukey's test

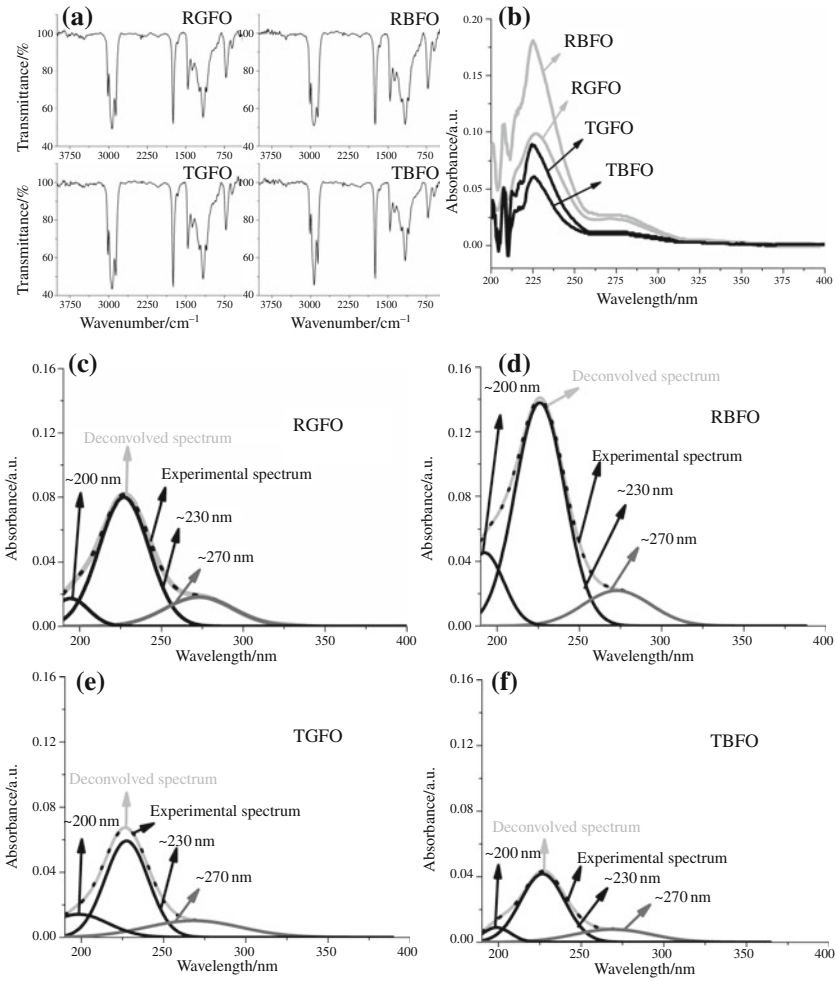

Fig. 1 Absorption spectra of the raw and toasted flaxseed oils: **a** infrared spectra, **b** UV–Vis spectra, **c**–**f** deconvolved UV–Vis spectra

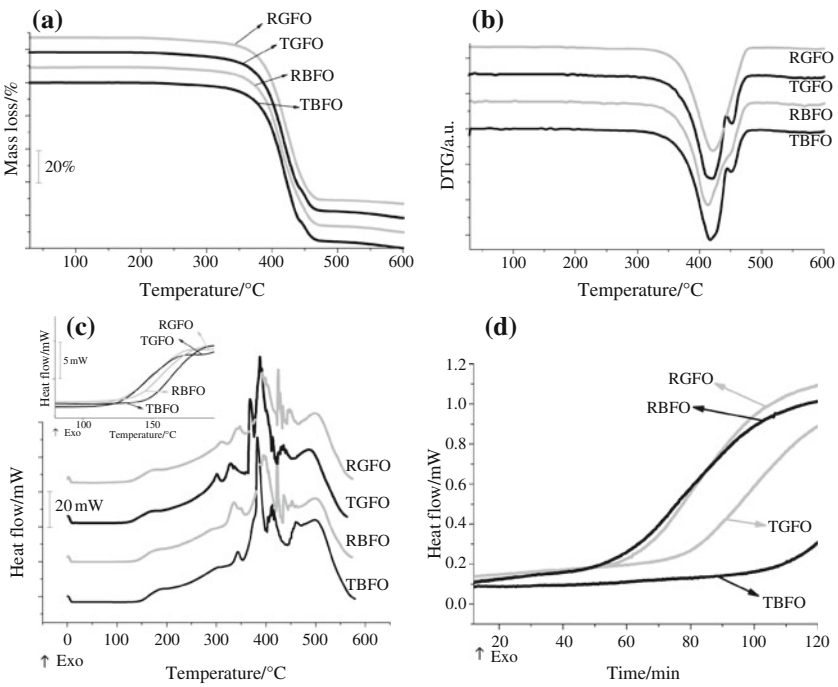

Fig. 2 Curves of the oils obtained from toasted and raw flaxseeds. **a** TG, **b** DTG, **c** non-isothermal DSC, and **d** isothermal, at 110 °C

Table 3 Thermogravimetric and calorimetric data of the flaxseed oil samples

Samples	TG					DSC	
	Step	$T_{initial}$/ °C[a]	T_{final}/ °C[b]	T_{peak} DTG/ °C[c]	Δm/ %[d]	OT_{onset}/ °C[e]	OIT_{onset}/ min at 110 °C[f]
Raw seed oils							
Golden	1st	208	327	214	3.2	153	55
	2nd	327	479	422	94.5		
	3rd	479	600	584	2.4		
Brown	1st	209	312	275	2.2	162	51
	2nd	312	476	414	93.1		
	3rd	476	601	569	3.5		
Toasted seed oils							
Golden	1st	200	305	203	2.6	159	69
	2nd	305	442	420	79.1		
	3rd	442	478	452	13.8		
	4th	478	601	576	4.4		
Brown	1st	202	313	208	2.3	165	99
	2nd	313	442	416	80.6		
	3rd	442	479	452	12.6		
	4th	479	600	578	4.3		

[a] Initial temperature

[b] Final temperature

[c] Peak temperature

[d] Mass loss

[e] Onset oxidation temperature

[f] Oxidative induction time

agreement with the chemical and physico-chemical properties (Tables 1, 2). Rudnik et al. [19] studied flaxseed oil samples without antioxidants and obtained OT_{onset} values of 186 °C and OIT_{onset} values of 23 min (isotherm at 130 °C) using DSC analysis, under oxygen atmosphere, heating rate of 20 °C min^{-1} and flow rate of 60 mL min^{-1}.

The thermal analysis of the oils obtained from the toasted flaxseeds showed a different behavior in relation to the oils obtained from the raw flaxseeds. One more mass loss step was observed, besides a slight increase in the OT_{onset} values and a meaningful increase in the OIT_{onset} values for both flaxseed varieties (Fig. 2; Table 3). These results can be assigned to the formation of carbonic chains with higher molecular weight, as a consequence of the oxidation of compounds present in the flaxseed. According to Cämmerer and Kroh [20], toasting process damages lipid storage cellular structure, favoring the action of lipolytic enzymes, the water elimination and the consumption of antioxidants, making lipids more susceptible to oxidation reactions. These results are in agreement with the physico-chemical properties and with the UV–Vis spectra, indicating that toasting process leads to oxidation reactions.

Conclusions

The oils obtained from golden and brown raw flaxseeds displayed similar thermal and oxidative stabilities, with an initial oxidation process indicated by UV–Vis spectroscopy. Oxidative processes were higher in oils obtained from toasted flaxseed. These results were observed by the physico-chemical properties, UV–Vis spectroscopy, and thermal analysis—TG and DSC.

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