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Evaluation of Bioactive Compounds and Antioxidant Activity of Refined Vegetable Oils

Avaliação de compostos bioativos e Atividade Antioxidante de óleos vegetais refinados

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ABSTRACT

The objectives of this study were to evaluate the refined soybean, canola, corn and sunflower oils different brands and quantify the bioactive compounds and investigate the antioxidant activity of such oils. Corn oil showed higher content of phenolic compounds, while soybean oil obtained higher of total carotenoid content. For all oil, the highest total phytosterol content was obtained for brand M2. The γ-tocopherol was the predominant tocol in soybean oil. Refined soybean and corn oils showed greater effectiveness in DPPH●, FRAP, and β-carotene/linoleic acid trials. It can be considered that these oils are of high quality, presenting bioactive compounds and antioxidant activity through the methods used.

Keywords: Refining. Vegetable oils. Bioactive compounds. Antioxidant activity.

RESUMO

Os objetivos deste trabalho foram avaliar os óleos refinados de soja, canola, milho e girassol de diferentes marcas e quantificar os compostos bioativos e averiguar a atividade antioxidante de tais óleos. O óleo de milho apresentou maior teor de compostos fenólicos totais, enquanto que o óleo de soja obteve maior teor de carotenoides totais. Para todos os óleos, os maiores teores de fitosteróis totais foram obtidos para a marca M2. O γ-tocoferol foi o tocol predominante no óleo de soja. Os óleos refinados de soja e milho apresentaram maior efetividade nos ensaios DPPH•, FRAP e β-caroteno/ácido linoleico. Pode-se considerar que esses óleos são de elevada qualidade, apresentando substâncias bioativas e atividade antioxidante pelos métodos utilizados.

Palavras-chave: Refinação. Óleos vegetais. Compostos bioativos. Atividade antioxidante.

1. INTRODUCTION

Edible oils are derived from crude oils, which are obtained by mechanical pressing or by solvent extraction process. In sequence, the mixture obtained from this process, known as miscella, passes through the distillation stage. The oil distillate still undergoes a degumming process which consists in the separation of the triglycerides from other undesirable elements, neutralization, clarification and product deodorizing.

The use of crude oils by consumers is not common due to their color and odor characteristics that are generally unacceptable. This causes industrial processing to be necessary, and efficient, leading to the removal of these unpleasant compounds and refining also has the purpose of removing impurities that affect the quality of the final product, however, this process is should aim for the least possible effect on the desired components (tocopherols, sterols, phenol) and minimum oil losses (GHARBY, 2022).

The vegetable oils may contain significant concentrations of bioactive compounds such as phytosterols, tocopherols, carotenoids and phenolic compounds. However, despite the bioactive compounds being of great interest in the food field, these components can be removed excessively during the steps of industrialization of vegetable matrices to obtain refined oils.

The identification and quantification of bioactive compounds in vegetable oils is of fundamental importance. Many of these compounds have antioxidant activity, acting as substances that retard or prevent the action of free radicals in the body, as well as acting on blood cholesterol control and may have potential for preventing cardiovascular diseases (SZYDŁOWSKA-CZERNIAK et al. 2008; FLAKELAR et al., 2022).

Refined vegetable oils are the raw material for the margarine industry, frying oils and other food products, used also to make special lipids as fat substitute of human milk for infant food, edible oils enriched with essential short and medium chain fatty acids. Vegetable oils provide more power than any other food group. They are also carriers of fat-soluble vitamins and can provide essential fatty acids (GHAZANI et al. 2013).

This study aimed to evaluate refined soybean, canola, corn and sunflower oils through quantify the bioactive compounds and to investigate the antioxidant activity of such oils.

2. MATERIALS AND METHODS

Materials

This study used refined soybean, canola, corn and sunflower oils of five brands named M1, M2, M3, M4 and M5. The samples were donated by different processing Brazilian industries

of vegetable oils. All samples were within the expiration date. In the Oils and Fats laboratory, samples were stored in amber glass bottles and inerted with nitrogen gas and then stored in the freezing chamber (-18 °C), protected from light until the time of analysis. All reagents used in this study were of analytical grade.

Analysis of bioactive compounds

Total phenolic compounds of grape seed extract and oil treatments were quantified spectrophotometrically (UV-mini-1240 model, Shimadzu, Kyoto, Japan) at 765 nm, using the Folin-Ciocalteu reagent and the standard curve of gallic acid (SINGLETON; ROSSI, 1965). Total phenolic compounds were expressed in milligrams of gallic acid equivalents per kilogram of oil (mg GAE/kg).

The content of the total carotenoids was performed by scanning spectrophotometer (UV-mini-1240 model, Shimadzu, Kyoto, Japan), according to the methodology described by Rodriguez-Amaya and Kimura (2004). The quantification was performed by absorption in the wavelength of maximum absorption and with an absorptivity value of 2592, in petroleum ether. The values were expressed as µg of β-carotene per gram of oil (µg β-carotene/g).

The composition of phytosterols was measured using gas chromatography with prior saponification of the samples (50-80 mg). Saponification was performed according to the methodology published by Duchateau et al. (2002). For the determination of the content of phytosterols, AOCS method Ch 6-91 (2009) was used, with adaptations. The analysis was performed using the GC-2010 Plus gas chromatograph (Plus-2010 model, Shimadzu, Tokyo, Japan), equipped with flame-ionization detector (GC-FID), split injector, and automatic sampler. Conditions of analysis: fused silica capillary column (30 x 0.25mm id, 0.25 µM film thickness, Restek RTX 5, Shimadzu, Tokyo, Japan). The programming of the column temperature started at 100 °C for 2 min, heated at 15 °C/min to 260 °C, and maintained in isothermal state for 35 min. The temperatures employed in the injector and detector were 280 and 320 ° C, respectively. Samples of 1.0 uL were injected, adopting a split ratio of 1:50. The carrier gas was hydrogen with a linear speed of 40 mL/min. The phytosterols (campesterol, stigmasterol, and β-sitosterol) were identified by comparison with the retention times of pure standards (Supelco, Bellefonte, USA) analyzed under the same conditions of the samples. The quantification of each isomer was performed by internal standardization (5α-cholestan-3β-ol), based on the areas of the peaks. nd: not detected

(detection limits of: campesterol ≤ 5.20 mg/100 g, stigmasterol ≤ 5.60 mg/100 g, stigmastanol ≤ 4.25 mg/100 g).

The composition of tocopherols was determined by AOCS Ce 8-86 (2009) using an HPLC system (210-263 model, Varian Inc., Walnut Creek, USA) equipped with fluorescence detector. Forty milligrams of each oil treatment were diluted with n-hexane, and 20 µL of the sample were injected. The operating conditions Were λ excitation of 290 nm and λ emission of 330 nm. A normal phase column (100 Si, 250 mm x 4.6 mm id, 0.5 µM particle size, Microsorb, Varian Inc., Walnut Creek, USA) was used, with n-hexane-isopropanol (99.5-0.5, v/v) mobile phase. The system was operated isocratically at a flow rate of 1.2 mL/min. The identification of tocopherols (α-, β-, γ- and δ-tocopherol) was conducted by comparing the HPLC retention time with those of standard compounds (Supelco, Bellefonte, USA) under the same operating conditions, and the quantification was based on an external standard method. Nd: not detected (detection limits of α- ≤ 3.15 mg/kg, β ≤ 1.10 mg/kg, γ ≤ 8.65 mg/kg, δ ≤2.30mg/kg).

Antioxidant activity

ABTS $^{\bullet+}$ measurement was performed as described by Re et al. (1999). Absorbance values at 730 nm were taken after 6 min in UV-vis spectrophotometer (UV-mini-1240, Shimadzu, Kyoto, Japan). Aqueous solutions of Trolox Concentrations (between 0 and 2000 µM) were used for calibration. Results were expressed in micromolar of Trolox per 100 gram of oil (µM Trolox/100 g).

DPPH method. The antioxidant capacity of oils was determined as described by Kalantzakis et al. (2006). This assay consists of spectrophotometric measurement of the intensity of color change in solution, depending on the amount of DPPH. The absorbance of the resulting solution was measured at 515 nm using a UV-vis spectrophotometer (Shimadzu, Kyoto, Japan). The results were expressed in percentage (%).

FRAP method. The method was carried out for the oil as previously described by Szydłowska-Czerniak et al. (2008). Maximum absorbance values were taken at 595 nm after 30 min using a UV-vis spectrophotometer (UV-mini-1240 model, Shimadzu, Kyoto, Japan). Aqueous solutions of Trolox concentrations (between 0 and 2000 µM) were used for calibration. Results were expressed in micromolar of Trolox per 100 gram of oil (µM Trolox/100 g).

β-carotene/linoleic acid method, according to the method described by Marco (1968) and modified by Miller (1971), an aliquot of the β-carotene solution (0.2 mg/mL in chloroform)

was mixed to 50 mg of linoleic acid and 200 mg of Tween 40 and, after this, the chloroform completely evaporated with nitrogen. After addition of 50 ml of distilled water saturated with oxygen, 5.0 mL aliquots of the β-carotene/Linoleic acid emulsion were mixed to 0.5 ml of the ethanolic solution of the sample (20 mg/mL) in test tubes. The absorbance at 470 nm was monitored every 15 min for 2 h, with the tubes kept in a water bath at 50 °C during the readings.

Statistical analysis

The experimental design was completely randomized in a 5 x 4 factorial scheme with five brands and four types of oils. A completely randomized design was conducted when no data was detected. Analyses were performed in triplicate. Results were expressed as mean values and standard deviation and were evaluated using one-way analysis of variance (ANOVA) and Tukey test to check the difference between brands and oils. The Assistat 7.7 beta software was used. Differences were considered significant when $p \leq 0.05$.

3. RESULTS AND DISCUSSION

Analysis of bioactive compounds

In general, the refining process reduces the phenolic compounds in oils because they are very polar compounds and dissolve in the water used during the washing step for the removal of soaps (WU et al., 2019). Among the types of oils, corn, showed higher content of phenolic compounds and less variation between the brands, which may be related to total phytosterol content, because in corn oil, the levels of these components were quite high. Further, the sunflower (brand M4), soybean and canola (brand M1) oils had the largest quantities of these compounds (Table 1). The lower content of phenolic compounds was quantified in canola oil of brand M5, which may be related to the steps of obtaining oil.

Variations in the quantities of phenolic compounds from refined oils and brands show that the content of phenolic compounds is affected by factors such as cultivar, degree of grain maturation, seasonal variation and climate as well as extraction conditions, storage and refining processes used. The type of extraction solvent influences in obtaining total phenolic compounds, since the polarity of the solvent affects the amount of phenolic compounds extracted.

Despite the low amount of carotenoids found in refined oils and the variation presented between different types of oils and brands (Table 1), soybean oil showed higher total carotenoid content of 7.02 µg of β-carotene/g, followed by 6.74 µg of β-carotene/g of

corn oil, both of the brand M4; and the lowest level was observed for sunflower oil of brand M5 with 4.10 µg of β-carotene/g.

Table 1. Content of total phenolics (mg GAE / kg) and carotenoids (µg of β-carotene / g of oil) to refined oils of different brands.

Compounds/ Brands	Oil			
	Soybean	**Canola**	**Corn**	**Sunflower**
Total phenolic				
M1	121,07 ± 3,33^{aA}	106,62 ± 2,69^{cA}	125,07 ± 2,00^{aB}	112,84 ± 3,36^{bB}
M2	103,96 ± 0,38^{bB}	104,84 ± 1,39^{bAB}	125,96 ± 2,04^{aB}	105,49 ± 1,30^{bC}
M3	81,29 ± 1,68^{dD}	95,62 ± 2,40^{cC}	128,40 ± 1,33^{aB}	101,73 ± 2,00^{cCD}
M4	105,07 ± 1,70^{cB}	101,29 ± 0,38^{cB}	116,62 ± 1,67^{bC}	162,73 ± 2,67^{aA}
M5	89,29 ± 2,34^{cC}	86,18 ± 3,01^{cD}	143,07 ± 2,91^{aA}	98,40 ± 0,67^{cD}
Total carotenoids				
M1	4,56 ± 0,03^{cC}	4,75 ± 0,05^{bcC}	5,33 ± 0,03^{aC}	4,89 ± 0,05^{bB}
M2	5,13 ± 0,11^{bB}	5,96 ± 0,13^{aB}	6,16 ± 0,33^{aB}	4,98 ± 0,05^{bAB}
M3	4,34 ± 0,15^{cC}	6,02 ± 0,22^{aB}	4,50 ± 0,22^{cD}	5,35 ± 0,26^{bA}
M4	7,02 ± 0,28^{aA}	4,45 ± 0,07^{cC}	6,74 ± 0,17^{aA}	4,77 ± 0,21^{bB}
M5	6,68 ± 0,20^{aA}	6,64 ± 0,09^{aA}	5,08 ± 0,07^{bC}	4,10 ± 0,14^{cC}

Means ± standard deviations of the analyzes performed in triplicate followed by lowercase letters in the rows and uppercase letters in columns do not differ by Tukey test ($p > 0.05$).

The reduction in the total carotenoid content occurs during the stages of neutralization and clarification and also in deodorizing due to the temperature used, which is generally higher than 150 °C when carotenoids can be degraded, thus resulting in the reduction of these compounds. Sánchez-Machado et al. (2015) observed this pigment loss at every stage of refining, 69.23% in neutralization and 81.54% in the clarification.

The proportion of carotenoids in the seeds and/or plants are primarily determined by genotype and varies according to climatic conditions, degree of ripeness, cultivation location, and conditions used by processing industries which explains the differences of carotenoids obtained in all evaluated oils. The presence of carotenoids in refined conventional vegetable oils is interesting because of the benefits presented by this constituent to human health.

Regardless of oils, higher total phytosterol content were obtained for the brand M2. Soybean oil ranged from 226.34 - 255.62 mg/100 g; canola from 476.48 - 615.67 mg/100 g; corn 738.15-1170.89 mg/100 g and sunflower 276.79 - 401.48 mg/100 g (Table 2). The Δ-

7-avenasterol is an isomer identified in low amounts in vegetable oils and in this study it was found only in corn and sunflower oils.

In the corn oil, it was identified only in the brands M3, M4 and M5 whose values ranged from 0.56 to 5.56 mg/100 g. In the refined canola oil, brassicasterol isomer, unique to this oil, was identified. For all refined oils, β-sitosterol was found in higher concentrations than other isomers. In the sunflower oil stigmastanol isomer was also identified in all brands, having an average of 11.73 mg/100 g.

Among the oils, soybean showed lower amount of total phytosterols while the largest amount was obtained for the corn oil. Corn oil is known to have high phytosterol content which can be up to three times greater than the value found in soybean or sunflower oils. This may be related to higher levels of unsaponifiables of corn oil which is larger in this oil (BAE et al., 2022) when compared with other types of oils of this study.

During refining, the amount of phytosterols decreased, mainly during the steps of neutralization and deodorization. During deodorization, distillation and partial esterification, dehydration of free sterols occurs due to high temperature and low pressure conditions which contribute to their loss. Moreover, clarifier earth also contributes to this reduction because it cause the decomposition of phytosterols in unsaturated hydrocarbons as a result of heating or hydrolysis catalyzed by esters (GHAZANI, et al. 2013). Considering the action of bioactive compounds, the presence of phytosterols in refined oils is important since these oils are used daily in the diet of people from all walks of life, which facilitates the intake of these compounds and, consequently, can contribute to the balance of health.

The α- and γ-tocopherols were the main tocol detected in refined vegetable oils, except for sunflower oil in which α-tocopherol prevailed with significant variations between brands. The γ-tocopherol was the predominant tocol in soybean oil (340.70 - 389.57 mg/kg). The β- and δ-tocopherols were tocols that had the lowest levels in the studied oils (Table 3). The absence or low content of γ- and δ-tocopherols isomers in the oil may for example contribute to the low oxidative stability of sunflower oil compared to other oils, it is proposed that these isomers are the most effective for the protection of vegetable oils against lipid peroxidation (LIU et al. 2023).

Variations are observed in the results for the same isomer of the same type of oil. These differences, in addition to the characteristics related to raw material can also be associated with the refining conditions used by each company, since these components are sensitive to heat forming tocoquinones and loose antioxidant properties or are removed in the refining steps (GHAZANI et al. 2013).

Table 2. Phytosterols (mg/100 g) of refined oils of different brands.

Phytosterols / Brands	Oils			
	Soybean	**Canola**	**Corn**	**Sunflower**
Campesterol				
M1	13.40 ± 0.20^{cB}	36.05 ± 0.43^{aB}	32.28 ± 0.16^{bC}	7.69 ± 0.59^{dB}
M2	12.67 ± 0.75^{cBC}	45.19 ± 0.13^{aA}	41.76 ± 0.31^{bA}	10.48 ± 0.08^{dA}
M3	12.53 ± 0.41^{cC}	45.35 ± 0.39^{aA}	26.59 ± 0.37^{bD}	8.02 ± 0.03^{dB}
M4	14.68 ± 0.27^{cA}	32.46 ± 0.11^{aD}	24.59 ± 0.50^{bE}	10.39 ± 0.13^{dA}
M5	12.83 ± 0.30^{cBC}	33.79 ± 0.28^{bC}	39.40 ± 0.15^{aB}	7.36 ± 0.25^{dB}
Brassicasterol				
M1	nd	30.37 ± 0.52^{C}	nd	nd
M2	nd	40.88 ± 0.09^{A}	nd	nd
M3	nd	41.52 ± 0.28^{A}	nd	nd
M4	nd	27.67 ± 0.34^{D}	nd	nd
M5	nd	32.37 ± 0.35^{B}	nd	nd
Stigmasterol				
M1	nd	nd	4.89 ± 0.03	8.02 ± 0.39^{A}
M2	nd	nd	nd	5.33 ± 0.27^{B}
M3	nd	nd	nd	8.13 ± 0.02^{A}
M4	nd	nd	nd	nd
M5	nd	nd	nd	5.51 ± 0.17^{B}
β-sitosterol				
M1	232.40 ± 0.25^{dB}	445.64 ± 0.13^{bD}	862.85 ± 1.02^{aC}	304.06 ± 0.54^{cB}
M2	242.97 ± 0.58^{dA}	529.69 ± 1.11^{bA}	1121.03 ± 0.45^{aA}	372.28 ± 1.86^{cA}
M3	229.75 ± 0.10^{dC}	507.83 ± 0.14^{bB}	800.51 ± 0.43^{aD}	299.79 ± 0.11^{cC}
M4	228.30 ± 0.14^{dC}	467.10 ± 1.16^{bC}	710.17 ± 0.14^{aE}	251.53 ± 0.40^{cD}
M5	213.52 ± 0.21^{dD}	410.32 ± 0.17^{bE}	1046.71 ± 0.27^{aB}	303.43 ± 0.06^{cB}
Stigmastanol				
M1	5.46 ± 0.24	nd	nd	15.34 ± 0.20^{A}
M2	nd	nd	8.10 ± 0.50	12.00 ± 0.34^{C}
M3	nd	nd	nd	13.51 ± 0.04^{B}
M4	nd	nd	nd	6.26 ± 0.26^{D}
M5	nd	nd	nd	11.44 ± 0.14^{C}
Δ-7-avenasterol				
M1	nd	nd	nd	1.73 ± 0.03^{C}
M2	nd	nd	nd	1.38 ± 0.02^{C}
M3	nd	nd	0.56 ± 0.05^{C}	1.59 ± 0.03^{C}
M4	nd	nd	3.38 ± 0.25^{B}	8.60 ± 0.25^{B}
M5	nd	nd	5.56 ± 0.42^{A}	12.26 ± 0.44^{A}
Total				
M1	251.26 ± 0.60^{dB}	512.07 ± 0.80^{bC}	900.02 ± 1.03^{aC}	336.84 ± 0.97^{cC}
M2	255.62 ± 1.10^{dA}	615.67 ± 1.02^{bA}	1170.89 ± 0.20^{aA}	401.48 ± 1.42^{cA}
M3	242.28 ± 0.46^{dC}	594.70 ± 0.27^{bB}	827.66 ± 0.43^{aD}	331.04 ± 0.06^{cD}
M4	242.99 ± 0.17^{cC}	527.23 ± 1.07^{dE}	738.15 ± 0.41^{aE}	276.79 ± 1.18^{bE}
M5	226.34 ± 0.26^{dD}	476.48 ± 0.55^{bD}	1091.67 ± 0.54^{aB}	340. 01 ± 0.20^{cB}

Means ± standard deviations of the analyzes performed in triplicate followed by lowercase letters in the rows and uppercase letters in columns do not differ by Tukey test ($p > 0.05$). nd: not detected.

Table 3. Tocopherols (mg/kg) of refined oils of different brands.

Tocopherols/ Brands	Oils			
	Soybean	**Canola**	**Corn**	**Sunflower**
α-tocol				
M1	63.33 ± 0.51^{dC}	123.80 ± 0.20^{bB}	107.27 ± 0.38^{cC}	339.87 ± 0.21^{aB}
M2	66.23 ± 0.70^{cA}	92.73 ± 0.06^{bD}	58.63 ± 0.15^{dD}	265.07 ± 0.47^{aD}
M3	58.60 ± 0.26^{dD}	109.87 ± 0.47^{cC}	115.57 ± 0.49^{bA}	354.43 ± 0.15^{aA}
M4	64.93 ± 0.83^{dB}	91.70 ± 0.20^{cE}	114.20 ± 0.44^{bB}	310.57 ± 0.12^{aC}
M5	52.87 ± 0.31^{dE}	135.30 ± 0.26^{bA}	106.47 ± 0.15^{cC}	250.83 ± 0.45^{aE}
β-tocol				
M1	nd	nd	nd	nd
M2	nd	32.63 ± 0.67^{B}	12.63 ± 0.15^{C}	nd
M3	nd	35.10 ± 0.20^{A}	20.47 ± 0.06^{A}	7.53 ± 0.06^{A}
M4	nd	17.13 ± 0.15^{C}	nd	nd
M5	nd	nd	17.13 ± 0.15^{B}	7.37 ± 0.06^{B}
γ-tocol				
M1	351.53 ± 0.38^{aC}	128.57 ± 0.58^{cC}	307.53 ± 0.15^{dB}	nd
M2	389.57 ± 0.55^{aA}	128.00 ± 0.26^{cC}	222.06 ± 0.06^{bD}	45.43 ± 0.32^{B}
M3	356.07 ± 0.57^{aB}	162.50 ± 0.46^{cA}	308.77 ± 0.23^{bA}	10.77 ± 0.75^{D}
M4	356.90 ± 0.30^{aB}	144.40 ± 0.36^{cB}	171.90 ± 0.80^{bE}	83.93 ± 0.35^{A}
M5	340.70 ± 0.75^{aD}	52.10 ± 0.17^{cD}	281.50 ±0.36^{bC}	19.80 ± 0.46^{C}
δ-tocol				
M1	82.83 ± 0.21^{aB}	10.33 ± 0.35^{bD}	13.50 ± 0.26^{C}	nd
M2	87.93 ± 0.45^{aA}	8.37 ± 0.12^{bE}	15.60 ± 0.20^{B}	16.63 ± 0.15^{B}
M3	82.37 ± 0.50^{aBC}	12.33 ± 0.06^{bC}	10.87 ± 0.35^{D}	nd
M4	80.47 ± 0.12^{aD}	18.50 ± 0.36^{bA}	23.00 ± 0.17^{A}	65.40 ± 0.26^{A}
M5	81.77 ± 0.15^{aC}	15.80 ± 0.26^{bB}	nd	11.47 ± 0.15^{C}
Total				
M1	497.70 ± 0.78^{aC}	262.70 ± 0.95^{dC}	428.30 ± 0.30^{bB}	339.87 ± 0.21^{cC}
M2	543.73 ± 0.83^{aA}	261.73 ± 0.80^{dC}	308.93 ± 0.15 ^{cD}	327.13 ± 0.38^{bD}
M3	497.03 ± 0.85^{aC}	319.80 ± 0.26^{dA}	455.67 ± 0.15^{bA}	372.73 ± 0.76^{cB}
M4	502.30 ± 0.44^{aB}	271.73 ± 0.65^{dB}	309.10 ± 0.36^{cD}	459.90 ± 0.62^{bA}
M5	475.33 ± 0.81^{aD}	203.20 ± 0.53^{dD}	405.10 ± 0.56^{bC}	289.47 ± 0.80^{cE}
Vitamin E*				
M1	123.24 ± 0.57^{dC}	155.48 ± 0.24^{cB}	164.13 ± 0.44^{bB}	373.98 ± 0.23^{aB}
M2	132.18 ± 0.73^{bA}	131.01 ± 0.25^{cC}	101.60 ± 0.17^{dB}	298.52 ± 0.48^{aC}
M3	118.71 ± 0.22^{dD}	155.77 ± 0.40^{cAB}	179.48 ± 0.55^{bA}	393.70 ± 0.22^{aA}
M4	125.78 ± 0.87^{dB}	127.68 ± 0.16^{cD}	151.42 ± 0.37^{aC}	138.93 ± 0.39^{bE}
M5	110.09 ± 0.31^{dE}	156.66 ± 0.30^{cA}	164.43 ± 0.22^{bB}	281.15 ± 0.58^{aD}
Vitamin E#				
M1	112.02 ± 0.52^{dC}	141.33 ± 0.21^{cB}	149.20 ± 0.40^{bB}	339.95 ± 0.21^{aB}
M2	120.16 ± 0.66^{bA}	119.09 ± 0.23^{cC}	92.44 ± 0.16^{dD}	271.26 ± 0.44^{aC}
M3	107.90 ± 0.20^{dD}	141.60 ± 0.37^{cAB}	163.25 ± 0.50^{bA}	357.88 ± 0.20^{aA}
M4	114.33 ± 0.79^{dB}	116.06 ± 0.15^{cD}	137.64 ± 0.34^{aC}	126.29 ± 0.35^{bE}
M5	100.07 ± 0.28^{dE}	142.40 ± 0.27^{cA}	149.52 ± 0.20^{bB}	255.56 ± 0.53^{aD}

Means ± standard deviations of the analyzes performed in triplicate followed by lowercase letters in the rows and uppercase letters in columns do not differ by Tukey test ($p > 0.05$). nd: not detected. * Expressed as (IU/kg). # Expressed as α-tocol (mg/kg).

In the neutralization, the decrease of tocopherols in vegetable oils can be of 10-20%, most likely due to absorption by these soaps during alkaline treatment (Assumpção at al. 2014). The residence time for some of the brands used in this study ranged from 15 to 30 minutes. In the clarification stage, tocopherols can be adsorbed by the earth used. Losses

in deodorization step may be related to thermal degradation due to high temperatures (> 240 °C) (NAZ et al. 2011). The temperatures used in this step may vary 180-280ºC and the time is of approximately 50 minutes.

Higher levels of tocopherols were found in soybean (475.33 - 543.73 mg/kg), in canola and corn oils of brand M3 (319.80 and 455.67 mg/kg, respectively), and in sunflower oil of M4 (459.90 mg/kg). Sunflower oil stood out in vitamin E, expressed as α -tocol in IU/kg, except for brand M4.

The presence of this component in refined oils is of great importance, because vegetable oils are part of the consumer diet and consequently, become major sources of tocopherols, especially γ-tocopherol since this is in substantial quantities in the soybean oil that is one of the most consumed. The γ-tocopherol has stimulatory action of urinary sodium excretion and contributes to the regulation of extracellular fluid volume. This protects the cardiovascular system by lowering blood pressure. Therefore, oils with lower levels of α-tocopherol and higher levels γ-tocopherol such as soybean, corn and canola have important nutritional application (Szewczyk; Chojnacka; Górnicka, 2021).

Antioxidant activity

In this study, higher values of antioxidant activity by ABTS method $^{\bullet+}$ were found in corn oil (21.33 μM Trolox/100 g) (Table 4), this fact may be due to the presence of tocopherols in the sample. Pellegrini et al. (2003) mentions that higher antioxidant capacity between different types of oils may be associated with a high amount of tocopherols present in the sample.

This variation in the values of the antioxidant activity by the ABTS$^{\bullet+}$ method may be because this radical reacts with the various types of phenolic compounds. A molecule moiety separates one electron or hydrogen atom from phenolic compound, forming a semiquinone radical and regenerating in ABTS. Furthermore, the semiquinone radical reacts with another ABTS$^{\bullet+}$ radical molecule, forming an unstable product (OSMAN et al. 2006).

In the antioxidant activity by DPPH$^{\bullet}$ method, samples that had lower antioxidant activities were: soybean oil of brand M5 with 89.15%; M3 canola oil with 75.20%; M2 corn oil with 87.22% and M2 sunflower oil with 83.94% (Table 4).

Despite the differences between the types of oils it can be said that the antioxidant activity for refined vegetable oils is considered effective. After evaluating the antioxidant activity of canola oil from three different batches, Szydłowska-Czerniak and Łaszewska (2015) reported that genetic influences, environmental and agronomic conditions and

technological factors affect the content of antioxidants, which may explain this variation in antioxidant capacity.

It is observed that, in general, soybean oil showed a higher antioxidant activity by this method, which can be explained by the fact that the oil has higher levels of γ- and δ-tocopherol which are more effective as antioxidants than the α-tocopherol, followed by corn oil.

Table 4. Antioxidant activity of refined oils of different brands.

Methods/	**Oil**			
Brands	**Soybean**	**Canola**	**Corn**	**Sunflower**
ABTS$^{\bullet+}$ (µM Trolox/100 g)				
M1	21,27 ± 0,19^{bB}	17,60 ± 0,33^{dB}	24,49 ± 0,38^{aB}	20,60 ± 0,19^{cB}
M2	27,60 ± 0,77^{bA}	26,60 ± 0,67^{cA}	29,82 ± 0,38^{aA}	23,60 ± 0,51^{dA}
M3	16,27 ± 0,58^{cC}	13,60 ± 0,67^{dC}	19,15 ± 0,38^{aC}	17,93 ± 0,33^{bC}
M4	13,27 ± 0,19^{cD}	13,60 ± 0,51^{cC}	14,93 ± 0,67^{bD}	17,70 ± 0,19^{aC}
M5	17,27 ± 0,19^{bC}	14,27 ± 0,67^{cC}	18,27 ± 0,33^{aC}	16,60 ± 0,77^{bC}
DPPH$^{\bullet}$(%)				
M1	94,60 ± 0,05^{aA}	80,69 ± 0,66^{dB}	92,17 ± 1,04^{bA}	86,85 ± 1,01^{cC}
M2	91,86 ± 0,64^{aB}	90,10 ± 2,17^{aA}	90,70 ± 0,13^{aA}	83,94 ± 0,76^{bD}
M3	91,34 ± 0,32^{aBC}	75,20 ± 0,89^{cC}	90,86 ± 0,24^{aA}	86,04 ± 0,44^{bC}
M4	91,49 ± 0,65^{aBC}	81,94 ± 1,89^{cB}	87,22 ± 0,22^{bB}	92,06 ± 0,55^{aA}
M5	89,15 ± 0,66^{bC}	80,53 ± 0,74^{dB}	92,67 ± 1,49^{aA}	89,08 ± 0,55^{cB}
FRAP (µM Trolox/100 g)				
M1	61,21 ± 2,42^{dE}	73,13 ± 1,92^{cC}	128,26 ± 2,40^{aB}	91,21 ± 2,38^{bC}
M2	113,74 ± 1,40^{cB}	128,01 ± 2,52^{bA}	144,04 ± 2,54^{aA}	102,51 ± 2,21^{dB}
M3	119,63± 1,26^{bA}	127,57 ± 1,13^{aA}	74,79 ± 2,17^{cC}	70,38 ± 1,92^{dD}
M4	104,96 ± 2,33^{cC}	88,90 ± 2,08^{dB}	141,96 ± 0,75^{aA}	115,69 ± 2,82^{bA}
M5	71,63 ± 1,95^{cD}	88,04 ± 2,71^{bB}	66,54 ± 0,67^{dD}	93,85 ± 2,83^{aC}
β-carotene/ linoleic acid (µg/g de β-carotene)				
M1	42,27 ± 2,18^{aC}	23,60 ± 0,65^{cC}	32,79 ± 1,50^{bC}	15,17 ± 0,70^{dD}
M2	48,86 ± 1,34^{dB}	59,78 ± 1,07^{cA}	74,09 ± 2,67^{aA}	64,35 ± 1,47^{bA}
M3	10,76 ± 0,45^{bD}	10,37 ± 0,23^{bD}	16,80 ± 0,82^{aD}	11,29 ± 0,60^{bE}
M4	42,88 ± 1,76^{aC}	27,19 ± 1,61^{dB}	33,44 ± 1,02^{cC}	38,70 ± 2,19^{bC}
M5	88,24 ± 0,93^{aA}	24,55 ± 0,22^{dBC}	55,67 ± 1,46^{bB}	47,40 ± 1,91^{cB}

Means ± standard deviations of the analyzes performed in triplicate followed by lowercase letters in the rows and uppercase letters in columns do not differ by Tukey test ($p > 0.05$).

Analyzing the oils by the FRAP method, there was a variation from 61.21 μM Trolox/100 g for the soybean oil, brand M1, to 144.04 μM Trolox/100 g for the corn oil, brand M2 (Table 5). Among the brands, M3 and M4 stood out, and between types of oil, the corn stood out in three of the five brands tested.

For β-carotene/Linoleic acid method, in general, brand M2 was highlighted with higher antioxidant activity for canola, corn and sunflower oils. Among the types of oil, the antioxidant activity was presented by soy and corn oils, whereas low antioxidant activity was observed for the oils of brand M3, which may be related to lack of synthetic antioxidant.

The difference in this activity by β-carotene/linoleic acid assay among the types of oils or even the same type of oil can be associated with the presence of metals such as copper, zinc and iron, and also between the ratio of β-carotene and water in the preparation of the emulsion, both have an influence on the concentration of β-carotene preventing their reaction and this may vary depending on the absorbance bands (DAWIDOWICZ; OLSZOWY, 2010).

Antioxidant activity can be affected by the type of process used in obtaining the oils, as phenolics, carotenoids and sterols are partially or completely removed or isomerized during the refining process. In addition, it is possible that carotenoids and chlorophylls present pro-oxidant action. Still, synthetic antioxidants were added to refined oils by processing industries, in order to protect them from oxidation, which can influence the results of such measures.

4. CONCLUSION

According to the results, corn oil has obtained the highest levels of phenolic compounds and total phytosterols and the sunflower can be considered the best source of vitamin E and essential fatty acids. Soybean oil showed more tocopherols, while in corn and canola oils were found higher levels of total carotenoids. Corn oil excelled in relation to the antioxidant activity by the $ABTS^{\bullet+}$ method. Refined soybean and corn oils showed greater effectiveness in the $DPPH^{\bullet}$, FRAP, and β-carotene/linoleic acid assays.

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