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Physicochemical characterization of chia (*Salvia hispanica*) seed oil from Argentina

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The physicochemical characteristics of chia oil from Argentina, which is one of the most efficient omega-3 (n-3) sources for enriching foods, have been studied. The results from analysis show that the chia oil has a relative density of 0.9288, refractive index 1.4810 and yellow color component that dominates over the red one. Its acidity index is 1.68 mg KOH/g, its saponification index is 197.9 mg KOH/g, iodine index is 208.3 g I_2/ 100g and the peroxide index is 1.95 meq O_2/kg. The fluorescence spectra for excitation wavelength 350 nm contain 3 peaks at about 472 nm, 503 nm and 670 nm, which are attributed to pigments, vitamins and oxidation products. Besides, the spectra in visible and UV range are used for determination of chlorophyll content, content of β-carotene, oxidation products and oxidant stability. Phase transition is observed at -36.9 ºC. The content of some essential, non essential and toxic elements in the solution obtained after microwave-assisted (MW) digestion of the examined oil were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). This method could be useful for quality control of the oil when used in food industry, medicine and cosmetics

Keywords: UV and visible spectroscopy, fluorescence, mineral contents, color characteristic

INTRODUCTION

Chia (*Salvia hispanica* L.) seed oil is an interesting source of polyunsaturated fatty acids (PUFA). It contains the highest proportion of α-linolenic acid (*60%) of any known vegetable sources [1]. This fatty acid (FA) belongs to the n-3 family which is essential for the normal growth and development of the human body and plays an important role in the prevention and treatment of coronary artery disease, hypertension, diabetes, arthritis, other inflammatory and autoimmune disorders, and cancer [2]. Further, chia oil is used as a base for face and body paintings. The activation energy of chia seed oil, calculated from the extrapolated temperature of the start of oxidation (T_e), was similar to that reported for pure α-linolenic acid (62–70 kJ/mol) [3], the main fatty acid presented in chia seed oil, and lower than the activation energy for corn oil (104.3 kJ/mol) [4]. The physicochemical characteristics and fatty acid composition of chia oils were investigated by Velasco Vargas, Alvarez-Chavez, Bushway [5-7]. However, no information was found about the mineral content and optical properties as fluorescence spectra and absorption spectra in UV region, which are connected with the presence of pigments and oxidative products. Obviously, further knowledge on chia seed oil properties is needed, which may lead to different uses in the food industry or medical, pharmaceutical and other non-food industrial applications. Based on that, the main objectives of this work are to study mineral content, some important physicochemical and quality characteristics of *Salvia hispanica* seed oil from Argentinahe .

EXPERIMENTAL

Chia (*Salvia hispanica*, L.) seeds were obtained in Argentina and the oil was extracted in a Bulgarian factory. The samples were poured into a 10-mm thick dish. The color parameters in two colorimetric systems XYZ and SIE Lab have been measured by Lovibond PFX 880 (UK). The refractive index of the oil was measured using an Abbe refractometer (Carl Zeiss, Germany) at 20°C.

The thermal characteristics of the chia oil samples were investigated in the temperature range of - 60°C to 20°C by differential scanning

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calorimeter DSC 204 F1 Phoenix (NETZSCH, Germany), equipped with intracooler. The DSC apparatus was calibrated with indium standart. In order to avoid condensation of water, argon gas was used to purge the furnace chamber at 20 ml min^{-1}. The samples (5-10 mg) were weighed into 40 μl aluminum standard crucible and hermetically sealed with aluminum standard lead. An empty aluminum crucible was used as a reference.

Iodine and saponified values and free fatty acid content were determined according to AOCS recommended practices Cd 1c-85, Ca 6a-40 and Ca 5a-40, respectively [8]. Oil oxidative stability was evaluated by the Rancimat (Mod 679, Metrohm) method, using 3 g of oil sample warmed at 100ºC with air flow of 20 L h^{-1}.

Determination of dynamic and kinematic viscosity was obtained by using degrees *Engler*. They are presented as ratio of the time of flow of 200 ml of the investigated oil to the time of flow of 200 ml of distilled water at the same temperature (usually 20ºC, but sometimes 50ºC or 100ºC).

Samples of about 0.3 g were weighed in Teflon vessels of microwave digestion system, then 8 ml 67% HNO_3 (supra pure) and 2 ml 30% H_2O_2 (supra pure) were added and samples were left to stay overnight. Microwave digestion was performed as follows: 15 min to reach 220ºC and 20 min left to stay at this temperature. After cooling the samples were transferred in 100 ml volumetric flask and diluted up to the mark with deionized water. A blank sample was passed through the whole analytical procedure. Inductively coupled plasma-mass spectrometer "X SERIES 2"– Thermo Scientific was used for the determination of elements.

The sources used to measure the fluorescence spectra are 250 nm, 300 nm, 350 nm, 400 nm and 450 nm light emitting diodes (LEDs). A fiber optic spectrometer (AvaSpec-2038, Avantes) with sensitivity in the 200-1100 nm range and a resolution of about 8 nm was used to measure the fluorescence spectra. The oil samples were placed in a 10 mm x 10 mm cuvette and irradiated by LEDs.

RESULTS

In the present study various techniques have been used for the characterization of chia (*Salvia hispanica*) seed oil from Argentina. The obtained main values for some physical and chemical characteristics are given in Table 1.

As seen, the relative density of Argentinian chia oil is greater than sunflower and soybean oils, but its value is very close to the relative density of Mexican chia oil 0.9241 [9]. According to Alvarado and Aguilera [10], the relative density is high to higher unsaturation's content in the fatty acids. The refractive index is greater than the values measured by the other author for Mexican chia oil 1.4761 and for Argentinian chia oil 1.4768 [12]. The Iodine value registered here (208.3 gI_2/100 g oil) showed the unsaturation grade of chia's oil, and that this parameter is proportional to the number of double bonds in the fatty acid chains.The Iodine index in chia oil could be compared only with the Iodine value in linseed oil (187 gI_2/100 g oil) [13]. The acidity value is similar to chia oil obtained by pressing seed from Guatemalan seeds with 1.64 mg KOH/g oil [12]. The oxidative stability of foods is dependent on the composition, concentrations and activity of reaction substrates and antioxidants. In order to minimize the use of food additives, the oxidative stability can be potentially improved by preserving or enhancing the endogenous oxidation control systems of foods [14]. The accelerated stability test showed that chia oils have a low oxidative stability of 2.4 h. In spite of the presence of antioxidant compounds, the high content of poly unsaturated fatty acids makes chia seed oil very instable. In this respect, some innovative technologies to protect from oxidation of this oil are needed.

Table 1 Physical and chemical properties of chia oils.

Physical and Chemical Properties	Argentinian chia oil
Peroxide value (meqO_2/kg oil)	1.95
Acidity value (mg KOH/g oil)	1.68
Saponification value (mg KOH/g oil)	197.9
Iodine value (g I_2/100 g oil)	208.3
Relative density	0.9288
Refractive index	1.4810
Oxidative stability (h)	2.4
Dynamic viscosity (Pa.s)	$4.25. 10^{-2}$

The color characteristics in two color systems XYZ and SIELab are shown in Table 2. On the base of transmission spectra in the visible region the pigments chlorophyll and β-carotene are determined. It is evident that color coordinates **x** and **y** are almost equals. Parameter *a** assumed a negative but low value, similar to data reported for β-carotene [15]. Besides, the chia seed oil samples showed positive values of parameter *b**, which is characteristic of yellow colors. Obviously, this oil is very rich of pigments.

There are data for fatty acid composition of chia oil in the literature, but the optical and especially fluorescence properties are not investigated. That's why in the present study the fluorescence spectra in the UV and visible region are recorded. The excitation – emission matrices are presented on the Fig 1.

Table 2 Color parameters of chia oils**.**

Color parameters	Argentinian chia oil
X	73.20
Y	79.81
Z	26.20
x	0.4085
y	0.4454
L	91,55
a	-10.03
b	64.31
Chlorophyll	22.08 ppm
β - carotene	0.156 ppm

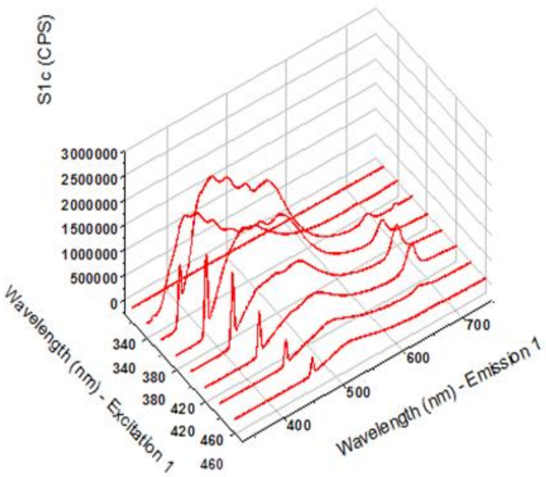

Fig. 1. Excitation-emission matrix for chia oil.

The fluorescence peaks give the connection between the optical and chemical properties of the sample and afford on the opportunity for its quality investigation. The good ratio between the intensities of emission and excitation is observed for excitation wavelength 350 nm. The distinct fluorescence peak is observed at about 440 nm, which is connected with phenol antioxidants. Among the primary oxidation products are hydroperoxides which further degrade to secondary products: aldehydes, alcohols, hydrocarbons and ketones [16]. It's important to notice that the known products formed during oxidation of vitamin E group are all non-fluorescent [17]. Changing in the content of tocopherols and phenols is also detected at about 503 nm. The fluorescence properties of the pigments are very similar and that's way signals in the wide wavelength range 600 - 720 nm are detected [17]. There is presence of the chlorophyll group in the studied sample and the band at 670 nm is attributed to it. The fluorescence maxima at 472 nm can be explained with the presence of β-carotene.

The extent of oxidation of chia oil has been estimated by the obtaining of absorption peaks in the UV region. The UV spectrum is presented on the Fig. 2.

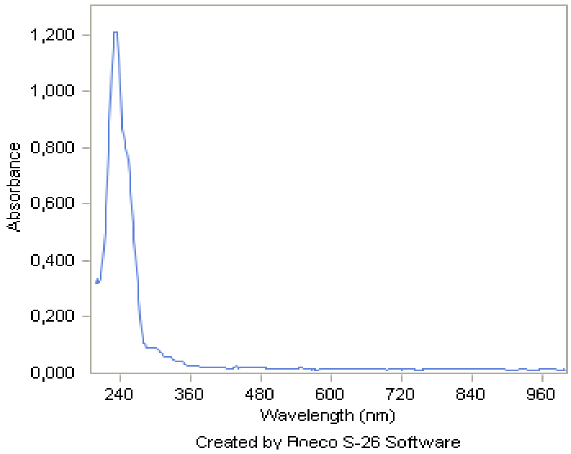

Fig. 2. UV spectrum for chia oil

The degree of oxidation of the studied sample is estimated through indirect determination of primary oxidation products (peroxides) of absorption of conjugated diene structures which are formed from linoleate units using UV spectroscopy at 232 nm and from the absorption of conjugate triene structures at 268 nm. The chia oil has a high content of polyunsaturated fatty acids (80%) and according to the obtained values of absorbance at 232 nm is oxidized. The absence of an absorption peak around 270 nm, however, proves the absence of by-products of the oxidation of carbonyl character. These results show that the oil of chia can be used for food purposes, but not recommended to be subjected to the heat treatment.

Further, the transmittance of the oil in the visible region has been investigated. It is seen that the oil strongly absorbs in the short wavelength of the spectrum from 400 nm to 500 nm. The transmittance is over to 90% of light flux from 550 nm to the end of the visible region.

Trace elements Fe, Cu, Ni and Mn [18] increased the rate of oxidation of the oil by the formation of free radicals of fatty acids and hydroperoxides. As mineral composition, chia oil is low in elements like all other oils (Ca=37.6 μg g^{-1}; K=6.78 μg g^{-1}; Mg=3.67 μg g^{-1}; Zn=2.35 μg g^{-1}; Cr=0.19 μg g^{-1}; Mn= 0.23 μg g^{-1}; Fe=2.32 μg g^{-1}; Co, Cu and Se<0.01 μg g^{-1}). There are no toxic elements (Ni=0.03 μg g^{-1}; Pb=0.06 μg g^{-1}; As, Cd, Tl and Hg<0.01 μg g^{-1}) and it can be used in food, medical and cosmetics industry. It is possible that concentrations of some elements are influenced by the manufacturing process and equipment.

Fig. 3 shows the DSC thermogram of chia oils stydied. The maximum of the largest peak takes place at around -32 °C, the maximum of the second largest peak is at around -10 °C.

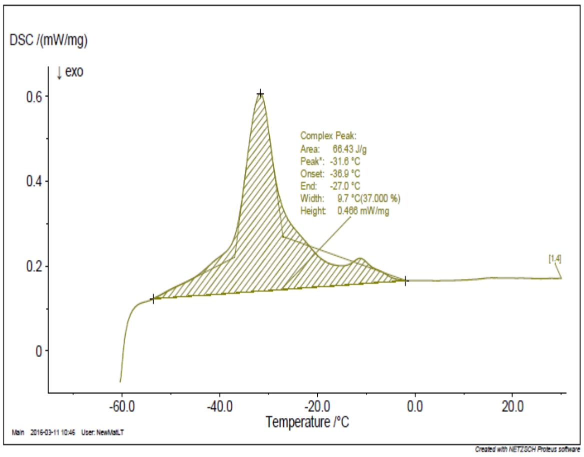

Fig. 3. DSC thermogram for chia oil

The relatively low melting temperatures could be related to the chia oil fatty acid composition - high amount of poly unsaturated triacylglycerols, like α-linolenic acid and linoleic acid [19]. As a consequence, the chia oil may be stored in a refrigerator, as it is not expected to partially crystallize (like other oils, such as olive oil). This ensures better storage conditions since the oxidative stability is low due to its high unsaturation.

CONCLUSION

Because of the increasing popularity of chia oil as a very important source of n-3 and n-6 fatty acids, this study presents a view of the characteristics of chia oil and the obtained parameters that could be used as a starting point to define quality standards since there are little specifications available for this nontraditional vegetable oil.

The chia oil has a high content of polyunsaturated fatty acids (80%) and according to the obtained values of absorbance at 232 nm it can serve as an evaluation of the degree of oxidation. The absence of an absorption peak at around 270 nm suggests that this oil can be used for food purposes, but it is not recommended to be used after heat treatment. The experimental results from fluorescence spectra show that the oil is reach of tocopherols and phenols (emission fluorescence peak at about 503 nm), chlorophyll group (λ_{em}= 670 nm), β-carotene (fluorescence maxima at 472 nm).

The absence of toxic elements shows that the product can be used in food, medical and cosmetics industry. An important problem is to improve the oxidative stability of the chia oil from Argentina, which could be resolved by the addition of natural antioxidants such as phenolic components.

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ФИЗИКОХИМИЧНИ ХАРАКТЕРИСТИКИ НА ЧИА (SALVIA HISPANICA) МАСЛО ОТ АРЖЕНТИНА

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(Резюме)

Изследвани са физикохимичните характеристики на масло от чиа /Аржентина/, което е един от най-ефективните омега-3 (N-3) източниците за добавка към храни. Резултатите показват, че маслото от чиа има относителна плътност - 0.9288, показател на пречупване - 1.4810 и жълта цветова компонента, която доминира над червената. Както и киселинно число: 1.68 mg KOH/g; индекс на осапуняване: 197.9 mg KOH/g; йодно число: 208.3 g I_2/100g, пероксидно число: 1.95 meq O_2/kg. Флуоресцентните спектри, получени при възбуждане с дължина на вълната 350 nm имат 3 пика: около 472 nm, 503 nm и 670 nm, които се дължат на пигменти, витамини и продукти на окисление. Освен това, спектри във видимата и UV област са използвани за определяне на съдържанието на хлорофил, β-каротин, продукти на окисление и оксидантна стабилност. Наблюдаван е фазов преход при -36.9ºC. Концентрацията на някой основни, есенциални и токсичните елементи в пробите са определени чрез ICP-MS, след микровълново разлагане на маслото. Този метод може да бъде полезен за контрол на качеството на маслото, когато се използва в хранително-вкусовата промишленост, медицината и козметиката