Oxidative stability of chia (Salvia hispanica L.) and sesame (Sesamum indicum L.) oil blends

Journal:	*Journal of the American Oil Chemists' Society*
Manuscript ID	JAOCS-19-0261.R1
Manuscript Type:	Original Article
Date Submitted by the Author:	18-Jan-2020
Complete List of Authors:	Rodriguez, Gilbert; Universidad Nacional del Santa, docente Villanueva, Eudes; Universidad Nacional Agraria La Molina Cortez, Danco; Universidad Nacional del Santa Sanchez, Esther; Universidad Nacional del Santa Aguirre, Elza; universidad nacional del santa Hidalgo, Alyssa; Universita degli Studi di Milano, DeFENS
Keywords:	Fats and oils, Oxidative Stability < Food and Feed Science / Nutrition and Health, Oilseeds

Oxidative stability of chia (*Salvia hispanica* L.) and sesame (*Sesamum indicum* L.) oil blends

Running title: Stability of chia and sesame oil blends

Gilbert Rodríguez[1,*]; Eudes Villanueva[2]; Danco Cortez[1]; Esther Sanchez[1]; Elza Aguirre[1]; Alyssa Hidalgo[3]

[1] Universidad Nacional del Santa, Urb. Bellamar s/n, Chimbote, Peru.

[2] Universidad Nacional Agraria La Molina, Av. La Molina, Lima, Peru.

[3] Department of Food, Environmental and Nutritional Sciences (DeFENS), University of Milan, Via Celoria 2, Milan, Italy.

* Corresponding author: giropape@yahoo.com (G. Rodriguez)

Abstract

Chia and sesame oils are important sources of essential fatty acids; however, their ω-3:ω-6 proportions do not comply with nutritional recommendation. A feasible approach to improve the ratio is to blend different oils, but only after understanding physical and chemical changes of the new matrix. Objective of the investigation was to determine the physico-chemical characteristics and the oxidative stability index (OSI), using the Rancimat method, of chia-sesame oil blends. The four ω-3:ω-6 blends tested (1:4, 1:6, 1:8 and 1:10) were exposed to temperatures of 110, 120 and 130 °C. The OSI values of the mixtures varied between 6.24-8.08 h, 3.07-4.00 h and 1.62-2.01 h for each temperature, respectively. In addition, their mean activation energy, enthalpy, entropy and Q_{10} were 88.4 kJ/mol, 85.2 kJ/mol, -41.1 J/mol K and 2.0. Finally, a shelf life prediction performed at 25 °C indicated stability times between 80 and 123 days. Therefore, combining chia and sesame oils produced blends with a good balance of essential fatty acids.

Keywords: chia, sesame, ω-3:ω-6 ratio, oil blends, oxidation stability

Introduction

Nutritional features, quality and stability of oils can be modified by hydrogenation, interesterification, fractionation and blending. Hydrogenation leads to trans isomers formation, interesterification and fractionation need special and expensive equipment, therefore blending oils with different compositions and properties represents the simplest method to achieve appropriate oil characteristics (Hashempour-Baltork et al., 2016). An edible oil blend is obtained mixing two or more oils (in a proportion greater than 5%) from different vegetable species (Guiotto et al., 2014). The mixing of different vegetable oils changes the fatty acids profile and may improve the nutritional and functional value. An increase in monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) intake contributes to reduce the risk of coronary heart disease, because ω-3 and ω-9 fatty acids have anti-inflammatory properties (Ramsden et al., 2013). However, previous research suggests that only ω-3 has a significant effect in the prevention of cardiovascular diseases (Griffin, 2008). Additionally, unsaturated oils with high MUFA and PUFA content are more prone to oxidation; therefore, properly balancing MUFA and PUFA may give oil blends with better nutritional value, high storage stability and even suitable for frying (Adhvaryu et al., 2000; Ramsden et al., 2013).

The ω-3 and ω-6 fatty acids play fundamental but different roles in the structure of the cells membrane. The different numbers and positions of double bonds in the chain give the fatty acids different physiological properties, making the relationship between ω-3:ω-6 fatty acids in the diet very important. Linoleic acid is metabolized to arachidonic acid and α-linolenic acid gives eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), all of which use the same metabolic pathways and compete for the same elongase and desaturase enzymes, thus ω-3:ω-6 balance in the diet is important (Huerta-Yépez et al., 2016).

The international nutrition and food committees convened by FAO/WHO established that fat in general should not contribute more than 30% of the total calories consumed by adults; in addition, the consumption should be evenly distributed between saturated fatty acids (SFA), MUFA and PUFA (1:1:1 ratio) (FAO, 2012). Simopoulos (2002) recommended a ω-3:ω-6 rate inferior to 1:4 to reduce the risks of chronic diseases. Gomes et al. (2019) evaluated the association of plasma and erythrocyte ω-3:ω-6 fatty acids with multiple oxidative stress biomarkers in breast cancer patients; they found that ω-3:ω-6 ratio (plasma) was associated with the anti-inflammatory factor.

Chia seeds have 28–32% oil, which presents the highest essential fatty acid content of any known vegetable source and other valuables components such as tocopherols, polyphenols, phytosterols, carotenoids, and phospholipids. The predominant fatty acids in chia oil are α-linolenic acid and linoleic acid, which comprise about 64% and 20%, respectively. The ω-3:ω-6 ratio of this oil is approximately 3:1, markedly higher than that of most vegetable oils (Julio et al., 2019).

Sesame seed, containing about 50% oil, is one of the oldest and most important oleaginous matrices, with an annual worldwide oil production of 1.63 million tons (FAOSTAT, 2014). The oil extracted from sesame is mainly used in China and Korea as a condiment oil along with fragrant peanut, safflower, perilla and red pepper oils (Ji et al., 2019). Sesame oil has been reported to contain ~80% unsaturated fatty acids (~42.36% linoleic acid) and many bioactive components including tocopherols, phytosterols and lignans (including sesamolin, sesamin, and sesamol) (Dossa et al., 2018). Sesame oil has very low content of ω-3 and high content of ω-6 fatty acids, thus to have a better combination of essential fatty acids their ratio should be balanced. For example, Hashempour-Baltork et al. (2017; 2018) proposed blending sesame oil with olive and flaxseed oils.

The widely used Rancimat method, an international standard performed under accelerated storage conditions at high temperatures (AOCS, 1998), is reliable, reproducible, does not involve reagents consumption and its measurements can be easily automated (Heidarpour and Farhoosh, 2018).

The main objective of this work was to determine, using the Rancimat method, the oxidative stability of chia and sesame oils blends with different ω-3:ω-6 proportions. Additionally, activation energy (*Ea*), enthalpy (ΔH^{++}), entropy (ΔS^{++}), energy of Gibbs (ΔG^{++}),, Q_{10} and shelf life of the blends were computed using the oxidative stability index values and extrapolating the results to standard storage temperatures.

Materials and methods

Materials

Oils extraction

The chia seeds (cv. Negra) were from the Arequipa region, Peru (15º52'S and 72º15'O) and the sesame seeds (cv. Negra) were from the Chanchamayo province, Junín, Peru (11º03'16"S and 75º19'45"W). The seeds had a moisture content of 8.13±0.12% and 10.43±0.07%, respectively. The oils were extracted by cold pressing using an Expeller Thor (Santa Maria, Brasil) with FA57/G Press (Sew-Eurodrive GmbH & Co KG, Bruchsal, Germany) at a screw speed of 35-40 rpm. The oils were stored at 4.00±0.5 °C in dark flasks under nitrogen atmosphere.

Preparation of the mixtures

The oil blends were formulated in order to obtain ω-3:ω-6 ratios of 1:4, 1:6, 1:8 and 1:10. The formulations (Table 1, expressed as percentage of each oil type) were calculated considering the content of ω-3 (linolenic acid) and ω-6 (linoleic acid) fatty acids, obtained by gas chromatography (see below), for each oil type reported in Table 2. The oils amounts (weight:weight) were thoroughly mixed for 30 s using a vortex (Velp Scientifica, Italy).

Methods

Physico-chemical characterization

Acidity, peroxide value (PV), expressed as milliequivalents of peroxides per kilogram of oil (mequiv O_2/kg oil) and *p*-anisidine value (*p*-AV) were determined according to AOCS methods Cd 3d-63, Cd 8-53 and Cd 18-90, respectively (AOCS, 1998). The total oxidation value (TotOx) was calculated from PV and *p*-AV as follows: TotOx = 2 PV + *p*-AV. The density was determined with an automatic digital densimeter (DOM 2911, Rudolph Research Analytical, USA). The iodine value was measured according to AOAC Official Methods 920.158 (AOAC, 2005). The fatty acid composition of the chia and sesame oils as well as of their blends was determined by gas chromatography according to method n. 991.39 (AOAC, 2005).

Oxidative stability index OSI

The oxidative stability index (OSI) of each oil and of the blends was evaluated by the method AOCS Cd 12b-92 (AOCS, 1998) using a 743 Rancimat equipment (Metrohm Schweiz AG, Zofigen, Switzerland). The assays were carried out using 3.0 ± 0.1 g of oil sample with an air flow of 15 L/h at 90, 100 and 110 °C for chia oil (Villanueva et al., 2017) and at 110, 120 and 130 °C for sesame oil (Villanueva et al., 2013) and blends. The temperatures were chosen according to the nature of the oil and its resistance to oxidation; a very high temperature originates very short analysis times and a very low temperature would require many hours of study (Bodoira et al., 2017; Martínez et al., 2015; Prasad-Timilsena et al., 2016). The oxidative stability index (OSI) was expressed in hours.

Thermodynamic analysis

The activation energy (*Ea*) was determined from the slope of the line representing the natural logarithm of the OSI values versus the inverse of the absolute temperature (1/T) (Villanueva et al., 2013).

$$\mathrm{Ln(OSI)} = \mathrm{Ln}\left(\frac{-\mathrm{Ln}(1-\alpha^*)}{\mathrm{Z}}\right) + \frac{E_a}{\mathrm{RT}}$$

where α^* represents the degree of transformation of unsaturated molecules for the induction time, R is the universal gas constant (8.314 J/mol K) and Z is the pre-exponential factor of the Arrhenius equation. The enthalpy (ΔH^{++}) and entropy (ΔS^{++}) of activation were obtained by regression of the logarithm of (K/T) vs. (1/T) (Heidarpour and Farhoosh, 2018):

$$\mathrm{Log}\left(\frac{\mathrm{K}}{\mathrm{T}}\right) = \mathrm{Log}\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^{++}}{2.303\mathrm{R}}\right) - \left(\frac{\Delta H^{++}}{\mathrm{RT}}\right)$$

where K is the inverse of OSI, k_B is Boltzmann constant (1.380658 x 10^{-23} J/K) and h is Planck's constant (6.6260755 x 10^{-34} Js).

The Gibbs free energy (ΔG^{++}) was calculated according to the Gibbs equation:

$$\Delta G^{++} = \Delta H^{++} - T\,\Delta S^{++}$$

The prediction of the shelf life was determined by extrapolation of the linear correlation of the logarithm of OSI vs. T for a 25 °C temperature (Heidarpour and Farhoosh, 2018):

$$\mathrm{Log(OSI)} = \alpha(\mathrm{T}) + \beta$$

While the Q_{10} number, which indicates the increase in reaction rate due to a 10 °C rise in temperature, was computed as: $\frac{\text{OSI at time T}}{\text{OSI at T} + 10\,°\text{C}}$ (Farhoosh, 2017)

Statistical analysis

All analyses were carried out in triplicate and the data were subjected to one-way analysis of variance (ANOVA). When significant differences were found ($p \leq 0.05$), Fisher's lowest significant difference (LSD) at 95% significance level was computed. The analyses were performed using the Statgraphics® Centurion XVI statistical program (Statpoint Technologies, Inc., Warrenton, Virginia, USA). The average values and the standard deviation were calculated using the Excel program (Microsoft® Office Excel 2016).

Results and discussion

Fatty acids characterization

Chia oil composition (Table 2) was 12.3% SFA ($C_{16:0} + C_{18:0}$), 7.6% MUFA ($C_{18:1}$) and 82.7% PUFA ($C_{18:2} + C_{18:3}$). The α-linolenic acid ($C_{18:3}$; ω-3) represented 63.5% of all fatty acids, a proportion very similar to those (63.26%, 65.2% and 61.8%) observed by Bodoira et al. (2017), Guiotto et al. (2014) and Villanueva et al. (2017), respectively. Sesame oil composition was 12.3% SFA, 39.5% MUFA and 45.2% PUFA. Linoleic acid ($C_{18:2}$; ω-6) was the predominant fatty acid (44.8% of total), a result close to 46.0% reported by Dossa et al. (2018), and within the range (36.9-47.9%) indicated by the Codex Alimentarius (2011).

The ω-3:ω-6 ratios of chia and sesame oils were 3.3:1 and 1:100.3 (Table 2), respectively, well outside the ranges recommended by FAO (2012). The ω-3:ω-6 fatty acid composition of the chia-sesame oil blends (Table 2), determined by gas chromatography, were 1:4.0 for the first formulation, 1:6.0 for the second, 1:8.0 for the third and 1:10.0 for the last.

In 80:20 and 90:10 (w:w) sunflower-chia oil blends, Guiotto et al. (2014) reported ω-3:ω-6 ratios of 1:2.68 and 1:5.31, i.e. within FAO (2012) recommendations. Similarly, Ract et al. (2015), in their quest for oil blends able to heal wounds by enzymatic interesterification, mixed sunflower-canola oils at 85:15 (w:w) and canola-flaxseed at 70:30 (w:w), obtaining ω-3:ω-9 ratios of 0.62:1 and 1.24:1.

The chia oil acidity (0.43%), peroxides (0.67 meq O_2/kg) and *p*-AV (0.36; Table 2) were similar to those reported by Guiotto et al. (2014) and Ixtaina et al. (2012); similarly, the density (0.870 g/mL) and iodine index (103.3 g/100 g; Table 2) were within the range of virgin and cold pressed oils (Codex Alimentarius, 2011), indicating the high quality of the oil used; sesame oil has density (0.903 g/mL), acidity (0.61%), iodine (108.1 g/100 g) and peroxide (1.14 meq O_2/kg) values similar to those reported by Gul et al. (2011). The blends, as expected, showed values within the range of the chia and sesame oils.

Oxidative stability index

The OSI of sesame oil, chia oil and blends (Table 3) showed that the rate of autooxidation doubled for each 10 °C increase in temperature. Therefore, the OSI values increased as the temperature decreases from 130 to 90 °C. The high concentrations of unsaturated fatty acids in the samples tested played a fundamental role in their oxidative stability, because high degrees of unsaturation are directly associated with lower OSI (García-Moreno et al., 2013). However, the lowest OSI did not always correspond to the highest PUFA, confirming that other factors, e.g. the presence of tocopherols and lignans, mainly sesamin and sesamolin, is related to the superior oxidative stability of this oil and the beneficial physiological effects of sesame (Hashempour-Baltork et al., 2018).

The OSI values of sesame oil (Table 3) were similar to those reported by Villanueva et al. (2013), i.e. 11.37 and 2.42 h at 110 and 130 °C. The OSI values for chia oil were similar to the data (1.49 h for 110 °C) by Villanueva et al. (2017) and the values (1.4 h for 110 °C) by Martínez et al. (2015). Lower OSI values (2.4 h at 100 and 3.2 h at 90 °C), but at a 20 L/h flow, were reported by González et al. (2016) and by Prasad-Timilsena et al., (2016), respectively.

Table 3 also shows the OSI of the oil blends. An increase in OSI due to the addition of sesame oil is observed; this stabilizing function can be attributed to the augment of linoleic acid and the reduction of linolenic acid in the oil blends. In trials of olive oil adulteration with palm oil or sunflower oil, Heidarpour and Farhoosh (2018) observed an improved OSI value as a consequence of the enrichment of the SFA and MUFA from palm oil. In sunflower-chia oil blends (80:20 and 90:10 w:w) with ω-3:ω-6 ratios of 1:32.7 and 1:5.3, respectively, at 98.5 °C and a 20 L/h flow, Guiotto et al. (2014) observed OSI values of 7.6 and 9.2 h and attributed the OSI boost to an increase in linoleic acid supplied by sunflower oil.

Thermodynamic study

The activation energy indicates the delay of the initial oxidation process due to the cleavage of the fatty acid chain junction that forms primary oxidation products. It has been suggested that *Ea* is influenced by the degree of oil polyunsaturation, so that a high content of linoleic (ω-6) and/or linolenic acids (ω-3) should decrease the *Ea* of lipid oxidation while a high oleic acid contents should increase it; on the contrary, an increase in saturated fatty acids content should improve the resistance to the initial thermal break (Adhvaryu et al., 2000). However, there are exceptions such as sacha inchi oil, whose degree of unsaturation and *Ea* values are both high, mainly because of the antioxidant activity that tocopherols exert in this oil matrix (Rodríguez et al., 2015).

As expected, Table 4 shows a greater influence of the unsaturated fatty acids on chia oil *Ea* (82.0 kJ/mol) than on sesame oil *Ea* (96.2 kJ/mol). The sesame oil *Ea* is similar to those (97.28, 98.79 and 96.86 kJ/mol) reported by Villanueva et al. (2013) using three different air flows (15, 20 and 25 L/h, respectively). The chia oil *Ea* is similar to the value reported by Villanueva et al. (2017; 81.98 kJ/mol) but higher than the values observed by Guiotto et al. (2014) and Ixtaina et al. (2012), i.e. 71.95 and 69.50 kJ/mol, respectively. The *Ea* of the new formulations obeys to the fatty acids nature, therefore it can be inferred that their increased ω-3:ω-6 ratio will result in an oxidation faster than sesame oil and a stability higher than chia oil. The ΔH^{++} and ΔS^{++} values showed a significant difference ($p \leq 0.05$) among treatments. The positive sign of the activation enthalpy ($\Delta H^{++} > 0$) reflected the endothermic nature of the formation of the activated complex (Farhoosh and Hoseini-Yazdi, 2014). Table 4 shows that sesame oil during the auto-oxidation absorbed more heat than all the mixtures including chia oil, an expected result since OSI was highest in sesame oil at 110 °C, as reported in Table 3. Rancimat-based studies in olive oil have ΔH^{++} values between 91.00 and 103.60 kJ/mol (Heidarpour and Farhoosh, 2018), in canola oil 86.78 kJ/mol, in soy oil 89.20 kJ/mol, in maize oil 84.92 kJ/mol and in sunflower oil 87.52 kJ/mol (Farhoosh et al., 2008). On the other hand, the activation entropy resulted negative ($\Delta S^{++} < 0$) with values from -44. 4 J/mol K in chia oil to -23.7 J/mol K in sesame oil. Negative entropy values suggest that the activated complexes are more ordered than their reactants, and high negative values imply that fewer species are involved in the activated complex state. In other words, the activated complex will have a lower potential for the oxidation reaction and, therefore, a slower rate. Studies in olive oil show ΔS^{++} between -78.8 and -95.4 J/mol K (Heidarpour and Farhoosh, 2018) and between -69.1 and -70.9 J/mol K (Farhoosh and Hoseini-Yazdi, 2014). In other vegetable oils they vary: in canola -112.99 J/mol K, in soybeans -104.35 J/mol K, in maize -112.28 J/mol K and in sunflower -107.73 J/mol K (Farhoosh et al., 2008). Finally, the energy of Gibbs was always positive (ΔG^{++}), suggesting that in Rancimat the autooxidation process is not spontaneous at different temperatures; sesame oil had a higher ΔG^{++} value (83.7 kJ/mol) than the other oil samples, showing lower oxidation reaction rates.

Shelf life

Table 5 shows the linear relationship between temperature and Log(OSI) for each chia-sesame oil blend, starting from the results of Table 5, where the α values vary between -0.0293 and -0.0326. Villanueva et al. (2013) reported similar values (α: -0.031 to -0.032) using sesame oil under different air flows (15, 20 and 25 L/h). The Q_{10} values ranged between 1.96 and 2.12, as in other vegetable oils such as soybean (1.99-2.09) (Farhoosh, 2007), olive (2.09-2.48) (Farhoosh and Hoseini-Yazdi, 2014), maize (2.00-2.01) and canola (2.00-2.01) (Farhoosh et al., 2008). All these Q_{10} around 2.0 represent the temperature acceleration factor, indicating that the reaction speed doubles for every 10 °C of temperature increase (Farhoosh and Hoseini-Yazdi, 2014).

Table 5 also shows the extrapolation values for the determination of the shelf life of the blends at 25 °C. All the oil samples present a significant difference ($p \leq 0.05$), reflecting the strong influence of the unsaturated fatty acids of chia oil; as expected, the OSI_{25} of the four chia-sesame oil blends (from 80.4 to 123.2 days) fell between the 25.8 days of chia oil and the 253.3 of sesame oil. The Rancimat extrapolation method has been successfully applied in the study of different oils, such as sacha inchi (Rodríguez et al., 2015); interestingly, soybean oil, whose ω-3:ω-6 ratio is around 1:6-7 (Kulkarni et al., 2017), shows a shelf life between 125 and 149 days (Farhoosh, 2007), similar to that of our 1:10 blend (Table 5). The shelf life was also determined under accelerated conditions, using combined models such as a regression model in storage at 50 °C and high temperatures (100-130 °C) which got a shelf life for olive oil between 1.14 and 1.63 years (Farhoosh and Hoseini-Yazdi, 2013). Finally, Guiotto et al. (2014) for the shelf life of chia oil, sunflower oil and their blends, tested under non-accelerated storage conditions at 20 °C, reported values between 120 and 240 days for a peroxide index not exceeding 10 meqv O_2/kg.

Conclusions

The results of this study show that the OSI of the chia-sesame oil blends, maintaining a ω-3:ω-6 ratio between 1:4 and 1:10, increased with the addition of sesame oil and decreased with that of chia oil. These results are directly related to the composition of the predominant fatty acids in the oils, which are α-linolenic in chia and linoleic in sesame. The process of accelerated oxidation of chia-sesame oil blends allowed to estimate the shelf life by extrapolation: the OSI obtained were outside the range of the experimental values at 25 °C, giving stability times ranging between 80 and 123 days. The thermodynamic behaviour was studied by calculating activation energy (86.7 - 89.1 kJ/mol), enthalpy (83.4 - 86.1 kJ/mol) and entropy (-44.3 - -39.1 J/mol) of the oxidation reaction.

The oil obtained from the mixture of chia and sesame oils has a better proportion of ω-3:ω-6 fatty acids, with a good oxidative stability that fluctuates between 6 to 8 h at 110 ºC and a shelf life at 25 ºC between 80 and 123 days.

References

Adhvaryu, A., Erhan, S., Liu, Z., & Perez, J. (2000). Oxidation kinetic studies of oils derived from unmodified and genetically modified vegetables using pressurized differential scanning calorimetry and nuclear magnetic resonance spectroscopy. *Thermochimica Acta*, 364:87–97. https://doi.org/10.1016/S0040-6031(00)00626-2

AOAC (2005). Official methods of analysis of the Association of Analytical Chemists International, (18th ed.) Gathersburg, MD U.S.A.: AOAC International.

AOCS (1998). Official methods and recommended practices of the AOCS, 5th edn. AOCS Press, Champaign.

Bodoira, R. M., Penci, C. M., Ribotta, P. D., & Martinez, M. L. (2017). Chia (*Salvia hispanica* L.) oil stability: study of the effect of natural antioxidants. *LWT – Food Science and Technology*, 75:107-113. https://doi.org/10.1016/j.lwt.2016.08.031

Codex Alimentarius (2011). Preliminary draft revision of the codex standard for specified vegetable oils. Penang, Malaysia.

Dossa, K., Wei, X., Niang, M., Liu, P., Zhang, Y., Wang, L., Liao, B., Cissé, N., Zhang, X., & Diouf, D. (2018). Near-infrared reflectance spectroscopy reveals wide variation in major components of sesame seeds from Africa and Asia. *The Crop Journal*, 6:202-206. https://doi.org/10.1016/j.cj.2017.10.003.

FAO (2012). Fats and fatty acids in human nutrition. Report of an expert consultation. 1st edition. FINUT. Granada, Spain. 204 pp.

FAOSTAT. (2014). Statistical data of food and agriculture organization of the united nations. http://www.fao.org/faostat/en/#data/QD.

Farhoosh, R. (2007). The effect of operational parameters of the Rancimat method on the determination of the oxidative stability measures and shelf-life prediction of soybean oil. *Journal of the American Oil Chemists' Society*, 84:205-209. https://doi.org/10.1007/s11746-006-1030-4

Farhoosh, R., Niazmand, R., Rezaei, M., & Sarabi, M. (2008). Kinetic parameter determination of vegetable oil oxidation under Rancimat test conditions. *European Journal of Lipid Science and Technology*, 110:587-592. https://doi.org/10.1002/ejlt.200800004

Farhoosh, R., & Hoseini-Yazdi, S.-Z. (2013). Shelf-life prediction of olive oils using empirical models developed at low and high temperatures. *Food Chemistry*, 141:557-565. http://dx.doi.org/10.1016/j.foodchem.2013.03.024

Farhoosh, R., & Hoseini-Yazdi, S.-Z. (2014). Evolution of oxidative values during kinetic studies on olive oil oxidation in the Rancimat test. *Journal of the American Oil Chemists' Society,* 91:281-293. https://doi.org/10.1007/s11746-013-2368-z

García-Moreno, P., Pérez-Gálvez, R., Guadix, A., & Guadix, E. M. (2013). Influence of the parameters of the Rancimat test on the determination of the oxidative stability index of cod liver oil. *LWT – Food Science and Technology*, 51:303-308. https://doi.org/10.1016/j.lwt.2012.11.002

Gomes, L., Esteves, R. M., Ferreira, A. A., Moreira, S. M., Rodrigues, G., Ferraz, E. A., & Teixeira, N. R. (2019). Plasma and erythrocyte ω-3 and ω-6 fatty acids are associated with multiple inflammatory and oxidative stress biomarkers in breast cancer. *Nutrition*, 58:194-200. https://doi.org/10.1016/j.nut.2018.07.115

González, A., Martínez, M. L., Paredes, A. J., León, A. E., & Ribotta, P. D. (2016). Study of the preparation process and variation of wall components in chia (*Salvia hispanica* L.) oil microencapsulation. *Powder Technology*, 301:868-875. https://doi.org/10.1016/j.powtec.2016.07.026

Griffin, B. A. (2008). How relevant is the ratio of dietary omega−6 to omega−3 polyunsaturated fatty acids to cardiovascular disease risk? Evidence from the OPTILIP study. *Current Opinion in Lipidology*, 19:57-62. https://doi.org/10.1097/MOL.0b013e3282f2e2a8.

Guiotto, E., Ixtaina, V., Nolasco, S., & Tomás, M. (2014). Effect of storage conditions and antioxidants on the oxidative stability of sunflower-chia oil blends. *Journal of the American Oil Chemists' Society,* 91:767-776. http://dx.doi.org/10.1007/s11746-014-2410-9

Gul, T., Zreen, Z., Anwar, F., Sarwar, S. (2011). Physico-chemical characteristics of two dDifferent varieties of sesame (*Sesamum indicum* L.) seed oil. *Asian J. Chem*., 23:2064-2068.

Hashempour-Baltork, F., Torbati, M., Azadmard-Damirchi, S., & Savage, G. P. (2016). Vegetable oil blending: A review of physicochemical, nutritional and health effects. *Trends in Food Science & Technology*, 57:52-58. https://doi.org/10.1016/j.tifs.2016.09.007

Hashempour-Baltork, F., Torbati, M., Azadmard-Damirchi, S., & Savage, G. P. (2017). Quality properties of sesame and olive oils incorporated with flaxseed oil. *Advanced Pharmaceutical Bulletin*, 7:97-101. https://doi.org/10.15171/apb.2017.012

Hashempour-Baltork, F., Torbati, M., Azadmard-Damirchi, S., & Savage, G. P. (2018). Chemical, rheological and nutritional characteristics of sesame and olive oils blended with linseed oil. *Advanced Pharmaceutical Bulletin*, 8:107-113. https://doi.org/10.15171/apb.2018.013

Heidarpour, M., & Farhoosh, R. (2018). A preliminary Rancimat-based kinetic approach of detecting olive oil adulteration. *LWT – Food Science and Technology*, 90:77-82. https://doi.org/10.1016/j.lwt.2017.12.015

Huerta-Yépez, S., Tirado-Rodriguez, A. B., & Hankinsona, O. (2016). Role of diets rich in omega-3 and omega-6 in the development of cancer. *Boletín Médico del Hospital Infantil de México*, 73:446-456. http://dx.doi.org/10.1016/j.bmhimx.2016.11.001

Ixtaina, V. Y., Nolasco, S. M., & Tomás, M. C. (2012). Oxidative stability of chia (*Salvia hispanica* L.) seed oil: effect of antioxidants and storage conditions. *Journal of the American Oil Chemists' Society,* 89:1077-1090. http://dx.doi.org/10.1007/s11746-011-1990-x

Ji, J., Liu, Y., Shi, L., Wang, N., & Wang, X. (2019). Effect of roasting treatment on the chemical composition of sesame oil. *LWT – Food Science and Technology*, 101:191-200. https://doi.org/10.1016/j.lwt.2018.11.008

Julio, L. M., Copado, C. N., Crespo, R., Diehl, B. W. K., Ixtaina, V. Y., & Tomás, M. C. (2019). Design of microparticles of chia seed oil by using the electrostatic layer-by-layer deposition technique. *Powder Technology*, 345:750-757. https://doi.org/10.1016/j.powtec.2019.01.047

Kulkarni, K. P., Kim, M.,·Song, J. T., Bilyeu, K. D., Lee, J. D. (2017). Genetic improvement of the fatty acid biosynthesis system to alter the ω-6/ω-3 ratio in the soybean seed. *Journal of the American Oil Chemists' Society*, 94:1403–1410. https://doi.org/10.1007/s11746-017-3049-01

Martínez, M. L., Curti, M. I., Roccia, P., Llabot, J. M., Penci, M. C., Bodoira, R. M., & Ribotta, P. D. (2015). Oxidative stability of walnut (*Juglans regia* L.) and chia (*Salvia hispanica* L.) oils microencapsulated by spray drying. *Powder Technology*, 270A:271-277. https://doi.org/10.1016/j.powtec.2014.10.031

Prasad-Timilsena, Y., Adhikari, R., Barrow, C. J., & Adhikari, B. (2016). Microencapsulation of chia seed oil using chia seed protein isolate-chia seed gum complex coacervates. *International Journal of Biological Macromolecules*, 91:347-357. https://doi.org/10.1016/j.ijbiomac.2016.05.058

Ract, J., Shafer, F., Gomes, H., Bortolon, J., Masahiro, G., Almeida, M., Hatanaka, E., Curi, R., & Gioielli, L. (2015). Production of vegetable oil blends and structured lipids effect on wound healing. *Brazilian Journal of Pharmaceutical Sciences*, 51:415-427. http://dx.doi.org/10.1590/S1984-82502015000200019

Ramsden, C. E., Zamora, D., Leelarthaepin, B., Majchrzak-Hong, S. F., Faurot, K. R., Suchindran, C. M., Ringel, A, Davis, J. M., & Hibbeln, J. R. (2013). Use of dietary linoleic acid for secondary prevention of coronary heart disease and death: evaluation of recovered data from the Sydney diet heart study and updated meta-analysis. *BMJ*, 346:e8707. https://doi.org/10.1136/bmj.e8707

Rodríguez, G., Villanueva, E., Glorio, P., & Baquerizo, M. (2015). Oxidative stability and estimate of the shelf life of sacha inchi (*Plukenetia volubilis* L.) oil. *Scientia Agropecuaria*, 6:155–163. http://dx.doi.org/10.17268/sci.agropecu.2015.03.02

Simopoulos, A. P. (2002). The importance of the ratio of omega-6/omega-3 essential fatty acids. *Biomedicine & Pharmacotherapy*, 56:365-379. https://doi.org/10.1016/S0753-3322(02)00253-6

Villanueva, E., Castillo, D., & Rodríguez, G. (2013). Influence of the Rancimat parameters on the determination of oxidative stability index of *Sesamum indicum* L. oil. *Scientia Agropecuaria*, 4:173-180. http://dx.doi.org/10.17268/sci.agropecu.2013.03.03

Villanueva, E., Rodriguez, G., Aguirre, E., & Castro, V. (2017). Influence of antioxidants on oxidative stability of the oil chia (*Salvia hispanica* L.) by Rancimat. *Scientia Agropecuaria*, 8:19-27. http://dx.doi.org/10.17268/sci.agropecu.2017.01.02

Table 1. Formulation of sesame and chia oil blends and their omegas ratios.

% oil (w/w)		Omegas ratio
Chía	Sesame	(ω-3:ω-6)
15.5	84.5	1:4
10.4	89.6	1:6
7.7	92.3	1:8
6.1	93.9	1:10

Table 2. Physico-chemical characteristics of chia oil, sesame oil and their blends. Mean value ± SD (n=3).

Profile	Chia	Sesame	ω-3:ω-6 ratios of chia–sesame oil blends			
			1:4	1:6	1:8	1:10
Fatty acid %						
$C_{16:0}$	$8.31^{e}\pm0.03$	$8.32^{d}\pm0.01$	$8.55^{c}\pm0.01$	$8.63^{b}\pm0.01$	$8.37^{d}\pm0.01$	$8.73^{a}\pm0.02$
$C_{18:0}$	$4.02^{c}\pm0.02$	$4.02^{c}\pm0.02$	$4.04^{c}\pm0.04$	$4.20^{b}\pm0.02$	$4.39^{a}\pm0.06$	$4.04^{c}\pm0.09$
$C_{18:1}$	$7.55^{e}\pm0.07$	$39.47^{a}\pm0.47$	$36.65^{d}\pm0.32$	$37.19^{c}\pm0.25$	$38.71^{b}\pm0.03$	$38.90^{b}\pm0.10$
$C_{18:2}$ (ω-6)	$19.18^{c}\pm0.85$	$44.76^{a}\pm0.16$	$40.33^{b}\pm2.85$	$43.19^{a}\pm0.23$	$43.52^{a}\pm0.45$	$43.87^{a}\pm0.64$
$C_{18:3}$ (ω-3)	$63.49^{a}\pm0.17$	$0.45^{e}\pm0.05$	$10.16^{b}\pm0.73$	$7.41^{c}\pm1.29$	$5.44^{d}\pm0.38$	$4.41^{d}\pm0.33$
ω-3:ω-6	3.3±0.2:1	1:100.3±11.4	1:4.0±0.4	1:6.0±1.1	1:8.0±0.6	1:10.0±0.7
Density (g/mL)	$0.870^{c}\pm0.00$	$0.903^{a}\pm0.01$	$0.873^{c}\pm0.01$	$0.877^{c}\pm0.01$	$0.890^{b}\pm0.00$	$0.897^{ab}\pm0.01$
Acidity (%)	$0.43^{d}\pm0.05$	$0.61^{a}\pm0.02$	$0.51^{c}\pm0.04$	$0.53^{bc}\pm0.02$	$0.55^{bc}\pm0.01$	$0.58^{ab}\pm0.01$
Iodine (g/100 g)	$103.3^{d}\pm0.6$	$108.1^{b}\pm1.0$	$105.4^{bcd}\pm1.3$	$106.4^{bc}\pm2.6$	$112.6^{a}\pm1.2$	$104.4^{cd}\pm1.8$
PV (meq O_2/kg)	$0.67^{c}\pm0.15$	$1.14^{a}\pm0.04$	$0.98^{b}\pm0.03$	$1.02^{ab}\pm0.03$	$1.05^{ab}\pm0.04$	$1.10^{ab}\pm0.03$
p-AV	$0.36^{d}\pm0.05$	$0.86^{a}\pm0.02$	$0.48^{c}\pm0.05$	$0.53^{c}\pm0.03$	$0.73^{b}\pm0.03$	$0.81^{a}\pm0.02$
TotOx	$1.69^{d}\pm0.26$	$3.14^{a}\pm0.07$	$2.44^{c}\pm0.08$	$2.57^{c}\pm0.08$	$2.83^{b}\pm0.10$	$3.01^{ab}\pm0.05$

Different letters in the same row indicate significant differences between samples ($p \leq 0.05$).

Table 3. Oxidative stability index (OSI; h) of chia oil, sesame oil and their blends. Mean value ± SD (n=3).

Temperature (°C)	Chia	Sesame	ω-3:ω-6 ratios of chia–sesame oil blends			
			1:4	1:6	1:8	1:10
	OSI±SD	OSI±SD	OSI±SD	OSI±SD	OSI±SD	OSI±SD
130	-	2.33^{a}±0.02	1.62^{e}±0.05	1.82^{d}±0.02	1.90^{c}±0.03	2.01^{b}±0.01
120	-	4.74^{a}±0.12	3.07^{e}±0.05	3.52^{d}±0.09	3.75^{c}±0.08	4.00^{b}±0.10
110	1.49^{f}±0.00	10.45^{a}±0.25	6.24^{e}±0.04	7.22^{d}±0.13	7.65^{c}±0.34	8.08^{b}±0.08
100	3.03±0.05	-	-	-	-	-
90	6.16±0.01	-	-	-	-	-

Different letters in the same row indicate significant difference between samples ($p \leq 0.05$).

Table 4. Activation energy (Ea), enthalpy (ΔH^{++}), entropy (ΔS^{++}), energy of Gibbs (ΔG^{++}) of chia oil, sesame oil and their blends.

Oil samples	Ea (kJ/mol)	ΔH^{++} (kJ/mol)	ΔS^{++} (J/mol K)	ΔG^{++} (kJ/mol)
Chia	82.0^{d}±0.1	78.9^{d}±0.1	-44.4^{b}±0.1	62.3^{c}±0.1
Sesame	96.2^{a}±2.0	93.0^{a}±2.0	-23.7^{a}±5.0	83.7^{a}±3.9
Blends (ω-3:ω-6 ratios)				
1:4	86.7^{c}±1.7	83.4^{c}±1.7	-44.3^{b}±4.5	66.0^{bc}±3.5
1:6	88.6^{bc}±0.9	85.3^{bc}±0.9	-40.7^{b}±2.1	69.3^{b}±1.7
1:8	89.4^{b}±2.0	86.1^{b}±2.0	-39.1^{b}±4.8	70.7^{b}±3.9
1:10	89.1^{bc}±0.9	85.9^{bc}±0.9	-40.2^{b}±2.3	70.1^{b}±1.8

Different letters in the same column indicate significant difference between samples ($p \leq 0.05$).

Table 5. Shelf life (oxidative stability index at 25 °C, OSI_{25}) and Q_{10} (increase of reaction rate due to a 10 °C temperature rise) of chia oil, sesame oil and their blends.

Oil samples	$\log OSI = \alpha(T) + \beta$			OSI_{25} (days)	Q_{10}
	α±SD	β±SD	R^2		
Chia	-0.0308±0.0000	3.5621±0.0038	0.999	$25.8^{d}\pm0.2$	2.03±0.00
Sesame	-0.0326±0.0007	4.5949±0.0773	0.999	$253.3^{a}\pm36.1$	2.12±0.12
Blends (ω-3:ω-6 ratios)					
1:4	-0.0293±0.0006	4.0168±0.0667	0.999	$80.4^{c}\pm9.8$	1.96±0.10
1:6	-0.0300±0.0003	4.1515±0.0409	0.999	$105.4^{bc}\pm8.3$	1.99±0.08
1:8	-0.0302±0.0007	4.2076±0.0862	0.999	$118.9^{b}\pm18.6$	2.01±0.05
1:10	-0.0302±0.0003	4.2242±0.0411	0.999	$123.2^{b}\pm9.5$	2.01±0.02

α and β: constants; $\mathbf{R^2}$: coefficient of determination. Different letters in the same column indicate significant difference between samples ($p \leq 0.05$).