



Chia Oil Microencapsulation by Spray Drying Using Modified Soy Protein as Wall Material [†]

Paola Alejandra Gimenez ¹, Antonella Estefanía Bergesse ², Nahuel Camacho ³, Pablo Daniel Ribotta ⁴,
Marcela Lilian Martínez ⁵ and Agustín González ^{1,*} 

¹ Faculty of Chemistry, National University of Córdoba, IPQA-CONICET, Córdoba 5000, Argentina

² Faculty of Agricultural Sciences, National University of Córdoba, IMBIV-CONICET, Córdoba 5000, Argentina

³ Faculty of Chemistry, National University of Córdoba, UNITEFA-CONICET, Córdoba 5000, Argentina

⁴ Faculty of Exact, Physical and Natural Sciences, National University of Córdoba, ICITAC-CONICET, Córdoba 5000, Argentina

⁵ Faculty of Exact, Physical and Natural Sciences, National University of Córdoba, IMBIV-CONICET, Córdoba 5000, Argentina

* Correspondence: agustingonzalez@unc.edu.ar

[†] Presented at the IV Conference Ia ValSe-Food CYTED and VII Symposium Chia-Link, La Plata and Jujuy, Argentina, 14–18 November 2022.

Abstract: Chia seed is the richest vegetable source of polyunsaturated fatty acids. A diet rich in these fatty acids decreases the risk of many chronic non-communicable diseases. The incorporation of omega-3-rich oils in processed foods seems to be an efficient way to increase its consumption; however, when these are exposed to processing conditions, oxidation reactions occur. Microencapsulation technology is an alternative method to enhance lipid stability. The use of vegetable proteins as wall materials is being widely developed. The objective of the present work was to study the effect of the microencapsulation using chemically modified soy protein as wall material on chia oil oxidative stability. The crosslinking effect on soy protein with different concentrations of gallic and tannic acids was evaluated. Chia oil was incorporated into the dispersions using a high-speed homogenizer and the emulsions were dried by Spray-Drying. The microcapsule moisture content and water activity were around 2.96–5.86% and 0.17, respectively. The encapsulation efficiency was among 54–78%. The oxidative stability determined by the Rancimat analysis showed a positive correlation between the amount of cross-linking agent used and the induction time, reaching a maximum of 11.97 h. In a storage test, the peroxide value was markedly lower for those crosslinked microcapsules respect to pure SPI wall material after 90 days. The results demonstrated that use of these polyphenols as crosslinkers of the wall material exerts a positive effect in the protection of the chia oil derived from obtaining an optimized wall material and from the intrinsic antioxidant properties of these crosslinkers.

Keywords: antioxidants; chia oil; crosslinking; microencapsulation; polyphenols



Citation: Gimenez, P.A.; Bergesse, A.E.; Camacho, N.; Ribotta, P.D.; Martínez, M.L.; González, A. Chia Oil Microencapsulation by Spray Drying Using Modified Soy Protein as Wall Material. *Biol. Life Sci. Forum* **2022**, *17*, 10. <https://doi.org/10.3390/blsf2022017010>

Academic Editors: Norma Sammán, Mabel Cristina Tomás, Loreto Muñoz and Claudia Monika Haros

Published: 25 October 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Chia seed oil with 61–70% of alpha linolenic acid (18:3) is the richest vegetable source of omega-3 fatty acids. The consumption of fatty acids of the omega 3 series provides numerous health benefits and can be incorporated in the form of triglycerides or ethyl esters [1]. A diet rich in these compounds reduces the risk of contracting coronary and neurodegenerative diseases, cancer, metabolic syndrome, rheumatism, type 2 diabetes, atherosclerosis, and Alzheimer's disease [1]. Although a higher consumption of these lipids is favorable from a nutritional and healthy point of view, some drawbacks are present due to its less oxidative stability and a short shelf life. One of the main challenges for the use and incorporation of these fatty acids in processed foods lies in the need to be stabilized by incorporating antioxidants and conveyed in a polymeric matrix that contains

and protects them. An effective technology for this purpose is microencapsulation in solid and polymeric matrices [2]. The use of plant proteins as wall material is being widely developed; however, it is necessary to study strategies that make it possible to obtain better microcapsules compared to those reported until now [3].

The antioxidant properties of polyphenols such as tannic and gallic acid have been reported by Shavandi et al. [4]. In addition, Kim et al. [5] reported an increase in the antioxidant properties of tannic acid after a thermal treatment.

Therefore, the objective of the present work was to study a challenging and novel strategy such as the chemical modification of the proteins used as wall material through cross-linking reactions with natural polyphenolic compounds. The influence on the chemical quality of the omega 3 rich oils containing microcapsules (MC) was analyzed, focusing on their degree of protection of the contained oil.

2. Materials and Methods

2.1. Materials

Soy protein isolate (SPI) (SUPRO E, 90% protein, fat-free dry basis) was obtained from DuPont Nutrition & Health (EEUU) and chia oil (CO) was obtained from seeds from the province of Salta, Argentina (Distribuidora Nicco SRL, Córdoba, Argentina). The reagents and solvents used were purchased from local distributors.

2.2. Oil Extraction and Microcapsule Preparation

Chia oil (CO) was extracted by cold pressing in a single step with a Komet screw-press (CA 59 G model, IBG Monforts, Mönchengladbach, Germany) according to Martinez et al. [6].

Aqueous dispersions of isolated soy protein (SPI) 8% *w/w* were prepared and brought to pH between 9 and 11. Natural crosslinkers such as tannic (TA), gallic acid (GA) and a heat-treated tannic acid (130 °C in autoclave for 15 and 30 min for increasing its antioxidant capacity [5]) (TA15 and TA30) were studied. Different amounts of the crosslinking agents were added (1–10% *w/w* respect to SPI amount) and allowed to react with stirring at 60 °C for 24 h. CO was incorporated dropwise into the dispersions at a 2:1 ratio (SPI:oil) for 15 min at 18,000 rpm using an Ultraturrax homogenizer (IKA T18, Staufen, Germany). The resulting emulsions were dried in a Mini Spray Dryer Büchi B-290 (Büchi Labortechnik AG, Flawil, Switzerland) with a two-fluid nozzle under the following conditions: air inlet and outlet temperature 130 and 80 °C, respectively, pump 10%, aspirator 100% and air flow 538 L/h.

2.3. Microcapsule Characterization

Moisture content was measured for each sample with a moisture analyzer with halogen heating (model HE53 Mettler Toledo, Columbus, OH, United States). Water activity was measured with Aqua-Lab (208 Series 3, Decagon Devices Inc., Pullman, WA, USA) at 25.0 ± 0.5 °C. Surface or free oil (SO), total oil (TO) and encapsulation efficiency (EE) were assessed following a previously reported methodology [2].

2.4. Oil Oxidative Stability Study

To study the oxidative stability of unencapsulated and encapsulated oil, samples were subjected to accelerated oxidation conditions (100 °C, air flow 20 L/h) in a Rancimat apparatus (METROHM, Herisau, Switzerland) and expressed as induction period (IP). The protection factor (PF) was defined as the ratio of IP of the microencapsulated oil and IP of unencapsulated oil. The hydroperoxide values (HPV) were assessed following the methodologies of González et al. [2].

The fatty acid composition of oil was analyzed by gas chromatography according to what was proposed by González et al. [7]. For the storage stability test, bulk CO and microencapsulated oil were placed in 250 mL amber glass bottles in a thermostated chamber at 25 °C. The samples were stored for 90 days. At different times, 5 g of samples were

extracted, and chia oil was extracted by immersing them in hexane for 24 h at 4 °C and evaporating the solvent in vacuum at 36 °C in order to evaluate their hydroperoxide value (HPV).

2.5. Statistical Analysis

Analytical determinations were the averages of duplicate measurements. Statistical differences among treatments were estimated from ANOVA test at the 5% level ($p < 0.05$) of significance, for all parameters evaluated.

3. Results and Discussion

3.1. Microcapsule Characterization

Dark green powders were obtained by spray-drying the prepared emulsions. The color of the powders darkened with increasing the amount of crosslinker initially added. The microcapsule moisture content and water activity were around 2.96 and 5.86% and 0.17, respectively, which is similar to reported in the literature (Bordon et al. [8]). With regard to the oil distribution in the microcapsules, the encapsulation efficiency was between 54 and 78%. Similar results were also obtained by González et al. [2] for SPI and maltodextrin microcapsules with values between 52 and 65%; Bordon et al. [8] for SPI and gum Arabic microcapsules with values between 68 and 87%. The relative abundance of the unsaturated fatty acids after oil microencapsulation was composed of 64.1%, 19.4% and 6.5% of linolenic, linoleic, and oleic acid, respectively. These results were in concordance with those reported in the literature (Martínez et al. [9]) for press-cold chia oil.

The protective effect of the microcapsules wall materials on the oxidative stability of chia oil was demonstrated by obtaining high induction periods in the Rancimat test. Microcapsules with wall materials with 1%, 5% and 10% of crosslinker agent showed IPs of 7.6 h, 7.6–11.9 h and 6.7–11.0 h, respectively. The maximum protection factor (PF) was around 4.0 for 5% of crosslinker agents. These results were higher than those reported by González et al. [2] with a maximum of 6.4 h and a PF of 2.7. In addition, the antioxidant properties of the natural crosslinkers were assessed adding the same amount of the polyphenols in bulk oils. The results of IP and PF for bulk chia oil with 5% of polyphenols were 5.6 h and 2.3, respectively. These results show that polyphenols exert an antioxidant effect, but this effect is smaller in respect to the protection obtained for microencapsulated oil. It could be seen that the simple addition of both effects in separately as microencapsulation (sample with microencapsulated oil in SPI wall material without crosslinker) and antioxidant effect (bulk oil with polyphenols samples) is smaller than both strategies combined (microencapsulated oil in crosslinked SPI wall material). This observation allows us to determine that there is a synergistic relationship between both protection strategies.

3.2. Storage Test

For this assay, microcapsules with 5% of crosslinker agent were selected due to their higher PF with the lower percentage of polyphenols used. Figure 1 shows that hydroperoxide values (HPV) gradually increased with storage time. After 90 days, all the samples analyzed presented HPV higher than the Codex acceptance limit for cold-pressed and virgin vegetable oils (15 milliequivalents of O₂/kg oil) (Codex Alimentarius, 2011). It is important to highlight that the microencapsulated samples whose wall material was composed by cross-linked protein presented a significantly lower HPV ($p < 0.05$) than the microcapsules with protein without chemical modification as wall material. The difference in oxidative stability of the microencapsulated chia oil with SPI in the present study compared with González et al. [2] could be due to the absence of the heating stage in the wall material preparation in which Maillard reaction occurs and the resulting compounds have shown antioxidant activity [10].

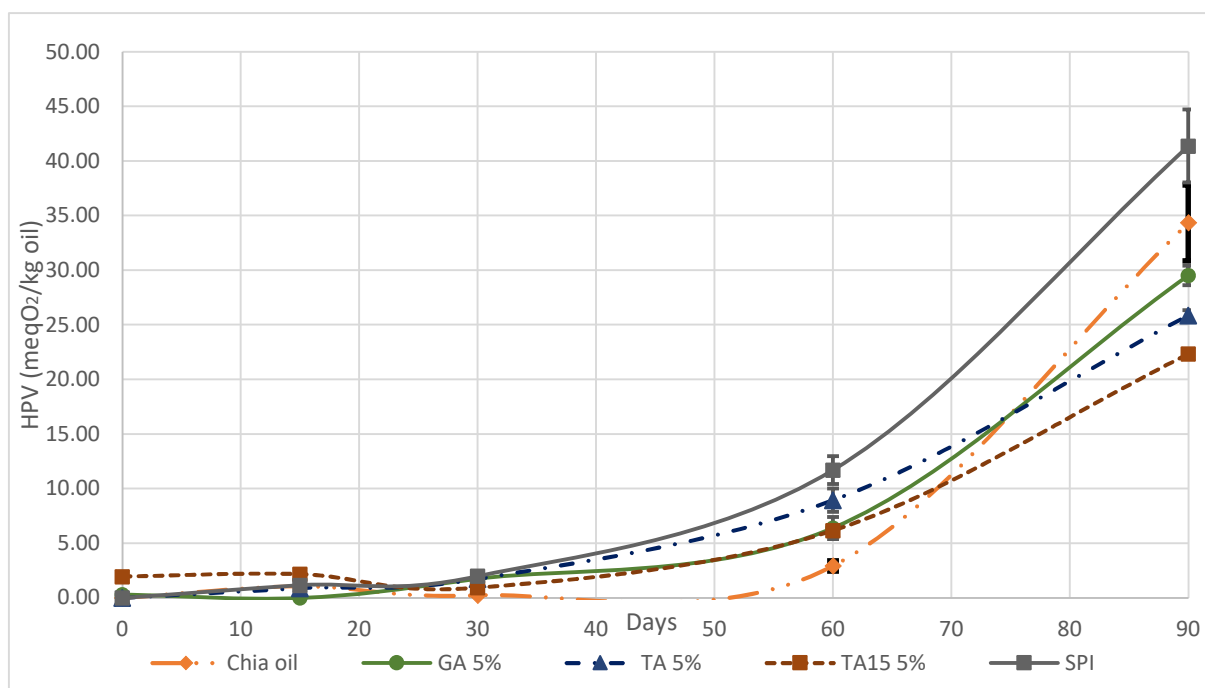


Figure 1. The peroxide value evolution for different storage times.

4. Conclusions

The results demonstrated that the use of these polyphenols as crosslinkers of the wall material for microencapsulation of chia oil exerts a positive effect on the protection of the oil derived from obtaining an optimized wall material and from the intrinsic antioxidant properties of these crosslinkers, allowing its potential application as an ingredient in processed foods.

Author Contributions: Conceptualization, M.L.M. and A.G.; methodology, P.A.G., M.L.M. and A.G.; validation, M.L.M. and A.G.; investigation, P.A.G., A.E.B. and N.C.; writing-original draft preparation, P.A.G.; writing-review and editing, M.L.M. and A.G.; supervision M.L.M. and A.G.; project administration P.D.R.; funding acquisition P.D.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was founded by La ValSe-Food-CYTED, grant number 119RT0567, FONCyT grant number PICT-2019-04265-II-B.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Racine, R.A.; Deckelbaum, R.J. Sources of the very-long-chain unsaturated omega-3 fatty acids: Eicosapentaenoic acid and docosahexaenoic acid. *Curr. Opin. Clin. Nutr. Metab. Care* **2007**, *10*, 123–128. [[CrossRef](#)] [[PubMed](#)]
2. González, A.; Martínez, M.L.; Paredes, A.J.; León, A.E.; Ribotta, P.D. Study of the preparation process and variation of wall components in chia (*Salvia hispanica* L.) oil microencapsulation. *Powder Technol.* **2016**, *301*, 868–875. [[CrossRef](#)]
3. Heck, R.T.; Lorenzo, J.M.; Dos Santos, B.A.; Cichoski, A.J.; de Menezes, C.R.; Campagnol, P.C.B. Microencapsulation of healthier oils: An efficient strategy to improve the lipid profile of meat products. *Curr. Opin. Food Sci.* **2020**, *40*, 6–12. [[CrossRef](#)]
4. Shavandi, A.; Bekhit, A.E.D.A.; Saeedi, P.; Izadifar, Z.; Bekhit, A.A.; Khademhosseini, A. Polyphenol uses in biomaterials engineering. *Biomaterials* **2018**, *167*, 91–106. [[CrossRef](#)] [[PubMed](#)]
5. Kim, T.J.; Silva, J.L.; Kim, M.K.; Jung, Y.S. Enhanced antioxidant capacity and antimicrobial activity of tannic acid by thermal processing. *Food Chem.* **2010**, *118*, 740–746. [[CrossRef](#)]

6. Martínez, M.L.; Marín, M.A.; Salgado Faller, C.M.; Revol, J.; Penci, M.C.; Ribotta, P.D. Chia (*Salvia hispanica* L.) oil extraction: Study of processing parameters. *LWT—Food Sci. Technol.* **2012**, *47*, 78–82. [[CrossRef](#)]
7. González, A.; Martínez, M.L.; León, A.E.; Ribotta, P.D. Effects on bread and oil quality after functionalization with microencapsulated chia oil. *J. Sci. Food Agric.* **2018**, *98*, 4903–4910. [[CrossRef](#)] [[PubMed](#)]
8. Bordón, M.G.; Bodoira, R.M.; González, A.; Piloni, R.; Ribotta, P.D.; Martínez, M.L. Spray-Drying, Oil Blending, and the Addition of Antioxidants Enhance the Storage Stability at Room Temperature of Omega-3-Rich Microcapsules Based on Chia Oil. *Eur. J. Lipid Sci. Technol.* **2022**, *124*, 1–11. [[CrossRef](#)]
9. Martínez, M.L.; Curti, M.I.; Roccia, P.; Llabot, J.M.; Penci, M.C.; Bodoira, R.M.; Ribotta, P.D. Oxidative stability of walnut (*Juglans regia* L.) and chia (*Salvia hispanica* L.) oils microencapsulated by spray drying. *Powder Technol.* **2015**, *270*, 271–277. [[CrossRef](#)]
10. Copado, C.N.; Diehl, B.W.K.; Ixtaina, V.Y.; Tomás, M.C. Application of Maillard reaction products on chia seed oil microcapsules with different core/wall ratios. *LWT—Food Sci. Technol.* **2017**, *86*, 408–417. [[CrossRef](#)]