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Oxidative stability of walnut (*Juglans regia* L.) and chia (*Salvia hispanica* L.) oils microencapsulated by spray drying

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ABSTRACT

This work was primarily aimed to evaluate the use of maltodextrin in combination with hydroxypropyl methylcellulose as wall materials for microencapsulation of both walnut and chia oils by spray drying. The effect of rosemary extract on the oxidative stability of the microencapsulated oils was examined under prolonged storage conditions. After a 45-day storage, the microencapsulated chia oil with rosemary extract showed lower formation of primary oxidation compounds than the control without additives, highlighting a protective effect of the antioxidant. Nevertheless, during the entire storage period the unencapsulated chia oil reported lower oxidative damage than their encapsulated counterparts, showing that the spray drying process affected its stability negatively. Walnut oil microencapsulation protected the oil from oxidation in comparison with its unencapsulated counterpart which was further apparent from the 30th day of storage. The addition of 1600 ppm of rosemary extract effectively protected microencapsulated walnut oil, showing – throughout the storage period – lower oxidation values in comparison with its analogous unencapsulated oil. The microcapsule surface oil and the images obtained by scanning electron microscopy at the beginning and at the end of the assay showed that the wall material has not been altered during storage.

1. Introduction

Currently, walnut and chia seeds are crops of high economic interest for the food, pharmaceutical and cosmetic industries. Both, walnut and chia seeds, contain high levels of oil, 52–70% and 25–38%, respectively [1–8]. The major components of these oils are triacylglycerols, in which monounsaturated (mainly oleic acid) and polyunsaturated (PUFA, linoleic and α-linolenic acids) fatty acids (FA) are present in high amounts [9,1,7,10]. Omega-3 fatty acids play an essential role in physiology, especially during fetal and infant growth [11], and in the prevention of cardiovascular diseases, and are antithrombotic, antiinflammatory, antiarrhythmic agents favoring plaque stabilization [12]. While these oils can be consumed directly as salad dressings, an interesting application would be to have them built into food products of mass consumption. Unsaturated fatty acids (ω−3, ω−6 and ω−9) are chemically unstable in the presence of oxygen, light, moisture and heat. Frankel [13] informed that in neat systems without an added initiator, linoleate was 40 times more reactive than oleate, and linolenate was 2.4 times more reactive than linoleate.

Microencapsulation of oils by spray drying in a polymeric matrix is an alternative that has been used by several researchers in order to protect unsaturated fatty acids [14–17]. This technology is defined as the process of enveloping a solid, liquid or gaseous substance within another substance in very small sealed capsules from which the core material is gradually diffused through the capsule walls at controlled rates under specific conditions [17]. Among the different techniques developed to encapsulate food ingredients, such as physical methods (e.g. pan coating, air-suspension coating, centrifugal extrusion, vibration nozzle and spray drying) and chemical methods (e.g. interfacial polymerization, in-situ polymerization, and matrix polymerization), the most common technique applied in this field is spray-drying because it is rather inexpensive and straightforward [18,17]. Spray drying involves the atomization of emulsions into a drying medium with high temperature, resulting in a very fast water evaporation, which results in a quick crust formation and in a quasi-instantaneous entrapment of the core material [14,18–20,16]. The main objective is to build a barrier between the component in the particle and the environment. This barrier may

Abbreviations: CO, chia oil; EE, encapsulation efficiency; FA, fatty acids; HPLC, high pressure liquid chromatography; HPMC, hydroxypropyl methylcellulose; HPV, hydroperoxide value; K_{232}, conjugated dienes; K_{270}, conjugated trienes; LSD, least significant difference; M, microcapsules; MD, maltodextrin; MUFA, monounsaturated fatty acid; ND, not detected; OSI, oxidative stability indexes; PUFA, polyunsaturated fatty acid; RE, rosemary extract; SEM, scanning electron microscopy; SO, surface oil; SY, solid yield; TO, total oil content; UV, ultra violet; WO, walnut oil.

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protect against oxygen, water, light, and also avoids contact with other ingredients. The efficiency of protection and controlled release depends mainly on the composition and structure of the established wall, and also on the operating conditions during the production and use of these particles (temperature, pH, pressure, humidity). An area of research of increasing interest is the use of biopolymer blends as wall materials that may allow the increase of the encapsulation efficiency and shelf life of microcapsules [21–23]. The selection of wall material influences the emulsion stability during its formation and after the drying process affecting the characteristics of the resulting microcapsules [24–27]. The usual encapsulating agents are proteins (e.g. milk and gelatine), gums (e.g. acacia and alginate), carbohydrates (e.g. sucrose, maltodextrins, modified starch, cyclodextrins and cellulose), lipids, fats, waxes, lecithins (emulsifiers) and fibers. Maltodextrin is a hydrolyzed starch commonly used as wall material in microencapsulation of food ingredients [18]. It offers advantages such as relatively low cost, neutral aroma and taste, low viscosity at high solid concentration and good protection against oxidation. However, the biggest problem of this wall material is its low emulsifying capacity. Also, it can be used in combination with other surface active biopolymers, such as gum Arabic [28,29], modified starches [30,29] and proteins [31,32], in order to obtain an effective microencapsulation by spray drying. Hydroxypropyl methylcellulose (HPMC), water soluble, non ionic cellulose derivative has been widely used in foods products. The presence of hydroxypropyl and methyl groups renders the cellulose molecules hydrophobic and makes them surface active and adequate for oil microencapsulation [14,18,30]. Most of the works found in the literature on microencapsulation of PUFA-rich oils have been carried out by using fish oils [31,33–35]. Fish oils are similar to walnut and chia oils because they are very rich in PUFAs, although their compositions differ largely. Some works have reported the microencapsulation of fish oils containing approximately 27% [34], 29% [17], or 33% [36] of ω−3 fatty acids. Walnut and chia oils contain about 15 and 60%, respectively, of α-linolenic (ω−3) FA [5,8,37]. Therefore, even though they could show a similar behavior when microencapsulated, their behavior may not be the same during spray drying and storage. Although encapsulation itself prevents lipid oxidation, additional stabilization with antioxidants is required to ensure maximum protection during processing and subsequent storage of microencapsulated bioactive ingredients [34]. Rosemary extract (*Rosmarinus officinalis*) has antioxidant properties and is widely used in food industry. The antioxidant activity of rosemary extract is associated with the presence of phenolic compounds, such as carnosic acid, rosmarinic acid, carnosol, rosmanol, rosmariquinone and rosmaridiphenol, which react with free radicals formed in the oxidation process [38].

Very little information is available on microencapsulation of walnut and chia oils [39–41] and none of the published works reported the influence of maltodextrin combined with hydroxypropyl methylcellulose as wall materials, on the oxidative stability of these oils.

This work was primarily aimed to evaluate the use of maltodextrin combined with hydroxypropyl methylcellulose as wall materials for microencapsulation of both walnut and chia oils by spray drying. In addition, the effect of rosemary extract on the oxidative stability of the microencapsulated oils was examined under prolonged storage conditions.

2. Materials and methods

2.1. Materials

Hydroxypropyl methylcellulose (HPMC, Methocel K99, Ciclo Química, Argentina), maltodextrin (MD, DE15, Distribuidora Nicco, Argentina) and soy lecithin (Distribuidora Nicco, Argentina) were used as an emulsion stabilizer and a protection for the oil drops in the emulsion and in the final powder.

Walnut oil (WO) was obtained from healthy and mature kernels from Franquette variety (Catamarca, Argentina); while, chia oil (CO) was obtained from seeds coming from the province of Salta, Argentina (Nutracéutica Sturla SRL). WO and CO extraction were performed as described elsewhere [6,8]. Briefly, walnut kernels were ground and particles between 2.4 and 4.8 mm were selected using an automated screen and conditioned to obtain 7.5% (w/w) moisture content. Chia seeds were only hydrated to obtain 10% (w/w) moisture content [8].

Oil expression was carried out with a Komet screw press (Model CA 59 G; IBG Monforts, Monchengladbach, Germany), with a 5 or 6 mm restriction die, as appropriate, and a screw speed of 20 rpm.

Guardian Rosemary Extract 08 (RE, oil soluble) was from Danisco (Copenhagen, Denmark).

2.2. Emulsion preparation

For spray drying, blends of both HPMC/MD/WO and HPMC/MD/CO in water emulsions were prepared. MD (6%) was dissolved in demineralized water at room temperature and then HPMC (3%) was slowly added and stored for 24 h at 4 °C [42]. RE was incorporated to the oil by magnetic stirring for 5 min at 90 rpm and under these conditions a homogenous oil appearance was achieved. Blends of oil: soy lecithin (0.3 g lecithin/9 g oil) were prepared and then incorporated drop by drop into the suspension in a ratio 2:1 (wall material: oil) for 10 min, using a homogenizer Ultraturrax T18. The resulting emulsions (200 mL lots) were stored at 4 °C before the spray drying process. The droplet size of the emulsions ranged from 0.06 to 29 and 0.13 to 24 μm, for CO and WO, respectively.

2.3. Spray-drying microcapsule preparation

The spray-drying process was performed in a laboratory-scale Mini Spray Dryer Büchi B-290 (Büchi Labortechnik AG). A two fluid nozzle with a cap orifice diameter of 0.5 mm was used; the air atomizing pressure was kept constant at 6 bars for all the experiments. The microcapsules were obtained in triplicate under the following operating conditions: air inlet temperature, 163 °C; atomization air flow rate, 279 L/h; pump setting, 10% and aspirator setting, 100% [42].

2.4. Experimental design for storage stability test

Microencapsulated and bulk WO and CO were separated in 250 mL dark glass bottles — samples. The RE was added to oil samples according to quantities stated in Table 1, based on a previous work [43]. After mixing (magnetic stirrer, 10 min, 90 rpm), a homogeneous oil appearance was achieved. The oil samples were utilized to prepare the blend and then incorporated to the emulsion. The microcapsules obtained were set in 250 mL amber glass bottles and placed inside a thermostated chamber at 25 ± 1 °C and 40% of relative humidity. Each treatment (consisting of a combination from oil plus additive) was prepared in triplicate. Bulk oil samples with and without RE were used as controls. Samples were stored for three months. Every fifteen days each individual sample was withdrawn from the chamber for scheduled analyses.

Table 1
Treatments for the storage stability study of bulk and microencapsulated walnut oil (WO) and chia oil (CO), with and without rosemary extract (RE).

Code	Treatment
WO (bulk oil)	WO without RE
M-WO (microcapsules)	WO without RE
CO (bulk oil)	CO without RE
M-CO (microcapsules)	CO without RE
WO + RE 1600 (bulk oil)	RE 1600 μg/g oil
M-WO + RE 1600 (microcapsules)	RE 1600 μg/g oil
CO + RE 1600 (bulk oil)	RE 1600 μg/g oil
M-CO + RE 1600 (microcapsules)	RE 1600 μg/g oil