

## Impact of the Encapsulation Process by Spray- and Freeze-Drying on the Properties and Composition of Powders Obtained from Cold-Pressed Seed Oils with Various Unsaturated Fatty Acids

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The aim of this study was to determine the influence of encapsulation methods on fatty acid composition and content of bioactive compounds in cold-pressed oils. Rape, flax, and safflower seed oils (10.2%) were mixed with water (70.0%) and wall components (19.8%) to obtain emulsions, which were then subjected to spray- and freeze-drying. Surface and total oil contents, and changes in contents of fatty acids, sterols, and tocopherols were compared in powders and natural oils.

The spray-drying was a more effective encapsulation method compared to the freeze-drying. Fatty acid composition of the oils was quite stable during the encapsulation process. Sterol degradation was high and only 35–40% of these compounds were determined in powders. In turn, tocopherol losses were dependent both on the encapsulation method and oil type. The encapsulation by freeze-drying allowed the retention of almost all tocopherols of cold-pressed flax and safflower seed oils.

### INTRODUCTION

Cold-pressed plant oils are used mainly by the pharmaceutical industry as a raw material for the production of dietary supplements, while their application is limited in the food industry. These oils constitute, first of all, an element of “slow food” [Miele & Murdoch, 2002], which is due to their poor storage stability, related to a high content of polyunsaturated fatty acids, like particularly in flax and safflower seed oils [Dorni *et al.*, 2018; Khattab & Zeitoun, 2013; Tańska *et al.*, 2016].

Cold-pressed oils obtained from such raw materials as rape, flax or safflower seeds are considered to be valuable edible fats from a nutritional point of view. Their value is a result of, among others, a high content of unsaturated fatty acids, oleic acid in rape seed oil (up to 60%), linoleic acid in safflower seed oil (up to 80%), and  $\alpha$ -linolenic acid in flax seed oil (up to 60%) [Ghazani *et al.*, 2014; Khalid *et al.*, 2017; Tańska *et al.*, 2016]. A beneficial effect of fatty acids of the rape seed oil on the blood lipid profile consists in reducing the concentration of total cholesterol and the low-density lipoprotein (LDL) fraction, without any effect on the concentration of the high-density lipoprotein (HDL) fraction [Nguemini *et al.*, 2010]. Additionally, results obtained by Nguemini *et al.* [2010] support the hypothesis that diet supplementation with rape seed

oil can enhance the treatment of ischemic stroke.  $\alpha$ -Linolenic acid, which belongs to the *n*-3 family (flax seed oil is a good source of this acid), may help protect against certain infections and in treating conditions including ulcers, migraine headaches, attention deficit/hyperactivity disorder, eating disorders, preterm labour, emphysema, psoriasis, glaucoma, Lyme disease, lupus, and panic attacks [Harper *et al.*, 2006]. The health-promoting properties of the above-mentioned cold-pressed oils are also affected by the native bioactive components they contain, such as: sterols (up to 835 mg/100 g in rape seed oil), tocopherols (up to 60 mg/100 g in flax seed oil), carotenoids (up to 28 mg/100 g in rape seed oil), squalene (up to 4 mg/100 g in flax seed oil), and polyphenols (up to 14 mg/100 g in safflower seed oil) [Ben Moumen *et al.*, 2015; Ghazani *et al.*, 2014].

The use of plant oils in the food industry can be increased by the application of the encapsulation process, which allows extending the oxidative stability of the core of the capsule and guarantees the controlled release of substances from the capsule during the technological process [Aksoylu & Günc Ergönül, 2017]. The most popular method of oil encapsulation is the spray-drying. It is considered to be an optimal solution for oils because it allows for the transformation of emulsion into powder, simultaneously preserving its valuable properties. Because of the large surface area of the droplets, water evaporates almost immediately and the droplets are transformed into particles. Another popular method used

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to prepare powdered oils is encapsulation by freeze-drying. It requires a much longer time but can be done at a very low temperature. During this process, water is frozen, followed by its removal from the sample, initially by sublimation (primary drying) and then by desorption (secondary drying) [Ogrodowska *et al.*, 2017].

Oil in a powdered form can be applied as a functional supplement to dairy products [Wang *et al.*, 2011], bakery products [Gallardo *et al.*, 2013], and fruit and vegetable products [Donsi *et al.*, 2011]. Although encapsulated oils are easier to apply in food products and more resistant to oxidative changes than the cold-pressed oils, there are still few studies that explain the effect of the encapsulation on the native oil components such as unsaturated fatty acids and bioactive compounds.

Our previous work [Ogrodowska *et al.*, 2019] showed that the encapsulation by spray- and freeze-drying had a significant impact on the content of bioactive compounds and oxidative stability of encapsulated bio-oils from evening primrose, borage, and blue weed seeds. We showed that despite the lower process efficiency, the encapsulation by freeze-drying would be more recommended for evening primrose seed oil. In turn, the encapsulated borage and blue weed oils should be produced by spray-drying. We hypothesized that the differences observed were connected to the initial chemical composition of the bio-oils used. Little is known, however, on this kind of a relationship. Generally, previous studies have focused on the physical properties of powders obtained with different encapsulation methods or under different process conditions [Bakry *et al.*, 2016].

In this work, we compared the influence of the most popular encapsulation methods (spray- and freeze drying) on the effectiveness of the encapsulation process and losses of sterols and tocopherols in powders obtained from cold-pressed oils with various unsaturated fatty acid composition.

## MATERIALS AND METHODS

### Materials

Three types of cold-pressed plant oils were investigated in this study. Seeds of rape, flax, and safflower were from “Szarlat” company (Łomża, Poland). The oils were produced by pressing the raw material on a IBG Monforts & Reiners, Komet CA59G (Nürnberg, Germany) laboratory expeller equipped with a nozzle giving 4 mm in diameter. The oils were purified by centrifugation on a centrifuge (type 5810R, Eppendorf AG, Hamburg, Germany) operated at 15,000×g. Whey protein concentrate was purchased from “Ostrowia” company (Ostrów Mazowiecka, Poland). Maltodextrin (DE 14–22) and guar gum were purchased from Edpol Food & Innovation Company (Łomża, Poland).

### Emulsification process

The composition of emulsions was the same for all samples: 19.8% (w/w) of wall materials (maltodextrin 15.4%, whey protein concentrate 3.9%, and guar gum 0.5%), 10.2% (w/w) of oil, and 70% (w/w) of water. The proportion of wall materials and oil loading were established based on the work of Ogrodowska *et al.* [2017]. The oils were blended with aqueous solutions of wall materials at 9,000 rpm for 120 s at 40°C

using Thermomix (Vorwerk, Wuppertal, Germany). Then, emulsions were further homogenized at 240 bar (I step) and 40 bar (II step) using a high-pressure laboratory valve homogenizer (Panda 2K, GEA Niro Soavi, Parma, Italy).

### Emulsion drying process

The spray-dried powders were prepared using a pilot-plant spray dryer (A/S Niro Atomizer, Copenhagen, Denmark) with disc having 110 mm in diameter as a spraying mechanism at 6400 rpm. The emulsion was pumped into a spray dryer chamber at a constant feeding speed. The inlet temperature was set at 130°C, whereas the outlet temperature at 90°C. The feed flow rate was 77 mL/min and the air flow rate was approx. 400 kg/h.

Freeze-dried powders were prepared using a lyophilizer (Cryolizer Freeze Dryer type B-64, New Brunswick Scientific Co., Inc., New Brunswick, NJ, USA). The emulsions were put into aluminium pans and frozen at -20°C for 24 h. Then, the emulsions were lyophilized, with an ice condenser set at -50°C at a pressure of 0.12 mbar and freeze-drying time reaching 72 h.

### Physical characterization of emulsions

Immediately after preparation, 50 mL of an emulsion sample was transferred to a graduated cylinder of 50 mL, sealed, and stored at 25°C for 24 h. The emulsion stability was evaluated by the phase separation observed throughout 24 h and expressed as % of upper phase separation.

The viscosity of the emulsions was measured using a Brookfield RV DV-II+ Pro Extra rheometer (AMETEK Brookfield, Middleboro, MA, USA) equipped with an RV-3 stainless steel spindle (disc with a diameter of 34.69 mm and a height of 1.65 mm). Measurements (100 mL of emulsion) were done at 25°C by a linear increase in shear stress from 0.01 to 1.64 Pa. Viscosities are given as the average viscosity of the linear part of the plot of shear stress *versus* viscosity and are expressed in mPa·s.

Droplet size of emulsions was measured using a Mastersizer 3000 particle size analyzer (Malvern Instruments, Ltd., Worcestershire, UK). Emulsion droplets were suspended in recirculating water (3,000 rpm), reaching an obscuration of 15–18%. Measurements were carried out at 25°C and emulsion droplet size was expressed as Sauter mean diameter D(4,3).

### Characterization of encapsulation process effectiveness

The content of surface oil was determined in the oils with the washing method [Ogrodowska *et al.*, 2017]. The surface oil was extracted three times with hexane for 5 min, filtered, and evaporated to dryness in the R-210 type rotary evaporator (Büchi Labortechnik AG, Flawil, Switzerland) under an N<sub>2</sub> stream.

The total oil content in the powders was determined according to the method described by Ogrodowska *et al.* [2017]. The total oil was extracted with a 2:1 (v/v) chloroform:methanol mixture, then the chloroform phase was isolated and evaporated to dryness in the R-210 type rotary evaporator (Büchi Labortechnik AG) under an N<sub>2</sub> stream.

The process efficiency (PE) of encapsulated oil production was determined as the ratio between the oil covered

by wall material and the total oil content in the powder [Kaushik *et al.*, 2015]. The content of oil covered by the wall material was computed from the difference between total oil content and surface oil content in the powder whose values were determined as described above.

### Morphological characterization of powders

The morphology of the powders was analyzed using scanning electron microscopy (SEM). The Quanta 200 SEM (FEI Company, Hillsboro, OR, USA) was applied to acquire images of the powder samples. Each powder sample was placed on double-sided adhesive carbon tabs, mounted on SEM tubs, and coated with palladium in a sputter coater. Then, the coated sample was analyzed using the SEM operating an accelerating voltage of 30 kV with 800× (spray-dried sample) or 100× (freeze-dried sample) magnifications.

### Fatty acid composition of oils and powders

Fatty acid composition was analyzed in the total oil extracted with a 2:1 (v/v) chloroform:methanol mixture.

Fatty acid esters were prepared according to the procedure described in a work of Zadernowski & Sosulski [1978]. The fatty acids were methylated by heating their solution in a chloroform:methanol:sulfuric acid mixture (100:100:1, v/v/v) at 70°C for 2 h. Fatty acids methyl esters were analyzed using a GC-MS QP2010 PLUS system (Shimadzu, Kyoto, Japan) equipped with a BPX70 capillary column (25 m × 0.22 mm × 0.25 μm; SGE Analytical Science, Victoria, Australia). Helium was used as the carrier gas with a flow rate of 0.9 mL/min. The temperatures were as follows: the injector – 230°C, the column was programmed in the range from 150°C to 250°C, interface of GC-MS – 240°C, the ion source – 240°C, and the electron energy was 70 eV. Individual fatty acids methyl esters were identified on the basis of their retention times and mass spectra, and results were expressed as the percentage (w/w) of each fatty acid in total fatty acids based on their peak areas.

### Content of bioactive compounds in oils and powders

Bioactive compounds were analyzed in the total oil extracted with a 2:1 (v/v) chloroform:methanol mixture.

The content of sterols was determined according to the procedure described in the work of Roszkowska *et al.* [2015]. The oil samples were dissolved in hexane, and a 5α-cholestane solution was added as an internal standard. The oil sample with the 5α-cholestane (internal standard) hexane solution was saponified in 2 M KOH in a methanolic solution at 70°C for 30 min. Sterols were extracted three times with diethyl ether. The collected extracts were evaporated to dryness in the R-210 type rotary evaporator (Büchi Labortechnik AG) under an N<sub>2</sub> stream. Then, the residue was re-dissolved in pyridine and *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% (w/w) trimethylchlorosilane (TMCS), and derivatized at 60°C for 60 min. The mixture was re-dissolved in heptane and analyzed using a GC-MS QP2010 PLUS system (Shimadzu, Kyoto, Japan) equipped with a ZB-5ms capillary column (30 m × 0.25 mm × 0.25 μm; Phenomenex, Torrance, CA, USA). Helium was used as the carrier gas with a flow rate of 0.9 mL/min. The temperatures were as follows: the injector

– 230°C, the column was programmed in the range from 70°C to 310°C, the interface of GC-MS – 240°C, the ion source – 220°C, and the electron energy was 70 eV. The sterols were identified on the basis of their retention times and mass spectra. Quantitative analysis of individual compounds was made based on the internal standard method with the use of 5α-cholestane.

The content of tocopherols was determined according to the procedure described in the work of Czaplicki *et al.* [2011]. The oil samples diluted in hexane were analyzed using an Agilent Technologies 1200 series apparatus with a fluorescence detector (Santa Clara, CA, USA). Individual compounds were separated on a LiChrospher Si60 column (250 mm × 4 mm, 5 μm; Merck, Darmstadt, Germany) with the use of 0.7% (v/v) iso-propanol solution in *n*-hexane as a mobile phase and the flow rate set at 1 mL/min. The fluorescence detector was used with excitation and emission wavelengths of 296 nm and 330 nm, respectively. Quantitative analysis of individual tocopherols was done based on external calibration curves prepared for α-, γ-, and δ-tocopherol. The sum of β- and γ-tocopherols was calculated as γ-tocopherol.

### Statistical analysis

The results obtained were analyzed statistically using Statistica 12.0 PL software (StatSoft, Kraków, Poland). The differences between mean values were determined using the analysis of variance (ANOVA) with Tukey's test at p ≤ 0.05 significance level.

## RESULTS AND DISCUSSION

### Characteristics of encapsulation effectiveness of cold-pressed oils

Table 1 presents the contents of surface oil and total oil, and process efficiency for cold-pressed oils encapsulated using the spray- and freeze-drying methods. The samples obtained as a result of spray-drying, regardless of oil type, had a much lower content of surface oil (2.91–5.30%, w/w) compared to those obtained by freeze-drying (10.25–10.76%, w/w). The total oil content in the powders obtained as a result of spray-drying ranged from 28.97% (w/w) for rapeseed oil to 29.85% (w/w) for safflower seed oil. In turn, the freeze-dried samples had by 1–3% lower content of total oil. The process efficiency for the powders obtained as a result of spray-drying ranged from 82.23% to 89.97% (w/w). A high content of surface oil and a similar content of total oil in the samples encapsulated by freeze-drying in comparison to those obtained by spray-drying resulted in the low efficiency of their encapsulation process (62.66–64.86%, w/w).

The results obtained correspond to the data presented by other authors. Gallardo *et al.* [2013], who spray-dried emulsions composed of flax seed oil and Arabic gum or its mix with maltodextrin and whey protein isolate, determined the surface oil and the total oil contents, as well as the process efficiency in the following ranges: 1.9–2.7% (w/w), 22.1–32.9% (w/w) and 87.8–91.4% (w/w), respectively. In turn, the use of maltodextrin and methyl cellulose for flax seed oil encapsulation brought about an increase in the surface oil content (24.5%, w/w), which resulted in a low PE (25.5%, w/w). The surface

TABLE 1. Surface and total oil contents, and efficiency of the encapsulation process of cold-pressed oils.

Type of cold-pressed oil	Emulsion drying method	Surface oil content (% w/w)	Total oil content (% w/w)	Process efficiency (% w/w)
Rape seed oil	SD	2.91±0.09 <sup>bc</sup>	28.97±0.07 <sup>ab</sup>	89.97±0.30 <sup>aA</sup>
	FD	10.57±0.24 <sup>aA</sup>	28.64±0.10 <sup>ba</sup>	63.08±0.95 <sup>ba</sup>
Flax seed oil	SD	3.68±0.03 <sup>bb</sup>	29.74±0.03 <sup>aA</sup>	87.63±0.25 <sup>aB</sup>
	FD	10.76±0.40 <sup>aA</sup>	28.82±0.54 <sup>ba</sup>	62.66±0.68 <sup>ba</sup>
Safflower seed oil	SD	5.30±0.17 <sup>ba</sup>	29.85±0.58 <sup>aA</sup>	82.23±0.92 <sup>aC</sup>
	FD	10.25±0.47 <sup>aA</sup>	29.18±0.18 <sup>ba</sup>	64.86±1.40 <sup>ba</sup>

Mean values in columns, for each type of oil separately (lowercase letters) and for each emulsion drying method separately (uppercase letters), denoted by the same letter do not differ statistically significantly at  $p > 0.05$  (Tukey test). SD – spray-drying, FD – freeze-drying.

oil content (4.73–5.57%, w/w), similar to the values presented in our study, was also determined by Goyal *et al.* [2015], who used lactose, milk proteins, and sodium caseinate to encapsulate refined flax seed oil by spray-drying. In turn, Chang *et al.* [2016] obtained a broad range of surface oil contents for spray-dried canola oil: from 2.4% (w/w) (the coat containing lentil protein isolate, maltodextrin, and sodium alginate) to 11.5% (w/w) (the coat containing lentil protein isolate, maltodextrin, sodium alginate, and lecithin). Carneiro *et al.* [2013] reported that the encapsulation efficiency was significantly influenced by the type of wall material used. In their experiment, PE determined for flax seed oil encapsulated by spray-drying varied from 62.3% (sample coated with whey protein concentrate and maltodextrin) to 95.7% (w/w) (sample coated with Hi-Cap waxy maize and maltodextrin). On the other hand, Umesha *et al.* [2013] studied the influence of oil and wall material proportion in emulsion on characteristics of garden cress seed oil encapsulation by spray-drying. They found that an increase in the oil/wall material ratio in the range from 0.1 to 0.75 decreased the PE by increasing the surface oil content. Those authors obtained a significantly higher surface oil content (7.8–13.6%, w/w) and a lower PE (47.5–73.3%, w/w) for an oil/wall material ratio of 0.5, that is comparable to the present study. Also Tonon *et al.* [2012] showed a relationship between oil loading and encapsulation efficiency of flax seed oil. They suggested lower oil loading (10–40%, w/w) in the encapsulation by spray-drying than in the present study. In turn, Hasani *et al.* [2015] confirmed the influence of different wall materials on the freeze-drying efficiency. In their study, fish oil was encapsulated with PE ranging from 70.74% for a maltodextrin, sodium caseinate, whey protein concentrate, and modified starch (Hi-Cap 100) mixture to 88.55% (w/w) for a mixture without sodium caseinate. The review of different methods of encapsulation presented by Ruiz Ruiz *et al.* [2017] showed that the key parameter in any of these processes was the selection of wall material. They reported that protein or polysaccharides were primarily used as shell materials in the spray-drying method.

Although most studies indicate the strong impact of wall material composition and oil loading on the process efficiency and the surface oil content, the emulsification method and drying parameters will also have an effect on the encapsulation process [Aksoylu & Günç Ergönül, 2017; Heinzelmann *et al.*, 2000]. Nonetheless, literature data shows that

PE decreased with an increasing surface oil content for both methods of powder production [Calvo *et al.*, 2011; Karaca *et al.*, 2013], as was noted in the present study.

As was pointed out in the present study, the oil samples encapsulated by freeze-drying had a higher surface oil content than the encapsulated by spray-drying. This phenomenon was also noticed by others researchers [Anwar & Kunz, 2011; Karaca *et al.*, 2013; Quispe-Condori *et al.*, 2011]. This is mainly due to the difference in the dehydration mechanism in these methods, which greatly affects the microstructure and integrity of the capsule wall. As a result of encapsulation by freeze-drying, the porous and irregular structure of flakes is observed (Figure 1). In particular, those particles of a larger size are easily destroyed, which can lead to powder structure opening and to oil leakage. Silva *et al.* [2016] explained that ice crystals are formed during the freezing stage preceding encapsulation, which contributes to the rupture of the emulsion droplets, thus releasing oil from the particle to the surface.

The results in Table 1 also show the effect of oil type on the encapsulation efficiency. In the case of encapsulation by spray-drying, the highest process efficiency was obtained for the rape seed oil, whereas the lowest was for the safflower seed oil. In turn, for freeze-drying, the safflower seed oil was slightly more effectively encapsulated than rape and flax seed oils. This property was strongly negatively correlated with the surface oil content. However, the total oil content differed only slightly among the samples (up to 4%) and the differences noted for each drying method separately were not statistically significant ( $p > 0.05$ ). Only sparse literature data address the encapsulation process of different oils under the same conditions. Shivakumar *et al.* [2012] found that safflower seed oil was effectively encapsulated by spray-drying at a higher percentage (up to 70% (w/w) total oil and 15% (w/w) free oil) compared to flax seed oil (up to 65% (w/w) of total oil and 19% (w/w) of free oil). In turn, Calvo *et al.* [2012] studied the influence of olive oil quality on the spray-drying effectiveness and observed no significant differences among monovarietal and blend-type extra-virgin olive oils. Mikulcová *et al.* [2017] studied the effect of oil type (refined and unrefined hemp seed oils) on the distribution of particles in an emulsion and showed that both oils performed similarly under high-intensity emulsification. The differences in surface oil content and process efficiency of the oil pow-



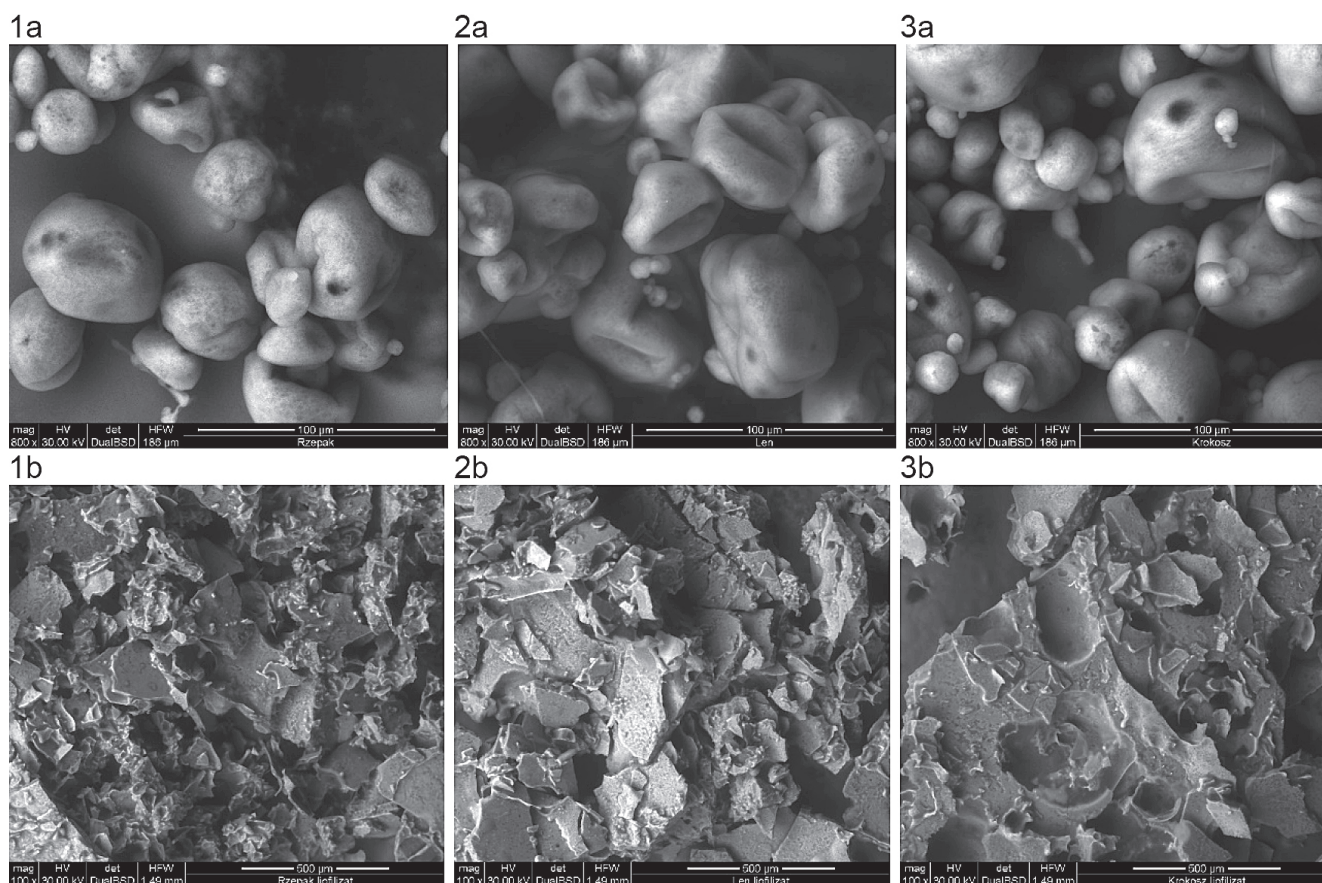


FIGURE 1. Scanning electron microscopy images of powders from cold-pressed rape (1), flax (2), and safflower (3) seed oils obtained by spray-drying (a, mag 800 $\times$ ) and freeze-drying (b, mag 100 $\times$ ) showing differences in powder morphology.

ders obtained by spray-drying were probably due to oil composition. The oils differ significantly in their fatty acid composition and unsaponifiable compounds content (including tocopherols), which could affect the emulsion droplet size and viscosity. Lindenstruth & Müller [2004] reported that the production process parameters (pressure and temperature) had a lesser influence on the emulsion properties than the composition of oil and surfactant phase. In their opinion, if a dispersed phase with small droplet sizes is needed, unsaturated components in the oil phase should be avoided. As shown by Tonon *et al.* [2012], the process efficiency decreased exponentially with droplet size and increased linearly with emulsion viscosity. This phenomenon was also observed in our study. It was noticed that the drying of the emulsion prepared with rape seed oil, which was characterized by a larger droplet size and greater viscosity (1.28 mPa·s), was more effective than the drying of emulsion with flax and safflower seed oils, whose emulsion viscosities were at 1.01 and 1.03 mPa·s, respectively (Table 2). This difference may be related to the fatty acid composition of the oils. Yalcin *et al.* [2012] reported that viscosity of the various vegetable oils depended on their fatty acid composition and increased as chain length and degree of saturation of fatty acids increased. Our results are in agreement with the finding from this study. Rape seed oil had the lowest amount of polyunsaturated fatty acids (PUFA) and the highest amount of monounsaturated fatty acids (MUFA) from all analyzed

oils (Table 3). Badke *et al.* [2019] also found a correlation between encapsulation efficiency and the chemical composition of encapsulated oil. According to their suggestion, when the core material is highly hydrophobic, it is necessary to use surfactants which will increase the affinity of the core with the shell, enhancing the encapsulation efficiency. Barbosa *et al.* [2005] reported that the encapsulation efficiency depended also on the emulsion stability. In their study, the lower amount of non-encapsulated material on particles surface was obtained from a more stable emulsion. However, in the present study, the results obtained for the encapsulation efficiency were not affected by the emulsion stability. All emulsions were stable over the 24-h storage at room temperature, showing no phase separation (Table 2).

TABLE 2. Characteristics of basic parameters of emulsions obtained from cold-pressed oils.

Type of cold-pressed oil	Stability after 24 h (% v/v)	Viscosity (mPa·s, w/w)	Droplet size D[4,3] ( $\mu$ m)
Rape seed oil	0.00 $\pm$ 0.01 <sup>a</sup>	1.28 $\pm$ 0.02 <sup>a</sup>	8.19 $\pm$ 0.34 <sup>a</sup>
Flax seed oil	0.00 $\pm$ 0.00 <sup>a</sup>	1.03 $\pm$ 0.01 <sup>b</sup>	4.58 $\pm$ 0.49 <sup>b</sup>
Safflower seed oil	0.00 $\pm$ 0.02 <sup>a</sup>	1.01 $\pm$ 0.01 <sup>b</sup>	4.37 $\pm$ 0.06 <sup>b</sup>

Mean values in columns, for each type of oil separately, denoted by the same letter do not differ statistically significantly at  $p > 0.05$  (Tukey test).

TABLE 3. Fatty acid composition of natural and powdered cold-pressed oils expressed as area percentage of each fatty acid in total area of all fatty acids and their changes after drying process.

Type of cold-pressed oil	Emulsion drying method	Fatty acids (area %)								
		Myristic C14:0	Palmitic C16:0	Stearic C18:0	Oleic C18:1 <i>n</i> -9	Linoleic C18:2 <i>n</i> -6	Linolenic C18:3 <i>n</i> -3	ΣSFA	ΣMUFA	ΣPUFA
Rape seed oil	-	n.d.	4.23±0.13 <sup>b</sup>	1.26±0.26 <sup>b</sup>	67.23±1.56 <sup>a</sup>	18.61±0.08 <sup>a</sup>	8.67±1.24 <sup>a</sup>	5.49±0.40 <sup>b</sup>	67.23±1.56 <sup>a</sup>	27.28±1.16 <sup>a</sup>
	SD	n.d.	5.09±0.06 <sup>a</sup>	1.92±0.04 <sup>a</sup>	68.28±0.58 <sup>a</sup>	17.31±0.43 <sup>b</sup>	7.41±0.25 <sup>b</sup>	7.01±0.10 <sup>a</sup>	68.28±0.58 <sup>a</sup>	24.71±0.68 <sup>b</sup>
		<i>n.d.*</i>	<i>+20.3</i>	<i>+52.4</i>	<i>+1.6</i>	<i>-7.0</i>	<i>-14.5</i>	<i>+27.7</i>	<i>+1.6</i>	<i>-9.4</i>
	FD	n.d.	4.80±0.18 <sup>a</sup>	1.87±0.01 <sup>a</sup>	67.73±0.25 <sup>a</sup>	17.74±0.44 <sup>b</sup>	7.86±0.01 <sup>ab</sup>	6.67±0.19 <sup>a</sup>	67.73±0.25 <sup>a</sup>	25.61±0.44 <sup>b</sup>
		<i>n.d.</i>	<i>+13.5</i>	<i>+48.4</i>	<i>+0.7</i>	<i>-4.7</i>	<i>-9.3</i>	<i>+21.5</i>	<i>+0.7</i>	<i>-6.1</i>
Flax seed oil	-	n.d.	5.55±0.35 <sup>c</sup>	3.26±0.04 <sup>c</sup>	16.53±0.06 <sup>a</sup>	11.26±0.13 <sup>b</sup>	63.41±0.33 <sup>a</sup>	8.81±0.39 <sup>b</sup>	16.53±0.06 <sup>a</sup>	74.67±0.45 <sup>a</sup>
	SD	n.d.	7.49±0.05 <sup>a</sup>	4.19±0.03 <sup>a</sup>	17.63±0.22 <sup>a</sup>	13.35±0.48 <sup>a</sup>	57.35±0.18 <sup>c</sup>	11.68±0.08 <sup>a</sup>	17.63±0.22 <sup>a</sup>	70.70±0.30 <sup>c</sup>
		<i>n.d.</i>	<i>+34.9</i>	<i>+28.5</i>	<i>+6.6</i>	<i>+18.7</i>	<i>-9.6</i>	<i>+32.3</i>	<i>+6.6</i>	<i>-5.3</i>
	FD	n.d.	6.46±0.28 <sup>b</sup>	3.72±0.37 <sup>b</sup>	17.17±0.16 <sup>a</sup>	11.34±0.01 <sup>b</sup>	61.33±0.82 <sup>b</sup>	10.17±0.65 <sup>a</sup>	17.17±0.16 <sup>a</sup>	72.67±0.81 <sup>b</sup>
		<i>n.d.</i>	<i>+16.4</i>	<i>+14.1</i>	<i>+3.9</i>	<i>+0.7</i>	<i>-3.3</i>	<i>+15.4</i>	<i>+3.9</i>	<i>-2.7</i>
Safflower seed oil	-	0.34±0.05 <sup>ab</sup>	6.80±0.07 <sup>c</sup>	2.50±0.27 <sup>a</sup>	11.99±0.17 <sup>b</sup>	77.69±0.47 <sup>a</sup>	0.69±0.01 <sup>a</sup>	9.64±0.29 <sup>a</sup>	11.99±0.17 <sup>b</sup>	78.38±0.46 <sup>a</sup>
	SD	0.46±0.12 <sup>a</sup>	7.80±0.01 <sup>a</sup>	2.56±0.08 <sup>a</sup>	18.73±0.90 <sup>a</sup>	69.13±1.14 <sup>c</sup>	1.34±0.28 <sup>a</sup>	10.82±0.02 <sup>a</sup>	18.73±0.45 <sup>a</sup>	70.46±0.43 <sup>c</sup>
		<i>+35.3</i>	<i>+14.7</i>	<i>+2.4</i>	<i>+56.2</i>	<i>-11.0</i>	<i>+94.2</i>	<i>+12.2</i>	<i>+56.2</i>	<i>-10.1</i>
	FD	0.29±0.06 <sup>b</sup>	7.11±0.06 <sup>b</sup>	2.44±0.08 <sup>a</sup>	18.34±0.23 <sup>a</sup>	71.03±0.13 <sup>b</sup>	0.81±0.05 <sup>a</sup>	9.83±0.05 <sup>a</sup>	18.34±0.23 <sup>a</sup>	71.84±0.18 <sup>b</sup>
		<i>-14.7</i>	<i>+4.6</i>	<i>-2.4</i>	<i>+53.0</i>	<i>-8.6</i>	<i>+17.4</i>	<i>+2.0</i>	<i>+53.0</i>	<i>-8.3</i>

Mean values in columns, for each type of oil separately, denoted by the same letter do not differ statistically significantly at  $p > 0.05$  (Tukey test). SFA – saturated fatty acids, MUFA – monounsaturated fatty acids, PUFA – polyunsaturated fatty acids, SD – spray-drying, FD – freeze-drying, n.d. – not detected.

\* Lines in italics present percentage changes in concentrations of individual compounds and their groups in the powdered oils relative to the natural cold-pressed oils.

### Fatty acid composition in cold-pressed oils and oil powders

The fatty acid composition of the examined cold-pressed oils is shown in Table 3. The major fatty acid in the natural rape seed oil was monounsaturated oleic acid (C18:1 *n*-9) with the percentage share of 67.23 area %. The contents of C18:2 *n*-6 and C18:3 *n*-3 acids in this oil were 18.61 and 8.67 area %, respectively. The content of saturated fatty acids (SFA) was low, and accounted for 5.49 area %. The results obtained for natural cold-pressed oil correspond to the results obtained by other researchers [Lewinska *et al.*, 2015; Roszkowska *et al.*, 2015]. Flax and safflower seed oils had a high level of polyunsaturated fatty acids, which accounted for 78 area % of all fatty acids. In turn, C18:3 *n*-3 acid prevailed in the flax seed oil, and its share was 63.41 area %. The second polyunsaturated fatty acid, C18:2 *n*-6, in this oil accounted for 11.26 area %. In turn, saturated fatty acids (SFA) and MUFA reached, on average, 10 area % and 17 area % in this oil. A similar composition of fatty acids in cold-pressed flax seed oil was reported in other studies [Khatab & Zeitoun, 2013; Tańska *et al.*, 2016]. C18:2 *n*-6 was the major acid in safflower seed oils (77.69 area %), while the share of C18:3 *n*-3 did not exceed 1.5 area %. A similar content of linoleic acid (76.58%) in safflower seed oil was reported by Dorni *et al.* [2018].

In rape seed oil powders obtained both as a result of encapsulation by spray- and freeze-drying, a reduction was

observed (by 4.7–14.5%) in the percentage share of polyunsaturated fatty acids: linoleic (C18:2 *n*-6) and  $\alpha$ -linolenic (C18:3 *n*-3). However, considerable changes were observed in saturated fatty acids: palmitic (C16:0) and stearic (C18:0), whose shares increased to 13.5–20.3% and 48.4–52.4%, respectively. Changes in percentage shares of PUFA only slightly affected the ratio of *n*-6 to *n*-3 fatty acids. In the natural rape seed oil, this ratio was at 2.01:1, while in the encapsulated rape seed oils it reached 2.03:1. In the encapsulated flax seed oil, C18:3 *n*-3 acid share was reduced by 9.6% (for spray-drying method) and by 3.3% (for freeze-drying method). The content of C18:2 *n*-6 was the highest in the oil encapsulated by spray-drying. Saturated fatty acids accounted for, on average, 10% and 17% in flax seed oils. The contents of SFA and MUFA increased after the encapsulation process, but statistically significant changes ( $p \leq 0.05$ ) were found only for SFA. Quispe-Condori *et al.* [2011] also encapsulated flax seed oil, using the spray- and freeze-drying methods. Although they observed no change in the  $\alpha$ -linolenic acid content after spray-drying process, the content of this acid decreased during freeze-drying. During encapsulation of flax seed oil by spray-drying, Barroso *et al.* [2014] also observed an increase in the content of SFAs and a decrease in linolenic acid content. The drying of an emulsion with safflower seed oil resulted in greater losses of PUFAs in comparison to rape and flax seed oils; these losses reached 10.1% with the spray-

-drying and 8.3% with the freeze-drying method. Additionally, noticeably greater changes were observed in the content of MUFAs in comparison to other oils. The share of those acids increased as a result of drying process by more than 50%, while in rape and flax seed oils their increase did not exceed 7%. The changes in the percentage share of fatty acids probably resulted from the drying temperature applied. However, it is not confirmed by the research conducted by Kwon *et al.* [2004] who did not observe any changes in the fatty acid composition of oils obtained as a result of safflower seed roasting at 140–180°C.

When comparing the results for encapsulated oils with the results for crude oils, a decrease in the percentage of the PUFAs was observed. The highest degradation of PUFAs was observed in spray-dried safflower seed oil powder (10.11%), while the lowest degradation was in freeze-dried flax seed oil powder (2.68%). Hue & Nyam [2018], who studied the encapsulation of kenaf seed oil by freeze-drying, noted a lower decrease of the PUFA share, which was 2.29%. Calvo *et al.* [2010] also observed only small changes in the fatty acid composition of extra-virgin olive oil during freeze-drying; including a decrease in the PUFA share (up to 4.3%) and an increase in the MUFA share (up to 1.3%). In contrast, the spray-drying of an emulsion with extra-virgin olive oils performed by Calvo *et al.* [2012] significantly modified the fatty acid composition. In that study, the PUFA share was reduced by 5.3–69.6% depending on the type of olive oil. Additionally, generally greater PUFA losses were found for oil samples along with higher percentage shares. This contradicts the results of our study, in which twofold greater changes were recorded for the encapsulated rape seed oils than for the encapsulated flax seed oils that were clearly richer in PUFAs. Wang *et al.* [2018] also reported no significant effect of the spray-drying method on the composition of fatty acids in peony seed oil characterized by a high PUFA share (39.24% (w/w) of C18:3 *n*-3 and 26.96% (w/w) of C18:3 *n*-6). Rubilar *et al.* [2012] also showed a reduction in MUFAs in flax seed oil as a result of the spray-drying process. In their study, the content of linolenic acid decreased slightly during the process, but the contents of oleic and linoleic acids decreased by almost 50%. In the work of Ogródowska *et al.* [2017], regardless of the drying method and processes temperature used, the PUFA losses in pumpkin seed oil ranged from 6.00 to 7.15%. The differences in the PUFA losses observed between the studied oils are likely to result from not only the content of prooxidants and antioxidants but also the droplet size of emulsions prepared with their use. This is consistent with our results where the emulsion containing safflower seed oil had particles with the smallest diameter D[4,3] (Table 2), and after drying the greatest degradation of PUFAs was observed.

Hogan *et al.* [2003] showed an antioxidative effect of 100 mg/kg  $\alpha$ -tocopherol addition on fish oil subjected to the spray-drying, while 500 mg/kg of  $\alpha$ -tocopherol contributed to a significant increase in the peroxide and anisidine values in encapsulated oil compared to the control sample. In turn, Coupland *et al.* [1996] demonstrated that the rate of lipid oxidation increased as the mean diameter of the droplet decreased because the droplet surface was increasing,

which increased the contact between the interface, oxygen and radicals in the solution and thus enabled the unsaturated lipid located on the interface to oxidize easily. Furthermore, they also suggested that the ratio of oxidizable-to-nonoxidizable compounds in emulsion droplets affected the rate at which the lipid oxidation proceeds.

A greater influence of the encapsulation by spray-drying on fatty acid composition compared to freeze-drying observed for the studied oils could be explained by the oil oxidation rate during the processes. The spray-drying requires using high temperatures, which can affect the labile components of oils. Considering even such factors as the cooling effect of water evaporation from the dried emulsion or the short time of its residence in the drying chamber, hydroperoxide formation is high as a result of accelerated oxidation [Aghbashlo *et al.*, 2013]. Anwar & Kunz [2011] also confirmed that even though spray-drying only needed a few seconds to produce a desirable size of granules, it had a high chance of lipid degradation by oxidation due to the high drying temperature in the process. Timilsena *et al.* [2017] reported that complex coacervation-based microencapsulation better protected PUFAs-rich oils than a simple spray drying. They explained that the higher encapsulation efficiency in the complex coacervation-based microencapsulation resulted from the better surface-active nature of the complex coacervates.

#### Content of sterols in cold-pressed oils and oil powders

The sterol content in the examined cold-pressed oils is presented in Table 4. All examined oils contained  $\Delta$ 5-avenasterol, campesterol,  $\beta$ -sitosterol, and  $\Delta$ 7-avenasterol. Additionally, brassicasterol (37.32 mg/100 g of oil) was present in rape seed oil and  $\Delta$ 7-sitosterol in flax and safflower seed oils (115.34 and 0.79 mg/100 g of oil, respectively).

The total sterols in rape seed oil amounted to 505.46 mg/100 g of oil. A higher content of sterols, ranging from 596.4 to 772.5 mg/100 g of oil, was presented in work by Krajičić *et al.* [2013], who examined rape seed oil obtained from seeds cultivated in Croatia. In turn, Roszkowska *et al.* [2015] found 338.6–411.8 mg/100 g sterols in commercial cold-pressed rape seed oils available in Poland. Both the spray- and the freeze-drying processes resulted in the similar degradation of sterols, by 61.34% and 61.93%, respectively (Table 4).

Flax seed oil had the highest content of total sterols (477.82 mg/100 g of oil) compared to the other oils tested. A similar content of total sterols in flax seed oil was determined by Zhang *et al.* [2018] and Tańska *et al.* [2016]. The results obtained (Table 4) demonstrated a higher degradation of total sterols in freeze-dried flax seed oil (by 65.82%) than in the spray-dried oil (by 59.91%).

The lowest total sterol level (303.97 mg/100 g of oil) in comparison to the other oils under analysis was determined in safflower seed oil. This result agrees with the findings reported by Nogala-Kalucka *et al.* [2010]. The process of safflower seed oil powder production contributed to significant sterol losses, amounting to 59.01% (spray-drying method) and 60.85% (freeze-drying method).

$\beta$ -Sitosterol was the major sterol in the examined cold-pressed oils, which has been confirmed in other studies



TABLE 4. Content of sterols in natural and powdered cold-pressed oils and their changes after drying process.

Type of cold-pressed oil	Emulsion drying method	Sterols (mg/100 g of oil)							Total (mg/100 g of oil)
		Brassicasterol	$\Delta 5$ -Avenasterol	Campesterol	$\beta$ -Sitosterol	$\Delta 7$ -Avenasterol	$\Delta 7$ -Sitosterol	Others	
Rape seed oil	-	37.32±4.60 <sup>a</sup>	18.98±2.30 <sup>a</sup>	177.88±4.92 <sup>a</sup>	237.02±4.29 <sup>a</sup>	26.65±2.33 <sup>a</sup>	n.d.	7.60±1.57 <sup>a</sup>	505.46±8.26 <sup>a</sup>
	SD	18.20±0.54 <sup>b</sup>	6.06±1.10 <sup>b</sup>	71.47±3.40 <sup>b</sup>	89.87±3.04 <sup>b</sup>	5.91±0.41 <sup>c</sup>	n.d.	2.68±0.47 <sup>c</sup>	195.43±7.49 <sup>b</sup>
		<i>-51.23*</i>	<i>-68.04</i>	<i>-59.82</i>	<i>-62.08</i>	<i>-77.80</i>	-	<i>-64.66</i>	<i>-61.34</i>
	FD	15.49±0.80 <sup>c</sup>	7.02±0.31 <sup>b</sup>	67.40±3.06 <sup>c</sup>	88.92±3.70 <sup>b</sup>	10.50±0.54 <sup>b</sup>	n.d.	3.08±0.27 <sup>b</sup>	192.41±2.75 <sup>b</sup>
		<i>-58.50</i>	<i>-63.02</i>	<i>-62.11</i>	<i>-62.48</i>	<i>-60.58</i>	-	<i>-59.49</i>	<i>-61.93</i>
Flax seed oil	-	n.d.	27.48±0.56 <sup>a</sup>	98.91±2.09 <sup>a</sup>	159.41±1.44 <sup>a</sup>	64.23±1.78 <sup>a</sup>	115.34±0.35 <sup>a</sup>	12.44±0.61 <sup>a</sup>	477.82±4.14 <sup>a</sup>
	SD	n.d.	2.46±0.09 <sup>b</sup>	37.59±2.56 <sup>b</sup>	80.54±0.10 <sup>b</sup>	14.48±0.51 <sup>b</sup>	44.22±2.15 <sup>c</sup>	12.24±0.85 <sup>a</sup>	191.53±3.40 <sup>b</sup>
		-	<i>-91.05</i>	<i>-62.00</i>	<i>-49.48</i>	<i>-77.45</i>	<i>-61.66</i>	<i>-1.68</i>	<i>-59.91</i>
	FD	n.d.	2.81±0.41 <sup>b</sup>	34.71±0.43 <sup>c</sup>	71.97±4.56 <sup>c</sup>	1.18±0.08 <sup>c</sup>	49.05±4.17 <sup>b</sup>	3.60±0.40 <sup>b</sup>	163.33±2.68 <sup>c</sup>
		-	<i>-89.78</i>	<i>-64.91</i>	<i>-54.85</i>	<i>-98.16</i>	<i>-57.47</i>	<i>-71.11</i>	<i>-65.82</i>
Safflower seed oil	-	n.d.	10.35±0.59 <sup>a</sup>	98.47±2.79 <sup>a</sup>	130.63±4.10 <sup>a</sup>	15.54±0.64 <sup>a</sup>	0.79±0.01 <sup>a</sup>	3.73±0.05 <sup>a</sup>	303.97±5.60 <sup>a</sup>
	SD	-	1.07±0.13 <sup>b</sup>	25.01±0.16 <sup>b</sup>	74.60±1.20 <sup>b</sup>	9.01±0.04 <sup>b</sup>	0.22±0.02 <sup>b</sup>	3.12±0.02 <sup>b</sup>	122.86±5.99 <sup>b</sup>
		-	<i>-89.59</i>	<i>-74.60</i>	<i>-42.89</i>	<i>-41.98</i>	<i>-72.98</i>	<i>-16.55</i>	<i>-59.01</i>
	FD	n.d.	1.23±0.16 <sup>b</sup>	24.71±1.509 <sup>b</sup>	71.35±0.83 <sup>c</sup>	6.96±1.05 <sup>c</sup>	0.20±0.01 <sup>b</sup>	3.50±0.28 <sup>a</sup>	112.62±2.87 <sup>b</sup>
		-	<i>-88.13</i>	<i>-74.90</i>	<i>-45.38</i>	<i>-55.16</i>	<i>-74.42</i>	<i>-6.23</i>	<i>-60.85</i>

Mean values in columns, for each type of oil separately, denoted by the same letter do not differ statistically significantly at  $p > 0.05$  (Tukey test). SD – spray-drying, FD – freeze-drying, n.d. – not detected.

\* Lines in italics present percentage changes in contents of individual compounds and their total content in the powdered oils relative to the natural cold-pressed oils.

[Czaplicki *et al.*, 2016; Nogala-Kalucka *et al.*, 2010; Rudzińska *et al.*, 2009]. The highest content of  $\beta$ -sitosterol was determined in rape seed oil (237.02 mg/100 g of oil), and the lowest one in oil obtained from safflower seed oil (130.63 mg/100 g of oil). Encapsulated oil production resulted in the significant degradation of  $\beta$ -sitosterol, although the range of these changes did not depend on the method applied, but on oil type. The greatest losses of this component (about 63%) were found for rape seed oil, while the smallest ones in the safflower seed oil (on average 44.5%). The flax and safflower seed oils were also characterized by the highest degradation of  $\Delta 5$ -avenasterol (by 88.13–91.05%). Additionally, the greatest degradation of brassicasterol was observed in the safflower seed oil, which was 88.94% (spray-dried sample) and 89.51% (freeze-dried sample). Hue & Nyam [2018] reported that the unsaturated bond in chemical structures was the major difference among various sterols and the main reason for the degradation of the sterols.  $\beta$ -Sitosterol has one double bond [Hue & Nyam, 2018], while brassicasterol and avenasterol have two double bonds in their molecules; and this may affect the rate of their degradation [Gawrysiak-Witulska *et al.*, 2015]. Our results generally confirmed this phenomenon, with the exception of brassicasterol in the rape seed oils and  $\Delta 7$ -avenasterol in the spray-dried safflower seed oil.

The available literature does not include many studies describing the effect of the powder production process on degradation of biologically active substances, including sterols. The studies on those compounds have been conducted

mainly in the context of their changes under the effect of applied technological operations or, generally, of heating. Sterols are among the compounds which are subject to degradation as a result of heat factors, which results in a variety of oxidative derivatives (oxysterols) formed [Rudzińska *et al.*, 2009]. Hernández Sánchez *et al.* [2016] found that during spray-drying, emulsion drops were in contact with hot air. During the process, at the beginning water is removed, drying liquid drops remain at the air wet bulb temperature (*e.g.* about 40°C) and their temperature may then start increasing at the end of drying when the air current has reached a temperature close to its outlet temperature (*e.g.* 94–110°C). Dry particles may therefore be exposed, for a very short time, to high temperatures, which can create favorable conditions for the formation of oxidation products. On the other hand, Soupas *et al.* [2006] reported that more sterol oxides were generated during storage of milk powder than during spray-drying.

Considering only the total content of sterols in the analyzed samples, it should be noted that the process of encapsulated oil production by freeze-drying contributed to their greater degradation. An opposite relationship was found in the experiment of Kim *et al.* [2014] who determined the content of bioactive compounds in rice bran subjected to different heat treatments. They observed that the sterol content in a freeze-dried and then dry-heated sample was slightly lower than in the control sample. Furthermore, the sterol content linearly decreased as the heating temperature or time increased. Kwon *et al.* [2004], who studied the effect of heat



TABLE 5. Content of tocopherols in natural and powdered cold-pressed oils and their changes after drying process.

Type of cold-pressed oil	Emulsion drying method	Tocopherols (mg/100 g of oil)			Total (mg/100 g of oil)
		$\alpha$	$\beta + \gamma$	$\delta$	
Rape seed oil	-	31.60±0.18 <sup>a</sup>	33.56±0.95 <sup>a</sup>	0.07±0.01 <sup>a</sup>	65.16±1.13 <sup>a</sup>
	SD	26.29±1.73 <sup>b</sup>	28.67±2.23 <sup>b</sup>	n.d.	54.95±3.97 <sup>b</sup>
		<i>-16.8*</i>	<i>-14.6</i>	<i>-100.0</i>	<i>-15.7</i>
	FD	21.80±2.22 <sup>c</sup>	27.71±2.64 <sup>b</sup>	0.05±0.01 <sup>a</sup>	49.51±0.42 <sup>c</sup>
		<i>-31.0</i>	<i>-17.4</i>	<i>-26.5</i>	<i>-24.0</i>
Flax seed oil	-	5.43±0.50 <sup>a</sup>	41.83±1.06 <sup>a</sup>	0.09±0.01 <sup>a</sup>	47.26±0.57 <sup>a</sup>
	SD	5.40±0.51 <sup>a</sup>	33.91±1.29 <sup>b</sup>	n.d.	39.31±0.78 <sup>b</sup>
		<i>-0.6</i>	<i>-18.9</i>	<i>-100.0</i>	<i>-16.8</i>
	FD	3.34±0.34 <sup>b</sup>	41.73±0.02 <sup>a</sup>	0.04±0.01 <sup>a</sup>	45.07±0.36 <sup>a</sup>
		<i>-38.5</i>	<i>-0.2</i>	<i>-49.4</i>	<i>-4.6</i>
Safflower seed oil	-	54.58±2.99 <sup>a</sup>	5.52±0.08 <sup>a</sup>	n.d.	60.11±3.06 <sup>a</sup>
	SD	24.71±4.02 <sup>b</sup>	5.01±0.10 <sup>a</sup>	n.d.	29.72±4.12 <sup>b</sup>
		<i>-54.7</i>	<i>-9.3</i>	<i>n.d.</i>	<i>-50.5</i>
	FD	54.28±0.72 <sup>a</sup>	5.03±0.02 <sup>a</sup>	n.d.	59.31±0.74 <sup>a</sup>
		<i>-0.9</i>	<i>-8.9</i>	<i>n.d.</i>	<i>-1.3</i>

Mean values in columns, for each type of oil separately, denoted by the same letter do not differ statistically significantly at  $p > 0.05$  (Tukey test). SD – spray-drying, FD – freeze-drying, n.d. – not detected. \* Lines in italics present percentage changes in contents of individual compounds and their total content in the powdered oils relative to the natural cold-pressed oils.

pre-treatment on the functional constituents of rice germ, reported that free sterols were degraded more easily when a high temperature or vacuum was applied because of their low boiling points. However, Hue & Nyam [2018] observed that loss of total sterols in kenaf seed oil was 59.76% during storage, while 32.86% during freeze-drying.

#### Content of tocopherols in cold-pressed oils and powders obtained from them

The tocopherol content in the examined cold-pressed oils is presented in Table 5. Tocopherols are the main antioxidants of rape seed oil. The analyzed rape seed oil samples contained tocopherols at the levels of 49.51–65.16 mg/100 g of oil. The oils had high amounts of  $\alpha$ - and  $\beta + \gamma$ -tocopherols, whereas  $\delta$ -tocopherol content was low. In natural rape seed oil,  $\alpha$ -tocopherol was present at the level of 31.60 mg/100 g of oil,  $\beta + \gamma$ -tocopherol at 33.56 mg/100 g of oil, and  $\delta$ -tocopherol at 0.07 mg/100 g of oil. These results concur with earlier reported findings, but most of the authors have reported that rape seed oil had high contents of  $\alpha$ - and  $\gamma$ -tocopherols, not  $\alpha$ - and  $\beta + \gamma$ -tocopherols [Azadmard-Damirchi *et al.*, 2010; Ghazani *et al.*, 2014]. Rape seed oil powder production resulted in the greatest changes in the  $\delta$ -tocopherol content, which was subject to complete degradation as a result of spray-drying. On the other hand, after encapsulation by freeze-drying, its content was reduced by 26.5%. However, freeze-drying proved to be a less favorable method for rape seed oil powder production in the case of  $\alpha$ -tocopherol. Its content in the freeze-dried oil was lower by 31.0%, while in the spray-dried oil its

decreased by 16.8%. However, in both encapsulated samples, the content of  $\beta + \gamma$ -tocopherol was at a similar level (approx. 28 mg/100 g of oil).

The content of total tocopherols in the natural flax seed oil was determined at 47.26 mg/100 g of oil, with prevailing  $\beta + \gamma$ -tocopherol, accounting for 88.5%. This oil contained also  $\alpha$ -tocopherol (5.43 mg/100 g of oil) and  $\delta$ -tocopherol (0.09 mg/100 g of oil). Similar contents of tocopherols were presented by Tańska *et al.* [2016], who characterized six samples of cold-pressed flax seed oil. A higher content of total tocopherols in flax seed oil, reaching 79.4 mg/100 of oil, was obtained by Bozan & Temelli [2008].

As a result of flax seed oil spray-drying,  $\beta + \gamma$ -tocopherol decreased by 18.93%. However, the freeze-drying process did not affect the degradation of those flax seed oil homologues. An opposite dependency was found for  $\alpha$ -tocopherol, the degradation of which (by 38.5%) occurred only after freeze-drying.

The content of tocopherols in natural safflower seed oil was comparable to that found in the rape seed oil and amounted to 60.11 mg/100 g of oil. However, the tocopherol profile of this oil was different, with  $\alpha$ -tocopherol found a major homologue, with the content reaching 54.58 mg/100 g of oil, *i.e. ca.* 90% of total tocopherols occurring in this oil. Safflower seed oil also contained  $\beta$ - and  $\gamma$ -tocopherols, the sum of which was 5.52 mg/100 g of oil. A similar tocopherol content was reported by Ben Moumen *et al.* [2015] who characterized the lipid fractions of safflower seeds cultivated in Morocco, Spain and India. As a result of spray-drying, the content

of  $\alpha$ - and  $\beta$ + $\gamma$ -tocopherols in safflower seed oil was reduced by 54.7% and 9.3%, respectively (Table 5). Freeze-drying affected the content of  $\beta$ + $\gamma$ -tocopherol to a degree comparable to spray-drying, but it did not affect the content of  $\alpha$ -tocopherol.

The encapsulation of flax and safflower seed oils by spray-drying had a greater impact on the degradation of total tocopherol content compared to the freeze-drying. Furthermore, the highest decrease in the sum of tocopherols was observed in encapsulated safflower seed oil (50.5%). However, an opposite relationship was found in the case of rape seed oil. Gawrysiak-Witulska *et al.* [2015] studied the effect of drying temperature on changes in individual homologues of tocopherols in the oil from yellow-seeded rape and found that during drying at 40°C and 60°C, losses of  $\alpha$ -,  $\beta$ - and  $\gamma$ -tocopherols did not exceed 2%, while  $\delta$ -tocopherol losses reached 6%. Increasing air temperature to 100°C and 120°C caused similar losses (23%) in the main tocopherol homologues in rape seed ( $\alpha$ - and  $\gamma$ -tocopherols). Also Hernández Sánchez *et al.* [2016] found only 10% degradation of  $\alpha$ -tocopherol added to the oil before spray-drying process. A slight effect of the freeze-drying process on the tocopherol content in encapsulated oils was confirmed for walnut and kenaf seed oils [Calvo *et al.*, 2011; Hue & Nyam, 2018]. The powders they obtained had similar contents of tocopherols compared to the raw oils. In contrast, Calvo *et al.* [2010] observed that the content of tocopherols slightly increased in encapsulated olive oil produced by freeze-drying. A similar trend was observed for a freeze-dried rice sample in an experiment performed by Kim *et al.* [2014]. The authors suggested that a significant amount of tocopherols was lost, being bound to proteins or phospholipids, and that applying thermal energy could break the linkages.

## CONCLUSIONS

Based on the research conducted, it was shown that the encapsulation efficiency and surface oil content depend not only on the encapsulation method but also on oil composition. The composition of oil, especially fatty acid composition, has a significant influence on the emulsion properties. In case of the spray-drying method, the use of rape seed oil allowed obtaining a higher encapsulation efficiency and lower surface oil content than the use of flax and safflower seed oils. For PUFAs, only a slight effect of the applied encapsulation method on their degradation was observed and it depended on oil type. In turn, sterol degradation did not depend on the drying method applied. In total, the losses of those bioactive substances in all types of oils were high and reached 60–66%. In most cases, the native tocopherols of the studied oils were degraded to a significantly lesser extent than sterols (up to 24%). The only exception was safflower seed oil encapsulated by spray-drying, which contained 50% less total tocopherols.

The results of our experiment show that the encapsulated rape, flax, and safflower seed oils had lower contents of bioactive compounds compared to the crude oils, regardless of the encapsulation method (spray- or freeze-drying). However, the degradation rate of the studied components is comparable to losses occurring in crude plant oils during culinary processes. Our results suggest that detailed analy-

sis of oil composition is necessary before the encapsulation process to enable the appropriate choice of the components of wall materials and drying parameters.

## CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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