Research Article

Chemical and Physical Properties of Meadowfoam Seed Oil and Extra Virgin Olive Oil: Focus on Vibrational Spectroscopy

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In food industry, vegetable oils are commonly used as functional ingredients. Cold pressed oils containing fatty acids show a variety of chemical properties, which are mainly dependent on the saturation of fatty acids. In this study, we have analyzed meadowfoam seed oil (MSO), obtained from seeds of Limnanthes alba, and extra virgin olive oil (EVO). Firstly, the fatty acids composition, denoted as Cox value, was determined for the oils that are considered as the most stable. The Cox value for MSO reached 0.032, while that for EVO was 1.780. We have also determined the content of fatty acids in both of the oils using gas chromatography, while the use of mid-infrared (MIR) and near-infrared (NIR) spectroscopy allowed us to assign bands corresponding to the vibrations present in the tested functional groups. Significant differences in the shape and intensity of some bands were observed due to different content of unsaturated fatty acids. Vibrational spectroscopy methods confirmed the presence of long chain fatty acids in MSO.

1. Introduction

The oxidation of vegetable oils starts during their isolation from natural raw materials. The oxidation process reduces the stability of end-products containing vegetable oils significantly. Oils known to have a high Oxidative Stability Index (OSI) number often have longer shelf lives, making them desirable for applications in food, pharmaceutical and cosmetic industries [1–3]. Generally, extra virgin olive oil (EVO) is recognized as the most stable oil and can be obtained by cold pressing olives from the olive tree (Olea europaea L.). Olive oil represents a greatly interesting product from the nutraceutical perspective. Its composition is primarily based on a diversity of triglycerides, also possessing diacyl- and monoacylglycerols, as well as free fatty acids and an extra component of nonlipid substances. According to the type of olive oil obtained (extra virgin, virgin, refined, etc.), the amount of free fatty acids is different, providing the possibility of being a main property to distinguish the grade of the oil [4]. In the composition of
olive oil, ingredients may be classified as derivatives of fatty acids, waxes and sterols, polyphenols, hydrocarbons, tocopherols, chlorophylls, and other compounds containing polarity. The oil is subject to several steps of refinement to remove phenol-derived compounds and phospholipids, but some fluctuations occur in other compounds. Olive oil is mainly composed of palmitic acid (7.5–20 wt.%), stearic acid (0.5–5 wt.%), palmitoleic acid (0.3–3.5 wt.%), oleic acid (55–85 wt.%), linoleic acid (7.5–20 wt.%), and linolenic acid (up to 1.5 wt.%). The oil also contains very small quantities of myristic, heptadecanoic, and eicosanoic acids. cis-Vaccenic and eicosenoic acids may also occur. The composition in fatty acids is dependent on the climate conditions, the variety of olive harvested, the latitude, and the stage of development of the fruit. Interestingly, the Italian, Greek, and Spanish olive oils are characterized by a lower profile of both linoleic and palmitic acids with a high amount of oleic acid. Contrarily, Tunisian olive oil is characterized by a high profile of linoleic and palmitic acids with a reduced amount of oleic acid [5]. Interestingly, unfinished biosynthesis of triglycerides or reactions of hydrolysis can lead to the presence of mono- and diacylglycerols in olive oil. Age and storage environment also impact on the distribution of these molecules. Fresh olive oil has a predominance of 1,2-diacylglycerols, which are exposed to isomerization along the time to 1,3-diacylglycerols. This feature helps to infer the age of a given oil as well as tracing a history of the storage conditions [6]. Moreover, tocopherols contained in EVO are a crucial group of lipophilic vitamins with antioxidant properties able to quench reactive species and are present in a nonesterified form. An interesting finding is that α-tocopherol has its antioxidant capacity increased in diminished concentrations (100 mg/kg) more than in higher concentrations (500 mg/kg to 1 000 mg/kg). Although the overall quantity of tocopherol in a sample of olive oil is subjected to some large disparities, between 5 mg/kg to 300 mg/kg, typical values in trustable sources of olive oil range from 100 mg/kg to 300 mg/kg. The quantity of tocopherol is reduced if the oil is exposed to refinement processes [7]. The most representative hydrocarbon present in Olea europaea is squalene that has anticancer properties, and it is considered as an effective antioxidant. This steroid precursor may be quantified in a range of 0.7 g/kg to 12 g/kg and is responsible for more than half of the portion of unsaponifiable matter in EVO [8, 9]. The oil contains pigments, such as carotenoids and chlorophylls. The former act as scavengers of reactive species avoiding oil degradation by oxidation and may vary in a concentration between 1 mg/kg and 20 mg/kg [10], while the latter provide green color to the oil. The concentration of chlorophylls in EVO usually ranges from 10 mg/kg to 30 mg/kg. The natural olive oil has also several other ingredients capable of quenching/antioxidizing the reactive species, and therefore the effect of singlet oxygen is not noticeable [11]. Additionally, four different types of sterols may be identified in EVO [12, 13], namely, desmethylsterols, 4α-methylsterols, 4,4-dimethylsterols (triterpene alcohols), and triterpene dialcohols. Fatty alcohols are also of high importance in the classification of olive oils due to the several subtypes. Thereupon, the overall content of aliphatic alcohol cannot surpass the limit of 350 mg/kg of olive oil [14, 15]. The composition of olive oil in waxes cannot surpass 350 mg/kg of olive oil [16]. Phytol (in a range of concentrations between 120 mg/kg and 180 mg/kg) and geranylgeraniol are the two acyclic diterpenoids isolated in alcoholic fractions of olive oil [17].

Depending on the desired effect of olive oil, owing to the constitution in polyphenols, the extraction process can be adapted. When dealing with olive oils containing a high fraction of these compounds, the extraction process adopted shall be the stone mill to prevent bitter taste and strong flavor of the final product. The system consisting in a hammer shall be preferred for final olive oils with a low content in polyphenols. Among the diverse phenomena that are prone to affect the content in polyphenol compounds are the surface area of the pieces used to crush the olives and the released enzymes that hydrolyze pectin. According to multiple studies carried out along the past years, these hold plenty of benefits to human well-being [18]. Polyphenol compounds are not the most abundant elements in olive oil but account for its good flavor and its pleasant effect [19]. Garcia et al. classified phenolic compounds with biological activity typical of olive oil into four groups: simple phenols, secoiridoid derivatives, lignans, and flavones [20]. Examples of specific compounds usually present in olive oil are oleuropein, tyrosol, hydroxytyrosol, and ligstroside; in addition, characteristic components are also caffeic acid, vanillic acid, and syringic acid [21, 22]. The recent review of Garcia-Martinez et al. is worth mentioning [23]; they have summarized the benefits of olive oil phenolic compounds in disease prevention. The content of virgin olive oil in phospholipids ranges from 40 mg/kg to 135 mg/kg when recently extracted. Crude olive residue oil has, however, a higher ratio of this class of molecules which are usually linked with proteins [24].

Meadowfoam (Limnanthes alba) is a herbaceous plant typical of northern California, Oregon, Vancouver Island, and British Columbia. The base of Limnanthes alba is branched with a system of thin fibrous roots, which allows simple transplantation during any phase of its development. Its physiology permits an adaptation to almost every type of soil although soils with less water-retaining capacity are less prone to withstand the growing of such species [25, 26]. Meadowfoam seed oil (MSO), obtained from the seeds of Limnanthes alba, is not as well-known as olive oil, although it is characterized by a high content of long chain fatty acids (C20-22). These fatty acids help the MSO to resist oxidation, making it a stable oil [27, 28]. Moreover, it consists of more than 98 wt.% of fatty acids, mainly monounsaturated fatty acids, which include gondola acid (C20: 1, ω-9) and erucic acid (C22:1, ω-9), but also vitamins A and E, both having antioxidant properties [29, 30]. The seeds of MSO are composed, in average, of 20 wt.% to 30 wt.% of oil, which is a combination of three fatty acid molecules. The stability of MSO is described as 20-fold higher than soybean oil, a fact inherent to the capacity of an oil to support oxidative processes. Once the seed is cracked and the oil removed through a special process of extraction, using a solvent, the remnants are available to be used as a foundation in the nourishment of cattle but with a daily limitation of consumption up to 25 wt.% of the overall food.
intake without negative outcomes to the weight gain in these animals. If it is vital for nourishing other animals, this food supplement must be cooked or subjected to a reduction in its proportion in the food, given the presence of glucosinolate residues, which are poisonous. The world market of oilseeds currently holds two large competitors—meadowfoam oil and rapeseed oil. To thrive in such markets, it is required from the newest competitor, meadowfoam oil, to present two main features: a competitive price and reliable suppliers [31,32]. The uses for MSO are wide since it can be transformed into a solid wax composed of a polymeric web of sulfur residues that has plenty of applications in rubber industry or may even undergo chemical modifications to be converted into ester of liquid wax, a replacement for oils of jojoba and sperm whale. According to Athar and Nasir, the Oxidative Stability Index (OSI), being a measure of the relative resistance of an oil to oxidation, amount to 50.6 h for EVO and 67.3 h for MSO [33]. In food and pharmaceutical industries, chemical methods are used for quality analysis on a regular basis. These analyses are usually costly and time-consuming. They often employ toxic solvents and reagents. Therefore, there is a growing demand for replacing these traditionally used analytical methods with instrumental methods, especially spectroscopic techniques. The infrared spectroscopy includes a part of the spectrum of electromagnetic radiation in the range between visible and microwave radiation. It is a method based on the absorption of infrared radiation by oscillating molecules. The infrared region is divided into three ranges. Near infrared (NIR) covers a range of 12500–4000 cm\(^{-1}\), in which mainly bands corresponding to overtones and combination vibrations occur. The medium infrared (MIR) is a range of 4000–400 cm\(^{-1}\), in which most of the vibrations of stretching and bending organic molecules take place. Far infrared (FIR) is a range of 400–10 cm\(^{-1}\) providing information on rotational transitions, crystal lattice vibrations, and skeletal vibrations of large molecules. The analysis of different parts of the infrared region provides more information about the analyzed product.

The aim of this work was to compare EVO and MSO using the vibrational spectroscopy (NIR and MIR region) to determine their chemical and physical properties.

2. Materials and Methods

2.1. Materials. Cold pressed Meadowfoam Seed Oil™ was obtained from Natural Plant Products, Inc. (Oregon, USA) and extra virgin olive oil was sourced from Costa d’Oro (Spoleto, Umbria, Italy). n-Hexane (HPLC grade) and sodium methoxide, used for gas chromatography analysis, were purchased from Sigma-Aldrich, whereas 37-component FAME mix were obtained from Supelco (Bellefonte, PA, USA).

2.2. Gas Chromatography. Fatty acids methyl esters were obtained by a direct methylation with 14 wt.% BF3-MeOH procedure. Fatty acids methyl esters were separated on a BPX-70 capillary column (60 m x 0.25 mm x 0.25 μm; SGE Analytical Science) installed in an Agilent Technologies 7820 gas chromatograph equipped with an autosampler. Helium was used as a carrier gas at a flow rate of 0.8 mL/min. Column temperature was programmed from 140 to 240°C at 6°C/min. Initial and final temperature were held for 5 and 20 min, respectively. Detector temperature was set at 270°C. Fatty acids were identified by comparison of the retention times with those of authentic standards. The relative content of individual components was calculated by area normalization method [34].

2.3. Calculated Oxidizability (Cox) Value. The potential stability of oils was evaluated through the calculated oxidizability (Cox) value, applying the following equation [35]:

\[
\text{Cox index} = \frac{(1 \times \% \text{ of oleic acid}) + (10.3 \times \% \text{ of linoleic acid}) + (21.6 \times \% \text{ of linolenic acid})}{100}\%
\]

2.4. Near-Infrared Spectroscopy. MPAFT-NIR spectrophotometer (Bruker Company) was used to measure the near-infrared (NIR) spectrum range using transmitted light. The oils tested in this experiment were placed into glass vials, having an optical path length of 8 mm. The spectra were measured between 12500 and 4000 cm\(^{-1}\). For each sample, ten spectra were recorded.

2.5. Mid-Infrared Spectroscopy. A Spectrum spectrophotometer 100 FT-IR with a technique of attenuated total reflection (ATR) was used to measure the of mid-infrared (MIR) spectrum. The spectra were measured (32 scans per sample or background) between 4000 and 400 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). The spectra were corrected using the background spectrum of air. The analysis was carried out at room temperature. Before recording the spectrum, the ATR crystal (ATR Pro One, produced by Jasco) was carefully cleaned with ethanol and acetone. The cleaned crystal was checked spectrally to ensure that no residue was retained from the previous sample. For a measurement, one droplet (20 μl) of the oil was placed on the surface of the ATR crystal and covered with a glass lid in order to avoid contamination with ambient moisture. For each sample, ten spectra were recorded.

3. Results and Discussion

The value of MSO was apparent immediately because of its unique composition of fatty acids, over 95 wt.% of which have chain lengths of 20 carbon atoms or longer [36]. The MSO is enriched in the unusual fatty acid Δ\(^5\)-eicosenoic acid (20:1Δ\(^5\)). This fatty acid has physical and chemical properties that make MSO useful for many industrial applications [25].
The high stability of MSO is due to the presence of double bonds which are not conjugated and the absence of oxidative susceptible polyunsaturated fatty acids common in other vegetable oils [37]. A total of twelve components were identified by GC, which varied from 0.13 to 63.16 wt.%, as shown in Table 1. The four major acids in MSO are 5-eicosenoic (C20:1), 5,13-docosadienoic (C22:2), 13-docosenoic (C22:1) and 5-docosenoic (C22:1). Collectively, these four acids constitute about 96 wt.% of total fatty acids in MSO. Table 1 shows the composition of fatty acids of MSO in comparison to EV.

The Cox value shows the level of oxidation of oils based on the unsaturated fatty acid. The lower the value of Cox index, the higher the stability of oil. The Cox value was obtained from

$$\text{COX index of MSO} = \frac{(1 \times 1.89\%) + (10.3 \times 0.78\%) + (21.6 \times 0\%)}{100\%}$$

(2)

The Cox value for MSO was found to be 0.032, which has been compared with the Cox values of olive oil (1.780 [38]), crude soybean oil (7.690 [39]), sunflower oil (6.600), and canola oil (4.140 [40]). Our results suggest that MSO is definitely more stable than these other oils. MSO contains a vast majority of monounsaturated fatty acids, such as gondoic acid (C20:1; ω-9) and erucic acid (C22:1; ω-9), the presence of which provides MSO with high resistance to oxidation [3]. Moreover, it has been reported that the relationship between the PUFA/SFA ratio and the Cox value in natural oils and their oxidative stability is usually the reverse [41].

As pointed out by Mahesar et al. [42], the application of NIR and MIR techniques to olive oils is increasing, from the perspective of a multidisciplinary study approach for food research [43]. Generally, infrared spectroscopy represents a rapid, less destructive, and high-throughput method for the analysis of food products. The MIR spectra of the analyzed oils are shown in Figure 1(a). Spectrum bands of triglycerides, the main components of oils, dominate the typical MIR spectra of the vegetable oil, although other components in the oil also contribute to the spectra [44]. The spectral profile of MSO is similar to the spectral profile of EVO. The only differences in the shape and intensity of some bands appear due to different unsaturated fatty acid contents (higher in MSO). The very intense band at 1743 cm⁻¹ of the stretching vibrations of carbonyl group (C=O) is attributed to the presence of glycerol-fatty acids ester bonds (COOR) of triglycerides [44]. This band is more intense in EVO sample.

### Table 1: The composition of fatty acids of MSO and of olive oil [source: own work].

<table>
<thead>
<tr>
<th>Oil name</th>
<th>Saturation of fatty acid</th>
<th>Common name of fatty acid</th>
<th>Systematic name of fatty acid</th>
<th>Numerical symbol</th>
<th>Percentage of fatty acid in the oil [wt.%, ±SD]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meadowfoam seed oil</strong></td>
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</tr>
<tr>
<td>Saturated fatty acids</td>
<td>Palmitic acid</td>
<td>Hexadecanoic acid</td>
<td>C16:0</td>
<td>11.37; ±0.31</td>
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<tr>
<td></td>
<td>Palmitoleic acid</td>
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<td>C16:1</td>
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<tr>
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<td>Octadecanoic acid</td>
<td>C18:0</td>
<td>3.27; ±0.15</td>
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<tr>
<td></td>
<td>Arachidic acid</td>
<td>Eicosanoic acid</td>
<td>C20:0</td>
<td>0.44; ±0.02</td>
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<tr>
<td></td>
<td>Behenic acid</td>
<td>Docosanoic acid</td>
<td>C22:0</td>
<td>0.13; ±0.00</td>
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<tr>
<td></td>
<td>Oleic acid</td>
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<td>C18:1; cis</td>
<td>72.15; ±0.31</td>
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<td>—</td>
<td>(Z)-5-Docosenoic acid</td>
<td>C22:1; cis</td>
<td>16.37; ±0.08</td>
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<tr>
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<td>—</td>
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<td>16.37; ±0.08</td>
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<td>Nervonic acid</td>
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<td>C24:1</td>
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<td><strong>Olive oil</strong></td>
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<td>Saturated fatty acids</td>
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<td>0.13; ±0.00</td>
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<td></td>
<td>Oleic acid</td>
<td>(Z)-9-Octadecenoic acid</td>
<td>C18:1; cis</td>
<td>72.15; ±0.31</td>
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<tr>
<td></td>
<td>Gondoic acid</td>
<td>(Z)-5-Eicosenoic acid</td>
<td>C20:1</td>
<td>0.28; ±0.00</td>
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<td>C22:1; cis</td>
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<td>—</td>
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<td>C22:2</td>
<td>16.37; ±0.08</td>
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<td>Unsaturated fatty acids</td>
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<td>C18:2; n-6; cis</td>
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<td>0.28; ±0.00</td>
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<td>C20:4</td>
<td>0.65; ±0.01</td>
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</table>
than in MSO. The characteristic band at 1653 cm\(^{-1}\) represents stretching vibrations of \(-C=\text{C-}\) of cis-olefins (of disubstituted olefins, RHC=CHR) [45]. In the fingerprint region (between 1500 and 900 cm\(^{-1}\)), several absorption bands appear, as seen in Figure 1(b). Generally, the fingerprint region represents a region rich in information, but, on the other hand, difficult to analyze due to its complexity [46]. The bands at approximately 1460 cm\(^{-1}\) and 1375 cm\(^{-1}\) are characteristic for CH\(_2\) and CH\(_3\) scissoring vibrations. The bands at 1238, 1160, 1117, and 1097 cm\(^{-1}\) arise from C-O stretching vibrations [47, 48]. These bands are more intense for EVO than for MSO, which confirms that EVO contains more oleic and \(\alpha\)-linolenic acid than MSO. The higher value of \(\alpha\)-linolenic acid, which is more prone to oxidation, may indicate that the olive oil will be less stable. In contrast to EVO spectrum, a peak in the wave at number 914 cm\(^{-1}\) is observed for MSO. This band is assigned to the bending vibration of cis-olefin group and vinyl groups

[49, 50]. The band at approximately 720 cm\(^{-1}\) is assigned to the overlapping peaks of CH\(_2\) rocking vibration and the out-of-plane vibration of cis-disubstituted olefins (CH\(_2\) rocking vibration) and is also more intense for the olive oil. The intensive bands with maxima at 2924 and 2852 cm\(^{-1}\) arise, respectively, to asymmetric and symmetric stretching vibrations of aliphatic \(\text{CH}_2\) methylene and terminal methyl groups of the fatty acid chains in triglycerides [47, 51]. These bands are more intense for MSO than for EVO, as seen in Figure 1(c).

The NIR spectra of oil exhibit broad overlapping bands, which are typical for overtones and combination tones of the fundamental vibrational modes [44]. The NIR spectra of the analyzed oils are depicted in Figure 2(a). Similar to the MIR spectra, bands originating from triglycerides also dominate the NIR spectra. The differences in the shape and intensity of some bands are also due to the differing contents of unsaturated fatty acids. The spectra of EVO and MSO are rather
similar, having few differences in the intensity of some bands. In the range 9000–6500 cm\(^{-1}\) (Figure 2(b)), the MSO has more intensive bands than EVO. The band at approximately 8264 cm\(^{-1}\) originates from the second overtones of the C-H stretching vibrations. The band with maxima at approximately 7187 cm\(^{-1}\) and 7074 cm\(^{-1}\) is characteristic for C-H combination vibrations [44, 52]. The first overtones of the C-H stretching vibrations in the methyl, methylene, and ethylene groups correspond to a band with two maxima at about 5791 cm\(^{-1}\) and 5676 cm\(^{-1}\). It was found that trans-unsaturated triglycerides absorbed light waves at 5797 cm\(^{-1}\) and 5681 cm\(^{-1}\) [52]. This band is more intense for MSO, meaning that this oil will be more stable than EVO (melting time is higher for trans-unsaturated triglycerides than for cis-unsaturated). The low-intensity bands at 4662 cm\(^{-1}\) and 4595 cm\(^{-1}\) correspond to the –HC=CH- stretching vibrations [53], Figure 2(d). There is only a little difference in the intensity of the oils analyzed (more intensive band is noticed for MSO).

The final composition of oils, particularly compounds present in the oil aromas, is dependent on the applied mechanical processes. Crushing process, for example, leads to an intensification from 20 wt.% to 50 wt.% of trans-2-hexenal in the final olive oil after 70 min of mechanical crushing. Another ingredient also affected was hexanal. Although its quantity was increased, it was still far distant from the higher level of trans-2-hexenal. Despite this, after finishing the processing methodology, the circumstances were inverted with an upsurge in hexanal and diminution in trans-2-hexenal, probably due to enzymatic action and reduction of the antioxidants present in the oil. Among the volatile and nonvolatile compounds responsible for the aroma and flavor of olive oil are those derived from polyunsaturated fatty acids/alcohols and 6-carbon aldehydes. The literature has stated that carotenoids and chlorophylls are likewise modified depending on the extraction methodology used. These components are present in higher levels when the oil is submitted to centrifugation using metallic
grinders, because they can extract more pigments. The presence of aliphatic alcohols and waxes may also be upgraded if the temperature of extraction increases.

During drying, olive oil shows an astonishing stability when compared to other oils such as soybean, corn, or cotton seed oil. Such fact is due to the capacity of olive oil to resist oxidant environments given its composition in abundant polar and nonpolar antioxidant molecules such as tocopherols and squalene and the complex constitution in fatty acids, allowing the oil to be reutilized. The reuse of the same olive oil for some occasions may also modify the diet lipid intake due to changes induced by temperatures during the frying process.

4. Conclusions

The composition of fatty acids of MSO and EVO was determined by gas chromatography. The high stability of MSO is due to the presence of double bonds which are not conjugated and the absence of oxidatively susceptible polyunsaturated fatty acids common in other vegetable oils. The results showed that the four major acids in MSO are 5-eicosenoic (C20:1), 5,13-docosadienoic (C22:2), 13-docosenoic (C22:1), and 5-docosenoic (C22:1). Collectively, these four acids constitute about 96 wt.% of total fatty acids in MSO. The determined value of α-linolenic acid, which was higher in EVO, may indicate that the olive oil will be less stable. The Cox value for MSO was found to be 0.032. If compared to the Cox values of olive oil (1.780), crude soybean oil (7.690), sunflower oil (6.600), and canola oil (4.140), MSO is more stable according to our results. The spectral results proved that methods of vibrational spectroscopy can be successfully used for analyzing the chemical composition of meadowfoam seed oil. Distinct regions, which pertain to unsaturated fatty acids, can be used as markers for differentiating between oils (MSO and EVO) and for monitoring their quality. The differences in the shape and intensity of some bands are due to the differing contents of unsaturated fatty acids. The NIR spectra of EVO and MSO are rather similar, having few differences in the intensity of some bands due to the differing contents of unsaturated fatty acids. The MIR spectra differ in the intensity and shape of the spectrum. Meadowfoam seed oil has a peak in the wave at number 914 cm$^{-1}$ which is not present in the olive oil spectrum. This band is assigned to the bending vibration of cis-olefin group and vinyl groups. The bands at 1238, 1160, 1117, and 1097 cm$^{-1}$ arise from C-O stretching vibrations being more intensive for EVO than for MSO, which confirms that EVO contains more oleic and α-linolenic acid than MSO. Based on the obtained results and studied literature, it could be concluded that MSO ensures higher stability compared to EVO.

Data Availability

The authors declare that the data supporting the findings of this study are available within the article. All the other data are available on reasonable request from the corresponding authors.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

Authors’ Contributions

AZ, KW, DK-P, and JDF contributed to methodology, formal analysis, investigation, resources, and data curation. AZ, KW, DK-P, and JDF wrote the original draft of the manuscript. ML, AD, AS, EBS, and IN participated in conceptualization, review and editing of the manuscript, project administration, supervision, and funding acquisition. All authors made a substantial contribution to the work and approved its publication.

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References


