

Fatty acids in seed oil of wild and cultivated rosehip (*Rosa canina* L.) from different locations in Serbia

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ABSTRACT

Rosehip (*Rosa canina* L.) seeds are rich in bioactive compounds and nutrients and hence with a great potential to be employed in production of functional foods. This work aimed to evaluate the fatty acid composition of seed oil from wild and cultivated rosehip collected at different locations in the Republic of Serbia. Unsaturated fatty acids were dominant in majority of seed oil samples, with linoleic (LA), α -linolenic (ALA) and oleic (OA) acids (24.53–46.68 %, 4.73–12.39 % and 3.89–13.82 %, respectively) as the most abundant ones. Based on the analyses of most dominant bands in Raman spectra of seeds (~ 1265 and ~ 1660 cm^{-1}) characteristic for unsaturated fatty acids, ANOVA revealed significantly higher content in two seed samples (5SW and 10SC). Ratios of UFAs/SFAs, ω -6/ ω -3 and LA/ALA and desirable fatty acids (DFA) indicated that most studied rosehip seed oils showed good quality. Factors such as genetic characteristics and agro-ecological conditions most likely affected FAs composition of seed oils.

1. Introduction

Dog rose (*Rosa canina*), belongs to the order Rosales, family Rosaceae, subfamily Rosoidae and genus *Rosa* L. which includes 100–250 species. The species name *canina* (in Latin means dog) may be attributed to writings of ancient Greek physician Hippocrates and Roman naturalist Pliny the Elder who suggested that a preparation of wild *R. canina* root could treat the bite of a rabid dog. It is estimated that *R. canina* is used during the last 4700 years of human history for their beauty, fragrance, and for cosmetic and medical purposes (Kazaz, 2009). Today, garden lovers dislike wild roses due to their lack of esthetic beauty and spiny nature (Maitra, 2016).

R. canina can be found wild in the temperature zones of Europe, Asia, North America, and northern Africa (Ercisli, 2007). It grows on the sunny side or semi-shade of hedgerows on a range of soils. The plant is in

flowers from May to June and fruit ripens from August to October. The flowers are large, pale pink, having faint sweet smell. A pseudo red-orange "hip" consists of achenes and an enlarged, red, fleshy floral cup (hypanthium) (Pećinar et al., 2021). Dog rose is used as a rootstock for ornamental varieties of roses. It can be planted to prevent soil erosion because it is adaptable to different soils and environmental conditions (Baktir et al., 2005).

Wild rosehips are rich in polyphenolic compounds, including flavonoids, anthocyanins, flavan-3-ols, procyanidins, catechin, quercetin, phenolic acids, such as gallic and ellagic acids, kaempferol, apigenin and resveratrol (Aptin et al., 2013; Dabić Zagorac et al., 2020; Fetni et al., 2020). Also rosehip is a valuable source of vitamins (A, B3, C, D, E, and P), and especially vitamin C which ranges from 250 to 2700 mg/100 g (Demir and Özcan, 2001; Daels-Rakotoarison et al., 2002). *R. canina* fruits are storing high levels of carotenoids, tocopherols as well as

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minerals (Ca, Fe, K, Mn, Na, P, and Zn), tannins, organic acids, amino acids, and pectin (Demir and Özcan, 2001; Tabaszewska and Najgebauer-Lejko, 2020). Due to that, rosehips are exhibiting antioxidant and anti-inflammatory action, antibacterial, antimutagenic, probiotic, antiulcerogenic, antinociceptive and anticarcinogenic effects (Gruenwald et al., 2019; Gulbagca et al., 2019). Also, they are helpful in osteoarthritis, against damaged liver parenchyma, regulates level of lipids and glucose in blood and arthralgia treatment (Shakibaei et al., 2012). In traditional medicine rosehips are used to treat infections of the bladder and kidney, diarrhea, skin problems, colds and flu, sore throat, fatigue, inflammation, scurvy, stress and nervousness. Rose honey is known to help soothe sore throats and wet rose petals can be placed on cuts and sores (Maitra, 2016).

The fruits are generally not consumed in fresh condition, but used for the production of marmalade, jams, juices, teas, sirups and wine, and recently, as a component of probiotic drinks, yoghurts and soups (Nadpal et al., 2016). The oil fraction of rosehip achenes, byproducts of rosehip industry products, is rich in polyunsaturated fatty acids (PUFAs), monounsaturated fatty acids (MUFAs) and saturated fatty acids (SFAs), as well as all-*trans*-retinoic acid (tretinoin) a naturally occurring derivative of vitamin A that regenerate damaged skin (Concha et al., 2006; Kulaitienė et al., 2020; Mannozi et al., 2020). In this respect, the oil is mainly used in the cosmetics and pharmaceuticals (Zlatanov, 1999; Özcan, 2002; Concha et al., 2006; Ilyasoğlu, 2014).

Lipids are considered one of the most important components in nutrition, as they are a main source of energy and precursors of many essential compounds in the human body (Ilyasoğlu, 2014). Among fatty acids (FAs) which are one of major lipid constituents, UFAs as well as omega-3 (ω -3) and omega-6 (ω -6) PUFAs, are the most important ones. Most naturally occurring UFAs have *cis* configuration, while those with *trans* configuration occur in products as a result of technology processing (i.e., hydrogenation). The human body cannot synthesize ω -3 and ω -6 PUFAs, due to the absence of relevant enzymes. Therefore, they are considered to be essential fatty acids (EFAs), and in order to satisfy human nutritional needs those acids have to be taken through food consumption (Orsavova et al., 2015; Murathan et al., 2016). Lately, EFAs have been considered as functional food and nutraceuticals, and many researchers have delineated their significant roles in metabolic processes, resulting in health benefits (Yoruk et al., 2008; Ilyasoğlu, 2014; Orsavova et al., 2015; Dąbrowska et al., 2019). PUFAs such as linoleic (LA), α -linolenic (ALA) and arachidonic (AA) contribute to the prevention of some diseases (diabetes, cardiovascular diseases and cancers) and have other important biological roles (Ristić-Medić et al., 2013; Ilyasoğlu, 2014; Murathan et al., 2016). Sterols and tocopherols which are found in rosehip seeds oil indicate their potential for use in functional food and dietary supplements (Ilyasoğlu, 2014; Mannozi et al., 2020).

The increasing demand for product quality improvement in chemical, pharmaceutical, cosmetic, food, and agricultural industries has triggered a significant renaissance of the vibration spectroscopic techniques, such as Raman, infrared (IR), and near-infrared (NIR) spectroscopy as more specific, non-destructive, efficient, enforceable and environmentally friendly analytical tools (Baranski et al., 2005; Schulz and Baranska, 2007). Moreover, a trend in recovery of nutritionally valuable components from plant food wastes is gaining attention (Gal-anakis, 2012), which provides a new perspective for use of rosehip seeds as nutritionally rich source.

In the Republic of Serbia, dog rose is classified as a protected wild plant species that has a special significance from the various aspects such as ecological, ecosystemic, biogeographical, scientific, health, economic and other (Official Gazette of RS, 2010). Despite the wide distribution of the rosehip plant and its significance from nutritional and health aspects, rosehip from Serbia is poorly studied (Nadpal et al., 2016; Popović-Djordjević et al., 2020; Pećinar et al., 2021). This especially refers to rosehip seed fatty acids.

Therefore, this work aimed to provide insightful data about fatty acid

composition of oil obtained from seeds of wild and cultivated rosehip grown at different locations in the Republic of Serbia. In this respect, *in situ* Raman spectroscopy (RS) provided primary information on fatty acids in studied seeds, whereas gas chromatography (GC-MS) was used for determination of fatty acids in seed oil samples.

2. Material and methods

2.1. Plant material

Rosehip (RH) fruits (*Rosa canina* L.) were collected at the stage of full physiological maturity from September to October 2018, at eight locations in Serbia. Two cultivated varieties ('Laksa' and 'Polimerijana'), have been grown (and manually harvested) in orchards located in two regions (Valjevo and Nova Varoš), whereas wild fruit samples were collected from six different locations (Fig. 1). Bright red fruits were randomly taken from different bushes at each location.

Schematic presentation of collection and preparation of plant material is given in Fig. 2. Briefly, about 60 mature rosehip fruits were harvested randomly according to color evenness (bright color) from each location. Plant samples were deposited in the Herbarium of the Faculty of Agriculture, Belgrade-Zemun, Serbia (voucher numbers: UBFA1353A-J). For the purpose of Raman microspectroscopy and GC analysis, collected rosehips were first washed by tap water and dried at room temperature. Later, seeds were separated from hypanthium (Figs. S1, S2 in Supplementary material). Total of 10 composite seed samples was prepared, labeled and used for further analyses.

2.2. Raman microspectroscopy

Raman microspectroscopy of longitudinal section of rosehip seed samples (Figs. S3-12 in Supplementary material, Table 1) was done using XploRA Raman spectrometer (Horiba Jobin Yvon), Raman scattering was excited by laser at a wavelength of 785 nm. In total, 100 spectra (ten spectra per seed sample) were recorded in the range of 200–1800 cm^{-1} following the procedure described in our previous work (Pećinar et al., 2021). The spectra preprocessing was realized using Spectragryph software, version 1.2.14. (Menges, 2021 <http://www.ffmpeg2.de/spectragryph/>).

2.3. Oil extraction

Separated seeds were ground in a blender (BOSCH MKM6000, 180 W, Slovenia). Approximately 0.5 g of each sample of ground seeds was weighed on an analytical balance in a glass vial to which 5 mL of *n*-hexane was added. A total of ten samples were prepared. Samples were extracted in an ultrasonic bath (Vabsonic SB-8 L T, Serbia) for 1 h, after which they were left at room temperature for 68 h to be extracted by maceration with occasional shaking. The extraction was repeated on the ultrasonic bath for an additional 30 min. After the extraction was complete, the samples were filtered through quantitative filter paper, and the solvent was evaporated at room temperature. Oil yields (in %) were: 1SWO - 7.5; 2SWO - 5.5; 3SWO - 5.3; 4SWO - 5.8; 5SWO - 5.5; 6SWO - 5.9; 7SCO - 6.9; 8SCO - 6.6; 9SCO - 6.1; 10SCO - 6.6.

Samples were further subjected to fatty acids (FAs) analysis by gas chromatography (GC). Seed and relevant oil samples labels are given in Table 1.

2.4. Determination of FAME by GC-FID

The fatty acid methyl esters (FAMES) were determined by GC-FID instrument (Agilent Technologies 6890, USA). The FAs were dissolved in 1 mL *n*-hexane (HPLC gradient grade, Baker ultra resi-analyzed, Holland) and derivatized to FAME's with 1 mL of 14 % BF_3/MeOH reagent (Supelco, Bellefonte, USA) as described in literature (Kostić et al., 2017; Barać et al., 2018). SP-2560 (length 100 m, i.d. 0.25 mm, film



Fig. 1. Sampling locations.

thickness 0.20 μm , Supelco, Bellefonte, USA) column was used for separation for all components. GC conditions for analyzing FAMES are given in [Supplementary material \(Table S1\)](#). The chromatographic peaks in the samples were identified by comparing retention times of FAME peaks with peaks in Supelco 37 Component FAME mix standard (Supelco, Bellefonte, USA). Total analysis time was 72.5 min and good separation was provided for all 37 FAMES. Fatty acids content was expressed in relative quantities as mass % of total fatty acids.

2.5. Lipid indices

According to literature, desirable fatty acids (DFA) ([Barać et al., 2018](#)) and the ratios: UFA/SFA, ω -6/ ω -3 ([Kostić et al., 2017](#)) and LA/ALA (linoleic acid/ α -linolenic acid) ([Sharma et al., 2012](#)) were calculated in rosehip seed oil samples. For calculation of DFA following equation was used:

$$\text{DFA} = \Sigma\text{MUFA} + \Sigma\text{PUFA} + \text{C18:0}$$

UFA/SFA ratio was obtained by dividing the sum of unsaturated FAs content and sum of saturated FAs content. ω -6/ ω -3 ratio was calculated by dividing the sum of ω -6 FAs content and sum of ω -3 FAs content, while LA/ALA ratio was obtained by dividing contents of linoleic and α -linolenic acids.

2.6. Statistical analyses

All recorded Raman spectra (10 per each sample) were statistically analyzed using Minitab statistical software. Prior to statistical analysis, the raw data were pre-processed, i.e. the Raman spectra were smoothed using Savitzky-Golay filters with 5 points and a second-order polynomial function. All Raman scattering intensities were normalized by the highest intensity band. One-way analysis of variance (ANOVA) was performed in order to investigate differences between rosehips grown at eight locations in Serbia, for $\sim 1265\text{ cm}^{-1}$ and $\sim 1660\text{ cm}^{-1}$ vibrational bands. If ANOVA test had indicated a statistically significant difference between the means ($p < 0.05$), Tukey's test was performed to indicate where the differences occurred. The test compares all possible pairs of means. The statistical analysis of FAMES by GC-FID was performed using one-way analysis of variance (ANOVA) and significant differences among means were determined by Duncan's comparison test. Differences at a confidence level of 95% were considered significant.

3. Results and discussion

3.1. Characterization and differentiation of rosehip seeds according to Raman spectra

Many studies show that rosehip seed oil possesses high amounts of PUFAs, especially with two double bonds (linoleic acid), followed by linolenic and oleic acids (with three double bonds and one double bond,

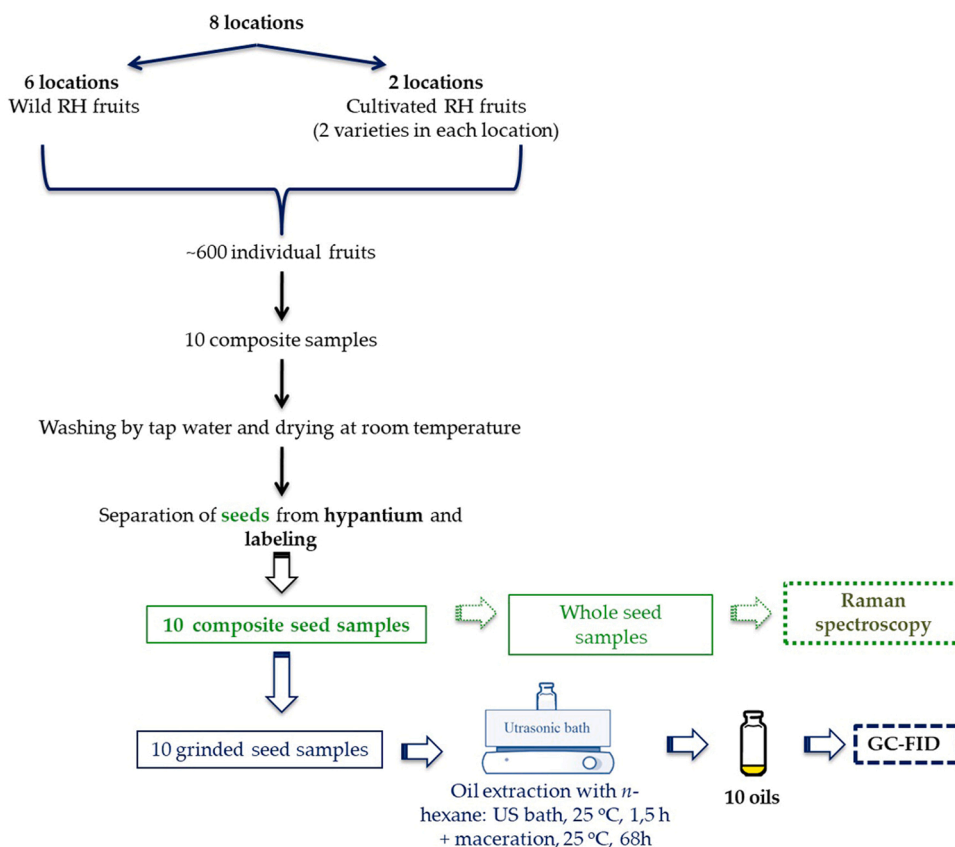


Fig. 2. Collection and preparation of plant material for instrumental analyses.

Table 1
Seed and oil samples labels.

Location ^a	Coordinates	Elevation	Seed sample	Seed oil sample
1	44° 22' N/20° 25' E	209	1SW ^b	1SWO ^d
2	43° 30' N/20° 42' E	611	2SW	2SWO
3	44° 15' N/20° 02' E	186	3SW	3SWO
4	43° 45' N/20° 33' E	250	4SW	4SWO
5	44° 38' N/20° 18' E	175	5SW	5SWO
6	43° 52' N/20° 19' E	268	6SW	6SWO
7	43° 23' N/19° 45' E	1000	7SC ^{c,f}	7SCO ^{e,f}
8	44° 05' N/19° 53' E	210	8SC ^f	8SCO ^f
7	43° 23' N/19° 45' E	1000	9SC ^g	9SCO ^g
8	44° 05' N/19° 53' E	210	10SC ^g	10SCO ^g

^a see in Fig. 1;

^b SW – seed from wild rosehip;

^c SC– seed from cultivated rosehip;

^d SWO – seed oil from wild rosehip;

^e SCO – seed oil from cultivated rosehip;

^{f,g} – 'Laksa' and 'Polimerijana' varieties, respectively.

respectively) (Da Silva et al., 2008; Mannozi et al., 2020).

According to Raman spectra of rosehip seed samples recorded in the region from 1200 to 1800 cm⁻¹ (Table 2 and Figs. S3-S12 in Supplementary material), bands associated to unsaturated fatty acids have been observed. The UFAs are fluids, so their Raman spectra show broad bands. The most characteristic band with high intense signal in examined seeds (Fig. 3, Table 2) occurred at ~1660 cm⁻¹, which indicate C=C stretching vibration of the *cis*-unsaturated fatty acids (De Gelder et al., 2007; Sharma et al., 2015; Martini et al., 2018; Farber et al., 2020). Also broad but medium intensity band at ~1266 cm⁻¹ assigned to C-H bending deformation of esterified unsaturated fatty acids was notable in spectra (Da Silva et al., 2008; Sharma et al., 2015; Wiercigroch et al., 2017; Martini et al., 2018; Zeise et al., 2018; Farber et al.,

Table 2
Raman spectra vibrational bands and their tentative assignments for seeds of rosehips grown at different locations in Serbia.

Sample	Band assignments (cm ⁻¹)		
	Esterified fatty acids	Unsaturated fatty acids (<i>cis</i> isomers)	Esterified unsaturated fatty acids (<i>cis</i>)
1SW	1731	1650	1262
2SW	1730	1658	1271
3SW	/	1658	1273
4SW	1757	1652	1262
5SW	1749	1658	1266
6SW	1731	1654	1264
7SC	1749	1653	1262
8SC	/	1661	/
9SC	1734	1652	1263
10SC	1732	1650	1262
Wavenumber range (cm ⁻¹)	1730–1757	1650–1661	1262–1273
Literature data (cm ⁻¹)	1730–1747 (Schulz and Baranska, 2007; Martini et al., 2018; Farber et al., 2020)	1655–1660 (De Gelder et al., 2007; Schulz and Baranska, 2007; Da Silva et al., 2008; Agarwal et al., 2011; Wiercigroch et al., 2017; Martini et al., 2018; Farber et al., 2020)	1265 (Da Silva et al., 2008; Sharma et al., 2015; Wiercigroch et al., 2017; Martini et al., 2018; Zeise et al., 2018; Farber et al., 2020)

2020; Pećinar et al., 2021).

The lower intensity band at ~1750 cm⁻¹ (Table 2) maybe related to the presence of fatty acid ester (Da Silva et al., 2008; Farber et al., 2020). It was found that studied seeds obtained from rosehips grown at

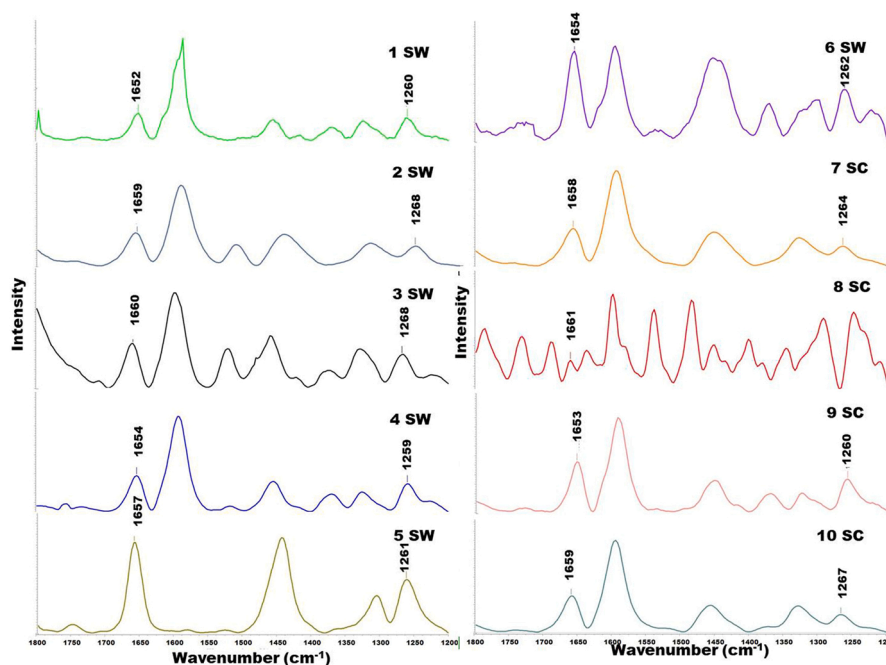


Fig. 3. Normalized Raman spectra of seed samples 1–10 with marked bands assigned to unsaturated fatty acids (*cis*) at ~1265 cm⁻¹ and ~1660 cm⁻¹.

different locations had no similar spectral profiles. Moreover, different intensities and positions of vibrational bands were observed, which indicated the differences in fatty acids composition.

These results could indicate the possible differentiation of seeds in chemical composition through different location and possible differences between wild and cultivated rosehips. The differences are especially pronounced for the bands in the region from 1260 to 1750 cm⁻¹. Namely, band positioned at ~1730 cm⁻¹ was not detected in spectra of seed sample 3SW, whereas bands at ~1265 and 1730 cm⁻¹ were not observed for seed sample 8SW (Table 2 and Figs. S3-S12). Spectra of FAs standards clearly show differences between SFAs and UFAs (Fig. S13). According to literature bands at 1260 cm⁻¹ (=C-H *cis* stretch) and 1650 cm⁻¹ (C=C stretch) indubitably distinguish UFAs from SFAs. In addition, bands at 1300 and 1440 cm⁻¹ are associated to aliphatic chains of fatty acids (Sharma et al., 2015; Martini et al., 2018). Results obtained in the present study were in line with these literature findings, especially in terms of UFAs bands.

Therefore, normalized intensities of ~1265 and 1660 cm⁻¹ vibrational bands were used to predict the differences in a relative content of unsaturated fatty acids in rosehips from studied locations. Results based on the band ~1265 cm⁻¹ indicated that sample 5SW rosehip had the statistically higher fatty acid content comparing to all other rosehips (Table 3, Fig. 4). At the same time, 9SC significantly differed from all

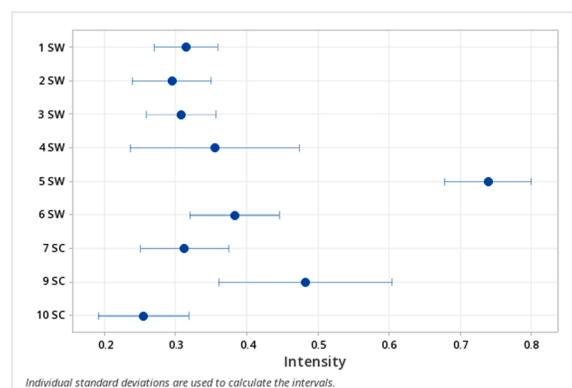


Fig. 4. Means (circles) and confidence intervals for the intensities of the rosehip seed (1–6SW, 7–10SC) spectra at ~1265 cm⁻¹ (unsaturated fatty acids).

Table 3
Tukey pairwise comparisons of rosehip seeds Raman spectra data.

Sample	Mean	Tukey test ^a	Sample	Mean	Tukey test ^a
	~1265 cm ⁻¹			~1660 cm ⁻¹	
5SW	0.7391	A	5SW	0.77864	A
9SC	0.4823	B	9SC	0.5437	B
6SW	0.3829	BC	10SC	0.4003	C
4SW	0.3550	BC	7SC	0.3990	C
1SW	0.3148	C	2SW	0.3694	C
7SC	0.3127	C	4SW	0.3611	C
3SW	0.3083	C	6SW	0.3608	C
2SW	0.2948	C	1SW	0.3359	C
10SC	0.2550	C	3SW	0.2897	C
			8SC	0.01950	D

^a Grouping information using the Tukey method and 95% confidence; means that do not share a same letter are significantly different

samples, with the exception of samples 4SW and 6SW. In general, the fatty acid content of the wild and cultivated rosehip seeds had no significant impact on samples differentiation, except for 5SW, 9SC, and sample 8SC where the band positioned at ~1265 cm⁻¹ was not clearly detected.

Differences between rosehip seeds for vibrational band at 1660 cm⁻¹, which can be assigned to unsaturated fatty acids, revealed that samples 5SW, 8SC and 9SC were significantly different from other seed samples (1–4 and 6SW, and 7 and 10SC) as well as from each other (Table 3, Fig. 5). Samples 5SW and 9SC had higher content of fatty acids, while their content in sample 8SC was significantly lower. The results of statistical analysis of fatty acids bands intensities indicated the absence of clear significant differences between wild and cultivated rosehips, which is in a agreement with previous theories that fatty acid composition is probably dependent on the abiotic ecological factors such as sunlight, temperature, soil properties, land exposition, elevation, etc (Güney, 2020; Mannozi et al., 2020). The findings of the study indicated that Raman spectroscopy coupled with advanced statistical analysis was able to predict the differences in the fatty acids content in a faster and easier way comparing with traditional analytical tools.

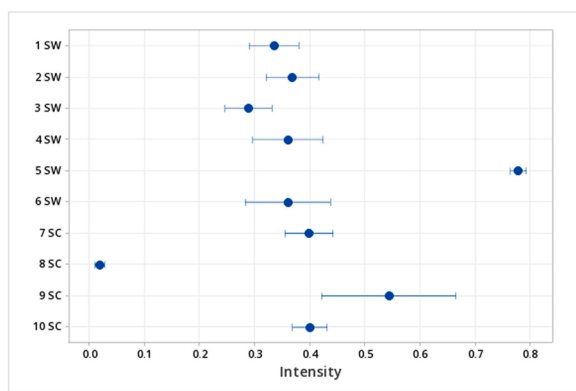


Fig. 5. Means (circles) and confidence intervals for the intensities of the rosehip seed (1–6SW, 7–10SC) spectra at ~1660 cm⁻¹ (unsaturated fatty acids, *cis* isomers).

3.2. Fatty acid profiles of rosehip seed oil samples

Although dog rose is classified as a protected wild plant species in Serbia that has a special significance from the various aspects, data about fatty acid composition of rosehip seeds are scarce. Results of GC analysis for seed oil (SO) obtained from rosehips collected at different locations in the R. Serbia are presented in Table 4.

Among the MUFAs, palmitoleic and oleic acid were the most abundant compounds in fatty acid profile, while erucic acid was found only in 5SWO sample (Table 4). Oleic acid was found in amount 3.89–13.82 % (Table 4), while this fatty acid was the one of the main FAs in rosehip SO studied by some authors (Zlatanov, 1999; Yilmaz et al., 2011; Güney, 2020). Due to high level of linoleic and oleic acid, rosehip SO has a higher oxidative stability than other unsaturated oils and could be used in diet as a functional food, giving a special flavor to food products

(Yoruk et al., 2008). In studied SO samples palmitoleic acid was detected in a relatively high percentage, especially in oil obtained from wild rosehip seeds (16.24–35.68 %, Table 4), while substantially lower content of this acid was reported in literature (Çelik et al., 2010; Güney, 2020).

Among PUFAs, α-linolenic acid (ALA), linoleic acid (LA) and arachidonic acid (AA) which are omega-3 (ω-3) and omega (ω-6) fatty acids, respectively, have been considered as the most important ones. Besides, linoleic and linolenic acids are essential fatty acids (EFAs).

Both LA and ALA are abundant in plants, especially in seeds (Simopoulos, 2016). In extracted rosehip SO samples LA was the most abundant FA (24.53–46.68 %, Table 4), which is in line with results of FA composition of rosehip seed oils reported in literature (Özcan, 2002; Murathan et al., 2016; Javanmard et al., 2018; Turan et al., 2018; Güney, 2020). It is interesting to point out that the highest relative content of LA was reported in samples from different regions in Turkey, 54.80 % (Turan et al., 2018) and 54.41 % (Özcan, 2002). However, LA was not detected in 1SWO sample, while the sample 7SCO had the highest content (46.68 %, Table 4). The obtained results corroborate with literature data which reported LA as predominant fatty acid in rosehip SO (Jakovljević et al., 2018; Mannozi et al., 2020). As for ALA (ω-3) lower amount was noted in studied oil samples, except for 1SWO, 6SWO and 8SCO where it was not detected at all. The important role of this fatty acid in metabolic processes and physiological functions in the human body and its cardioprotective and central nervous system effects have been known for many years (Stark et al., 2008). Linoleic, α-linolenic and oleic acids were reported as the main UFAs in oil extracted from rosehip seeds waste from one Serbian food factory (Milić et al., 2020), which is supported by results obtained for order of LA, ALA and OA (24.53–46.68 %, 4.73–12.39 % and 3.89–13.82 %, respectively) in the present study. Arachidonic acid (AA) was detected in samples 2SWO-4SWO, 7SCO, 10SCO. Other authors also reported this FA but in significantly lower amounts (Kulaitienė et al., 2020; Mannozi et al., 2020).

Table 4
Fatty acid (FA) profiles of rosehip seed oils (SOs).

Sample	1SWO	2SWO	3SWO	4SWO	5SWO	6SWO	7SCO	8SCO	9SCO	10SCO
FA	Content (%)									
C16:1	27.33 ^b ± 1.31	21.38 ^c ± 1.01	22.41 ^c ± 0.96	22.63 ^c ± 0.99	16.24 ^d ± 0.68	35.68 ^a ± 1.22	16.95 ^d ± 0.71	11.77 ^e ± 0.34	9.77 ^e ± 0.21	18.02 ^d ± 0.71
C18:0	11.87 ^a ± 0.48	/	7.94 ^b ± 0.12	/	/	11.73 ^a ± 0.48	/	6.30 ^c ± 0.14	/	/
C18:1ω9c	13.32 ^a ± 0.72	8.48 ^d ± 0.24	9.83 ^c ± 0.31	8.46 ^d ± 0.21	6.47 ^e ± 0.19	11.58 ^b ± 0.32	6.92 ^e ± 0.08	3.89 ^g ± 0.02	5.26 ^f ± 0.04	13.82 ^a ± 0.60
C18:2ω6c	/	26.77 ^{de} ± 1.17	30.51 ^c ± 1.10	26.10 ^{de} ± 1.03	33.00 ^b ± 1.11	27.65 ^d ± 1.13	46.68 ^a ± 1.34	25.28 ^e ± 0.84	31.51 ^{bc} ± 0.97	24.53 ^e ± 0.96
C18:2ω6t	/	/	/	/	/	/	3.49 ± 0.05	/	/	/
C18:3ω3	/	8.21 ^d ± 0.26	9.37 ^c ± 0.37	12.39 ^a ± 0.55	8.13 ^d ± 0.15	/	8.01 ^d ± 0.16	/	4.73 ^e ± 0.08	10.94 ^b ± 0.38
C20:0	16.19 ^b ± 0.63	11.63 ^c ± 0.20	4.48 ^f ± 0.08	5.20 ^f ± 0.14	10.68 ^d ± 0.44	/	/	16.91 ^b ± 0.41	26.52 ^a ± 1.02	7.68 ^e ± 0.22
C20:3ω6c	/	/	/	/	/	/	/	/	6.30 ± 0.15	/
C20:4ω6	/	10.61 ^b ± 0.24	8.09 ^c ± 0.22	16.02 ^a ± 0.76	7.01 ^d ± 0.27	/	10.27 ^b ± 0.22	/	/	7.12 ^d ± 0.12
C21:0	19.02 ^a ± 0.44	5.17 ^e ± 0.13	/	/	6.64 ^d ± 0.12	/	/	14.77 ^b ± 0.33	12.73 ^c ± 0.34	4.66 ^e ± 0.09
C22:0	12.27 ^b ± 0.57	7.74 ^d ± 0.09	7.36 ^d ± 0.18	9.19 ^c ± 0.32	5.13 ^e ± 0.13	13.36 ^a ± 0.47	7.68 ^d ± 0.19	5.08 ^e ± 0.06	3.19 ^f ± 0.04	13.23 ^a ± 0.43
C22:1ω9c	/	/	/	/	6.70 ± 0.21	/	/	/	/	/
C24:0	/	/	/	/	/	/	/	16.01 ± 0.41	/	/
ΣSFA	59.35	24.54	19.78	14.39	22.45	25.09	7.68	59.07	42.44	25.57
ΣUFA	40.65	75.45	80.21	85.60	77.55	74.91	92.32	40.94	57.57	74.43
ΣMUFA	40.65	29.86	32.24	31.09	29.41	47.26	23.87	15.66	15.03	31.84
ΣPUFA	/	45.59	47.97	54.51	48.14	27.65	68.45	25.28	42.54	42.59

^a not detected; ^a, ^b, ^c, ... Means with at least one similar letter did not show significant differences at the *p* < 0.05 level. All data are means ± standard deviation (*n* = 3). 16:1 - Palmitoleic acid; 18:0 - Stearic acid; 18:1ω9c - Oleic acid; 18:2ω6c - Linoleic acid; 18:2ω6t - Linoleilaidic acid; 18:3ω3 - α-Linolenic acid; 20:0 - Arachidic acid; 20:3ω6 - cis-8,11,14-Eicosatrienoic acid; 20:4ω6 - Arachidonic acid; 21:0 - Heneicosanoic acid; 22:0 - Behenic acid; 22:1ω9c - Erucic acid; 24:0 - Lignoceric acid

Linolenic and *cis*-8,11,14-eicosatrienoic acid, were detected in low percentage (Table 4) in only two samples (7SCO and 9SCO, respectively). It is worth to mention that in the 1SWO sample PUFAs were not detected at all.

Behenic, stearic, arachidic, heneicosanoic and lignoceric acid are among saturated FAs that were detected in extracted rosehip seed oils (Table 4). Behenic acid was found in all samples, while lignoceric acid was identified only in sample 8SCO. These SFAs were also reported in rosehip seed oils by other authors (Ercisli, 2007; Çelik et al., 2010; Adamczak et al., 2011).

Numerous studies on this topic, including the present, have shown many differences in fatty acid profiles of rosehip seed oils, as well as the FAs quantity. Results support observations that fatty acid composition of rosehip oil is probably dependent on the variety of rosehip fruit (genetic factors), the growing conditions (climate, soil, and ecological factors), harvest time, as well as applied extraction methods (Özcan, 2002; Topkafa, 2016; Dąbrowska et al., 2019; Güney, 2020; Mannozi et al., 2020). Besides, results obtained in this study revealed differences in the fatty acid composition between wild and cultivated rosehip, which could be attributed to genetic characteristics of studied varieties, applied agro-technical measures in rosehips cultivation (i.e. fertilization), and different uptake of certain nutrients from the soil, etc. Literature data demonstrated that the SO content and the biosynthesis of fatty acids in dragon's head plant were affected by fertilizer sources and fertilizer application method in combination with ecological factors (Mohammadghasemi et al., 2021).

3.3. Lipid indices and nutritional potential of rosehip seed oil samples

Nutritive recommendations given by WHO (World Health Organization)/FAO (Food and Agriculture Organization) (WHO Technical Report Series 916, 2003) indicate that higher UFAs relative to SFAs content are preferable in food. Besides, the presence of PUFAs in food or food supplements, the balanced intake of ω -3 and ω -6 FAs is very important (Ristić-Medić et al., 2013; Kostić et al., 2017). These FAs are metabolically and functionally specific, and often have antagonistic physiological effects (Simopoulos, 2016). Besides the proper and adequate intake of ω -3 and ω -6 FAs, the LA/ALA ratio in the diet is even more important as suggested by the World Health Organization report (Ristić-Medić et al., 2013). Calculated lipid indices of studied SO samples are given in Table 5.

UFA/SFA ratio - The results showed that UFAs were dominant in all samples, except samples 1SWO and 8SCO, where SFAs were found in higher percentage (Table 4). In that respect, results indicate favorable composition of studied rosehip SO samples. For the assessment of food or food supplements nutritional value, the ratio between unsaturated and saturated FAs is a good indicator and according to literature recommended ratio should be above 1.6 (Kostić et al., 2017). Most of studied rosehip seed oils had UFAs/SFAs ratio from 2.9 to 11.6, with the exception of samples 1SWO and 8SCO where the ratio was substantially lower (0.7) and sample 9SCO where it was close to the acceptable ratio value (1.4). The highest UFAs/SFAs ratio was observed for SO (7SCO) obtained from cultivated rosehip. This indicator showed favorable nutritional properties of SOs expressed through the fatty acid content.

ω -6/ ω -3 ratio - The great importance of the intake of ω -6 and ω -3 fatty acids is evident, but it is perhaps even more significant, in what

ratio ω -6/ ω -3 FAs are represented in daily nutrition. In human diet, during evolution, this ratio increased from 1:1–20:1, and higher, which contributed to the "obesity epidemic", and resulted in the frequency of diabetes, atherosclerosis and numerous inflammatory processes of the vascular system (Simopoulos, 2016). Since these essential fatty acids are not interconvertible, and exhibit different physiological and functional properties, it is clear that their well-balanced intake is necessary. Numerous studies have shown that health beneficiary ω -6/ ω -3 ratio is 1–2/1 (Simopoulos, 2016), while nutritional recommendation for French population allows the ration of 5/1 (AFSSA, 2001; Kostić et al., 2017). It is notable that the foods from wild edible plants and some vegetable oils contain a good balance of these essential FAs. It was observed that chicken food enriched with flaxseed and fishmeal lead to the substantial decrease in ω -6/ ω -3 ratio (Simopoulos, 2016). The ω -6/ ω -3 ratio (taking into account all detected FAs belonging to these classes) in most studied SO samples ranged from 2.9 (10SCO) to 8.0 (9SCO), indicating not very favorable balance of ω -6 and ω -3 FAs. Literature data on some wild *Rosa* spp. show that the ω 6: ω 3 ratio varies from 1.8:1–3.4:1 (Sharma et al., 2012). If only LA/ALA ratio is considered, then its values in studied samples were lower (2.2–6.7) (Table 5). Oil samples 2–5SWO and 10SCO could be considered as oils with quite fair balance of $\Sigma\omega$ -6 and $\Sigma\omega$ -3 as well as LA and ALA, according to French recommendations (AFSSA, 2001). In general, it is indicated that lowering the LA/ALA ratio in animals prevents overweight and obesity (Simopoulos, 2016).

Desirable fatty acids (DFA) - This indicator represents one of the health lipid indices (Barać et al., 2018), and for most studied samples (2–6SWO and 7SCO) it was over 75 %. Due to the low content of UFAs (40.94 %), the sample 8SCO was characterized with the most unfavorable DFA (47.24 %). On the other hand, the most favorable DFA value was obtained for the sample 7SCO (92.32 %), due to the highest content of UFAs (Tables 4 and 5).

4. Conclusions

This research provided new information on fatty acid characterization of rosehip seeds and relevant oils obtained from wild and cultivated rosehip grown in the Republic of Serbia. Raman spectra of studied seeds pointed out the complexity of natural matrix with certain differences observed between samples in spectral profiles. Based on the intensity of two most prominent bands associated to unsaturated fatty acids (\sim 1260 and \sim 1660 cm^{-1}) ANOVA revealed significant differences between the seeds, and samples 5SW and 10SC stood out. Differences in fatty acid profile observed between analyzed seed oil samples from rosehip collected in different locations were probably affected by agro-ecological conditions and genetic characteristics of studied rosehips. In most oil samples UFAs were the dominant acids, with linoleic, α -linolenic and oleic as the most abundant ones. Nutritional lipid indices (DFA, UFAs/SFAs, ω -6/ ω -3 and LA/ALA ratios) were favorable for most of studied oils, which could be useful in turning rosehip seeds from a food industry waste into a valuable source of bioactive compounds with health and nutrition benefits.

CRediT authorship contribution statement

Jelena Popović-Djordjević: Conceptualization, Resources, Writing

Table 5
Lipid indices in studies rosehip seed oil samples.

Sample	1SWO	2SWO	3SWO	4SWO	5SWO	6SWO	7SCO	8SCO	9SCO	10SCO
DFA (%)	52.42	75.45	88.15	85.60	77.55	86.64	92.32	47.24	57.57	74.43
Σ UFAs/ Σ SFAs	0.7	3.1	4.1	5.9	3.5	3.0	11.6	0.7	1.4	2.9
$\Sigma\omega$ -6/ $\Sigma\omega$ -3 ratio	/	4.6	4.1	3.4	4.9	/	7.5	/	8.0	2.9
LA/ALA	/	3.3	3.3	2.1	4.1	/	5.8	/	6.7	2.2

/- not calculated

– original draft, Writing – review & editing, Visualization, Supervision. **Bojana Špirović-Trifunović:** Formal analysis. **Ilinka Pećinar:** Software, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Luiz Fernando Cappa de Oliveira:** Data curation, Writing – review & editing, Supervision. **Đurđa Krstić:** Methodology, Validation, Formal analysis. **Dragana Mihajlović:** Investigation, Writing – original draft. **Milica Fotirić Akšić:** Investigation, Writing – original draft, Writing – review & editing. **Jesus Simal-Gandara:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request. The datasets supporting this article have been uploaded as part of the Supplementary Material.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.indcrop.2022.115797](https://doi.org/10.1016/j.indcrop.2022.115797).

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