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Assessment of the Nutritional Potential and Resistance to Oxidation of Sea Buckthorn and Rosehip Oils

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Featured Application: Cold-pressed oils provide valuable substances necessary for the proper development and functioning of the body. They are rich in essential unsaturated fatty acids, which cannot be synthesized by the organism. New oils intended for consumption, previously very popular in cosmetics, such as pressed from wild rose and sea buckthorn, are becoming more popular. By determining the potential nutritional properties, resistance to oxidation, and melting profile, it is possible to assess the processing suitability of oils.

Abstract: Cold-pressed oils from non-typical materials, such as wild rose and sea buckthorn, should meet certain requirements to be approved for consumption. The aim of this study was to evaluate the nutritional potential and selected quality parameters with particular emphasis on oxidative stability of two commercially available cold-pressed oils: rose hip oil and sea buckthorn oil. The fatty acid composition, including nutritional indexes (polyunsaturated fatty acid/saturated fatty acid ratio PUFA/SFA; atherogenicity index IA is as follows: hypocholesterolemic/hypercholesterolemic index HH; health-promoting index HPI), positional distribution of fatty acids, melting profile and oxidative stability were analyzed. The tested oils were characterized by a high content of unsaturated fatty acids, which were mainly represented by oleic and linoleic acids. In the case of one of the analyzed rosehip oil oils (R1), α-linolenic acid was also found at the level of 26%, which contributed to obtaining the recommended ratio of omega-6 to omega-3 fatty acids. The lowest value of IA and the highest values of HH and HPI were also recorded for R1 rosehip oil. This oil was also characterized by the highest resistance to oxidation, as indicated by induction times measured at various temperatures. The distribution of fatty acids in triacylglycerols molecules in the analyzed oils was typical for vegetable oils. In the case of tested oils, similar melting profiles with endothermic peaks recorded at negative temperatures, which resulted from the presence of triacylglycerol fractions with a high proportion of mono- and polyunsaturated fatty acids, were observed.

Keywords: rosehip oil; sea buckthorn oil; cold-pressed oils; oxidative stability; polyunsaturated fatty acids; health indexes; melting characteristic

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1. Introduction

Nowadays, consumers are increasingly choosing cold-pressed oils for their health-promoting properties and high nutritional value. Both refined and cold-pressed oils contain omega-3 and omega-6 fatty acids, but refined oils, depending on the degree of refining, contain fewer other bioactive substances: tocopherols, tocotrienols, sterols, carotenoids and chlorophylls, phospholipids and phenolic compounds [1]. Oils obtained from unconventional sources have gained popularity among consumers. New oils intended for consumption and previously very popular in cosmetics are rosehip and sea buckthorn oils.

The rose genus includes about 120–200 species that are widespread in Europe, Asia, the Middle East, and North America. *Rosa canina* L., known as 'Dog Rose', is considered a

valuable source of polyphenols and vitamin C [2]. Rosehips are a valuable ingredient in the preparation of functional foods, pharmaceuticals, and nutraceuticals due to the content of functional compounds, including vitamin C, phenolic compounds, minerals, essential fatty acids and carotenoids [3,4]. Rosehip seeds are a waste product in the production of juices and syrups. They contain from 4.9% to 17.82% oil, and due to their desirable composition, they are successfully used in the production of food and cosmetic oils [5]. Twenty-three fatty acids have been identified in cold-pressed rosehip oil with the largest share of the following fatty acids: linoleic (35.9–54.8%), α-linolenic (16.6–26.5%), oleic (14.7–22.1%). Saturated fatty acids are present in smaller amounts and represented by palmitic (3–5%), stearic (1.5–2.5%), and myristic (<0.5%) fatty acids [5,6]. Rosehip oil also contains phytosterols with a total content of 589.2–648.5 mg/100 g, mainly β-sitosterol (475.3–529.7 mg/100 g), campesterol (19.2–20.5 mg/100 g), stigmasterol (6.0–7.8 mg/100 g), Δ5-avenasterol (24.2–37.9 mg/100 g), Δ7-avenasterol (3.7–5.6 mg/100 g) [7].

Sea buckthorn (*Hippophae rhamnoides*) belongs to the olive family (*Elaeagnaceae*); it is found in Europe, Siberia, the Caucasus, and Asia. Sea buckthorn berries contain many biologically active substances such as vitamin C (87.45–149.37 mg/100 g, even 1004.85 mg/100 g, depending on the variety, place, and growing conditions), polyphenolic compounds—mainly flavonols (128.66–282.75 mg/100 g), carotenoids (7.94–28.16 mg/100 g to even 106.25–216.04 mg/100 g), phospholipids (123.40–181.16 mg/100 g), phytosterols (7.68–47.84 mg/100 g) and tocopherols (3.35–6.27 mg/100 g) [8]. Sea buckthorn contains 17–20% of oil in fruit, while in seeds, the content is approx. 10%, although in some varieties, it can reach up to 16%. The oil is the most important product currently obtained from sea buckthorn berries, it has the form of a thick, dark brown liquid, strongly coloring the skin, with a characteristic taste and aroma [9,10]. The seed oil contains more unsaturated fatty acids, sterols, vitamins K and E, and fewer carotenoids, tocopherols, and saturated fatty acids than fruit oil. The content of tocopherols in the sea buckthorn oil is 101–1128 mg/100 g of oil, mainly α-tocopherol, γ- and β-tocopherol. Sea buckthorn oil is a source of carotenoids with a total content of 314–2139 mg/100 g, among which 30% is γ-carotene, 20%—β-carotene, and 30%—lycopene [8].

The number of methods for determining the stability of edible oils and their resistance to oxidation is constantly increasing [11]. Some of the methods available make it possible to determine one or more oxidation reaction products. Color and fat values are widely used to assess the degree of oxidative degradation of fats: peroxide value (PV), which measures the concentration of hydroperoxides; anisidine value (LA), which is used to determine the level of secondary oxidation products, such as unsaturated ketones and aldehydes; acid value (AV), which indicates the content of free fatty acids, Rancimat index determined on the basis of conductometry [12]. These oil stability tests do not provide comprehensive information about the presence of the product in various oxidation states. Therefore, the assessment of oil resistance to oxidation determined by the concentration of peroxides or volatile products can be unclear [5]. Nowadays, there is an urgent need to apply thermoanalytical methods, e.g., differential scanning calorimetry (DSC), for testing the susceptibility of fats to oxidation. There are two basic techniques: isothermal, in which the sample is heated at a constant temperature, and dynamic, with a controlled temperature ramp [13]. In isothermal experiments, as a result of the reaction between unsaturated fatty acids and oxygen, oxidation induction times are recorded. In non-isothermal conditions, the starting and/or maximum temperature of the oxidation reaction, which occurs under the influence of oxygen or air, is determined [5,13].

The purpose of this research includes the evaluation of the nutritional potential and chosen quality parameters and resistance to oxidation of two cold-pressed oils: rosehip oil and sea buckthorn oil. The oxidative stability of oils was tested using the isothermal DSC method by determining the induction times and kinetic parameters of oxidation.

2. Materials and Methods

2.1. Materials

Commercially available rosehip (*Rosa canina* L.) cold-pressed oil (from two manufacturers, R1 and R2) and sea buckthorn (*Hippophae rhamnoides*) cold-pressed oil also from two manufacturers (B1 oil was pressed from seeds, B2 oil originated from pulp) were purchased in Poland in October 2022 directly from the oil manufacturer and stored at −20 °C until analysis. The analyses were performed at least in triplicate.

2.2. Acid Value and Peroxide Value Analysis

The acid value and peroxide value of oils were determined according to the ISO method [14,15] using the automatic titrator TitraLab AT1000 Series (Düsseldorf, Germany), equipped with a combined pH electrode for titrations in non-aqueous solutions (in acid value analysis) and combined electrode with a platinum ring for titration of ORP—oxidation–reduction potential (in peroxide value analysis).

2.3. Fatty Acid Profile

Fatty acids methyl esters were analyzed according to the ISO method [16] with the use of a YL6100 (Young Lin Bldg., Anyang, Hogyedong, Korea) gas chromatograph equipped with a flame ionization detector and a BPX-70 capillary column (SGE Analytical Science, Milton Keynes, UK). The procedure for analyzing fatty acid methyl esters has been described in previous studies [17]. Conditions used for the separation of methyl esters: initial temperature 70 °C, held for 0.5 min; temperature increase from 70 °C to 160 °C at a rate of 15 °C/1 min; temperature increase from 160 °C to 200 °C at a rate of 1.1 °C/1 min; temperature increase from 200 °C to 225 °C at a rate of 30 °C/1 min; final temperature 225 °C held for 1 min; injector temperature 225 °C, detector temperature 250 °C. The qualitative determination of individual fatty acids was made on the basis of a comparison of retention times with the standard, while the percentage content of individual fatty acids was determined on the basis of the areas of individual peaks in the chromatogram.

The nutritional indexes were calculated based on the results of fatty acid profile Equations (1)–(4).

Polyunsaturated fatty acid/saturated fatty acid ratio PUFA/SFA [18]:

$$\text{PUFA/SFA} = \sum\text{PUFA}/\sum\text{SFA} \quad (1)$$

Atherogenicity index IA [19]:

$$\text{IA} = [\text{C12:0} + (4 \times \text{C14:0}) + \text{C16:0}]/\Sigma\text{UFA} \quad (2)$$

Hypocholesterolemic/hypercholesterolemic index HH [20]:

$$\text{HH} = (\text{C18:1cis9} + \text{SPUFA})/(\text{C12:0} + \text{C14:0} + \text{C16:0}) \quad (3)$$

Health-promoting index HPI [21]:

$$\text{HPI} = \Sigma\text{UFA}/[\text{C12:0} + (4 \times \text{C14:0}) + \text{C16:0}] \quad (4)$$

2.4. Fatty Acid Positional Distribution

The study was conducted using pancreatic lipase, which hydrolyzes ester bonds in the external positions sn-1 and sn-3, assuming their equivalence. This enabled the determination of unhydrolyzed fatty acids located in the sn-2 position of triacylglycerols. The determination of fatty acids in the sn-2 position in the first stage involved the enzymatic deacylation of triacylglycerols. The procedure was described by Bryś et al. [22]. In the second step, preparative thin-layer chromatography was performed to separate the products obtained by enzymatic deacylation. The procedure of this part of the experiment was also

described in a previous publication by Bryś et al. [22]. The composition of fatty acids in the sn-2 monoacylglycerols obtained in this way was determined by gas chromatography.

2.5. DSC Measurements

The Q200 DSC (TA Instruments, Newcastle, DE, USA) was used to register melting profiles according to the procedure applied by Aguedo et al. [23] and Wirkowska-Wojdyła et al. [24]. Next, 3–4 mg of each oil was weighted into aluminum pans, which were hermetically closed. The reference sample was an empty measuring pan. Measurements were performed under the following conditions: nitrogen flow rate of 50 mL/min at normal pressure, the melted samples were heated to 80 °C and held at this temperature for 10 min. Then, the samples were cooled to −80 °C at a rate of 10 °C/min and kept at this temperature for 30 min. The samples were heated to 80 °C at a rate of 15 °C/min.

The Q20 DSC equipped with a pressure chamber (PDSC—pressure differential scanning calorimeter) was used to analyze oxidative stability according to the procedure described by Wirkowska-Wojdyła et al. [24]. Oil samples were oxidized in isothermal conditions at five different temperatures (100, 110, 120, 130, 140 °C) and under oxygen pressure of 1350–1400 kPa. Curves of heat flow versus oxidation time were obtained. From the curves, the time of reaching the maximum of the exotherm peak (induction time) was determined [25].

A graph of the logarithm of the induction time (τ) versus the reciprocal temperature (in absolute scale) was plotted. Equation (5) was used to determine regression lines:

$$\log \tau = a\, T^{-1} + b \quad (5)$$

where a and b are adjustable coefficients.

The activation energy of the oxidation process was calculated using the Ozawa–Flynn–Wall relationship Equation (6):

$$Ea = 2.19 \times R \times a \quad (6)$$

where R is the gas constant, and a is a coefficient from Equation (5).

2.6. Statistical Analysis

Experimental data were statistically analyzed using Statgraphics Plus software, version 4.1. (Statistical Graphics Corporation, Warrenton, VA, USA). Each determination was performed in triplicate. The results obtained were presented as mean ± standard deviation. Experimental data were analyzed by one-way analysis of variance (ANOVA). The significance of the differences was verified by Tukey's post hoc HSD test at the significance level $\alpha = 0.05$.

3. Results and Discussion

3.1. Nutritional Potential of Sea Buckthorn and Rosehip Oils

One of the basic quality features on the basis of which the nutritional value of fat can be determined is the composition of fatty acids.

Sea buckthorn seed oil B1 contained 87.71% of unsaturated fatty acids, mainly represented by linoleic acid (57.78%) and oleic acid (28.83%) (Table 1). The remaining unsaturated fatty acids were palmitoleic acid, α-linolenic acid, eicosenoic acid, and eicosatrienoic acid. The share of these acids did not exceed 1.5%. Saturated fatty acids determined at a level of 12.29% were mainly represented by palmitic acid (8.17%) and stearic acid (3.78%). The share of other saturated acids, such as myristic and arachidic acids, did not exceed 1%. The content of unsaturated fatty acids in sea buckthorn B2 oil was 79.21%, including 40.14% of linoleic acid, 23.19% of oleic acid, and 15.09% of palmitoleic acid. The analyzed oil contained 20.79% of saturated fatty acids, including 17.6% of palmitic acid and 2.64% of stearic acid. The analyzed oil also contained trace amounts of myristic and arachidic acids, not exceeding 1%. According to Zheng et al. [26], the content of fatty acids in sea buckthorn oils differed significantly depending on the part of the plant from which the oil was pressed.

The authors report that the palmitoleic, palmitic, and oleic acids were the dominating fatty acids in the pulp oils, whereas the linoleic and α-linolenic acids were the main ones in the seed oils. This may explain the differences in the content of fatty acids in the analyzed oils because B1 oil was pressed from seeds, while B2 oil was pressed from pulp. The observed differences mainly concern the content of linoleic, palmitic, and palmitoleic acids. B1 oil was characterized by approximately 18% higher linoleic acid content than B2 oil. B2 oil contained approximately twice as much saturated palmitic acid in comparison to B1 oil. Palmitoleic acid was also detected in the B2 oil in an amount of 15.09%, which is characteristic of oils obtained from the pulp [27]. In both tested oils similar contents of oleic and stearic acids were detected.

Table 1. Fatty acids composition (%) and health indexes of sea buckthorn and rosehip oils.

Type of Fatty Acid	Rosehip Oil R1	Rosehip Oil R2	Sea Buckthorn Oil B1	Sea Buckthorn Oil B2
C14:0	-	0.11 ± 0.03	0.14 ± 0.07	0.36 ± 0.11
C16:0	4.30 ± 1.03 ^{a}	7.28 ± 1.21 ^{b}	8.17 ± 1.32 ^{b}	17.60 ± 2.64 ^{c}
C16:1	0.13 ± 0.07	0.17 ± 0.02	0.29 ± 0.02	15.09 ± 1.38
C18:0	2.44 ± 0.38 ^{a}	4.56 ± 0.95 ^{b}	3.78 ± 0.63 ^{b}	2.64 ± 0.52 ^{a}
C18:1 cis	16.02 ± 1.68 ^{a}	24.99 ± 1.98 ^{b}	28.83 ± 1.92 ^{b}	23.19 ± 2.11 ^{b}
C18:2 n-6	49.37 ± 3.25 ^{a}	60.97 ± 2.87 ^{b}	57.78 ± 2.38 ^{b}	40.14 ± 2.68 ^{a}
C18:3 n-6	0.09 ± 0.01	0.02 ± 0.01	-	-
C18:3 n-3	26.02 ± 1.32 ^{c}	0.44 ± 0.12 ^{b}	0.11 ± 0.03 ^{a}	0.36 ± 0.12 ^{b}
C20:0	0.96 ± 0.30	0.35 ± 0.11	0.23 ± 0.09	0.19 ± 0.08
C20:1	0.39 ± 0.11	0.23 ± 0.10	0.13 ± 0.05	0.09 ± 0.03
C20:2	0.15 ± 0.06	0.02 ± 0.01	-	-
C20:3	0.14 ± 0.07	0.84 ± 0.24	0.54 ± 0.11	0.35 ± 0.10
SFA	7.70 ± 1.71 ^{a}	12.30 ± 2.30 ^{b}	12.32 ± 2.11 ^{b}	20.79 ± 3.35 ^{c}
MUFA	16.54 ± 1.85 ^{a}	25.39 ± 2.10 ^{b}	29.25 ± 1.99 ^{b}	38.37 ± 3.52 ^{c}
PUFA	75.77 ± 4.71 ^{c}	62.29 ± 3.25 ^{b}	58.43 ± 2.52 ^{b}	40.85 ± 2.90 ^{a}
PUFA/SFA	9.840	5.064	4.743	1.965
IA	0.047	0.088	0.100	0.240
HH	21.347	11.811	10.501	3.566
HPI	21.467	11.358	10.044	4.161

Data denoted by the same letter are not statistically different (α = 0.05). SFA—saturated fatty acids; MUFA—monounsaturated fatty acids; PUFA—polyunsaturated fatty acids. IA—atherogenicity index; HH—hypocholesterolemic/hypercholesterolemic index; HPI—health-promoting index.

Rosehip oil R1 was rich in unsaturated fatty acids, the content of which was 92.3% of all fatty acids, including 75.5% of polyenic acids (Table 1). The dominant unsaturated fatty acids in this oil were linoleic acid (49.37%), α-linolenic acid (26.02%), and oleic acid (16.02%). Among saturated fatty acids, the most abundant were palmitic acid—4.3%, stearic acid—2.44%, and arachidic acid—approximately 1%. The content of other fatty acids was as follows: palmitoleic, γ-linolenic, eicosenoic, eicosadienoic, and eicosatrienoic fatty acids did not exceed 1%. R2 rosehip oil was also rich in unsaturated fatty acids, which constituted 87.64% of all fatty acids, including 60.97% of linoleic acid. The second unsaturated fatty acid with the highest share was oleic acid (24.99%). The remaining unsaturated fatty acids: palmitoleic, margaroleic, γ-linolenic, α-linolenic, eicosenoic, eicosadienoic, and eicosatrienoic acids accounted for a total of approximately 2%. Saturated fatty acids accounted for 12.36%. The analyzed rosehip oils were characterized by a similar total content of unsaturated acids, but they differ in the content of individual fatty acids. R1 oil contained a significantly higher amount of α-linolenic acid (26.02%), while R2 oil contained only 0.44% of this acid. It was also noticed that R2 oil was characterized by a significantly higher content of linoleic acid. The obtained results only for R1 oil correspond to those obtained by Grajzer et al. [5]. The authors determined the content of unsaturated fatty acids at the level of 89.7–91.5%, including the content of linoleic acid (44.4–51.7%), α-linolenic acid (21.5–31.8%) and oleic acid (14.7–16.3%).

In order to provide a more complete characterization of the analyzed oils, nutritional indexes indicating possible health-promoting properties were calculated. PUFA/SFA is an indicator typically used to study the influence of fats/oils on cardiovascular disease. A lower ratio of PUFA/SFA might correspond to a negative effect. Rosehip oil R1 was characterized by the highest PUFA/SFA index (9.840), while in rosehip oil R2 and sea buckthorn B1 oil, this index reached the levels of 5.064 and 4.743, respectively, which was similar to that in sunflower oil (4.75–4.94) [18]. This index for sea buckthorn oil B2 was similar to some red seaweeds (*Gracilaria dura*, *Gracilaria corticata*, *Sarconema filiforme*) [18]. Since n-6 and n-3 fatty acids have different effects on cardiovascular diseases, the PUFA/SFA index may be insufficient to assess the nutritional value of fats. The recommended ratio of n-3/n-6 PUFA (1:2 and 1:5) has anti-inflammatory effects, while a high ratio of n-6 to n-3 acids (even 20:1) demonstrates a negative effect on the body's lipid metabolism [28]. Among the tested oils, only rosehip oil R1 met these recommendations with the n-6 to n-3 ratio 1.9:1. Atherogenicity index (IA) indicates a relationship between the sum of pro-atherosclerotic SFAs and the sum of unsaturated acids, considered as anti-atherogenic, inhibiting the accumulation of atherosclerotic plaque and lowering the level of phospholipids and cholesterol [29]. Therefore, consuming foods or products with a lower IA index can reduce the levels of total cholesterol and LDL in human blood plasma [30]. IA in R1 (0.047) and R2 (0.088) oils were at a similar level as in linseed oil [31], sunflower oil [17], and strawberry seed oil [31]. In B1 and B2 oils, this index was at a similar level as in blackcurrant seed oil [32], guar seed oil [33], and oil from fish (*Hemiramphus brasiliensis*, *Hyporhamphus unifasciatus*) [34]. Another index, HH, characterizes the relationship between hypocholesterolemic fatty acids (cis-C18:1 and PUFA) and hypercholesterolemic fatty acids (C12:0, C14:0, and C16:0). Compared to the PUFA/SFA index, the HH ratio can more accurately reflect the influence of fatty acids on cardiovascular diseases. The calculated index for the tested R1, R2, and B1 oils indicated the health-promoting properties of these oils comparable to linseed oil [31], strawberry seed oil, cranberry seed oil, and blackcurrant seed oil [32]. B2 oil was characterized by the lowest HH index value (3.566). The calculated index was close to the HH index characterizing some shellfish (*Cervimunida johni, Pleuroncodes monodon*) and was higher than the HH index of most fish [35]. The last indicator that was calculated based on the composition of individual fatty acids was the health-promoting index, currently used to compare dairy products [21]. Generally, products with a high HPI value are considered to be more beneficial to human health. It is worth emphasis that the values of HPI for analyzed oils (4.161–21.467) were higher compared to dairy products, where for which the value of this indicator reached 0.16–0.68 [18].

The properties of fat are influenced not only by the composition of fatty acids but also by their distribution of acids in triacylglycerol molecules. Vegetable fats may contain various fatty acids, which may occupy different positions in triacylglycerols—external (sn-1 or sn-3) or internal (sn-2). The sn-1,2,3 positions are not equal and have different distributions depending on the type of oil. The most beneficial from the nutritional point of view and bioavailability is the distribution of fatty acids in the sn-2 location because they are intact at all stages of digestion [36]. Figure 1 shows the distribution of selected fatty acids in the sn-2 position of triacylglycerol molecules of the tested sea buckthorn and rosehip oils.

It was found that the external TAG positions in rosehip oil R1 were occupied by saturated acids—palmitic and stearic acids (from 73–77%). Polyunsaturated α-linolenic acid was also present in a large share of 74% in these positions. The distribution of linoleic acid in the TAG molecule was practically equal: 34.2% in the sn-2 position and 65.8% in the sn-1 and 3 positions. Oleic acid mainly occupied the internal sn-2 position, where its share was 43.02%. In rosehip oil R2, the highest share in external positions was determined in the case of saturated acids—palmitic and stearic acids (from 82% to 88%). The distribution of unsaturated oleic and linoleic fatty acids in the internal and external positions was practically equal. Sea buckthorn oils were characterized by a similar distribution of saturated fatty acids as rosehip oils, i.e., these acids were esterified mainly in

the external positions of triacylglycerols. Unsaturated oleic acid was located mainly in the internal position. 36.13% and 38.91% of this acid was in the sn-2 position in oils R1 and R2, respectively. Polyunsaturated linoleic acid in R2 oil was also esterified primarily in the sn-2 position, while in R1 oil, the distribution of this acid between all triacylglycerol positions was equal. These results correspond to the studies of other vegetable oils obtained from non-typical sources. Górska et al. [32] found that in strawberry, cranberry, and blackcurrant seed oils, saturated fatty acids were esterified in external positions, while oleic and linoleic acids tended to occupy internal TAG positions.

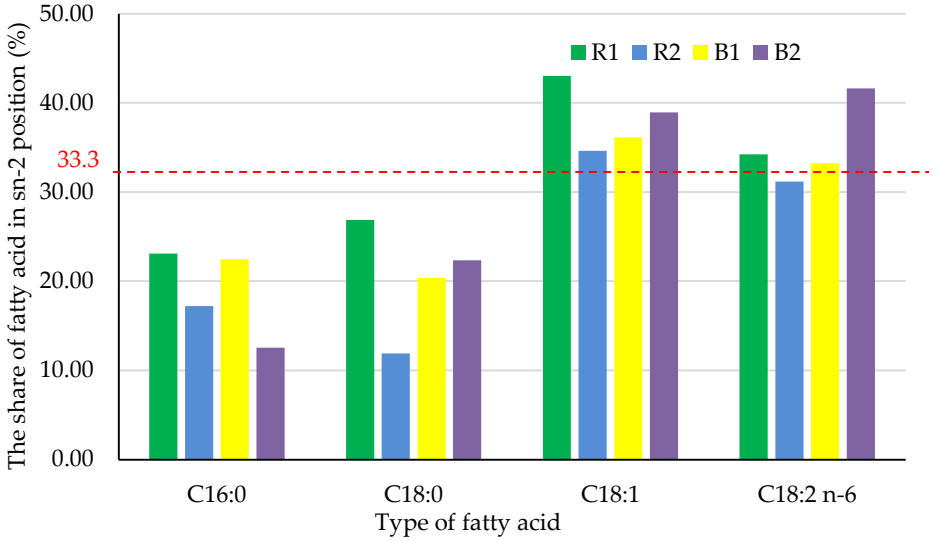


Figure 1. The distribution of selected fatty acids (palmitic, stearic, oleic, linoleic) in the sn-2 position of triacylglycerols molecules of sea buckthorn and rosehip oils.

3.2. Melting Profiles of Sea Buckthorn and Rosehip Oils

The fatty acid composition may also influence the melting profiles of the fats. Melting profiles of sea buckthorn and rosehip oils are shown in Figures 2 and 3, respectively. Two endothermic peaks were recorded on the melting curves of sea buckthorn oils at temperatures −37.05 °C and −26.76 °C for B2 oil and −36.55 °C and −24.71 °C for B1 oil. For sea buckthorn oil B2, an additional distinct peak was recorded at a temperature of −8.57 °C because this oil contained over 8 percentage points more saturated fatty acids and 17 percentage points less polyunsaturated fatty acids than sea buckthorn oil B1. On the melting curve of rosehip oil R1, one peak was observed with a maximum at a temperature of −37.75 °C, while in rosehip oil R2, two peaks were recorded with a maximum at a temperature of −38.05 °C and −29.5 °C. Rosehip oil R2 was characterized by a higher content of saturated acids and a lower content of polyunsaturated α-linolenic acid, which may affect the occurrence of the second peak. Generally, the analyzed oils were characterized by the presence of endothermic peaks at low temperatures [24,37]. This corresponded to the triacylglycerol fraction with a high share of mono- and polyunsaturated fatty acids, which were confirmed by the chromatographic analysis of the oils. Górska et al. [32], in the studies on the properties of the lipid fraction obtained from strawberry, cranberry, and blackcurrant seeds, also observed the occurrence of endothermic peaks at low temperatures related to the melting of triacylglycerols containing mainly polyunsaturated fatty acids.

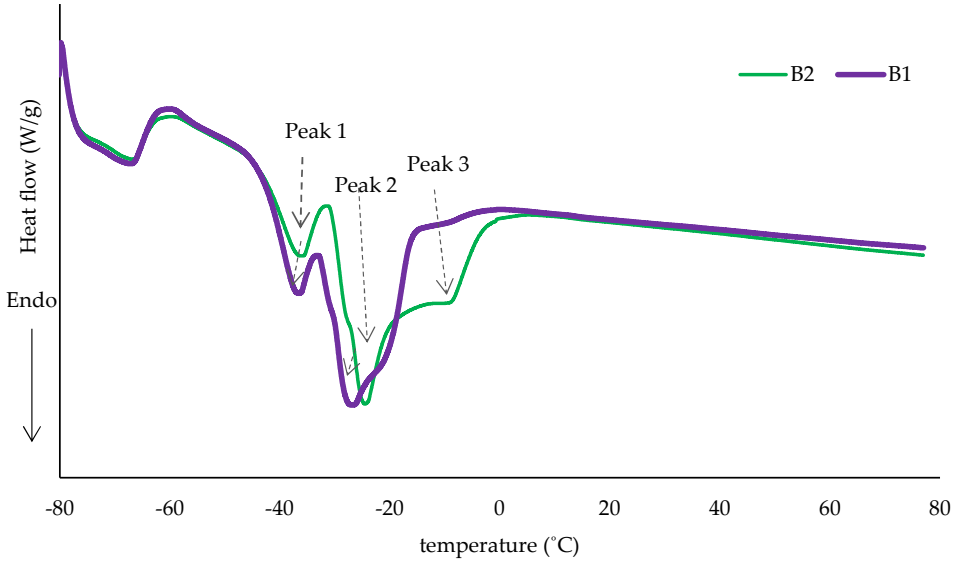


Figure 2. DSC melting profile of sea buckthorn oils.

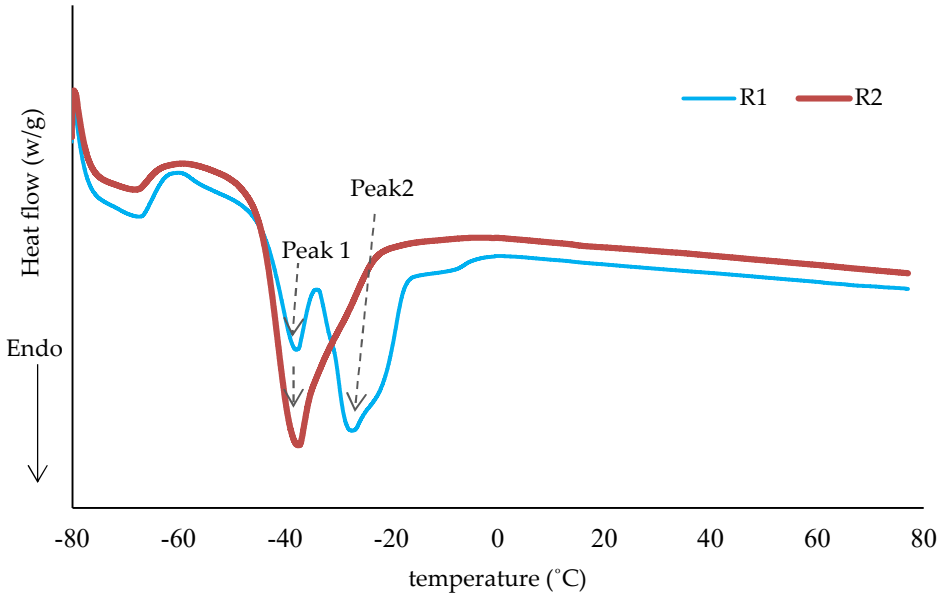


Figure 3. DSC melting profile of rosehip oils.

3.3. Oxidative Stability of Sea Buckthorn and Rose Hip Oils

The PDSC induction times recorded for sea buckthorn and rosehip oils are shown in Table 2. Rosehip oil R1 was characterized by a statistically longer induction time at each measurement temperature than rosehip oil R2. In the case of R2 rosehip oil, which contained over 20 percentage points less α-linoleic acid, a shorter induction time was recorded in comparison to R1 oil. The longer induction time of rosehip oil R1 corresponded to the level of the peroxide value, which determined the content of primary oxidation products. The peroxide value was determined at a lower level in the case of R1 oil (2.04 meq O_2/kg) compared to R2 oil (3.21 meq O_2/kg) (Table 2), but in general, in both oils, it did not exceed the value of 15 meq O_2/kg, as specified in Codex Alimentarius for cold-pressed oils [38]. Grajzer et al. [39] recorded the peroxide value in rosehip oil at the level of 1.24 meq O_2/kg, which indicated that this oil was characterized by a lower content of primary oxidation products than the analyzed R1 and R2 oils. The lower induction time of R2 oil could also be influenced by the content of free fatty acids, measured by the acid value. Free fatty

acids formed during the hydrolysis of ester bonds in triacylglycerol molecules may induce oxidation reactions [40] because they oxidize faster than acylated fatty acids due to the prooxidant effect of free carboxylic groups [5]. Rosehip R2 oil was characterized by an acid value almost 11 times higher than R1 oil (Table 2).

Table 2. Induction time at temperatures 100, 110, 120, 130, and 140 °C; acid value and peroxide value of sea buckthorn and rosehip oils.

Parameter	Rosehip Oil R1	Rosehip Oil R2	Sea Buckthorn Oil B1	Sea Buckthorn Oil B2
AV (mg KOH/g of fat)	0.26 ± 0.09^{a}	2.91 ± 0.84^{c}	1.00 ± 0.32^{b}	1.50 ± 0.29^{b}
PV (meq O_2/kg of fat)	2.04 ± 0.32^{a}	3.21 ± 0.43^{b}	5.21 ± 0.54^{c}	4.01 ± 0.35^{b}
Induction time at 100 °C (min)	203.36 ± 13.98^{c}	137.61 ± 6.10^{b}	80.36 ± 0.73^{a}	149.12 ± 1.95^{b}
Induction time at 110 °C (min)	88.42 ± 0.91^{c}	56.35 ± 0.23^{b}	36.52 ± 1.86^{a}	71.20 ± 1.67^{d}
Induction time at 120 °C (min)	40.58 ± 2.50^{c}	24.45 ± 1.77^{b}	17.81 ± 1.44^{a}	36.56 ± 3.51^{c}
Induction time at 130 °C (min)	19.32 ± 1.43^{b}	10.85 ± 0.30^{a}	8.65 ± 1.48^{a}	17.57 ± 1.41^{b}
Induction time at 140 °C (min)	8.96 ± 0.77^{b}	4.07 ± 0.27^{a}	3.60 ± 0.46^{a}	8.40 ± 0.87^{b}

Data denoted by the same letter are not statistically different ($\alpha = 0.05$).

In the case of sea buckthorn oil, the influence of polyunsaturated fatty acid content on oxidative stability has been found. Sea buckthorn oil B2, with a lower content of polyunsaturated fatty acids, was characterized by longer induction times at each measurement temperature compared to sea buckthorn oil B1, with shorter induction times (Table 2) and a higher content of polyunsaturated fatty acids. The degree of hydrolysis of ester bonds in the analyzed sea buckthorn oils did not affect the induction times because sea buckthorn oils were characterized by similar levels of acid value (no statistically significant differences were found) (Table 2). The peroxide value for sea buckthorn oil B1 was about 1.3 times higher than for oil B2 (Table 2). In both B1 and B2 oils, the peroxide value did not exceed the value of 15 meq O_2/kg specified by Codex Alimentarius [38]. The oxidative stability of sea buckthorn oils may be influenced by the content of bioactive compounds such as flavonoids, carotenoids, and polyphenols [27]. According to Zheng et al. [26], sea buckthorn oil obtained from fruit pulp contained more flavonoids, carotenoids, and polyphenols than oil obtained from seeds. The authors determined the content of flavonoids in the sea buckthorn pulp oil and seeds oil at the level of 9.54–14.18 mg quercetin equivalents/100 g and 4.11–4.58 mg QE/100 g, respectively. The carotenoid content reached 70.2–104.6 mg/100g for sea buckthorn pulp oil and 15.1–15.4 mg/100g for sea buckthorn seeds oil, and the total polyphenols—129.3–170.1 mg GAE/kg oil for sea buckthorn pulp oil and 86.9–90.1 mg GAE/kg oil for sea buckthorn seeds oil. Differences in the content of these compounds may explain the higher oxidative stability of B2 oil pressed from pulp compared to B1 oil pressed from seeds. Zheng et al. also reported that pulp oils showed better oxidative stability than seed oils [26].

Based on the induction times recorded at five measurement temperatures (100, 110, 120, 130, and 140 °C), the activation energy of the oxidation reactions of the tested rosehip and sea buckthorn oils was determined. Based on the kinetic parameters of the oxidation reaction, it was possible to determine the processing suitability of oils. Figures 4 and 5 show a graphical relationship between the logarithm of the induction time and the reciprocal of the measurement temperatures of sea buckthorn and rosehip oils, respectively. Table 3 presents the activation energy and adjustable coefficients for the oxidation reaction of sea buckthorn and rosehip oils.

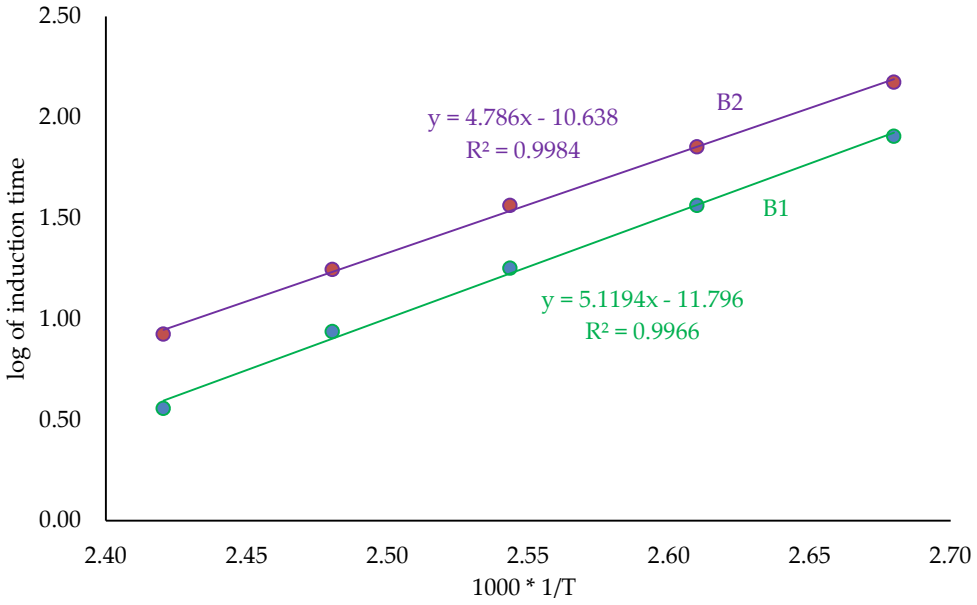


Figure 4. Log induction time versus reciprocal oxidation temperature of sea buckthorn oils.

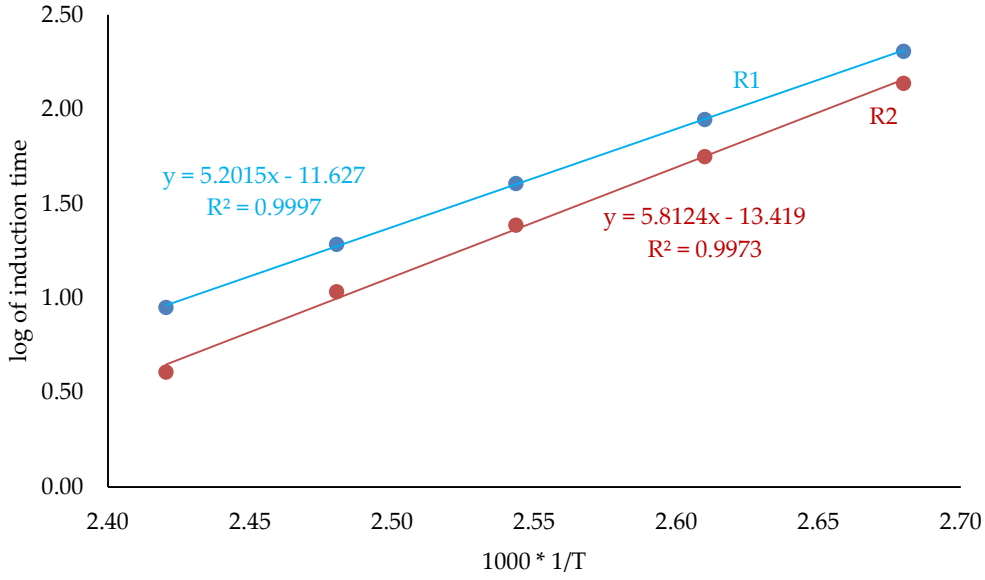


Figure 5. Log induction time versus reciprocal oxidation temperature of rosehip oils.

Table 3. Adjustable coefficients and activation energy of oxidation reaction of sea buckthorn and rosehip oils.

Parameters	Rosehip Oil R1	Rosehip Oil R2	Sea Buckthorn Oil B1	Sea Buckthorn Oil B2
a	5.2015 ± 0.06 ^{b}	5.8124 ± 0.16 ^{b}	5.1194 ± 0.24 ^{b}	4.786 ± 0.20 ^{a}
b	11.627 ± 0.19 ^{b}	13.419 ± 0.41 ^{c}	11.796 ± 0.65 ^{b}	10.638 ± 0.53 ^{a}
R^2	0.999	0.997	0.996	0.998
Ea (kJ/mol)	94.74 ± 1.17 ^{b}	105.85 ± 2.93 ^{c}	93.93 ± 4.41 ^{b}	87.23 ± 3.58 ^{a}

Data denoted by the same letter are not statistically different (α = 0.05).

Data from this equation describing the linear relationship were the starting point for calculating the activation energy of the analyzed rosehip and sea buckthorn oils. The activation energy of an oxidation reaction is defined as the smallest amount of energy

necessary to initiate oxidation processes in a molecule. The activation energy was at the level of 87.23–93.93 kJ/mol in sea buckthorn oil and 94.74–105.85 kJ/mol in rosehip oil. Although rosehip oil R1 and sea buckthorn oil B2 were characterized by longer induction times, lower values of activation energy were determined for these oils compared to oils R2 and B1, for which lower values of induction times and higher values of activation energy were recorded. A similar tendency was observed by Grajzer et al. [5] in a study on rosehip oil, stating that fatty acid composition strongly affected the activation energy of oils. Moreover, the authors concluded that Ea determined for a single MUFA (e.g., oleic acid) was much higher than for PUFA. This may explain the higher activation energy for rosehip oil R2 with a higher share of monounsaturated fatty acids compared to oil R1, for which a lower activation energy and a lower share of monounsaturated fatty acids were recorded. No such relationship was found for sea buckthorn oils.

4. Conclusions

Food analysis is currently a big challenge for laboratories and institutions controlling the safety and quality of food products in order to meet the increasing demands of consumers. Consumers are eager to buy products that they believe are beneficial from a nutritional point of view but may pose a threat to a balanced diet. For this reason, scientific research is conducted to assess the quality and nutritional potential of various product groups.

R1 rosehip oil turned out to be the most valuable in terms of fatty acid composition and health indexes. It was characterized by the lowest share of saturated fatty acids and the highest share of polyunsaturated fatty acids (including alpha-linolenic acid). Additionally, the share of n-3 to n-6 fatty acids was in line with current nutritional recommendations. In the case of this oil, the lowest AI and the highest HH and HPI were observed. Due to the above characteristics, it is worth considering including this oil in the diet. This oil turned out to be the most resistant to oxidation, as indicated by the induction time values. However, sea buckthorn oil B2 pressed from pulp, with a high content of unsaturated fatty acids, was characterized by the least favorable nutritional parameters. The consumption of oils characterized by a high ratio of n-6 to n-3 acids can influence the occurrence of many cardiovascular diseases. It is worth emphasizing that oils pressed from non-typical materials should be subjected to detailed tests, including not only fatty acids composition but also nutritional indexes, fatty acids distribution in triacylglycerol molecules, and oxidative stability before being approved for consumption.

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