

Article

Berry Seeds—A By-Product of the Fruit Industry as a Source of Oils with Beneficial Nutritional Characteristics

Agata Górka * , Iga Piasecka , Magdalena Wirkowska-Wojdyła , Joanna Bryś , Kinga Kienc, Rita Brzezińska and Ewa Ostrowska-Ligeza 

Department of Chemistry, Institute of Food Sciences, Warsaw University of Life Sciences, 166 Nowoursynowska Str., 02-787 Warsaw, Poland

* Correspondence: agata_gorska@sggw.edu.pl; Tel.: +48-22-5937611

Featured Application: By-products of the fruit industry such as fruit seeds can be considered as a source of valuable nutrients that should be regained and reused in processing. Berry seed oils with favorable nutritional characteristics, including the composition and distribution of confirmed beneficial fatty acids in triacylglycerol structure, oxidative stability, melting profile and health indices that meet the requirements to be allowed for human consumption, may have applications in the food industry by reintegration into the production chain, which is in agreement with EU politics of circular economy and sustainable development.

Abstract: Proper management of waste is one of the major challenges for the food industry. Fruit seeds are an example of by-products that are rich in bioactive substances and generated in significant amounts during fruit processing. Oils, including those obtained from seeds, should meet certain requirements to be allowed for human consumption. The aim of this study was to determine the quality of oils from black currant, strawberry and cranberry seeds by determining the following parameters: fatty acid composition by gas chromatography, distribution of fatty acids between sn-2 and sn-1,3 positions of triacylglycerols by partial enzymatic hydrolysis, oxidative stability by pressure differential scanning calorimetry and melting characteristics by differential scanning calorimetry. Additionally, health indices of atherogenicity (IA), thrombogenicity (IT) and hypocholesterolemic/hypercholesterolemic (HH) ratio were calculated. It was found that the oils studied were a rich source of unsaturated fatty acids. Linoleic acid was found to occupy the internal position of triacylglycerols in the highest proportion. Black currant and strawberry seed oils were of lower oxidative stability and, in the case of cranberry seed oil, high oxidative stability was determined. The shape of melting curves for black currant and strawberry seed oils indicated the presence of low-melting fractions of triacylglycerols containing polyunsaturated fatty acids. It can be concluded that cranberry seed oil, with low values of IA and IT, high values of HH index and the highest oxidative stability, can be considered the most favorable from a nutritional point of view concerning human health.

Keywords: black currant seed oil; strawberry seed oil; cranberry seed oil; quality assessment; fatty acid composition; fatty acid distribution; oxidative stability; melting profile; health indices



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1. Introduction

In 2012, the European Commission (EC) adopted a strategy aimed at counteracting the conflict between ensuring food security and the use of renewable resources, entitled “Innovation in the service of sustainable growth: the bioeconomy for Europe”. The document was updated by the EC in 2023 in the form of an analysis of the drivers of food security [1]. Taking into account the growing number of people requiring food, the demographics of societies, progressing climate change and loss of biodiversity, as well as the previously irresponsible management of natural resources, the idea of an innovative bioeconomy was

born. This term covers the sectors of the national economy, including food, pharmaceutical, agriculture, energy and many other industries, using biomass. Biomass refers to renewable resources of biological origin that can be included in processing. In this way, bio-waste can be transformed into a value-added bio-product which can be food, feed or bioenergy. Proper management of waste generated during food production and processing is currently a major challenge for the food industry. The concept of a closed-loop supply chain in the configuration of internal recycling is becoming more and more popular, i.e., a food producer includes its own waste as a raw material for further production, internally or externally. For example: an entity producing cured meats sells waste in the form of animal bones and organs to an entity producing feed, cosmetics or pharmaceuticals [2–4].

Fruit and vegetable processing generates large amounts of waste in the form of unused raw material. Due to the perishable nature of fruit and vegetables, tons of bruised, damaged and rotting raw material are discarded. In the fruit industry, many tons of waste in the form of seeds are generated each year, for example during the processing of cherries, because seeds can constitute up to 15% of the fruit weight. It is important to consider that by-products of the fruit processing industry can be a source of biologically active substances that can be isolated and reused, which is in agreement with the EU politics of circular economy and sustainable development. In many studies, researchers have confirmed the presence of bioactive substances in by-products of the fruit industry. The content of lignins and cellulose qualifies cherry seeds as a raw material for the production of activated carbon, which is used in the wine industry to remove ochratoxin A [5]. The hulls can be added to pig feed, enriching it with fiber and minerals. They can also be used as a filler in children's toys or microwave-responsive hot water bottles. In the cosmetics industry, they can be applied as an ingredient for mechanical exfoliation of the epidermis and for the production of oil with anti-wrinkle properties. Raspberry seed oil, with anti-inflammatory properties, was patented in 1973 and was used in the prevention of gingivitis, eczema and various types of rashes. The patent also mentions its use as an ingredient in shampoos, antiperspirants, lipsticks, toothpastes and after shave lotions [6]. Peach kernel oil is characterized by a low content of saturated fatty acids (approximately 10%) and a high content of linoleic acid, oleic acid and vitamins A and E, which makes it a material of interest in the cosmetics industry. The cake, which is a residue after pressing the oil, is rich in amygdalin and emulsin, i.e., an enzyme that hydrolyzes this glycoside under specific conditions. The reaction product, benzaldehyde, can be distilled off and used as a raw material in the production of the known fragrance cinnamaldehyde. The amygdalin-free cake can then become a high-protein feed with a quality similar to that of linseed or rapeseed cake. On the other hand, apart from pressing the oil, the kernels of the seeds can be reused by the confectionery industry as a raw material for the production of peripan mass [7]. Fruit pomace, e.g., from chokeberry, rosehip, blackcurrant or strawberries, can be used as an ingredient in fruit teas to impart antioxidant properties to the composition. In confectionery products, the addition of expeller can successfully provide a source of precious fiber. Apple pomace, due to its chemical composition, is a good breeding ground for lactic bacteria. Helbig et al. [8] indicate that even the extraction meal, i.e., blackcurrant seeds after pressing the oil, contained valuable ingredients. Researchers identified essential amino acids, iron and fiber in amounts similar to that of fresh pomace.

Black currant seeds, which are the primary waste when obtaining juice from these fruits, consist of approximately 20.3% protein, 55.8% carbohydrates, 1.6% minerals and 14.8% valuable fat. The fatty acids present in the oil are mainly unsaturated: 73.6% are polyunsaturated and 17.3% are monounsaturated. Among polyunsaturated fatty acids, linoleic acid constitutes as much as 47.8% [9]. Black currant seed oil, compared to oils obtained from red currant or gooseberry seeds, is characterized by the highest content of vitamin E, i.e., 1716 mg/kg. At the same time, it contains the most alpha-tocopherol (34.8% of detected tocopherols), which is the most active among the tocopherols [10]. Supplementation with black currant seed oil, according to Tahvonon et al. [11], reduces the level of LDL cholesterol more effectively than supplementation of the most famous fish oil.

Strawberry seeds can consist of up to 20% fat in dry matter. The oil obtained from them is characterized by a high content of polyenic (74.5%) and monoenoic (17.9%) fatty acids. Among them, three main fatty acids can be distinguished: linoleic acid, which constitutes approximately 40% of total fatty acids, alpha-linolenic acid—approximately 34%—and oleic acid—approximately 17%. It should be noted that the high content of alpha-linolenic acid makes this oil a unique source of valuable omega-3 acids [12]. Pieszka et al. [13] detected a significant amount of gamma-tocopherol, i.e., approximately 49 mg/100 g, small amounts of other tocopherol isoforms and trace amounts of tocotrienols in strawberry seed oil.

Cranberry seed oil contains approximately 30–35% alpha-linolenic acid, 35–40% linoleic acid and 20–25% oleic acid. Compared to oils from conventional raw materials, it is therefore characterized by a unique share of omega-3, omega-6 and omega-9 fatty acids [14]. Due to its composition, cranberry seed oil can be potentially used both in the food industry and in the pharmaceutical, cosmetics or perfumery industries. It contains a particularly high content of beta-sitosterol, which is a factor that lowers the content of lipoproteins in the blood; the presence of campesterol and stigmasterol has also been confirmed. It can be used in the treatment of eczema and rashes and the production of face creams, bath oils, toothpastes, hair products and antiperspirants. Yu et al. [15] also noted the impressive ability of cranberry seed oil to chelate Fe^{2+} ions. Metals can act as catalysts in food oxidation reactions, and chelating agents prevent these chain reactions. Cranberry seed oil contains 0.341 g/100 g of alpha-tocopherol and 0.110 g/100 g of gamma-tocopherol [16]. It should be noted that gamma-tocotrienol (1.235–1.50 g/100 g) is the dominant tocochromanol, which is unique compared to other oils obtained from fruit seeds [14].

The present study aimed to accurately evaluate the quality of black currant, cranberry and strawberry seed oils, including important parameters such as: composition and distribution of fatty acids in triacylglycerol structure, oxidative stability and melting profile. Additionally, health indices of atherogenicity, thrombogenicity and hypocholesterolemic/hypercholesterolemic ratio were assessed to provide information on the impact of fatty acids present in oils on human health, regarding the risk of atherosclerosis and the likelihood of blood clots, atheroma and thrombus occurrence. Such thorough analysis will be helpful in defining the potential of applying black currant, cranberry and strawberry seed oils in food, cosmetics and pharmaceutical industries.

2. Materials and Methods

2.1. Materials

The research material consisted of oils obtained by extraction with an organic solvent (hexane) using the Soxhlet apparatus from seeds:

- black currant (*Ribes nigrum* L.);
- strawberries (*Fragaria* L.);
- cranberries (*Vaccinium macrocarpon*).

The seeds, presented in Figure 1, were purchased in local eco shops.

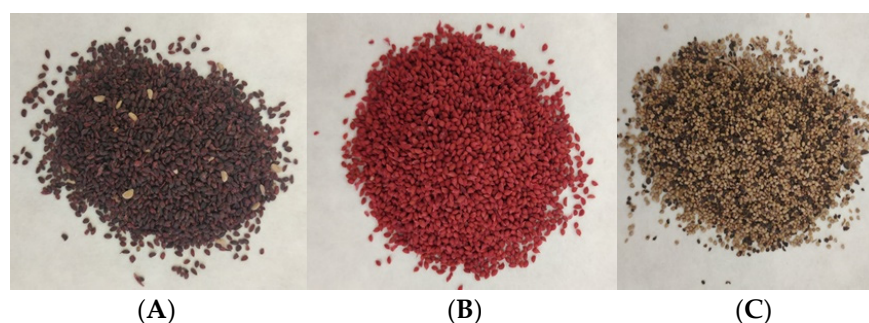


Figure 1. Black currant (A), cranberry (B) and strawberry (C) seeds.

2.2. Methods

2.2.1. Oil Extraction from Black Currant, Cranberry and Strawberry Seeds

In order to obtain the oils by hexane extraction using a Soxhlet apparatus, 10 g (± 0.001 g) of seeds were weighed on an analytical balance and ground in an IKA Tube Mill (IKA Works GmbH & Co. KG, Staufen, Germany) control with a speed of 10,000 rpm. The seeds crushed in this way were transferred to a thimble which was placed in a Soxhlet apparatus. Hexane (150 mL) was added to the round-bottom flask. Multiple extraction was carried out to obtain 30 overflows in the apparatus in accordance with PN-EN ISO 659:2010 [17]. The obtained extracts were dried with anhydrous magnesium sulfate, which was then filtered off. The solvent was distilled off using a Buchi Rotavapor R-210 vacuum evaporator. Hexane residues from the samples were removed under a nitrogen atmosphere.

2.2.2. Determination of the Fatty Acid Composition of Oils by Gas Chromatography

In order to determine the fatty acid composition by gas chromatography, fatty acids were converted to volatile methyl esters in accordance with PN-EN ISO 5509:2001 [18]. The gas chromatography apparatus YL6100 GC equipped with a flame ionization detector (FID) and a BPX 79 capillary column (filled with stationary phase, length 30 m, internal diameter 0.22 mm, film thickness 0.25 μ m) was used. Nitrogen was applied as the carrier gas. The following conditions were used: starting temperature 70 °C/0.5 min; then increasing the temperature from 70 °C to 160 °C at a rate of 15 °C/min; temperature rise from 160 °C to 200 °C at a rate of 1.1 °C/min; 200 °C/12 min; temperature rise from 200 °C to 225 °C at a rate of 30 °C/1 min; end temperature 225 °C/1 min. The detector temperature was 250 °C and the injector temperature was 225 °C. The fatty acids were then identified by comparing the retention times with FAME standard (Supelco 37 Component FAME Mix). For the quantitative analysis of fatty acids, the peak area in the chromatogram was determined and the percentage of a given acid was calculated [19]. The determinations were conducted in 3 replications.

2.2.3. Determination of the Distribution of Fatty Acids between the sn-2 and sn-1,3 Positions of Triacylglycerols by Enzymatic Hydrolysis

In order to determine the structure of triacylglycerols, the method of partial hydrolysis of triacylglycerols with pancreatic lipase was used. For this purpose, 0.1 g of the tested oil was weighed, and then the following were added: 8 cm³ of TRIS-HCl solution with concentration of 1 mol/dm³, pH = 8; 0.5 cm³ of 2.2% CaCl₂ solution; 0.2 cm³ of 1% aqueous solution of bile salts. The sample was shaken for 30 s, 20 mg of pancreatic lipase was added and it was shaken again for 30 s. The sample was then incubated in a water bath at 40 °C for 10 min. In order to stop the reaction, 15 cm³ of ethyl alcohol and 5 cm³ of 6 mol/dm³ hydrochloric acid were added. The sample was placed in the centrifuge for 5 min. The top organic layer was then removed. The obtained products were separated by preparative thin layer chromatography (TLC) using silica gel plates, and the chromatogram was developed in a chromatographic chamber. The composition of fatty acids in the sn-2 position of monoacylglycerols was determined by gas chromatography [19]. The comparison of the obtained data and the known initial profile of triacylglycerols allowed determination of the percentage of fatty acids in the sn-1,3 position and fatty acids in the sn-2 position. The following formulas were used:

$$\text{sn-1,3} = \frac{3 \times (\text{FA in TAGi}) - (\text{FA in sn-2 MAG})}{2}$$

$$\text{sn-2} = \frac{(\text{FA in sn-2 MAG}) \times 100\%}{3 \times (\text{FA in TAGi})}$$

where:

sn-1,3—content of a given fatty acid in sn-1 and sn-3 positions [%];

sn-2—content of a given fatty acid in the sn-2 position [%];

FA in TAGi—content of a given fatty acid in the initial TAG [%];

FA in sn-2 MAG—content of a given fatty acid in sn-2 MAG [%].

2.2.4. Assessment of Oxidative Stability of Oils by Means of Pressure Differential Scanning Calorimetry

The time of induction of the oil oxidation reaction was determined by pressure differential scanning calorimetry with a TA Instruments DSC Q20 apparatus. For this purpose, 3–4 mg of the tested oil was weighed into an aluminum pan. The pan was placed in the pressure chamber with the reference sample, i.e., an identical empty pan. Measurements were carried out in an oxygen atmosphere at a pressure of approx. 1350 kPa. The samples were oxidized at 100 °C and 120 °C [20]. For each sample, 3 replications were performed at each temperature.

2.2.5. Determination of the Melting Characteristics of Oils by Differential Scanning Calorimetry

The melting characteristics were determined by differential scanning calorimetry method using a TA Instruments Q200 DSC apparatus. For this purpose, 3–4 mg of the tested oil was weighed into an aluminum vessel. An identical empty pan was used as a reference sample. The process was carried out under normal pressure with a nitrogen flow of 50 mL/min. The samples in the apparatus were heated to 80 °C, held at this temperature for 10 min, cooled to −80 °C at a rate of 10 °C/min and held at this temperature for 30 min. The melting profile was obtained by heating the samples to 80 °C at a rate of 15 °C/min [20]. Three repetitions were performed for each sample.

2.2.6. Health Indices of Black Currant, Cranberry and Strawberry Seed Oils

Based on the saturated, unsaturated and polyunsaturated fatty acid profiles and n-3:n-6 fatty acid ratio, health indices, such as the index of atherogenicity (IA) and index of thrombogenicity (IT), defined by Ulbricht and Southgate [21], and hypocholesterolemic/hypercholesterolemic ratio (HH) proposed by Santos Silva et al. [22], were calculated according to equations:

$$IA = \frac{C12 : 0 + (4 \times C14 : 0) + C16 : 0}{\Sigma UFA}$$

$$IT = \frac{C14 : 0 + C16 : 0 + C18 : 0}{0.5 \times \Sigma MUFA + (0.5 \times \Sigma n - 6 \text{ PUFA}) + (3 \times \Sigma n - 3 \text{ PUFA}) + \frac{n-3}{n-6}}$$

$$HH = \frac{cis - C18 : 1 + \Sigma PUFA}{C12 : 0 + C14 : 0 + C16 : 0}$$

2.2.7. Statistical Analysis

The results were analyzed in the statistical program Statistica 13 using the analysis of variance (ANOVA) and Tukey's test at the significance level of $\alpha = 0.05$. Microsoft Excel 2010 was used to calculate the means with standard deviation.

3. Results

3.1. Fatty Acid Composition and Distribution between sn-2 and sn-1,3 Positions of Triacylglycerols

As a result of extraction process, strawberry, black currant and cranberry seed oils were obtained with the yield of 11%, 5% and 12%, respectively. The studied oils were tested using gas chromatography to analyze the composition of fatty acids. The results obtained for cranberry, black currant and strawberry seed oils, the percentage content of fatty acids from particular groups of saturated (SFA), monounsaturated (MUFA) and polyunsaturated fatty acids (PUFA) and the ratio of n-3 to n-6 fatty acids are presented in Table 1. Black currant seed oil was characterized by a very high content of linoleic acid (18:2 n-6c). It also contains large amounts of oleic acid (18:1 n-9c), alpha-linolenic acid (18:3 n-3) and

gamma-linolenic acid (18:3 n-6). According to Martysiak-Żurowska and Drapała [12], the high content of gamma-linolenic acid is characteristic of black currant seed oil. Strawberry seed oil was a source of large amounts of linoleic acid (18:2 n-6c), alpha-linolenic acid (18:3 n-3) and oleic acid (18:1 n-9c). These values are consistent with the literature, despite the use of different extraction methods. Among the oils tested in the study, strawberry seed oil was distinguished by a low content of saturated acids (SFA), especially palmitic acid (16:0), and a lack of gamma-linolenic acid. Cranberry seed oil was characterized by the highest content of oleic acid (18:1 n-9c) and alpha-linolenic acid (18:3 n-3) among the tested oils, and the lowest content of linoleic acid (18:2 n-6c). Close to trace amounts of gamma-linolenic acid (18:3 n-6) have been detected. Based on the obtained results, it can be stated that black currant, strawberry and cranberry seed oils are a rich source of polyunsaturated fatty acids. They are also characterized by a high content of monounsaturated fatty acids and low content of saturated fatty acids. Consuming products rich in polyunsaturated fatty acids is very beneficial for human health; additionally, it is crucial to maintain the right proportion of n-3 to n-6 fatty acids. The Western diet is characterized by an increased ratio of n-6 to n-3 fatty acids. Medicine associates this fact with an increased incidence of diseases, such as diabetes, rheumatoid arthritis, inflammatory bowel disease, obesity, asthma, cancer or depression, among the population, because when excessive amounts of n-6 fatty acids are consumed, pro-inflammatory eicosanoids are produced and, consequently, it can result in an inappropriate pro-inflammatory response of the immune system. On the other hand, eicosanoids, which are formed from n-3 fatty acids in the metabolic pathway, are thought to have anti-inflammatory and health benefits. It is proved that the optimal ratio of n-3 to n-6 fatty acids should be between 1:1 and 1:4 [23,24]. The oils tested in the study are characterized by an appropriate ratio of n-3 to n-6 acids. The ratio of these fatty acids for black currant seeds, strawberry seeds and cranberry seed oils are 1:4, 1:1.5 and 1:1.2, respectively.

Table 1. Fatty acid composition [%] and health indices of cranberry, black currant and strawberry seed oils.

Fatty Acid	Cranberry Seed Oil	Black Currant Seed Oil	Strawberry Seed Oil
12:0	0.01	0.06	-
14:0	0.04	0.19	0.13
15:0	0.01	0.05	0.03
16:0	5.89	7.95	4.71
16:1	0.07	0.10	0.23
17:0	0.05	0.09	0.05
17:1	0.04	0.05	0.06
18:0	1.34	1.93	1.87
18:1 n-9c	23.99	16.09	17.26
18:2 n-6c	36.59	48.07	44.01
18:3 n-6c	0.12	8.92	-
18:3 n-3c	31.39	15.02	29.76
20:0	0.11	-	1.09
20:1	0.23	1.19	0.34
22:1 n-9c	0.12	-	0.07
other	-	0.29	0.39
ΣSFA	7.45 ± 0.46 ^a	10.27 ± 1.21 ^b	7.88 ± 0.74 ^a
ΣMUFA	24.45 ± 1.89 ^b	17.43 ± 0.97 ^a	17.96 ± 1.02 ^a
ΣPUFA	68.1 ± 2.28 ^a	72.01 ± 2.75 ^b	73.77 ± 2.03 ^b
n-3:n-6 ratio	1:1.2	1:4	1:1.5
Health indices			
IA	0.065	0.098	0.057
IT	0.058	0.122	0.055
HH	15.50	10.74	18.81

Data denoted by different letters (^a, ^b) are statistically different ($\alpha = 0.05$).

From nutritional point of view, in addition to the composition of fatty acids, their distribution among internal and external positions in triacylglycerol structure is essential. The three positions where fatty acids can attach via an ester linkage to the glycerol backbone to form triacylglycerol are not equivalent. Fatty acids achieve the best bioavailability at the sn-2 position because it is preserved at all stages of the molecule's digestion. In natural vegetable oils, it is observed that the most important fatty acids for the human body are esterified in this position [25]. In the study, the distribution of fatty acids between the n-2 and n-1,3 positions of triacylglycerols was studied by enzymatic hydrolysis. The results are shown in Tables 2–4 for cranberry seed oil, black currant seed oil and strawberry seed oils, respectively.

Table 2. Fatty acid composition in sn-2 and sn-1,3 positions of TAG and the share of fatty acids in internal position (sn-2) of TAG in cranberry seed oil.

Fatty Acid	Fatty Acid Composition in sn-2 Position of TAG [%]	Fatty Acid Composition in sn-1,3 Positions of TAG [%]	Fatty Acid Share in sn-2 Position of TAG [%]
16:0	2.19	7.74	12.39
18:1 n-9c	29.53	21.22	41.03
18:2 n-6c	40.85	34.46	37.21
18:3 n-3c	26.78	33.70	28.44

Table 3. Fatty acids composition in sn-2 and sn-1,3 positions of TAG and the share of fatty acids in internal position (sn-2) of TAG in black currant seed oil.

Fatty Acid	Fatty Acid Composition in sn-2 Position of TAG [%]	Fatty Acid Composition in sn-1,3 Positions of TAG [%]	Fatty Acid Share in sn-2 Position of TAG [%]
16:0	4.43	9.71	18.57
18:1 n-9c	21.63	13.32	44.82
18:2 n-6c	49.04	47.59	34.01
18:3 n-3c	13.47	15.80	29.90
18:3 n-6c	9.17	8.80	34.27

Table 4. Fatty acids composition in sn-2 and sn-1,3 positions of TAG and the share of fatty acids in internal position (sn-2) of TAG in strawberry seed oil.

Fatty Acid	Fatty Acid Composition in sn-2 Position of TAG [%]	Fatty Acid Composition in sn-1,3 Positions of TAG [%]	Fatty Acid Share in sn-2 Position of TAG [%]
16:0	3.57	5.29	25.25
18:1 n-9c	20.82	15.48	40.21
18:2 n-6c	49.85	41.09	37.76
18:3 n-3c	24.38	32.45	27.31

Cranberry seed oil was characterized by the highest content of linoleic acid (18:2 n-6c) in the inner position, i.e., 40.85%. The share of this acid in the sn-2 position was 37.21%. This oil also contained 29.53% of oleic acid (18:1 n-9c) in the internal position, the share of which in the sn-2 position was 41.03%. The share of alpha-linoleic acid (18:3 n-3) in the sn-2 position was 28.44%, while this fatty acid was present in this position in the amount of 26.78%. The share of saturated fatty acid (palmitic, 16:0) in the internal position was only 12.39%. Based on the obtained results, it can be stated that the internal position of triacylglycerol in cranberry seed oil was occupied mainly by unsaturated fatty acids, which is typical for oils from plant sources. Similarly, in the case of black currant seed oil, the highest content of linoleic acid (18:2 n-6c) (49.04%) was observed in the internal

position. The share of this acid in the sn-2 position was 34.01%. This oil also contained 21.63% of oleic acid (18:1 n-9c) in the internal position, with 44.82% share of this fatty acid in the sn-2 position. Alpha-linolenic acid (18:3 n-3) was present in the sn-2 position of triacylglycerol in 13.47% with the share in this position reaching 29.90%. Black currant seed oil contained 9.17% of gamma-linolenic acid (18:3 n-6) in the internal position, and its share in sn-2 position was detected at the level of 34.27%. The share of saturated fatty acids represented by palmitic fatty acid (16:0) in the internal position amounted to 18.57%. These results correspond to the studies of Martysiak-Żurowska and Drapała [12], who obtained the following shares of fatty acids in the sn-2 position in black currant seed oil: linoleic acid 37.8%, oleic acid 47.5%, alpha-linolenic acid 16.3%, gamma-linolenic acid 37.4% and palmitic acid 19.5%. Strawberry seed oil was characterized by the highest content of linoleic acid (18:2 n-6c) in the internal position, i.e., 49.85%. The share of this acid in the sn-2 position was 37.76%. The share of alpha-linoleic acid (18:3 n-3) in the sn-2 position was 27.31%, while the content of this fatty acid in the internal position reached 24.38%. This oil contained also 20.82% of oleic acid (18:1 n-9c) in the internal position, the share of which in the sn-2 position was detected at the highest level of 40.21%. The share of saturated fatty acid (palmitic acid, 16:0) in the internal position was 25.25%. These results correspond to the studies of Martysiak-Żurowska and Drapała [12], who obtained the following shares of fatty acids in the sn-2 position in strawberry seed oil: linoleic acid 40.2%, alpha-linolenic acid 29.1%, oleic acid 38.2%. This distribution of fatty acids is typical for vegetable oils. In quinoa and amaranth seed oils, unsaturated fatty acids tended to be located in the internal position sn-2 of triacylglycerols. The proportion of saturated fatty acids in the sn-2 position was below 33.3%, which means that saturated fatty acids were mainly located in the external sn-1,3 positions [26]. Similar results for the distribution of fatty acids in triacylglycerol molecules were obtained for avocado pulp oils, that the sn-2 position was occupied mainly by oleic acid. The content of oleic acid in the sn-2 position was about 63% for Hass and 55.3% for the Reed cultivar, and its share in this position reached 34% and 29% for Hass and Reed, respectively [27].

3.2. Oxidative Stability of Cranberry, Black Currant and Strawberry Seed Oils

The induction time of the oxidation reaction at 100 °C and 120 °C was determined for cranberry, black currant and strawberry seed oils in order to assess oxidative stability using pressure differential scanning calorimetry. The results are given in Table 5.

Table 5. Oxidation induction time (OIT) of cranberry, black currant and strawberry seed oils at 100 °C and 120 °C.

Oil	OIT at 100 °C [min]	OIT at 120 °C [min]
Cranberry seed oil	212.04 ± 3.55 ^e	46.09 ± 0.63 ^c
Blackcurrant seed oil	73.00 ± 2.29 ^d	17.33 ± 0.41 ^b
Strawberry seed oil	50.04 ± 2.33 ^c	9.39 ± 0.46 ^a

Data denoted by different letters (a, b, c, d, e) are statistically different ($\alpha = 0.05$).

Exemplary pDSC curves of oxidation induction time for cranberry seed oil, black currant seed oil and strawberry seed oils at 120 °C are presented in Figure 2 and at 100 °C in Figure 3. Cranberry seed oil was characterized by the longest induction time of the oxidation reaction both at 120 °C and 100 °C. This was probably due to the high content of oleic acid (18:1 n-9) and the lower content of polyunsaturated fatty acids in comparison to the tested strawberry and black currant seed oils. Oleic acid makes oils such as olive oil or rapeseed oil more stable and resistant to oxidation in comparison to oils rich in polyunsaturated fatty acids. Cranberry seed oil contained the highest amount of oleic acid (23.99%) and the lowest amount of polyunsaturated fatty acids (68.1%) among all the tested oils, and therefore, the induction time of the oxidation reaction in this case was extended and demonstrated good oxidative stability. In addition, cranberry seed oil was characterized by an intense yellow color, which may indicate the presence of natural

antioxidants [28]. Strawberry seed oil, with oxidation induction time reaching 50.04 min. at 100 °C and 9.39 min. at 120 °C, was the least stable.

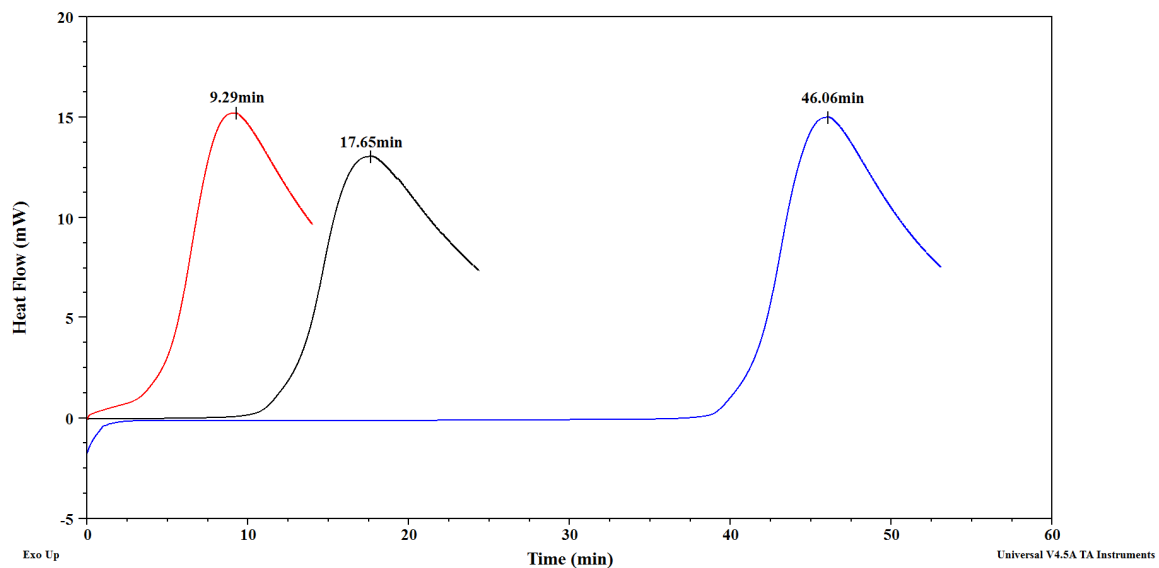


Figure 2. Exemplary pDSC curves of oxidation induction time for cranberry (blue), black currant (black) and strawberry (red) seed oils at 120 °C.

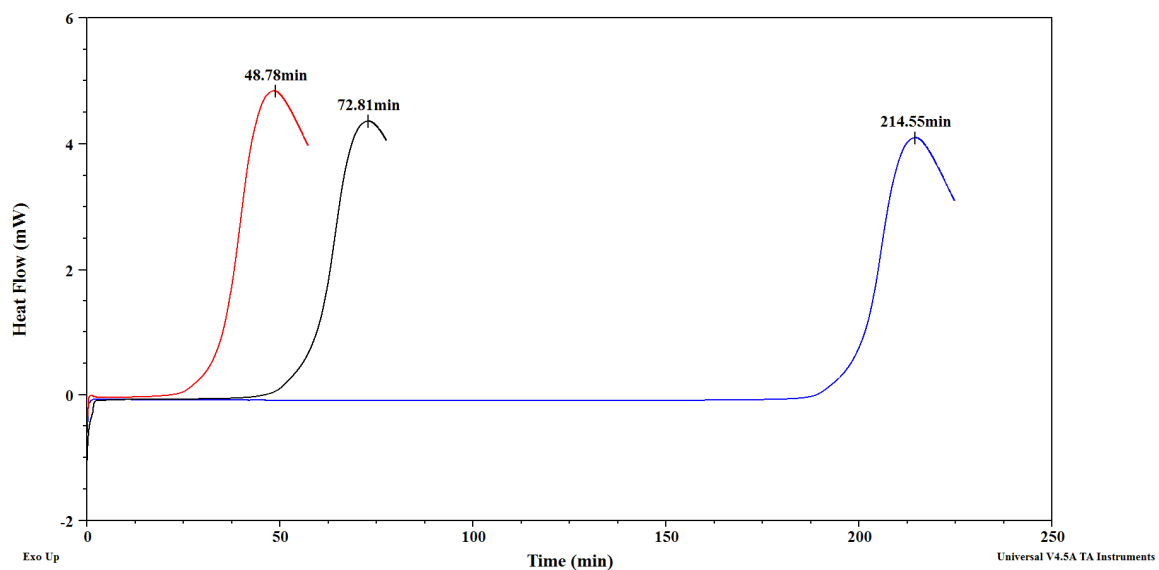


Figure 3. Exemplary pDSC curves of oxidation induction time for cranberry (blue), black currant (black) and strawberry (red) seed oils at 100 °C.

3.3. Melting Characteristics of Cranberry, Black Currant and Strawberry Seed Oils

The melting characteristics of the oils were determined using differential scanning calorimetry. Melting profiles of cranberry, black currant and strawberry seed oils are presented in Figure 4. In the case of the melting curve for cranberry seed oil, two endothermic events were defined. The first phase transition at -33.62 °C indicated the presence of low-melting fractions of triacylglycerols containing polyunsaturated fatty acids. The second peak at -20.80 °C indicated the presence of triacylglycerols rich in monounsaturated fatty acids [29]. Only the curve for cranberry seed oil showed the second endotherm, because this oil contained about seven percentage points more oleic acid than the others and was placed in a statistically separate homogeneous group in the statistical analysis of monounsaturated acids. The presence of the endotherm on the course of melting curve for black currant

seed oil, at $-37.41\text{ }^{\circ}\text{C}$, proved the presence of low-melting fractions of triacylglycerols containing mainly polyunsaturated fatty acids, which was in agreement with the fatty acid composition of this oil. Similarly, in the case of the melting profile for strawberry seed oil, one endotherm at $-40.23\text{ }^{\circ}\text{C}$ could be observed. This transformation proved the presence of low-melting fractions of triacylglycerols containing mainly polyunsaturated fatty acids. Piasecka et al. [29], who studied other berry seed oils, also determined an endothermic event occurring at $-40.35\text{ }^{\circ}\text{C}$ for blackberry seed oil and $-40.01\text{ }^{\circ}\text{C}$ for raspberry seed oils.

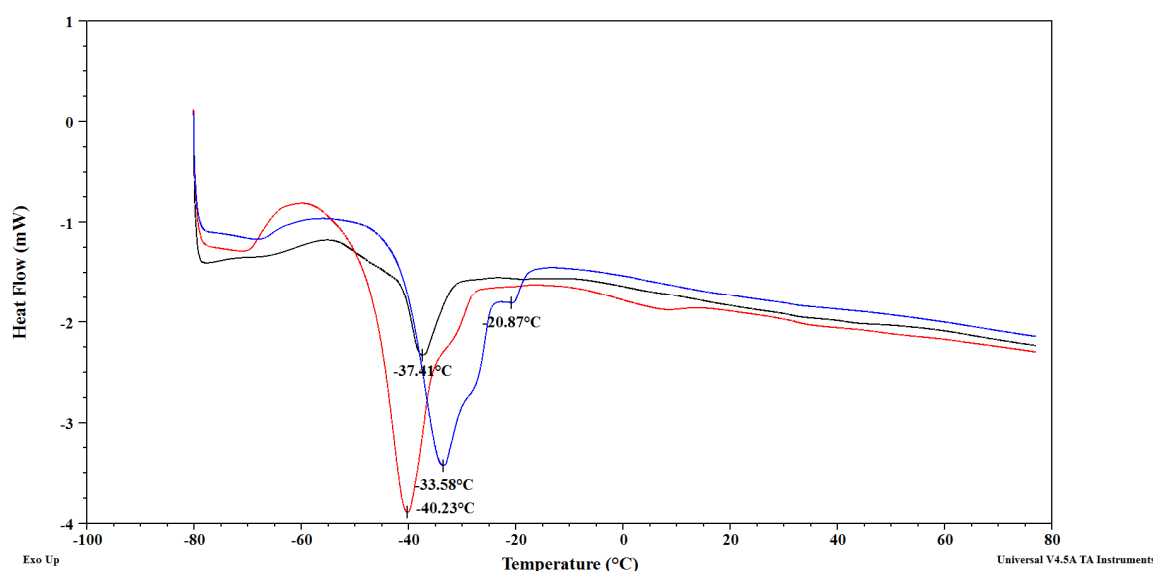


Figure 4. Melting curves of cranberry (blue), black currant (black) and strawberry (red) seed oils.

3.4. Health Indices of Blackcurrant, Cranberry and Strawberry Seed Oils

Taking into account results obtained for cranberry, black currant and strawberry seed oils concerning health indices, such as the atherogenicity index (IA), thrombogenicity index (IT) and hypocholesterolemic/hypercholesterolemic ratio (HH) (Table 1), it can be stated that the studied oils are of favorable nutritional and health values. The lowest atherogenic index was observed for strawberry seed oil ($IA = 0.057$), whereas the highest value of IA was observed for black currant seed oil ($IA = 0.098$). Considering the thrombogenicity index, the lowest value was found for strawberry seed oil and the highest value for black currant seed oil. In the case of strawberry and cranberry seed oils, IA and IT values were close, indicating a low incidence of coronary heart disease and beneficial health effects. Strawberry seed oil was also characterized by the highest value of HH index. Black currant seed oil showed a higher IA and IT compared to other studied oils and the lowest value of HH index, which can result in increased risk of cardiovascular disease. Importantly, both IA and IT are proven valuable and well-known indices that can be successfully applied to assess the potential impact of the fatty acid profile of fat on the risk of incidence of cardiovascular disease and the occurrence of blood clots, atheroma and thrombus. Oils with lower IA and IT values are thought to possess health benefits and minimize the risk of cardiovascular diseases [30,31]. Fats with IA values below 1.0 and IT values below 0.5 are particularly recommended for human consumption. In general, owing to the low IA value, all categories of nut oils have beneficial health effects. In the nut and seed product category, the highest atherogenic index was found for cocoa butter ($IA = 0.67$). Despite having polyphenolic compounds, cocoa butter lipid contains approximately 60% SFA, 35% MUFA, and a very low amount of PUFA (below 5%) ($IA = 0.67$, $IT = 3.09$), showing an increased risk of cardiovascular diseases [32].

4. Conclusions

The study proved that the characteristics of black currant seed, strawberry seed and cranberry seed oils, considering fatty acid composition and distribution in triacylglycerol structure, oxidative stability, melting profile and health indices, allowed the classification of the oils as nutritionally beneficial with potential applications in food, pharmaceutical and cosmetic industries. Taking into account the obtained results, it can be summarized that cranberry seed oil, with favorable fatty acid composition and distribution, low values of atherogenicity and thrombogenicity indices and a high value of hypocholesterolemic/hypercholesterolemic ratio, in addition to the longest oxidation induction time, is the most favorable from a nutritional point of view concerning human health. The oil was characterized by the highest content of oleic acid (18:1 n-9c) and alpha-linolenic acid (18:3 n-3) and a low content of saturated fatty acids, among the tested oils. Additionally, the n-3:n-6 ratio was beneficial and in agreement with dietary recommendations. It is also important to mention that cranberry seed oil had the highest oxidative stability and high nutritional quality, confirmed by low atherogenicity and thrombogenicity indices. The study concluded that oils with lower IA and IT values have health benefits and minimize the risk of cardiovascular diseases. Future research should be focused on searching for new sources of oils from food industry by-products with beneficial nutritional characteristics.

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References

1. European Commission. *Commission Staff Working Document. Drivers of Food Security*; European Commission: Brussels, Belgium, 2023.
2. Simonetto, M.; Sgarbossa, F.; Battini, D.; Govindam, K. Closed loop supply chains 4.0: From risks to benefits through advanced technologies. A literature review and research agenda. *Int. J. Prod. Econ.* **2022**, *253*, 108582. [\[CrossRef\]](#)
3. Zhang, Q.; Dhir, A.; Kaur, P. Circular economy and the food sector: A systematic literature review. *Sustain. Prod. Consum.* **2022**, *32*, 655–668. [\[CrossRef\]](#)
4. Aschemann-Witzel, J.; Asioli, D.; Banovic, M.; Perito, M.A.; Peschel, A.O.; Stancu, W. Defining upcycled food: The dual role of upcycling in reducing food loss and waste. *Trends Food Sci. Technol.* **2023**, *132*, 132–137. [\[CrossRef\]](#)
5. Olivares-Marín, M.; Fernández, J.A.; Lázaro, M.J.; Fernández-González, C.; Macías-García, A.; Gómez-Serrano, V.; Stoeckli, F.; Centeno, T.A. Cherry stones as precursor of activated carbons for supercapacitors. *Mater. Chem. Phys.* **2009**, *114*, 223–227. [\[CrossRef\]](#)
6. Oomah, B.D.; Ladet, S.; Godfrey, D.V.; Liang, J.; Girard, B. Characteristics of raspberry (*Rubus idaeus* L.) seed oil. *Food Chem.* **2000**, *69*, 187–193.
7. Kowalczyk, R.; Piwnicki, Ł. Pestki owoców jako cenny surowiec wtórny przemysłu spożywczego. (Fruit seeds as a valuable by-product of the food industry). *Postępy Tech. Przetwórstwa Spożywczego* **2007**, *2*, 62–66.
8. Helbig, D.; Bohm, V.; Wagner, A.; Schubert, R.; Jahreis, G. Berry seed press residues and their valuable ingredients with special regard to black currant seed press residues. *Food Chem.* **2008**, *111*, 1043–1049. [\[CrossRef\]](#)
9. Pacholek, B.; Małecka, M. Pestki czarnej porzeczki jako źródło naturalnych przeciwutleniaczy. (Blackcurrant seeds as a source of natural antioxidants). *Rośliny Oleiste* **2000**, *21*, 675–682.
10. Goffman, G.D.; Galletti, S. Gamma-linolenic acid and tocopherol contents in the seed oil of 47 accessions from several rubes species. *J. Agric. Food Chem.* **2001**, *49*, 349–354. [\[CrossRef\]](#)
11. Tahvonon, R.L.; Schwab, U.S.; Linderborg, K.M.; Mykkänen, H.M.; Kallio, H.P. Black currant seed oil and fish oil supplements differ in their effects on fatty acid of plasma lipids, and concentrations of serum total and lipoprotein lipids, plasma glucose and insulin. *J. Nutr. Biochem.* **2005**, *16*, 353–359. [\[CrossRef\]](#)

12. Martysiak-Żurowska, D.; Drapała, Ł. Struktura triacylogliceroli olejów z nasion truskawki, maliny i czarnej porzeczki. (Structure of triacylglycerols of strawberry, raspberry and blackcurrant seed oils). *Żywność Jadalna* **2010**, *45*, 11–20.
13. Pieszcza, M.; Migdał, W.; Gašior, R.; Rudzińska, M.; Bederska-Łojewska, D.; Pieszcza, M.; Szczurek, P. Native oils from apple, blackcurrant, raspberry, and strawberry seeds as a source of polyenoic fatty acids, tocopherols, and phytosterols: A health implication. *J. Chem.* **2015**, *4*, 1–8. [\[CrossRef\]](#)
14. Ahmad, N.; Anwar, F.; Abbas, A. *Fruit Oils: Chemistry and Functionality*, 1st ed.; Springer: Cham, Switzerland, 2019; pp. 663–674.
15. Yu, L.L.; Zhou, K.K.; Parry, J. Antioxidant properties of cold-pressed black caraway, carrot, cranberry, and hemp seed oils. *Food Chem.* **2005**, *91*, 723–729. [\[CrossRef\]](#)
16. Heeg, T.; Lager, H.; Bernard, G. Cranberry Seed Oil, Cranberry Seed Flour and a Method for Making. U.S. Patent US 2012/0148687 A1, 14 June 2012.
17. PN-EN ISO 659:2010; Oilseeds-Determination of Oil Content (Reference Method). Polish Committee for Standardization: Warsaw, Poland, 2010.
18. PN-EN ISO 5509:2001; Vegetable and Animal Oils and Fats. Preparation of Fatty Acid Methyl Esters. Polish Committee for Standardization: Warsaw, Poland, 2001.
19. Bryś, J.; Vaz Flores, I.F.; Górka, A.; Wirkowska-Wojdyła, M.; Ostrowska-Ligeza, E.; Bryś, A. Use of GC and PDSC methods to characterize human milk fat substitutes obtained from lard and milk thistle oil mixtures. *J. Therm. Anal. Calorim.* **2017**, *130*, 319–327. [\[CrossRef\]](#)
20. Dolatowska-Żebrowska, K.; Ostrowska-Ligeza, E.; Wirkowska-Wojdyła, M.; Bryś, J.; Górka, A. Characterization of thermal properties of goat milk fat and goat milk chocolate by using DSC, PDSC and TGA methods. *J. Therm. Anal. Calorim.* **2019**, *138*, 2769–2779. [\[CrossRef\]](#)
21. Ulbricht, T.L.V.; Southgate, D.A.T. Coronary heart disease: Seven dietary factors. *Lancet* **1991**, *338*, 985–992. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Santos-Silva, J.; Bessa, R.J.B.; Santos-Silva, F. Effect of genotype, feeding system and slaughter weight on the quality of light lambs: II. Fatty acid composition of meat. *Livest. Prod. Sci.* **2022**, *77*, 187–194. [\[CrossRef\]](#)
23. Patterson, E.; Wall, R.; Fitzgerald, G.F.; Ross, R.P.; Stanton, C. Health implications of high dietary omega-6 polyunsaturated fatty acids. *J. Nutr. Metab.* **2012**, *2012*, 1–16. [\[CrossRef\]](#)
24. Simopoulos, A.P. The importance of the ratio of omega-6/omega-3 essential fatty acids. *Biomed. Pharmacother.* **2002**, *56*, 365–379. [\[CrossRef\]](#)
25. Dubois, V.; Breton, S.; Linder, M.; Fanni, J.; Parmentier, M. Fatty acid profiles of 80 vegetable oils with regard to their nutritional potential. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 710–732. [\[CrossRef\]](#)
26. Wirkowska-Wojdyła, M.; Ostrowska-Ligeza, E.; Górka, A.; Bryś, J. Application of Chromatographic and Thermal Methods to Study Fatty Acids Composition and Positional Distribution, Oxidation Kinetic Parameters and Melting Profile as Important Factors Characterizing Amaranth and Quinoa Oils. *Appl. Sci.* **2022**, *12*, 2166. [\[CrossRef\]](#)
27. Brzezińska, R.; Górka, A.; Gotowicka, K.; Bryś, J.; Ostrowska-Ligeza, E.; Wirkowska-Wojdyła, M. Quality Assessment of Avocado Pulp Oils during Storage. *Proceedings* **2021**, *70*, 14.
28. Kamal-Eldin, A. Effect of fatty acids and tocopherols on the oxidative stability of vegetable oils. *Eur. J. Lipid Sci. Technol.* **2006**, *58*, 1051–1061. [\[CrossRef\]](#)
29. Piasecka, I.; Górka, A.; Ostrowska-Ligeza, E.; Kalisz, S. The study of thermal properties of blackberry, chokeberry and raspberry seeds and oils. *Appl. Sci.* **2021**, *11*, 7704. [\[CrossRef\]](#)
30. Khalili Tilami, S.; Kourimská, L. Assessment of the Nutritional Quality of Plant Lipids Using Atherogenicity and Thrombogenicity Indices. *Nutrients* **2022**, *14*, 3795. [\[CrossRef\]](#) [\[PubMed\]](#)
31. Acay, A.; Ulu, M.S.; Ahsen, A.; Ozkececi, G.; Demir, K.; Ozuguz, U.; Yuksel, S.; Acarturk, G. Atherogenic index as a predictor of atherosclerosis in subjects with familial Mediterranean fever. *Medicina* **2014**, *50*, 329–333. [\[CrossRef\]](#)
32. Kourimska, L.; Pokhrel, K.; Bozik, M.; Khalili Tilami, S.; Horcicka, P. Fat content and fatty acid profiles of recently registered varieties of naked and hulled oats with and without husks. *J. Cereal Sci.* **2020**, *99*, 103216. [\[CrossRef\]](#)

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