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Research Article

Native Oils from Apple, Blackcurrant, Raspberry, and Strawberry Seeds as a Source of Polyenoic Fatty Acids, Tocochromanols, and Phytosterols: A Health Implication

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The oils from strawberry, blackcurrant, raspberry, and apple seeds were characterized by a high content of unsaturated fatty acids (90.8%, 88.6%, 94.0%, and 86.9%, resp.). Strawberry and raspberry oils had high levels of C18:2 (45.4% and 49.0%) and αC18:3 (29.0% and 33.0%, resp.). Blackcurrant oil was the richest source of γC18:3 (18.5%) and C18:4 (3.6%). Apple oil had high levels of C18:2 (55.5%) and C18:1 (29.4%). Blackcurrant oil had 229.5 mg/100 g of tocochromanols, predominantly γ-tocopherol (117.8 mg/100 g) and α-tocopherol (84.3 mg/100 g). Raspberry oil was rich in γ-, α-, and δ-tocopherol (193.5; 65.6; and 32.2 mg/100 g, resp.). Strawberry oil contained γ- and δ-tocopherol, 49.0 and 6.1 mg/100 g, respectively. Apple contained all isomers of α-, β-, γ-, and δ-tocopherols at 41.7, 62.7, 13.6, and 21.8 mg/100 g, respectively. The level of tocotrienols in the analysed oils ranged from 0.85 to 6.73 mg/100 g. Ten different phytosterols were found in the tested oils. The richest sources of phytosterols were blackcurrant oil (6824.9 μg/g) followed by raspberry (5384.1 μg/g), strawberry (4643.1 μg/g), and apple oil (3460.0 μg/g). The dominant compound in the analysed oils was sitosterol, from 2630 μg/g in apple oil to 3630 μg/g in blackcurrant oil.

1. Introduction

Poland is the leading European manufacturer of fruit juice, in particular concentrated apple juice. Fruit juice and drink production was 1100 thousand tons in the 2005/2006 season and varied between 900 and 1300 thousand tons in the subsequent years, whereas the amount of berries produced for juice is almost 500 thousand tons [1, 2]. A valuable coproduct of juice production is pressing residue known as pomace, which in addition to being high in nutrients is a rich source of biologically active substances called nutraceutics, that is, unsaturated fatty acids, natural antioxidants (phenolic acids, flavonoids, anthocyans, tocopherols, and tocotrienols), carotene pigments, phytosterols, minerals, aromatic substances, pigments, bacterial and viral inhibitory substances, ballast compounds, fibre, and pectins [2–7]. Dried pomace is put through a sifting process to produce seeds that form 5–70% of total pomace weight depending on type of dried fruit. Increasing attention has been paid during the last decade to the fact that some seeds may contain fats of high nutritional, dietetic, and even therapeutic value. The major lipid components of oils are triacylglycerols (esters of glycerol and fatty acids). Less important components found in much smaller amounts are nontriacylglycerol compounds such as phospholipids, sterols, tocopherols, and carotenoids [8, 9]. These components not only determine the nutritional value of the oils but also have a significant effect on their stability, in particular the oxidative stability.

Seeds of berries, including strawberries, raspberries, blackcurrant, and apples, are a rich source of polyenoic

fatty acids (EUFA). These acids are not synthesized in the human body and have to be supplied through diet. Human nutritionists recommend that Poles should consume diets lower in fats with the change of its structure by increasing the intake of fats that contain polyenoic fatty acids. In addition to linoleic acid (LA) and long-chain polyenoic fatty acids (LC PUFA), an important role among them is played by 18-carbon polyenoic fatty acids having a triene structure—α-linolenic (ALA) and γ-linolenic (GLA)—which belong to two biochemically different families of n-3 and n-6. It has recently been emphasized that n-3 fatty acids serve important physiological and health-promoting roles, especially in preventing cardiovascular diseases [10]. Considerable attention has also been given to the health-promoting role of γ-linolenic acid, especially with regard to inflammatory, allergic, and cardiovascular diseases [11].

In addition to these fatty acids, the oils from strawberry, raspberry, blackcurrant, and apple seeds contain a number of antioxidant, anti-inflammatory, antiatherosclerotic, and anticancerous substances, including tocochromanols, carotenoids, flavonoids, phytosterols, and phenolic acids [5, 8, 12–14]. Plant fatty acids, which belong to a group of essential unsaturated fatty acids (EUFA), are characterized by high biological activity.

Recent years have seen much more intensive research on compounds that protect the body from the harmful effects of free radicals and other active forms of oxygen. Lipophilic components of vegetable oils, which show antioxidant activity and an ability to scavenge free radicals, are worthy of special notice. To date, vegetable oils rich in 18-carbon polyenoic fatty acids having a triene structure were used as pharmaceutical preparations available in capsules. However, the current oil production technology that uses cold-pressing in nitrogen gas or supercritical carbon dioxide extraction enables the oils to be obtained in almost unchanged form. They are more abundant in side compounds of high biological and antioxidant activity. Occurrence of antioxidants that inhibit unfavourable changes and knowledge of their activity and stability is essential not only to technologists but also to nutritionists. The shelf life of oils can be extended by using a variety of procedures that protect freshly extracted oils, such as limiting or eliminating oxygen contact, light exposure, and contact with prooxidative metal (copper and iron) ions, as well as supplementing the oil with oxidation inhibiting substances. Various antioxidants are used for this purpose. Efforts are made to limit the use of synthetic antioxidants on the grounds of health risks. Considerable emphasis is placed on the use of natural or nature-identical antioxidants. Their broad antioxidative properties may help to limit autoxidation of vegetable oils rich in polyenoic fatty acids having a triene structure. When they are added to the diet, they may have beneficial effects on the human body because of their free radical scavenging capacity.

In a search for new sources of these biologically valuable fats, we performed chemical analyses of oils obtained from the pressing of strawberry, raspberry, blackcurrant, and apple seeds in terms of the composition and content of fatty acids, tocopherols, tocotrienols, and phytosterols.

2. Materials and Methods

2.1. Materials and Extraction of Fat from the Seeds. Oils from blackcurrant, raspberry, strawberry, and apple seeds originated from Mega-Sort company (Poland), which specializes in the drying and packaging of fruit pomace produced after extraction of fruit and vegetable juices. Pomace with about 55% moisture content, originating from Hortex company (Poland), was dried on drum driers to reduce the moisture below 10%. Dried fruit pomace was then cut and ground and the seeds were separated. The production line (Scorpion, Poland) included a chopper, a separator, and a pneumatic tunnel, in which the seeds were separated from the other parts. Oils were obtained from the seeds on a standard technological line used for cold-pressing of oilseeds (Farmet, Czech Republic) and equipped with a UNO screw press, a sedimentation tank, and board and candle filters. Seeds were subjected to a press head temperature of 55°C for 20 s. The pressed and filtered oils from raspberry and strawberry seeds were placed in dark glass containers with added N_2, tightly closed, and refrigerated at 4°C until further analyses.

2.2. Analytical Methods

2.2.1. Determination of Fatty Acid Composition in Oils. Gas chromatography was used to determine higher fatty acids in fruit seed oils in the form of methyl esters, following saponification of the fatty acids contained in the sample.

Reagents. Gradient grade n-hexane for HPLC analysis, BF_3/methanol (Merck, Germany) and (pure for analysis) NaOH, chloroform, methanol, and NaCl (Chempur, Poland) were used. Sodium chloride (0.58%) and potassium hydroxide solutions (0.5 N) were made using double-distilled water.

Equipment. A Varian 3400 gas chromatograph (USA) equipped with an 8200 CX autosampler and FID detector was used. Data were integrated using Varian Star 4.5 software. Conversion was carried out using Excel. Sample preparation also involved the use of 7 mL screw-cap tubes (Schott), chromatography vials, a water bath, and a nitrogen solvent evaporation system.

Conditions of Chromatographic Analysis. Chromatographic separation was performed on CP Wax 58 column (0.53 mm × 1 μm) (Chrompack, USA) using temperature programmes of 60–188°C (4°C/min) followed by 60–220°C (5°C/min). Injector and FID detector temperature were 200 and 260°C, respectively. Helium was used as a carrier gas (6 mL/min). Hexane sample solutions (1 μL) were injected onto the column.

Procedure for PUFA Determination. Oil samples (about 100 mg) were weighed into 7 mL screw-cap tubes (Schott), saponified with 0.5 N NaOH in methanol (80°C), and esterified with BF_3 in methanol [15, 16]. Methyl esters of fatty acids were extracted with hexane. After salting out with saturated NaCl solution (0.58%), the hexane layer was collected into a chromatography vial and determined by gas chromatography.

The analyses were performed using standard solutions containing a mixture of standards (0.02–3.3 mg/mL in hexane) of the following fatty acids: caprylic (C8), capric (C10), lauric (C12), myristic (C14), palmitic (C16), palmitoleic (C16:1), stearic (C18), oleic (C18:1), linoleic (C18:2), linolenic (C18:3), γ-linolenic (gC18:3), stearidonic (C18:4), arachidic (C20), arachidonic (C20:4), behenic (C22), erucic (C22:1), eicosapentaenoic (EPA, C20:5), docosahexaenoic (DHA, C22:6), eicosenoic (C20:1), eicosadienoic (C20:2), and eicosatrienoic (C20:3, ω6) acids, all purchased from Sigma-Aldrich (USA), and conjugated linoleic acid isomers (CLA: c9-t11, t10-c12, and c9-c11) purchased from Larodan AB (Sweden). Final results were adjusted for fatty acid content in a blank sample, which was prepared in a similar manner to the sample but without weighed sample.

2.3. Determination of α-, β-, γ-, and δ-Tocopherols and Tocotrienols in Oils. Tocopherols (α-, β-, γ-, and δ-tocopherols) and tocotrienols (α-, β-, γ-, and δ-tocotrienols) in fruit seed oils were determined according to the method described by Gąsior et al. [17] using normal-phase high-performance liquid chromatography (NP-HPLC) [18]. Tocopherols and tocotrienols were determined after saponification of the sample in the presence of potassium hydroxide and ethanol, followed by extraction with a mixture of ethyl acetate/hexane (1/9, v/v). Analyses were performed with standard solutions (0–24 μg/mL) containing a mixture of tocol standards, using α-tocopherol from Fluka (USA), β-, γ-, and δ-tocopherols from Calbiochem (USA), and tocotrienols from Davos Life Science Pte Ltd. (Singapore). Final results were corrected for tocol content in a blank sample and recovery determined by the standard addition method (89–102%).

2.3.1. Reagents. Gradient grade *n*-hexane for HPLC analysis (Merck, Germany) and (pure for analysis) ethyl acetate, acetic acid, isopropyl alcohol (2-propanol), and ethanol 95-96% (Chempur, Poland) were used in addition to potassium hydroxide, sodium chloride (POCH, Poland), and pyrogallol (>98%, Fluka, USA). Sodium chloride (10 g/L) and potassium hydroxide solutions (600 g/L) were made using double-distilled water.

2.3.2. Equipment and Standardization of Standards. An Agilent Series 1100 HPLC system (USA) equipped with a pump, autosampler, and fluorescence detector was used. Data were integrated using Agilent ChemStation software. Calculations were carried out using Excel. Sample preparation also involved the use of 12 mL screw-cap tubes (Schott), screw-cap bottles (15 mL), a shaker (Vortex, Germany), an ultrasound bath, and a water bath. Standards (alcohol solutions) were standardized [17] using a Beckman DU 640 spectrophotometer based on tabular data for reference extinction values (E_1 cm 1%) of 75.8, 89.4, 91.4, 87.3, 86.0, 86.2, 91.0, and 85.8 for α-tocopherol, β-tocopherol, γ-tocopherol, δ-tocopherol, α-tocotrienol, β-tocotrienol, γ-tocotrienol, and δ-tocotrienol, respectively [19].

2.3.3. Conditions of HPLC Chromatographic Analysis. Chromatographic separation was performed on a LiChroCART 250-4 Lichrospher Si 60 column (5 μm, Merck, Germany) under the following conditions: FL detector, λ wavelength: Ex290 nm Em330 nm; injection 50 μL; eluent (flow rate 1.6 mL/min), *n*-hexane : ethyl acetate : acetic acid (97.3 : 1.8 : 0.9 v/v/v), duration of analysis 37 min, pressure 58–68 bar. Prior to analysis, the eluent was degassed in an ultrasound bath. Between analyses of each sample, the column was conditioned for 70 min using 10% isopropanol solution in *n*-hexane (v/v).

2.3.4. Determination Procedure. Oil samples (about 20 mg) were weighed into 12 mL Schott tubes with an accuracy of 0.0001 g. 1 mL of pyrogallol in ethanol (60 g/L), 0.5 mL of aqueous solution of potassium hydroxide (600 g/L), 0.5 mL of aqueous solution of sodium chloride (10 g/L), and 0.5 mL of ethanol were added to these. Vials were screw-capped, agitated on a Vortex shaker for about 10 s, and then transferred to a water bath (70°C), where the samples were saponified for 45 min. After cooling, 4 mL of aqueous solution of sodium chloride (10 g/L) was added and this was extracted twice (4 mL each) with a mixture of ethyl acetate and *n*-hexane (1 : 9, v/v), shaking (Vortex) the screw-capped tube for about 0.1 min. The extracts were pooled and evaporated dry under nitrogen (15 mL bottles) in a water bath (40°C). After dissolving the residue in 0.5 mL of a 1% mixture of isopropanol and *n*-hexane (v/v), the solutions (50 μL) were injected onto a chromatographic column. The same procedure was carried out when making blank samples except that no sample was added.

2.4. Determination of Phytosterols in Oils. The sterol content of lipids from the fruits was analysed according to the AOCS Official Method Ch 6-91 [20]. Phytosterol standards originated from Calbiochem (USA). 0.05 g of oils was weighed with an accuracy of 0.001 g into the reaction tubes, adding 100 μL of 5 α-cholestan as an internal standard and the samples were saponified in 2 mL of 1 M KOH in methanol for 18 h. After adding 2 mL of water, sterols were extracted three times with a mixture of hexane and MTBE (1 : 1) for 5, 3, and 2 min. Then the solvent was evaporated under a stream of nitrogen and the samples were dissolved in anhydrous pyridine and silylated with Sylon BTZ reagent (Sigma-Aldrich, USA). Sterols were separated using capillary column DB-35 ms (25 m × 0.2 mm × 0.33 μm; J & W Scientific, Folson, CA, USA) on a HP 5890 Series II gas chromatograph. Hydrogen was used as a carrier gas at a flow rate of 1.5 mL min^{-1}. The following temperature programme was used for the column from 100°C to 250°C (25°C/min) for 1 min then to 290°C (3°C/min). The initial and final temperature were held for 5 and 15 min, respectively. Injector and detector temperature were 300°C. Sample injection was performed by injecting 1 μL of the sample onto the column, using the splitless mode of injection for 1 min. Sterols were identified by comparing the retention times of these authentic standards.

2.5. Determination of Acid Value in Oils. About 5 g of oil was weighed into a 250 mL flask with an accuracy of 0.01 g. The sample was dissolved in 50 mL of hot ethanol. Titration was performed by mixing the flask content with KOH solution in

ethanol to the end point in the presence of phenolphthalein. The end point was when adding one drop of lye which caused a weak but perceivable change in colour for at least 15 s. The blank sample was titrated [21].

The acid value was calculated using the following formula:

$$\mathrm{LK} = 56.1 * (V - V0) * \frac{c}{m}, \quad (1)$$

where m: weight of fat, V: volume of potassium hydroxide solution used for fat sample titration, $V0$: volume of potassium hydroxide solution used for blank sample titration, and c: concentration of KOH solution (0.1 N).

2.6. Determination of Peroxide Value in Oils. About 2 g of oil was weighed with an accuracy of 0.001 g and transferred into a conical flask. The flask was filled with 10 cm^3 of chloroform, mixed until the fat was completely dissolved, filled with 15 cm^3 of acetic acid and 1 cm^3 of KI solution, and closed with a ground-in stopper. Flask content was agitated for 1 min and then left in the dark for 5 min. 75 cm^3 of distilled water (rinsing the stopper thoroughly) and 5 drops of starch solution were added to this, which after mixing was titrated with a 0.002 N solution of sodium thiosulfate. The blank sample was prepared simultaneously [22].

Peroxide value was calculated using the following formula:

$$\mathrm{LOO} = 0.002 * (a - b) * \frac{1000}{m} \quad \left[\text{milliequivalents of active } O_2/\text{kg}\right], \quad (2)$$

where a: volume of sodium thiosulfate solution used for fat sample titration (cm^3), b: volume of sodium thiosulfate solution used for blank sample titration (cm^3), and m: weight of sample (g).

2.7. Statistical Analysis. Analysis of the chemical composition, the content of bioactive compounds, and physicochemical properties in the oils was performed in 3 replications; the results were expressed as mean and coefficients of variation (CV) (Table 1).

3. Results and Discussion

Biooils are biologically the most valuable plant fats due to their composition that reflects the actual structure of all substances found in the seeds from which the oil was extracted. The WHO/FAO Codex Alimentarius Commission provided a definition of biooil that corresponds to virgin oil and determines the conditions for its extraction. Only mechanical extraction methods that ensure high quality of biooils are allowed. Pressing of oilseeds using hydraulic or screw press at low temperature regimes is therefore the only expression method. The procedures allowed to remove impurities from oil include water washing and centrifugation as well as sedimentation and filtration. No phospholipids, tocopherols, sterols, or carotenoids are removed from these oils. The high quality of these oils is conditional on the use of selected, fully mature seeds. The moisture content of the seeds obtained was in the range of 7.5–9.5%. Most oil was found in apple seeds, followed by strawberry, blackcurrant, and raspberry seeds (20.2, 18.5, 16.2, and 13.5%, resp.). These results are confirmed by the findings of other authors [14, 23, 24] and the small differences are due to the quality of extracted seeds and oil extraction technique (including press type and filtration method). The analysed oils were characterized by increased peroxide values (within the normal range) of 8.78, 8.39, 9.45, and 10.59 mq O_2/kg for strawberry, blackcurrant, raspberry, and apple seed oils, respectively. Cold-pressed virgin oils are characterized by increased peroxide and acid values as a result of protein, mineral, and other impurities that favour oxidation processes being left after oil extraction [5, 25].

3.1. Fatty Acids in Oils from Strawberry, Blackcurrant, Raspberry, and Apple Seeds. In addition to lifestyle and living conditions, diet is one of the most important determinants of our health and well-being. Advances in understanding the action of diet ingredients that may have a beneficial effect on the human body made it possible to design and produce food with specific health-promoting effects, rich in various bioactive components. Among these, polyenoic fatty acids are important, which play a significant role in preventing metabolic diseases of modern civilization. Polish fat products (oils, margarines, spreads, 100% fats) contain small amounts of n-3 polyenoic fatty acids but practically have no γ-linolenic acid. For this reason, efforts are made to increase their dietary content. Some vegetable oils are a rich source of these acids.

Oils considered a rich source of PUFA having a triene structure (α-linoleic acid C18:3 Δ 9,12,15 and γ-linolenic acid C18:3 Δ 6,9,12)—such as linseed, false flax, hemp, borage, and vipers bugloss, as well as strawberry, blackcurrant, raspberry, and apple seed oils—are characterized by widely different composition and content of individual fatty acids. This particularly refers to the group of polyenoic acids, including those having a triene structure. The composition of fatty acids in the oils from strawberry, blackcurrant, raspberry, and apple seeds was characterized by a high content of unsaturated fatty acids (90.8%, 88.6%, 94.0%, and 86.9%, resp.) (Table 2). The largest differences in the fatty acid profile of the analysed oils were observed within α-linolenic and linoleic acids. Oils from strawberry and raspberry seeds had high levels of linoleic acid C18:2 (45.4% and 49.0%) and alpha-linolenic acid αC18:3 (29.0% and 33.0%, resp.). The richest source of gamma-linoleic (γC18:3) and stearidonic acids (C18:4) was blackcurrant seed oil (18.5% and 3.6%, resp.). Apple seed oil had a high content of oleic acid C18:1 (29.4%), which is in agreement with the findings of Yukui et al. [24]. Linseed oil is one of the richest sources of α-linolenic acid, whose average content in commercial oil is 57.3%, as confirmed by Choo et al. [26].

The analysed oils were found to be high in α-linolenic acid; this especially concerned oils from strawberry, raspberry, and blackcurrant seeds (29.0%, 33.0%, and 13.5%, resp.). In the apple seed oil, the level of α-linolenic acid did not exceed 1%. In addition, considerable amounts of this acid are found in linseed, false flax, vipers bugloss, and hemp oils [14, 26–29].

Table 1: Physicochemical properties of oils from strawberry, raspberry, blackcurrant, and apple seeds.

Characteristics	Strawberry seed oil	Raspberry seed oil	Blackcurrant seed oil	Apple seed oil
Content of oil (% dry matter)	18.56 ± 0.32	13.52 ± 0.31	16.20 ± 0.29	20.22 ± 0.32
Moisture content of seeds (%)	7.78 ± 0.11	6.96 ± 0.10	8.01 ± 0.12	8.84 ± 0.13
Acid value (mg KOH/g)	2.09 ± 0.004	1.74 ± 0.002	4.10 ± 0.006	1.36 ± 0.002
Peroxide value (mq O_2/kg)	8.78 ± 0.02	8.39 ± 0.01	9.45 ± 0.03	10.59 ± 0.04

Values are mean± and coefficients of variation (CV).

Table 2: Composition of fatty acids in oils from strawberry, raspberry, blackcurrant, and apple seeds (% of total fatty acids).

Fatty acids	Strawberry seed oil	Raspberry seed oil	Blackcurrant seed oil	Apple seed oil
C 10	0.01	0.00	0.01	0.00
C 16	6.20	4.19	9.63	9.50
C 16:1 (*n*-7)	0.25	0.14	0.17	0.00
C 18	1.89	1.19	1.39	1.82
C 18:1 (*n*-9)	15.51	11.70	12.09	29.36
C 18:2 (*n*-6)	45.45	49.01	38.64	55.54
γ 18:3 (*n*-6)	0.04	0.04	18.54	0.34
C 18:3 (*n*-3)	29.05	33.02	13.57	0.85
C 18:4 (*n*-3)	0.00	0.00	3.58	0.00
C 18:2 (CLA) c9-c11	0.00	0.00	0.11	0.00
C 20	0.91	0.45	0.21	1.56
C 20:1	0.27	0.00	1.26	0.57
C 20:2 (*n*-6)	0.11	0.00	0.49	0.09
C 20:4 (*n*-6)	0.00	0.00	0.01	0.00
C 22	0.12	0.13	0.07	0.18
C 22:1	0.08	0.04	0.07	0.07
C 22:5 (*n*-3)	0.10	0.09	0.14	0.11
C 22:6 (DHA) (*n*-3)	0.00	0.01	0.01	0.01
SFA	9.14	5.95	11.32	13.06
UFA	90.86	94.05	88.68	86.94
PUFA *n*-6	45.60	49.05	57.68	55.97
PUFA *n*-3	29.16	33.12	17.30	0.96
PUFA *n*-6/*n*-3	15.63	1.48	3.33	58.30

3.2. Tocopherols and Tocotrienols in Oils from Blackcurrant, Raspberry, Strawberry, and Apple Seeds. In the analysed oils, the highest concentrations of tocols were identified in raspberry and blackcurrant seed oils (301.9 and 229.5 mg/100 g) and lower levels in apple and strawberry seed oils (143.6 and 58.4 mg/100 g, resp.). The dominant isomers of tocopherols in oils from raspberry, blackcurrant, and strawberry seeds were γ- and α-tocopherol, and the same oils were poor in β isomer (Table 3). A different pattern was evident for the profile of tocopherols in apple seed oil, in which the concentration of β isomer was highest (62.7 mg/100 g) compared to α, δ, and γ isomers of 41.7, 21.2, and 13.6 mg/100 g, respectively. In comparison with the results of Helbig et al. [3], the oil extracted from blackcurrant seeds had higher concentration of tocols and a similar profile. Goffman and Galletti [30] reported blackcurrant seed oil to contain a total of 1716 mg/kg tocopherols, of which 34.8% was α-tocopherol, 60.2% was γ-tocopherol, and 5.0% was δ-tocopherol. Meanwhile, Velasco and Goffman [31] found that blackcurrant seed oil contained a total of 531 mg/100 g tocopherols on average, of which 89.6% was γ isomer. Shahidi and Shukla [9] reported that blackcurrant seed oil contained a total of 1500 mg/kg tocopherols on average.

The tocopherol content of oils from blackcurrant and raspberry seeds was comparable to commercial oils rich in tocopherol, that is, maize and soybean oils at 162 and 180 mg/100 g oil, respectively [32]. We can attribute differences in tocol levels to oil extraction method. The tocopherol content of oils is considerably affected by the refining process, which removes about 40% of tocopherol. In a study on oxidative stability of oils, Kamal-Eldin [33] found that problems in stabilizing vegetable oils by the addition of tocopherols are due to the fact that native tocopherols in these oils are at optimal levels necessary for their stabilization.

3.3. Phytosterols in Oils from Blackcurrant, Raspberry, Strawberry, and Apple Seeds. In most vegetable oils, sterols are the principal component of unsaponifiable substances, whose

Table 3: Tocochromanol (tocopherol and tocotrienol) content of oils from strawberry, raspberry, blackcurrant, and apple seeds.

Tocochromanols	Strawberry seed oil	Raspberry seed oil	Blackcurrant seed oil	Apple seed oil
Tocopherols (mg/100 g):				
α-Tocopherol	2.46 ± 0.8	65.61 ± 14.5	84.32 ± 7.5	41.75 ± 1.5
β-Tocopherol	nd	3.83 ± 5.4	4.44 ± 2.4	62.77 ± 1.3
γ-Tocopherol	49.02 ± 0.6	193.58 ± 29.9	117.88 ± 13.8	13.60 ± 2.4
δ-Tocopherol	6.15 ± 0.7	32.17 ± 13.3	18.41 ± 4.6	21.28 ± 3.3
Tocotrienols (mg/100 g):				
α-Tocotrienol	nd	1.84 ± 2.5	1.67 ± 0.9	1.21 ± 0.6
β-Tocotrienol	nd	nd	nd	nd
γ-Tocotrienol	0.85 ± 0.6	4.18 ± 2.2	2.07 ± 1.2	3.05 ± 1.7
δ-Tocotrienol	nd	0.71 ± 0.7	0.78 ± 0.6	nd
Sum of tocols (mg/100 g)	58.48 ± 5.7	301.92 ± 2.3	229.57 ± 23.1	143.66 ± 3.5

nd (not detected), limit of quantitative for each tocol is 0.5 mg/100 g.
Values are mean± and coefficients of variation (CV).

Table 4: Phytosterol content of oils from apple, blackcurrant, strawberry, and raspberry seeds (μg/g).

Phytosterols	Apple seed oil	Blackcurrant seed oil	Strawberry seed oil	Raspberry seed oil
Campesterol	219.8 ± 16.4	513.4 ± 5.7	328.9 ± 12.4	254.7 ± 20.2
Stigmasterol	13.2 ± 13.1	44.6 ± 3.0	97.9 ± 2.5	60.7 ± 3.7
Sitosterol	2629.3 ± 168.5	3637.3 ± 225.7	2656.6 ± 95.14	3341.9 ± 32.7
Sitostanol	249.9 ± 56.8	300.9 ± 36.3	291.9 ± 10.7	364.6 ± 18.4
Avenasterol	347.8 ± 6.3	124.2 ± 3.4	47.5 ± 3.2	80.3 ± 2.4
D7-Stigmasterol	0	76.2 ± 9.2	108.2 ± 3.7	94.7 ± 5.6
Cycloartenol	0	775.6 ± 26.9	642.7 ± 25.3	449.8 ± 21.2
D7-Avenasterol	0	146.4 ± 6.1	158.7 ± 9.2	66.6 ± 5.2
24-Methylene-cycloartenol	0	931.9 ± 47.7	99.9 ± 12.6	523.8 ± 17.1
Citrostadienol	0	274.5 ± 10.5	210.7 ± 13.4	147.0 ± 3.2
Sum of phytosterols	3460.0	6824.9	4643.1	5384.1

Values are mean± and coefficients of variation (CV).

content in blackcurrant and borage oil is 1.2% [9]. The main sterols of vegetable oils reported by Warner and Mounts [34] and Rudzińska et al. [35] are β-sitosterol, campesterol, stigmasterol, brassicasterol, Δ5-avenasterol, Δ7-stigmasterol, and Δ7-avenasterol (Table 4). In most oils, their total content ranges from 400 to 800 mg/100 g, but there can be considerable differences in the content of these compounds between some oils [9, 36].

Chromatographic analysis of the oils revealed 10 different phytosterols. Oils from blackcurrant, raspberry, strawberry, and apple seeds contain considerable amounts of phytosterols. The richest sources of phytosterols were blackcurrant seed oil (6824.9 μg/g) followed by raspberry (5384.1 μg/g), strawberry (4643.1 μg/g), and apple seed oil (3460.0 μg/g).

The dominant compound in the analysed oils was sitosterol, whose content ranged from 2630 μg/g in apple seed oil to 3630 μg/g in blackcurrant seed oil. Sitosterol is an important phytosterol that reduces the absorption of cholesterol, which helps to maintain a low level of total cholesterol in peripheral blood. The analysed samples also contained considerable amounts of other phytosterols such as campesterol, sitostanol, cycloartenol, and citrostadienol. Unlike cholesterol, phytosterols generally have a positive effect on human health. They bind bile acids and reduce the risk of high blood levels of total cholesterol without affecting the levels of HDL cholesterol [37]. Another positive effect of phytosterols is that they inhibit the development of intestinal cancer. In human and animal bodies, phytosterol shows mainly anticarcinogenic, antioxidative, and cholesterol-lowering activities [38].

4. Conclusions

The oils obtained from strawberry, blackcurrant, raspberry, and apple seeds are a rich source of essential unsaturated fatty acids (EUFA), tocochromanols and phytosterols, which could find wide application in the cosmetic, pharmaceutical, and food industries.

The native oils from strawberry, raspberry, blackcurrant, and apple seeds can be regarded as special oils (biooils), which, due to their possible nutraceutical effects, could find broader use not only in the cosmetic but also in the food industry. They could find special application in the design and production of foods with specific health-promoting effects, rich in various bioactive components helpful in preventing metabolic diseases of modern civilization.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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