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Characterization of Saskatoon Berry (*Amelanchier alnifolia* Nutt.) Seed Oil

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The seeds of 17 cultivars of Saskatoon berries (*Amelanchier alnifolia* Nutt.) were evaluated for their seed mass, oil content, fatty acid and triacylglycerol (TAG) composition, tocopherol profile, and sterol content. The oil content of the seeds ranged from 9.4% (cv. 'Pasture') to 18.7% (cv. 'Thiessen'). The seed oils contained mainly linoleic acid in the range from 47.3% (cv. 'Success') to 60.1% (cv. 'Lee 3') and oleic acid in the range from 26.3% (cv. 'Lee 3′) to 38.1% (cv. 'Success'). The total tocopherol content ranged from 1053 to 1754 mg/kg of oil. α-Tocopherol was the major vitamin E compound in all berry seed oils investigated, accounting for 87% of total tocopherols. The predominant sterols were β-sitosterol, Δ^5-avenasterol, and campesterol. The sterols content in seed oil ranged from 7357 mg/kg of oil (cv. 'Success') to 15771 mg/kg of oil (cv. 'Lee 3'). Thirteen triacylglycerols (TAG) were identified in seed oils, among which LLL, LLO, LOO, LLP, LOP (L, linoleoyl; O, oleoyl; P, palmitoyl) represented 88% of the total TAG. TAG composition suggests good oxidative stability of the Saskatoon berry seed oil, which could be suitable for food and industrial applications. Moreover, Saskatoon berry seed oil may serve as potential dietary source of tocopherols, sterols, and unsaturated fatty acids.

KEYWORDS: Saskatoon berry; berry seed oil; tocopherols; sterols; triacylglycerols; fatty acid composition

INTRODUCTION

Saskatoon (*Amelanchier alnifolia* Nutt.), a fruit-producing shrub or small tree of the Rosaceae family, is native to the North American Great Plains. In the United States it is commonly called the juneberry or serviceberry. The fruits, collected from wild stands, were traditionally used by aboriginal people and early settlers on the prairies. Today, there are more than 1200 ha of commercial Saskatoon berries planted in the Canadian prairies, Saskatchewan, Manitoba, and Alberta, accounting for an estimated 6−8 million kilograms of Saskatoon berries (personal communications). Traditionally, Saskatoon berries were consumed mostly fresh, baked in pies, or processed into jams and spreads, but recent innovations in processing and freezing have greatly increased the potential for these berries to be used in industry, for example, by juice, wine, cereal, snack food, and ice cream processors (*1*). Fruit seeds are one of the major byproducts from the manufacture of fruit wine and juice. A number of edible oils from fruit seeds have been shown to contain high levels of unsaturated fatty acids and other biologically active phytochemicals such as tocopherols and phytosterols (*2*, *3*). For instance, black currant seed oil contains 12−23% γ-linolenic acid (*4*). Cranberry seed oil is a rich source of essential fatty acids, containing between 35 and 44% linoleic acid (18:2*n*-6) and 23−35% α-linolenic acid (*5*, *6*), along with significant levels of β-sitosterol and α- and γ-tocopherols (*7*). Woods' rose and hawthorn seed oils contain high amount of sterols (862 and 705 mg/100 g, respectively) and tocopherols (236 and 284 mg/100 g, respectively) (*2*). These data suggest that fruit seed oils might serve as potential dietary sources for natural antioxidants and other phytochemicals. Further investigation of the chemical compositions of fruit seed oils is required to evaluate the potential of fruit seed lipids as sources of valuable oil for food applications.

Although Saskatoon berries from the Canadian prairies have been investigated for their nutritional, medicinal, and antioxidant properties, no research has been conducted on the lipid profiles of their seeds. Therefore, the objective of the present research was to evaluate the fatty acid, triacylglycerol, tocopherol, and sterol compositions of the seed oil from 17 Saskatoon berry cultivars native to western Canada. The information obtained from this study can be used to evaluate the potential use of this berry seed oil in food products and to confirm product authenticity.

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MATERIALS AND METHODS

Chemicals. Boron trifluoride, hexane, methanol (ACS grade), acetonitrile (HPLC grade), 2-propanol (HPLC grade), sodium chloride, potassium chloride, potassium hydroxide, pyrogallol, cyclohexane, and anhydrous sodium sulfate were purchased from Fisher Scientific (Ottawa, ON, Canada). Pyridine was obtained from Pierce (Rockford, IL) and 5α-cholestane from Sigma-Aldrich (St. Louis, MO). *N*,*O*-Bis(trimethylsilyl)trifluoroacetamide and trimethylchlorosilane were from Alltech (Guelph, ON, Canada). Fatty acid methyl ester standards were purchased from Nu-Chek Prep Inc. (Elysian, MN). The plant sterol mixture and tocopherol standards were obtained from Matreya LLC (Pleasant Gap, PA), and triacylglycerol standards were purchased from Sigma-Aldrich (St. Louis, MO).

Berry Material. Ripe Saskatoon berries from 17 cultivars (Success, Lee 3, Martin, Parkhill, Forestburg, Lee 8, Lee 2, Pembina, Honeywood, Northline, Thiessen, Pasture, Nelson, Pearson, Quaker, Smokey, and Regent) were harvested in July 2006 on the Dn'A Garden commercial plantation, Elnora, AB, Canada. The seeds were removed from the berries, washed with tap water, and air-dried at room temperature. Two different samples of each cultivar were collected and analyzed individually in duplicate.

Oil Content. The oil content in berry seeds was analyzed according to the method of Troeng (*7*). Seeds were ground in a commercial grinder. Two and a half grams of accurately weighed and well-mixed sample was transferred into a "Swedish Tube" containing ball bearings [manufactured according to specification of the American Oil Chemists' Society (AOCS)], and 35 mL of petroleum ether (boiling range 36−60 °C as specified by the AOCS) was added. The samples were then shaken on a reciprocating shaker (Eberbach Corp., Ann Arbor, MI) for 20−30 min. After shaking, the contents were filtered under vacuum. The filtrates of petroleum ether were collected into a tared flask, and the solvent was removed under vacuum at 60 °C using a rotary evaporator. Oil content was expressed on a dry seed weight.

Moisture Content. Moisture content in Saskatoon berry seed was analyzed according to AOCS Method Ba 2a-38 (*8*). For this purpose, 3 g of seed was dried for 2 h at 130 °C.

Fatty Acid Composition. Fatty acid composition of seed oils was determined by gas−liquid chromatography of fatty acid methyl esters according to AOCS Official Methods Ce 2-66, Ce 1e-91, and Ce 1b-89 (*9*). One-fourth of a gram of oil was hydrolyzed with 6 mL of 0.5 N NaOH in methanol solution. When the oil was completely dissolved (indicating complete hydrolysis), 6 mL of 14% boron trifluoride in methanol solution was added and refluxed under heat for approximately 5 min. Subsequently, 10 mL of hexane was added, and the mixture was cooled to ambient temperature. Twenty milliliters of 15% NaCl solution was then added to the flask. The clear hexane solution was transferred to an autosampler vial using a Pasteur pipet. Analyses were performed on an Agilent 6890 gas chromatograph equipped with an Agilent 7683 autosampler and a flame ionization detector, and a 30 m × 0.32 mm i.d., 0.25 μm, DB225 capillary column (Agilent Technologies, Mississauga, ON, Canada). The temperature program was as follows: 200 °C for 9 min, raised at 4 °C/min to 220 °C, held at 220 °C for 7 min. The detector and injector temperatures were 280 and 250 °C, respectively. The carrier gas was helium at a constant pressure of 15 psi. The samples (1 μL) were injected at a split rate of 1:100.

Tocopherol and Sterol Composition. The tocopherol and sterol composition of seed oils was analyzed by gas−liquid chromatography according to the method of Slover et al. (*10*) with modifications. The oil (0.1 g) was saponified with 0.5 mL of saturated aqueous KOH in the presence of 8 mL of 3% ethanolic pyrogallol for 8 min in a water bath at 80 °C. Eight milliliters of water was added, unsaponifiables were extracted three times with 10 mL of cyclohexane, and the internal standard was added to samples. After solvent removal, the tocopherols and sterols were derivatized with pyridine, *N*,*O*-bis(trimethylsilyl)trifluoroacetamide, and trimethylchlorosilane, and TMS derivatives were analyzed using an Agilent 6890 gas chromatograph (Agilent Technologies) equipped with a 30 m × 0.32 mm, i.d., 0.25 μm, HP-1 capillary column. The temperature program was as follows: 240 °C for 20 min, raised at 5 °C/min to 260 °C, held at 260 °C for 26 min. The detector and injector temperatures were 300 and 280 °C, respectively. The carrier gas was helium at a constant pressure of 15 psi. The samples (2 μL) were injected at a split rate of 1:50. 5α-Cholastane was used as internal standard at the concentration of 0.2 mg/mL. The response factors (tocopherols versus 5α-cholestane and sterols versus 5α-cholestane) used for calculation were 1.08 and 1.0, respectively.

HPLC-DAD-APCI-MS Determination of Triacylglycerols. The HPLC-DAD-APCI-MS determination of triacylglycerols (TAG) in Saskatoon seed oil was conducted according to the method of Lisa and Holcapek (*11*) with modifications. For this purpose, the seed oils were dissolved in an acetonitrile/2-propanol (1:1, v/v) solvent mixture yielding 3% (w/v) solutions. The chromatographic system consisted of an 1100 Series Agilent Technologies LC-MSD system equipped with a diode array detector (DAD) coupled to a mass spectrometer (quadruple analyzer) equipped with an atmospheric pressure chemical ionization (APCI) interface (Agilent Technologies). The separation was performed on two 250 mm × 4.6 mm, i.d., 4 μm, RP C12 columns (Synergi Max-RP 80A, Phenomenex, Torrance, CA) using gradient elution with acetonitrile (A) and 2-propanol (B). The elution system was as follows: 0 min, 100% A; 129 min, 31% A; 132 min, 100% A. MS parameters were as follows: vaporizer temperature, 400 °C; drying gas temperature, 350 °C; gas flow (N_2), 3.0 L/min; nebulizer pressure, 60 psi. The instrument was operated in positive ion mode scanning from *m*/*z* 100 to 1200 at a scan rate of 2.0 s/cycle.

Statistical Analysis. Data are presented as mean values ± standard deviation of two samples of each cultivar, analyzed individually in duplicate. Analysis of variance (ANOVA) was performed using Statgraphic software (StatPoint, Inc., Sainte-Fey, QC, Canada). A probability value of $P \le 0.05$ was considered to denote a statistically significant difference.

Table 1. Seed Mass of Berries and Oil Content of Saskatoon Berry Seeds[a]

cultivar	seed mass (% FW)	oil content (% DW)
Northline	2.9 ± 0.04d	13.96 ± 1.2c
Pasture	2.3 ± 0.06e	9.44 ± 0.9e
Success	4.3 ± 0.10a	14.42 ± 0.4b
Honeywood	3.0 ± 0.04c	10.76 ± 0.7d
Regent	3.8 ± 0.05b	11.80 ± 0.5d
Lee 2	3.4 ± 0.06c	15.21 ± 0.7b
Pembina	3.8 ± 0.10b	14.84 ± 0.8b
Thiessen	2.6 ± 0.02e	18.67 ± 1.0a
Quaker	2.6 ± 0.09d	11.12 ± 0.6d
Lee 8	3.3 ± 0.06c	14.27 ± 0.8b
Forestburg	3.5 ± 0.05c	14.66 ± 1.0b
Nelson	4.0 ± 0.09b	12.98 ± 0.9c
Pearson	3.5 ± 0.11c	13.80 ± 0.4c
Martin	2.3 ± 0.04e	11.67 ± 0.6d
Lee 3	2.7 ± 0.09d	10.90 ± 0.5d
Parkhill	3.8 ± 0.06b	17.01 ± 1.1a
Smokey	4.4 ± 0.05a	16.21 ± 1.0b
av	3.3	13.63

[a] Different letters within each column represent significance difference ($p < 0.05$); values are mean ± SD of two samples of each cultivar, analyzed individually in duplicate.

RESULTS AND DISCUSSION

Seed Mass of the Berries. The seed mass of 17 Saskatoon berry cultivars, calculated as weight percent of fresh weight, varied considerably (**Table 1**). The cultivars 'Smokey' and 'Success' contained the highest amount of seeds (>4%) in the berries, whereas cultivars 'Martin', 'Pasture', and 'Thiessen' contained the lowest seed mass (<2.6%). The Saskatoon berry contained seed mass similar to those of blueberry, bearberry, and crowberry but higher than those of lingonberry and cranberry (*3*).

Oil Content. Data for the total oil content in 17 Saskatoon berry cultivars are presented in **Table 1**. The seed oil yields (9.4−18.7%) varied significantly among the cultivars analyzed. 'Thiessen', 'Parkhill', and 'Smoky' cultivars contained the highest amount of oil in the seeds, whereas cultivar 'Pasture' had the lowest lipid content. The oil content in most of the cultivated Saskatoon berry seeds was higher than in wild Saskatoon berry seeds, for which an average of 13% was reported (*12*). The oil content of analyzed Saskatoon seeds was higher than the oil content reported for Canadian raspberry seeds (10.7%) (*13*). Also, thorny buffaloberry, chokecherry, hawthorn, and Woods' rose fruits collected in western Canada contained lower amounts of oil in their seeds than Saskatoon berries (11.5, 10.4, 3.4, and 3.7%, respectively) (*2*). Chokeberries and black currants showed higher concentrations of oil in seeds (19 and 23%, respectively) than Saskatoon berries (*14*).

Table 2. Fatty Acid Composition (Percent) of Saskatoon Berry Seed Oil[a]

cultivar	16:0	16:1	18:0	18:1	18:2n-6	18:3n-3	20:0	20:1	20:2	22:0	24:0	others	SA	MUFA	PUFA
Northline	7.80a	0.37	1.05	29.25d	57.13a	0.81c	1.35	0.97	0.09	0.46	0.19	0.53	10.85b	30.59 d	58.03 b
Pasture	6.44b	0.28	1.31	28.63d	57.99a	1.12a	1.47	1.15	0.13	0.52	0.18	0.78	9.92 c	30.06 e	59.24 a
Success	7.04a	0.37	2.03	38.08a	47.32d	0.80c	1.96	1.02	0.07	0.58	0.22	0.51	11.83 a	39.47 a	48.19 f
Honeywood	7.03a	0.31	1.31	31.15c	55.83b	0.92b	1.30	0.86	0.08	0.44	0.16	0.61	10.24 b	32.32 d	56.83 c
Regent	6.94a	0.38	2.08	37.46a	47.88d	0.95b	1.90	0.98	0.07	0.60	0.22	0.54	11.74 a	38.82 a	48.9 f
Lee 2	5.47c	0.27	1.50	33.50b	53.63c	0.91b	1.95	1.26	0.10	0.60	0.19	0.62	9.71 c	35.03 c	54.64 d
Pembina	5.59c	0.27	1.47	33.06b	54.02b	0.93b	1.93	1.28	0.10	0.59	0.19	0.57	9.77 c	34.61 c	55.05 d
Thiessen	6.94a	0.28	1.13	29.26d	57.43a	1.05a	1.39	1.17	0.12	0.47	0.16	0.60	10.09 c	30.71 d	58.6 b
Quaker	6.95a	0.29	0.90	28.03d	58.75a	1.09a	1.21	1.31	0.15	0.44	0.21	0.67	9.71 c	29.63 e	59.99 a
Lee 8	7.48a	0.36	1.10	30.11c	56.65b	0.75c	1.38	0.96	0.09	0.44	0.18	0.50	10.58 b	31.43 d	57.49 c
Forestburg	6.69b	0.30	1.11	32.07c	54.90b	0.89b	1.40	1.26	0.10	0.50	0.19	0.59	9.89 c	33.63 c	55.89 d
Nelson	6.41b	0.43	1.37	34.27b	52.99c	0.84c	1.44	1.00	0.08	0.46	0.18	0.53	9.86 c	35.70 b	53.91 e
Pearson	6.91b	0.30	1.06	32.65b	54.10b	0.93b	1.30	1.27	0.11	0.48	0.23	0.66	9.98 c	34.22 c	55.14 d
Martin	6.76b	0.27	1.06	29.42c	57.47a	1.01a	1.39	1.24	0.12	0.50	0.18	0.58	9.89 c	30.93 d	58.60 b
Lee 3	7.29a	0.29	0.82	26.27e	60.12a	1.16a	1.17	1.30	0.16	0.47	0.22	0.74	9.97 c	27.86 f	61.44 a
Parkhill	5.93c	0.43	1.58	34.44b	53.03c	0.96b	1.54	0.96	0.01	0.50	0.21	0.41	9.76 c	35.83 b	54.00 e
Smokey	6.64b	0.30	1.03	30.22c	57.00a	0.82c	1.30	1.30	0.12	0.48	0.22	0.57	9.67 b	31.82 d	57.94 b
av	6.72	0.32	1.29	31.64	55.07	0.94	1.49	1.13	0.11	0.50	0.20	0.59	10.20	33.10	55.11

[a] Different letters within each column represent significance difference ($p < 0.05$).

Table 3. Molecular Mass and Fragmentation Ions Obtained for TAG Identified in Saskatoon Seed Oil by HPLC-DAD-APCI-MS

TAG[a]	t_R (min)	$[M + H]^+$ (m/z)	$[M + H - R_iCOOH]^+$ (m/z)	$[R_iCO]^+$, $R_iCOO + 58]^+$ (m/z)
LLLn	71.3	877.7	599.5 (95),[b] 597.5 (60)	
LLL	77.2	879.7	599.5 (100)	337.2 (80), 263.2 (10)
LLO	83.8	881.8	599.5 (100), 601.6 (55)	339.3 (100), 263.2 (20)
LLP	85.5	855.7	599.5 (100), 575.4 (65)	
LLG	89.3	909.8	599.5 (100), 629.5 (55)	367.3 (80), 337.3 (30), 339.3 (25)
LOO	90.4	883.7	603.5 (80), 601.5 (60)	265.2 (80), 339.3 (40)
LOP	91.5	857.7	601.5 (100), 577.5 (75), 575.5 (70)	313.2 (70)
PLP	92.5	831.6	575.5 (100), 551.5 (30)	313.3 (55), 239.1 (20)
LLA	96.2	911.8	631.6 (80), 599.5 (50)	337.3 (30)
OOO	96.9	885.8	603.6 (90)	265.3 (90)
OOP	97.8	859.7	577.5 (85), 603.5 (70)	265.3 (60), 239.3 (45)
unknown	101.1	939.9	659.7 (90), 599.5 (75), 629.5 (15)	
OLA	102.0	913.8	631.6 (80), 601.5 (65), 633.6 (63)	339.3 (100), 265.3 (70), 337.1 (65), 263.3 (25)
POS	104.0	861.8	605.4 (100), 577.4 (80), 579.5 (25)	265.3 (40), 239.1 (15)
LgLL	106.1	967.9	687.7 (60), 599.5 (35)	337.1 (60)

[a] Abbreviations: Ln, linolenate; L, linoleate; O, oleate; S, stearate; P, palmitate; A, arachidate; Lg, lignocerate. [b] Relative abundance of the fragment ion.

Fatty Acid Composition. The fatty acid profile is presented in **Table 2**. Eleven acids were identified, among which linoleic (18:2) contributed 55% to the total (average), followed by oleic (18:1) acid at 32% and palmitic (16:0) acid at 6.7%. These predominant acids in Saskatoon berry seed oil were significantly different among 17 cultivars tested (**Table 2**). The highest level of linoleic acid was observed in the 'Lee 3' seed oil (60.1%), and the lowest levels were found in 'Regent' and 'Success' seed oils (47.9 and 47.3%, respectively). Conversely, due to low linoleic acid content, 'Success' and 'Regent' seed oils had significantly higher oleic acid content than other cultivars. At the same time 'Lee 3' seed oil (high in linoleic acid) contained the lowest level of oleic acid (26%). All seed oils also contained low levels of α-linolenic acid, the *n*-3 essential fatty acid. The fatty acid composition of the oil extracted from the seeds of cultivated Saskatoon berries is comparable to the fatty acid composition of the oil extracted from seeds of wild Saskatoon berries (*12*). The contents of saturated fatty acids in analyzed seed oils were below 12% (**Table 2**). The level of saturated fatty acids in Saskatoon berry seed oil was comparable to that reported for Woods' rose, hawthorn, boysenberry, and blueberry seed oils (*2*, *15*), but lower than that presented for pumpkin seed oil (>20%) (*16*). Saskatoon berry seed oils contained high levels of total unsaturated fatty acids (from 87.7% for 'Success' to 89.8% for 'Parkhill'), but the differences in the content of mono- and polyunsaturated fatty acids between cultivars were significant (**Table 2**). For instance, 'Success' and 'Regent' seed oils contained the lowest levels of polyunsaturated fatty acids (48.2 and 48.9%, respectively), whereas 'Lee 3' and 'Quaker' seed oils contained the highest amounts of polyunsaturated fatty acids (61.4 and 60.0%, respectively). The differences in the content of polyunsaturated fatty acids were related to the concentration of linoleic acid, *n*-6 essential fatty acid, in the seed oils. Essential fatty acids cannot be synthesized in the human body and have to be obtained through the diet. Because the Saskatoon berry seeds are byproducts from fruit processing, development of food applications of the Saskatoon berry seed oils may add value to berry fruit production and provide opportunities for diversification.

Triacylglycerol Composition. The fatty acid composition can be used to evaluate the stability and nutritional quality of fats and oils. However, to understand their physical and functional properties, determination of the type and amounts of TAG species present in the oil is also essential. The TAG composition in Saskatoon seed oil was determined by HPLC method using

Table 4. Triacylglycerol Composition[a] of Saskatoon Seed Oil

cultivar	LLLn	LLL	LLO	LLP	LLG	LOO	LOP	PLP	LLA	OOO	OOP	unknown	OLA	POS	LgLL
Northline	1.76	27.61b	28.83b	9.76a	1.50	10.22d	5.15b	0.50	2.45	1.63	0.57	0.71	0.81	0.32	0.27
Pasture	2.42	30.77a	27.22c	8.51b	1.77	10.14d	4.06c	0.50	2.38	1.67	0.30	0.63	0.76	0.31	0.23
Success	1.71	21.03d	29.89b	8.39b	1.96	16.24a	6.57a	0.54	3.09	3.94	0.89	0.63	1.34	0.45	0.39
Honeywood	2.01	26.93b	34.70a	5.09c	1.05	11.98c	5.29b	0.40	1.69	2.35	0.78	0.41	0.56	0.24	0.22
Regent	1.79	21.66d	33.71a	6.75c	0.95	15.31a	7.64a	0.25	2.78	3.48	0.97	0.96	0.70	0.26	0.21
Lee 2	2.12	26.56b	32.40a	6.19c	1.92	13.64b	2.48d	1.64	3.31	2.80	0.46	0.95	0.39	0.26	0.21
Pembina	2.21	26.27b	32.55a	5.79c	2.02	13.00b	4.48c	0.28	3.23	2.67	0.46	0.96	0.38	0.11	0.11
Thiessen	2.40	30.17a	30.29b	8.17b	1.71	9.73d	4.79c	0.33	2.49	1.74	0.57	0.24	0.34	0.17	0.09
Quaker	2.37	31.04a	29.99b	9.35a	2.09	12.30c	1.76d	0.33	2.39	1.14	0.34	0.47	0.20	0.11	0.11
Lee 8	1.96	28.55b	29.51b	9.95a	1.39	10.90d	5.88b	0.27	2.50	1.53	0.41	0.30	0.56	0.26	0.10
Forestburg	1.90	24.01c	29.45b	8.87b	1.97	11.21c	5.20b	0.23	2.66	2.09	0.39	0.59	0.30	0.12	0.16
Nelson	1.87	26.88b	30.09b	8.59b	1.05	13.28b	5.61b	0.30	2.27	2.85	0.29	0.95	0.11	0.19	0.20
Pearson	1.88	23.53c	30.88b	9.00b	2.11	11.35c	6.10b	0.22	2.62	2.22	0.39	0.64	0.22	0.13	0.12
Martin	2.48	28.60b	28.29b	9.09b	2.03	9.81d	5.64b	0.37	2.66	1.76	0.36	0.57	0.24	0.09	0.10
Lee 3	2.83	31.16a	27.57c	10.77a	2.00	8.37e	5.00b	0.38	2.30	1.01	0.38	0.46	0.22	0.12	0.14
Parkhill	2.05	26.33b	32.06a	8.42b	1.00	14.37b	5.58b	0.24	2.65	3.18	0.38	0.71	0.36	0.12	0.14
Smokey	1.73	24.38c	31.28b	7.42b	2.10	9.85d	5.84b	0.22	2.65	1.75	0.44	0.56	0.26	0.16	0.18
av	2.09	26.49	30.83	8.13	1.69	12.07	5.19	0.40	2.62	2.30	0.50	0.63	0.41	0.19	0.17

[a] TAG composition presented as DAD peak area (%) recorded at 205 nm. Ddifferent letters within each column represent significance difference ($p < 0.05$).

Table 5. Content of Tocopherols in Saskatoon Berry Seed Oil[a]

cultivar	α-tocopherol (mg/kg of oil)	δ-tocopherol (mg/kg of oil)	γ-tocopherol (mg/kg of oil)	total (mg/kg of oil)
Northline	1292.8 ± 22.1b	15.2 ± 3.6b	134.8 ± 12.2ef	1442.8d
Pasture	1166.1 ± 27.3c	18.7 ± 3.0a	197.5 ± 20.1b	1382.3e
Success	1098.4 ± 19.1c	7.1 ± 0.6c	125.2 ± 24.3f	1230.7f
Honeywood	1140.6 ± 28.5c	6.9 ± 0.2c	209.4 ± 30.1b	1356.9e
Regent	960.1 ± 31.1e	8.1 ± 0.4c	130.9 ± 27.6f	1099.1h
Lee 2	1234.0 ± 42.2b	12.2 ± 0.3b	139.7 ± 29.2e	1385.9e
Pembina	1211.5 ± 36.8b	8.2 ± 1.0c	128.0 ± 18.3f	1347.7e
Thiessen	1147.2 ± 28.1c	7.3 ± 0.2c	203.2 ± 19.1b	1357.7e
Quaker	1326.1 ± 32.1b	7.0 ± 0.7c	203.0 ± 22.8b	1536.1c
Lee 8	1312.5 ± 37.6b	8.1 ± 1.1c	123.1 ± 12.1f	1443.7d
Forestburg	1102.9 ± 16.1c	6.7 ± 0.9c	142.0 ± 28.7e	1251.6f
Nelson	1452.1 ± 39.1a	8.9 ± 0.8c	188.5 ± 32.4c	1649.5b
Pearson	1090.0 ± 29.3c	6.5 ± 0.6c	157.1 ± 30.0d	1253.6f
Martin	903.0 ± 22.8e	7.1 ± 0.3c	142.9 ± 26.6e	1053.0h
Lee 3	1485.7 ± 29.7a	6.6 ± 0.4c	261.8 ± 27.1a	1754.1a
Parkhill	1000.0 ± 17.1d	5.2 ± 0.6c	124.5 ± 17.9f	1129.7g
Smokey	1019.5 ± 25.1d	7.4 ± 0.2c	152.7 ± 22.8d	1179.6g
av	1173.1	8.7	162.6	1344.4

[a] Different letters within each column represent significance difference ($p < 0.05$); values are mean ± SD of two samples of each cultivar, analyzed individually in duplicate.

DAD (used to obtain the profile of TAG in the oil) and MS (used to identify TAG in the oil) detectors. The TAG composition and identification of Saskatoon berry seed oil are presented in **Tables 3** and **4**. Overall, the TAG compositions of all 17 cultivars of Saskatoon berry oil were similar. HPLC-DAD-APCI-MS analysis revealed that Saskatoon berry seed oil consisted of five abundant TAG species containing mainly linoleic (18:2), oleic (18:1), and palmitic (16:0) acids, which comprised >88% of the TAG (**Table 4**). The most prominent components were detected at m/z 879.7, 881.8, 855.7, and 883.7 and were identified by MS/MS analysis as trilinoleoylglycerol (LLL), dilinoleoyl-oleoylglycerol (LLO), dilinoleoyl-palmiteoylglycerol (LLP), and linoleoyl-dioleoylglycerol (LOO), respectively (**Table 3**). The positional distribution of fatty acids within the TAGs was determined by the mass spectrometry according to the ratio of fragment ions, because the neutral loss of fatty acid from the middle *sn*-2 position is less favored in comparison to *sn*-1 and *sn*-3 positions, and therefore it provides the fragment ion with lower relative abundance than statistically expected (**Table 3**). Only small amounts of saturated fatty acids were found in Saskatoon seed oil (10.3% in average) (**Table 2**). Trisaturated TAG species were not detected, possibly because the UV detection shows low sensitivity for saturated TAG, making their quantification very difficult.

The TAG composition and structure affect functional properties of foods in which the oil was incorporated, such as melting point range, solid fat index, and crystal structure. These physical properties affect food properties from texture to taste (*17*, *18*). Also, the oil oxidative stability is, in part, dependent on TAG composition and structure (*19*). In previous studies it was found that triacylglycerol types such as LLLn, LnLP, LLP, LnLO, LLS, and PLP reduced and LLO, LOO, LOP, OOO, LOS, and POO increased oil oxidative stability (*20*, *21*). These results suggest that Saskatoon berry seed oil has good oxidative stability with respect to triacylglycerol composition and structure (high levels of LLO, LOO, and LOP; medium levels of LLP; and low levels of LLLn).

Table 6. Concentration of Sterols in Saskatoon Berry Seed Oil[a]

cultivar	campesterol (mg/kg ofoil)	stigmasterol (mg/kg of oil)	β-sitosterol (mg/kg of oil)	Δ^5-avenasterol (mg/kg of oil)	α-amyrin (mg/kg of oil)	Δ^7-avenasterol (mg/kg of oil)	citrostadienol (mg/kg of oil)	total (mg/kg of oil)
Northline	509.1 ± 15.3ef	236.9 ± 11.2c	8067.5 ± 56.5de	811.9 ± 35.1e	273.0 ± 16.6a	133.2 ± 15.5c	94.2 ± 21.4e	10125.8d
Pasture	818.7 ± 16.7b	373.7 ± 15.1a	8667.5 ± 45.2cd	884.2 ± 31.7cd	172.0 ± 12.7c	175.9 ± 30.0b	201.4 ± 16.9ab	11293.4bc
Success	517.0 ± 20.1e	139.6 ± 13.8e	5987.7 ± 58.4g	495.2 ± 19.3i	78.3 ± 9.9f	72.5 ± 43.2de	66.5 ± 14.7f	7356.8gh
Honeywood	743.3 ± 18.4c	234.7 ± 15.8c	8502.5 ± 64.2d	915.6 ± 65.4c	230.9 ± 56.9b	157.6 ± 24.6bc	186.3 ± 36.2bc	10970.9c
Regent	587.1 ± 13.2d	126.8 ± 21.4e	6981.8 ± 74.2f	578.3 ± 35.4h	119.9 ± 17.5e	96.3 ± 18.8d	85.9 ± 25.3e	8576.1f
Lee 2	498.7 ± 25.2ef	205.9 ± 23.6c	7230.7 ± 55.3ef	698.5 ± 43.2g	123.3 ± 23.9e	135.2 ± 35.7c	128.7 ± 27.1d	9021.0e
Pembina	530.2 ± 16.7de	215.9 ± 15.8c	7776.2 ± 35.8e	715.4 ± 44.8f	140.8 ± 15.4d	140.4 ± 21.4c	142.7 ± 20.7d	9661.6d
Thiessen	789.2 ± 18.3bc	232.5 ± 13.5c	9295.4 ± 67.4c	1002.1 ± 75.3b	219.2 ± 12.4b	165.6 ± 19.5b	201.6 ± 18.4ab	11905.6b
Quaker	810.6 ± 25.5b	294.3 ± 20.3b	10027.2 ± 73.9b	951.6 ± 43.5b	179.5 ± 31.8c	149.9 ± 26.4c	197.8 ± 17.9b	12610.9b
Lee 8	475.4 ± 22.3f	199.2 ± 17.7c	7621.7 ± 81.5e	740.5 ± 54.5f	228.4 ± 28.4b	108.8 ± 14.3d	82.6 ± 11.4e	9456.6de
Forestburg	527.6 ± 19.9de	189.5 ± 16.4cd	6952.6 ± 45.3f	614.0 ± 25.5h	175.9 ± 20.4c	133.1 ± 28.7c	146.6 ± 16.5.cd	8739.3ef
Nelson	730.6 ± 16.4c	177.9 ± 14.5d	6941.0 ± 62.7f	683.5 ± 38.1g	225.2 ± 25.6b	153.0 ± 19.5bc	124.9 ± 21.6d	9036.1e
Pearson	535.5 ± 11.9de	186.4 ± 29.5d	7200.5 ± 67.4ef	580.1 ± 17.9h	160.0 ± 21.2c	125.0 ± 28.1cd	150.9 ± 21.1c	8938.4e
Martin	617.7 ± 24.5d	229.0 ± 13.1c	7653.5 ± 44.4e	852.0 ± 30.4d	171.7 ± 18.4c	152.2 ± 15.6.bc	170.1 ± 18.1.c	9846.2d
Lee 3	1003.7 ± 36.7a	405.9 ± 25.1a	12294.6 ± 78.3a	1352.1 ± 81.2a	270.8 ± 11.4a	220.4 ± 10.3a	223.1 ± 16.4a	15770.6a
Parkhill	556.1 ± 14.4d	139.2 ± 13.8e	6570.8 ± 65.3f	422.0 ± 31.5j	87.5 ± 14.2f	99.5 ± 15.4d	129.0d ± 19.3	8004.1g
Smokey	525.6 ± 16.3e	126.3 ± 18.3e	6362.1 ± 71.1fg	448.2 ± 26.7j	140.3 ± 24.1d	81.2 ± 12.6d	131.0 ± 17.2d	7814.7g
av	633.4	218.5	7890.2	749.7	176.3	135.3	144.9	9948.712

[a] Different letters within each column represent significance difference ($p < 0.05$); values are mean ± SD of two samples of each cultivar, analyzed individually in duplicate.

Tocopherol Composition. The tocopherol content of the 17 Saskatoon berry cultivar seed oils is shown in **Table 5**. α-, γ-, and δ-tocopherols were found in all seed oils investigated, whereas β-tocopherol was not detected. Total tocopherol contents varied significantly within cultivars. The highest tocopherol content was found in cv. 'Lee 3' (1754.1 mg/kg of oil), whereas the lowest was observed in cv. 'Martin' (1053.0 mg/kg of oil). α-Tocopherol was the predominant vitamin E derivative and accounted for 84−91% of the total tocopherols, followed by γ-tocopherol (8−15%) and δ-tocopherol (0.4−1.4%). Cultivar 'Lee 3' contained the highest levels of α- and γ-tocopherols (1486 and 262 mg/kg of oil, respectively). The seed oil extracted from cv. 'Martin' contained the lowest concentration of α-tocopherol (903 mg/kg of oil) within the cultivars tested.

Thus, the Saskatoon berry seed oils contain higher levels of total tocopherols than commercial extra virgin olive oil, soybean, peanut, corn, sunflower, and canola oils (260−1000 mg/kg of oil) (*22*−*24*). They are also higher than those detected in cold-pressed blueberry, red raspberry, marionberry, boysenberry, Canadian chokecherry, and thorny buffaloberry seed oils (111−942 mg/kg of oil) (*2*, *15*). On the other hand, they are lower than that reported for hexane-extracted raspberry seed oil (3600 mg/kg of oil) (*13*). The Saskatoon berry seed oil contained high concentrations of α-tocopherol, the biologically most active of the four tocopherols and one of the most potent chain-breaking phenolic antioxidants known (*25*, *26*). Additionally, α-tocopherol protects polyunsaturated fatty acids from oxidation and thus prevents arteriosclerosis and cancer (*27*, *28*). The concentration of α-tocopherol in Saskatoon berry seed oil was much higher than that in Finish berry seed oils (21−151 mg/kg of oil) (*15*), hexane-extracted raspberry seed oil (710 mg/kg of oil) (*13*), or chokecherry, thorny buffaloberry, and Woods' rose seed oils (33, 184, and 399 mg/kg of oil, respectively) (*2*). The hawthorn seed oil contained a higher amount of α-tocopherol than Saskatoon seed oil (2673 mg/kg of oil) (*2*).

The high levels of tocopherols, especially α-tocopherol, detected in the analyzed Saskatoon berry seed oils would offer excellent protection against oxidative degradation of the oil during processing and storage.

Sterol Composition. Total sterol content of Saskatoon berry seed oil varies within the range of 7357−15771 mg/kg. As in most vegetable oils, the sterol fraction of Saskatoon berry seed oil was composed mainly of Δ^5-sterols. The most abundant sterols were β-sitosterol, Δ^5-avenasterol, campesterol, and stigmasterol (**Table 6**). Other sterols, detected at lower levels, include α-amyrin, Δ^7-avenasterol, and citrostadienol. 'Lee 3' contained the highest level of sterols in seed oil (15571 mg/kg of oil), followed by cvs. 'Quaker' and 'Thiessen' (12611 and 11906 mg/kg of oil, respectively). The lowest sterol contents were measured in the oil extracted from seeds of cvs. 'Parkhill', 'Smoky', and 'Success' (8004, 7815, and 7357 mg/kg, respectively). The Saskatoon berry seed oil contained higher levels of sterols than hawthorn, chokeberry, thorny buffaloberry, Woods' rose, or sea buckthorn seed oils (*2*, *29*). Also, commercial seed oils such as canola, sunflower, and soybean oil contained lower amounts of sterols than Saskatoon berry seed oil (*30*). β-Sitosterol is known to be the principal plant sterol found in many oilseeds. In Saskatoon berry seed oil the β-sitosterol levels varied in the range from 5987 to 12295 mg/kg of oil in the 'Success' and 'Lee 3′ cultivars, respectively, with an average content of 7890 mg/kg of oil, contributing 79% to total sterols. Plant sterols, primarily β-sitosterol, campesterol, and stigmasterol, are membrane constituents that effectively reduce serum LDL cholesterol and artherosclerotic risk (*31*). Hence, the consumption of Saskatoon berry seed oils that contain sterols could provide health benefits.

This study showed that the seed oil from 17 Saskatoon berry cultivars studied contained high levels of unsaturated fatty acids (88−90%). This feature makes the Saskatoon berry seed oil a valuable component for applications in the functional food and cosmetic industries.

Interestingly, the oils from cultivars contained different proportions of mono- and polyunsaturated fatty acids. For instance, cvs. 'Regent' and 'Success' contained low levels of polyunsaturated fatty acids (∼48%), whereas oil from 'Lee 3' contained 60% polyunsaturated acids. The level of mono- and polyunsaturated fatty acids is linked to the oxidative stability of particular oils and the food products containing them. In the seed of the Lee 3 cultivar, the high level of polyunsaturated fatty acids was associated with the highest level of tocopherols and sterols detected in studied oils.

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