

## Characteristics of raspberry (*Rubus idaeus* L.) seed oil<sup>☆</sup>

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### Abstract

Studies were conducted on properties of oil extracted from raspberry seeds. Oil yield from the seed was 10.7%. Physicochemical properties of the oil include: saponification number 191; diene value 0.837; *p*-anisidine value 14.3; peroxide value 8.25 meq/kg; carotenoid content 23 mg/100 g; and viscosity of 26 mPa.s at 25°C. Raspberry seed oil showed absorbance in the UV-B and UV-C ranges with potential for use as a broad spectrum UV protectant. The seed oil was rich in tocopherols with the following composition (mg/100 g):  $\alpha$ -tocopherol 71;  $\gamma$ -tocopherol 272;  $\delta$ -tocopherol 17.4; and total vitamin E equivalent of 97. The oil had good oxidation resistance and storage stability. Lipid fractionation of crude raspberry seed oil yielded 93.7% neutral lipids, 3.5% phospholipids, and 2.7% free fatty acids. The main fatty acids of crude oil were C18:2 *n*-6 (54.5%), C18:3 *n*-3 (29.1%), C18:1 *n*-9 (12.0%), and C16:0 (2.7%). The ratio of fatty acids, polyunsaturates to monounsaturates to saturates varied depending on lipid fraction. Polymorphic changes were observed in thermal properties of raspberry seed oil. © 2000 Published by Elsevier Science Ltd. All rights reserved.

**Keywords:** Raspberry seed; Raspberry oil; Oil quality; Tocopherols; Storage; DSC; Chemical and physical parameters

### 1. Introduction

About 18,000 metric tonnes of raspberries are produced annually in Canada with the total global production at 312 thousand metric tonnes. In the processing of raspberry juice, the seed becomes a byproduct which is currently under exploited. Oil from raspberry seed could amount to over 400 metric tonnes, assuming 10% of seed in fresh berries, 23% oil content of seeds (Johansson, Laakso & Kallio, 1997) and that all raspberry produced in Canada is processed as juice.

The composition of raspberry seeds compiled by Winton and Winton (1935) reveals that as early as 1907 oil expressed from the seed amounted to 14.6–18%. These raspberry seed oils contained 0.73–1.10% phytosterol, and had a saponification value of 187–192. Recently, Johansson et al. (1997) found that linoleic,  $\alpha$ -linolenic, oleic and palmitic acids were typically the most abundant fatty acids from seed oil of 22 common edible wild northern berries, including raspberry. The seed mass, 100 seed weight, and seed oil content for raspberry were 10.1% (fw), 180 mg, and 23.2%, respectively.

Storage studies by Carnat, Pourrat and Pourrat (1979) showed that raspberry seed oil oxidized very slowly even at 60°C with an increase in peroxide value from 3 to 39 mmol/kg over 7 days. At ambient temperature (22–23°C), oxidation was slower yet, with peroxide values varying from 3 to 18 mmol/kg after 5 weeks. This resistance to oxidation of raspberry seed oil was purported to be due to the presence of a minor component in the unsaponifiable fraction of the oil (Carnat et al.). In the quest to understand the oxidative stability of raspberry seed oil, Pourrat and Carnat (1981) stabilized the moisture content of raspberry seed to 5–6% by drying at 50°C for 4–5 h, then extracted oil with chloroform. The oil yield was 16–18% by that process and the fatty acid composition in percentage of the chloroform extracted oil was: C16:0, 2.7; C18:0, 0.2; C18:1, 18.7; C18:2, 55.5; and C18:3, 32.6 (Pourrat & Carnat, 1981). The definitive reason for the high stability of raspberry seed oil has not been fully clarified.

The incorporation of raspberry seed oil in cosmetics and pharmaceutical products based on its anti-inflammatory activity notably for the prevention of gingivitis, rash, eczema, and other skin lesions has been patented (Pourrat & Pourrat). The anti-inflammatory activity of raspberry seed oil was superior compared to those of other well-known oils such as virgin avocado oil, grape-seed oil, hazelnut oil, and wheat germ oil (Pourrat &

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Pourrat). According to this patent, raspberry seed oil can be used as a sun screen, in toothpaste, cremes for prevention of skin irritations, bath oil, aftershave cream, antiperspirants, shampoos, and lipsticks.

Red raspberry forms part of the Pacific Agri-Food Research Centre small fruit breeding program. In addition to the release of new cultivars with high yields of large fruits with excellent quality, pleasant flavor, firm fruit and low susceptibility to pre- and postharvest diseases, there is interest in the complete utilization of the fruit for food and non-food uses. Raspberry seed oil may be regarded as a speciality oil and as such may attract considerable attention because of its possible nutraceutical effects. It is a rare commodity and currently retails at \$52 a litre as a fragrant oil. Our aim is to transform raspberry seed into economically valuable ingredients for the food and nonfood industries. In this context, the chemical and physical properties of oil extracted from raspberry seed has been investigated to provide guidelines for innovative uses of this byproduct. The properties of raspberry seed oil was also compared with those of two commercial oils, grapeseed and safflower oils used in the food, cosmetic and pharmaceutical industries.

## 2. Materials and methods

Raspberry (*Rubus idaeus* L.) seeds from a mixture of different cultivars grown for processing were obtained from Valley Berry Inc., (Abbotsford, British Columbia). Since the moisture content of the seed was about 41.5%, the seed samples were air-dried in a fluid bed dryer (Lab-Line Instruments Inc., Melrose Park, IL) for 2 h at 25°C to reduce the moisture to 13.6%. Raspberry seeds were ground (Thomas Wiley Mill, Philadelphia, PA) to pass a 1mm screen. Oil from milled samples was extracted using hexane as described by Oomah, Mazza and Przybylski (1996). Briefly, the sample (100 g) was stirred for 2 h at 4°C with hexane (1 l). The solvent was removed by vacuum filtration and the sample was further extracted twice. After the last filtration, the extract was pooled, hexane removed (vacuum rotary evaporation, 35°C), purged with nitrogen and stored at –20°C until analysis. A sample of raspberry seed was hydraulically pressed (Carver Press, 280 kg/cm<sup>2</sup>) to extract cold-pressed oil. A commercial grapeseed oil produced and packed in Spain (Aceitas Borges Pont, S.A., Catalonia) and safflower oil (P.C.<sup>TM</sup> Product, Sunfresh Ltd., Toronto, Canada) purchased from a local food store were used as controls.

### 2.1. Analytical procedures

Official methods (American Oil Chemists' Society, AOCS, 1993) were used for the determination of the saponification value (method Cd 3-25) and *p*-anisidine

value (method Cd 18-90) of oils. Conjugated dienoic and trienoic acids were determined by the spectrophotometric method outlined in the Standard Methods for the Analysis of Oils, Fats and Derivatives (International Union of Pure and Applied Chemistry, IUPAC, 1985). The peroxide value of the oils was determined using the PeroXOquant quantitative peroxide assay kit (Pierce, Rochford, IL, USA). Absorptivity and transmission of oil solutions (0.1–10% v/v) in hexane were measured with a spectrophotometer (DU-640B, Beckman Instruments Inc., Fullerton, CA, USA).

The AOAC method (958.05, Association of Official Analytical Chemists, AOAC, 1990) with a few modifications was used to evaluate carotenoid content of oils. Carotenoid content, expressed as micrograms of  $\beta$ -carotene per gram of oil, was performed by applying a calibration curve constructed by preparing solutions of increasing concentration, from 0.5 to 2.5  $\mu$ g of  $\beta$ -carotene/ml hexane. Absorbance was recorded at 440 nm (DU-640B, Beckman Instruments Inc., Fullerton, CA, USA) using hexane as blank. Oil was diluted with hexane (10% v/v for grapeseed and safflower, 1% v/v for raspberry) to  $\beta$ -carotene standard range. Moisture content was determined by the AOAC method (AOAC, 1984). Viscosity of the oil was measured with a controlled stress Bohlin rheometer CVO (Bohlin Instruments Ltd., Gloucestershire, UK). Measurements were performed at 25°C with a steel cone-plate geometry (20 mm, 2°) under a ramping shear of 2.5–10 Pa.

Tocopherols were analyzed by an HPLC system (Waters 840 system, Milford, MA, USA) consisting of a pump (Model 510), an autosampler (Model 712) and a fluorescence detector (McPherson SF-749 spectrofluorometer, Acton, MA, USA) interfaced with a personal computer. A normal phase column (4.6 $\times$ 150 mm, Primesphere 5 silica 5  $\mu$ m) with guard column (4.6 $\times$ 30 mm) (Phenomenex, Torrance, CA, USA) was used with hexane/2-propanol/dimethyl propane (1000/5/1, v/v/v) as a mobile phase. The system was operated isocratically at a flow rate of 1 ml/min. Separations were carried out at 25°C (Waters TCM temperature controller) with the fluorescence detector excitation and emission wavelengths set at 297 and 325 nm, respectively. Typically, a 10 min equilibration period was used between samples, requiring about 40 min/sample. Quantitation was based on an external standard method; the calibration curves ranged from 3.97 to 15.87, 5.41 to 21.63 and 6.0 to 24.0  $\mu$ g/ml of reference compounds  $\alpha$ -,  $\delta$ -, and  $\beta$ -,  $\gamma$ -tocopherols, respectively (Sigma Chemical Co., St Louis, MO, USA). Prior to HPLC analysis, the oil was diluted with hexane to obtain a concentration of about 160 g/l, filtered (0.45  $\mu$ m, Gelman Science Inc., Ann Arbor, MI, USA) and 20  $\mu$ l sample was injected.

Crystallization and melting points were measured with a differential scanning calorimeter (DSC-2910

Modulated DSC-TA Instruments, New Castle, DE, USA). Oil (20–25 mg) was weighed in DSC-pan (aluminium open pan, TA Instruments T70529) and DSC runs were performed within the temperature range of 10 to  $-70^{\circ}\text{C}$ . A programmed cycle was followed in which the sample was cooled from 10 to  $-70^{\circ}\text{C}$  at  $1^{\circ}\text{C}/\text{min}$ , maintained at this low temperature for 5 min and heated back to  $10^{\circ}\text{C}$ . An empty DSC pan was used as an inert reference to balance the heat capacity of the sample pan. The DSC was calibrated for temperature and heat flow using mercury (mp  $-38.83^{\circ}\text{C}$ , TA Instruments standard), distilled water (mp  $0.0^{\circ}\text{C}$ ), gallium (mp  $29.76^{\circ}\text{C}$ , TA Instruments standard) and indium (mp  $156.6^{\circ}\text{C}$ ,  $\Delta$  28.71 J/g, Aldrich Chemical Co.).

Separation of individual lipid classes was performed using solid-phase extraction cartridge, (Bakerbond amino [NH<sub>2</sub>] disposable extraction column, 500 mg, J. T. Baker Inc., Phillipsburg, NJ), with aminopropyl packing, essentially as described by Carelli, Bredan and Crapiste (1997). The cartridge was preconditioned with 2 ml methanol, 2 ml chloroform, and 4 ml hexane before use. A micropipet was used to inject 50–150 mg of oil dissolved in chloroform. Lipid classes were recovered by sequential elution under vacuum (5–10 mm Hg) with 4 ml each of chloroform/isopropanol (2/1, v/v), diethyl ether/acetic acid (95/5, v/v), and methanol to separate neutral lipids, free fatty acids and phospholipids, respectively. The eluates were collected, evaporated under nitrogen, weighed, and stored at  $-20^{\circ}\text{C}$  for fatty acid analysis.

The lipids were esterified by the one-step methylation method of Ulberth and Henninger (1992) with some modifications. These included the omission of toluene in the reagent and centrifugation for phase separation. The top layer was transferred into a small vial and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . Samples were analyzed for their fatty acid methyl esters on a Hewlett–Packard model 5890 gas chromatograph (Avondale, PA), equipped with a split/splitless injector, a flame-ionization detector, an automatic sampling device, and a 100 M SP-2560 fused-silica capillary column (Supelco, Oakville, ON) with 0.25 mm i.d. The column temperature was programmed from 140 to  $240^{\circ}\text{C}$  at  $4^{\circ}\text{C}/\text{min}$ , and the injector and detector temperatures were set at  $260^{\circ}\text{C}$ . Helium was the carrier gas. Peak areas of duplicate injections were measured with a Hewlett–Packard 3396 computing integrator. All assays except thermal analysis were performed in triplicates.

### 3. Results and discussion

Raspberry seed at 13.6% moisture content had a yield of about 10.7% (db) oil by solvent extraction. Our oil yield was at the lower end of the seed oil content for *Rubus* species (10–23% dw) reported by Johansson et al.

(1997), and lower than (14–18%) those reported earlier for raspberry seed (Pourrat & Carnat, 1981; Winton & Winton, 1935). The lower oil yield obtained in this study could be partly due to different seed samples and solvent used for oil extraction. Raspberry seed oil is yellow with a slight “fishy” off-note. Crude raspberry seed oil showed some absorbance in the UV-C (100–290 nm) and UV-B (290–320 nm) range (Fig. 1). In the UV-B range, the wavelengths of ultraviolet light responsible for most cellular damage, raspberry seed oil can shield against UV-A induced damage by scattering (high transmission), as well as by absorption. The shielding power in the UV-A (320–400 nm) range depends mostly on the scattering effect. Thus, raspberry seed oil may act as a broad spectrum UV protectant and provide protection against both UV-A, an exogenous origin of oxidative stress to the skin, and UV-B. The optical transmission of raspberry seed oil, especially in the UV range (290–400 nm) was comparable to that of titanium dioxide preparations with sun protection factor for UV-B (SPF) and protection factor for UV-A (PFA) values between 28–50 and 6.75–7.5, respectively (Kobo Products Inc., South Plainfield, NJ).

Absorptivity at 245 nm, a wavelength which is approximately at the lower limit of detectability for the

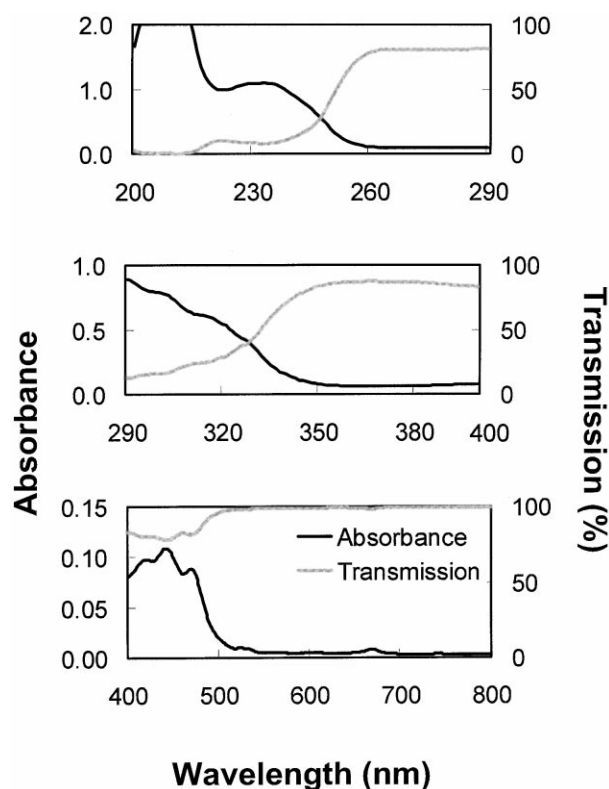


Fig. 1. Ultra violet/visible spectra of raspberry seed oil. Figure derived from scans ( $\lambda = 200\text{--}290$ ) of oil diluted 1:100; from scans ( $\lambda = 290\text{--}400$  and  $\lambda = 400\text{--}800$ ) of oil diluted 1:10, all in hexane. Black line is absorbance and gray line is transmission.

human eye, was low for raspberry seed oil, inferring low levels or absence of yellow pigments in the oil. Green pigments, particularly chlorophyll content, usually measured at 630, 670 and 710 nm, was negligible as indicated by very low absorbance (0.003–0.007) in the 600–750 nm range for raspberry seed oil (1% oil in hexane). The negligible amount of green pigments does not impart undesirable color to the oil and may be unable to promote oil oxidation, especially in the presence of light. Raspberry seed oil contained yellow coloring as indicated by absorbance between 0.084 and 0.108 at 440–460 nm for 1% oil in hexane and was equivalent to the Munsell 1.25 Y 8/16 rating. These yellow colors which include carotenoids are beneficial, since they simulate the appearance of butter without the use of primary colorants such as carotenes, annatos, and apocarotenals commonly used in the oil and fat industry. Actual carotenoid content of raspberry seed oil was 23 mg/100 g of oil (Table 1).

Table 1  
Physicochemical characteristics of raspberry, safflower and grape seed oils

Characteristic <sup>a</sup>	Raspberry	Safflower	Grape
Oil yield — dry matter (%)	10.7 ± 0.3	c	c
Seed moisture (%)	13.6 ± 0.1	c	c
Viscosity (mPas.s) <sup>b</sup>	26 ± 1.1	47.3 ± 0.4	49.4 ± 0.3
Saponification number	191 ± 0.1	191.6 ± 0.6	192.9 ± 0.4
Diene value	0.837 ± 0.0003	0.514 ± 0.006	0.467 ± 0.001
Triene value	<sup>d</sup>	0.134 ± 0.006	0.089 ± 0.001
<i>p</i> -Anisidine value	14.3 ± 0.2	5.36 ± 0.006	10.46 ± 0.03
Peroxide value (meq/kg)	8.25 ± 0.1	3.52 ± 0.04	0.96 ± 0.01
Carotenoid content (mg/100 g)	23 ± 0.04	<sup>d</sup>	<sup>d</sup>

<sup>a</sup> Means of 3.

<sup>b</sup> Means of 10 measurements over ramping stress range (2.5 to 10 Pa).

<sup>c</sup> Not applicable.

<sup>d</sup> Not detected.

Raspberry seed oil has a low viscosity (Table 1), a characteristic which may render it less occlusive than hydrocarbon oils. The viscosity of raspberry seed oil was lower than most vegetable oils and similar to that of oleic acid (Noureddini, Teoh & Clements, 1992). Conjugated diene value of the seed oil was 0.837, and significantly higher than those of commercial grapeseed and safflower oils analyzed under the same conditions. This difference is likely due to raspberry seed oil's high 18:3 content compared to the two commercial oils. Conjugated triene was not detected in raspberry seed oil suggesting absence or very low levels of linolenate oxidation in oil. *p*-Anisidine value of the oil was 14.3 and significantly higher than those of the commercial oils, indicating the presence of aldehydic carbonyl compounds or secondary oxidation of the raspberry seed oil. The peroxide value was 8.25 meq/kg oil, and lower than those generally recommended for commercial vegetable oils ( $\leq 10$ ). However, the oil hydroperoxides can be substantially lowered or reduced during bleaching with acid-activated bleaching earth. The total oxidation value (totox) of raspberry seed oil, calculated using the peroxide and anisidine values ( $2Px + Av$ ), was 30.8, and comparable to that of encapsulated fish oil, but higher than those of vegetable oils (Shukla & Perkins, 1998). Raspberry seed oil was twice as prone to auto-oxidation as safflower oil (totox value of 12.4) under the same test conditions. The saponification value of raspberry seed oil was high and comparable to those of common vegetable oils indicating very high content of low molecular weight triacylglycerols. It was similar to the saponification value of canola oil (Eskin et al., 1996) and within the values for raspberry seed oil (187–192) reported previously (Winton & Winton, 1935). Raspberry seed oil may be prone to peroxide formation based on its peroxide value and may be suitable for soap production judging from the high saponification value.

The major tocopherol in raspberry seed oil was the  $\gamma$  isomer at 75% of the total tocopherol.  $\alpha$ - and  $\delta$ -Tocopherol contents of the oil were 71 and 17.4 mg/100 g, respectively (Table 2). The  $\alpha$ - and  $\delta$ -tocopherol levels of

Table 2  
Tocopherol contents of raspberry, safflower and grape seed oils (mg/100 g)

Oils <sup>a</sup>	Tocopherol				Tocotrienol		Total	Vitamin E
	$\alpha$	$\beta$	$\gamma$	$\delta$	$\alpha$	$\gamma$		
Raspberry								
Hexane extracted	71 ± 0.5	<sup>b</sup>	272 ± 2.6	17.4 ± 0.5	<sup>c</sup>	<sup>c</sup>	360 ± 3.6	97 ± 0.8
Cold pressed	46.1 ± 2.2	<sup>c</sup>	144 ± 11.7	7.1 ± 0.7	<sup>c</sup>	<sup>c</sup>	198 ± 13.2	61 ± 3.3
Safflower	56.0 ± 0.09	2.0 ± 0.2	1.1 ± 0.1	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>	59.0 ± 1.0	57 ± 0.9
Grape	5.6 ± 0.0	2.3 ± 0.0	3.3 ± 0.3	<sup>c</sup>	15.7 ± 0.2	28.5 ± 0.5	55.4 ± 0.9	11.8 ± 0.1

<sup>a</sup> Means of 2.

<sup>b</sup> Trace.

<sup>c</sup> Not detected.

cold-pressed raspberry seed oil was about half that of the hexane-extracted oil. The reason for this difference is unclear, but could probably be due to the presence of non-lipid material in cold-pressed oil which may dilute the concentration of tocopherols. The biologically active vitamin E content relative to that of  $\alpha$ -tocopherol, calculated by using the formula proposed by McLaughlin and Weihrauch (1979), were 97.8 and 58.4 mg/100 g for the hexane-extracted and cold-pressed oils, respectively. Raspberry seed oil is a very rich source of gamma tocopherol since its level (137–272 mg/100 g) is much higher than those reported for other vegetable oils and foods (Eskin et al., 1996; McLaughlin & Weihrauch). The ratio of the tocopherol isomers  $\alpha$ : $\gamma$ : $\delta$  in raspberry seed oil was 20:75:5, and resembled that in commercial refined corn oil at 17:78:3 (McLaughlin & Weihrauch, 1979). The high  $\gamma$ -tocopherol concentration of raspberry seed oil may exert a significant biological effect in non-ruminant animals since  $\gamma$ -tocopherol concentration is easily detected in animals fed natural source of tocopherols at concentrations of 100 and 1000 ppm (Engberg, Jakobsen & Hartfiel, 1993). Raspberry seed oil with high levels of  $\gamma$ -tocopherol may be as important as  $\alpha$ -tocopherol in the prevention of degenerative diseases.

Storage studies carried out at 37°C in the dark showed similar trends of increase in peroxide value with time for raspberry and safflower oils (Fig. 2). However, the rate of increase in peroxide value for raspberry seed oil was lower than that of safflower oil. The data describing the rate of autoxidation fitted the polynomial model ( $y = ax^2 + bx + c$ ). The coefficients of regressions ( $R^2$ ) between the peroxide value and storage

time were 0.808 and 0.864 ( $P < 0.05$ ) for raspberry and safflower oils, respectively. At the end of the storage period (240 h) both oils were roughly equivalent in terms of oxidative degradation that had occurred. A clear induction period was not observed in this study, even when the storage period was extended to 900 h (data not shown). Similar observations have been reported for raspberry seed oil stored at ambient (22–23°C) temperature for 5 weeks (Carnat et al., 1979).

Raspberry seed oil consisted primarily of neutral lipid (93.8%) with minor amounts of free fatty acid and phospholipids (3.5 and 2.7% of the total crude oil, respectively) (Table 3). Similar high levels of neutral lipids (95.7–95.9%) have been reported for raspberry seed oil (Winton & Winton, 1935), and other berry fruit

Table 3  
Fatty acid composition of raspberry seed oil

Fatty acid	Composition (mass%)			
	Crude oil <sup>a</sup>	Neutral lipid	Free fatty acid	Phospholipid
Fractions (%) <sup>b</sup>		93.7 ± 2.0	3.5 ± 1.13	2.7 ± 3.1
C16:0	2.69 ± 0.14	2.68	10.46	10.92
C18:0	0.97 ± 0.01	1.02	1.26	<sup>c</sup>
C18:1	11.99 ± 0.01	12.11	26.62	19.24
C18:2	54.52 ± 0.10	55.12	47.28	63.55
C18:3	29.11 ± 0.05	28.74	14.35	6.29

<sup>a</sup> Means of 4.

<sup>b</sup> Means of 2.

<sup>c</sup> Not detected.

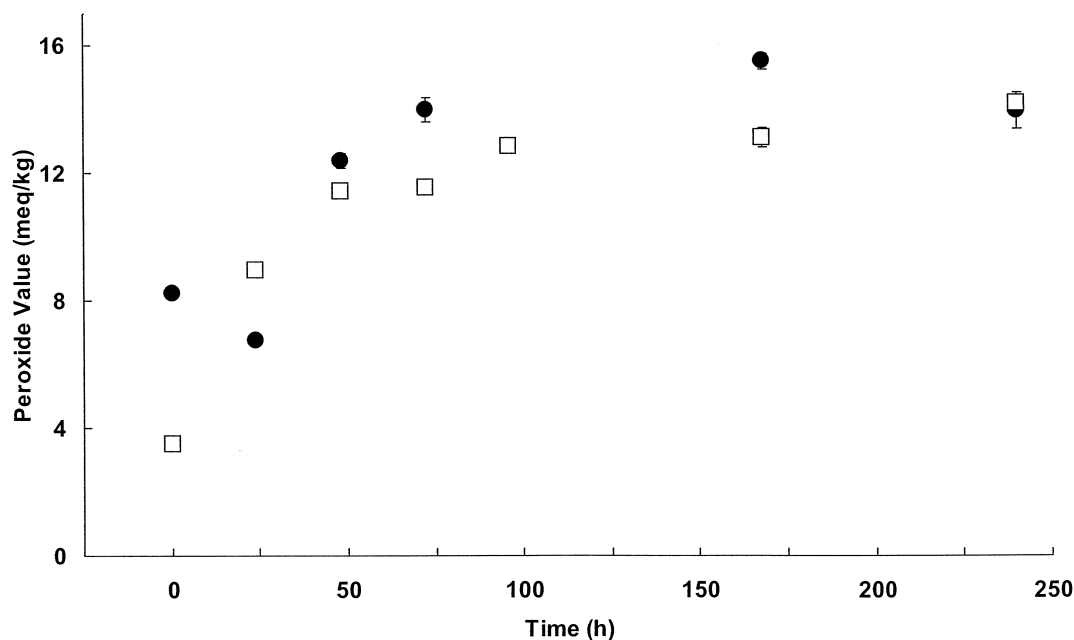


Fig. 2. Stability of raspberry seed oil at 37°C evaluated as peroxide value. ● = raspberry seed oil, □ = safflower seed oil.

oils such as sea buckthorn seed oil (92%) (Zadernowski, Nowak-Polakowska, Lossow, Nesterowicz, 1997). The phospholipid content of raspberry seed oil at 2.7% was higher than that of fruit stone oils from the *Rosaceae* species (0.4–1.1% for peach, apricot, and cherry seed oils) at the expense of neutral lipids (97.2–98.7%) (Zlatanov & Janakieva, 1998). Raspberry seed oil had higher free fatty acid content but comparable phospholipid content than those of common edible oils (canola, soybean, sunflower, corn) 0.3–1.8%, and 0.2–4.0%, respectively. For edible purposes, these non-triglycerides components are considered detrimental to oil quality and should be removed through processing.

The phospholipids are useful as emulsifiers in food and pharmaceutical applications. In raspberry seed oil, the phospholipids may act as a natural antioxidant (Rěblová & Pokorný, 1995) and consequently increase oil stability and shelf life.

The most abundant fatty acids of raspberry seed oil were linoleic,  $\alpha$ -linolenic, and oleic acids, which together comprised 96% of the total fatty acid. The fatty acid composition of raspberry seed oil was similar to that reported previously (Pourrat & Carnat, 1981) and to that of *Rosa dumalis* (Johansson et al., 1997). The linoleic acid content of raspberry seed oil was similar to that of walnut oil (56–59%) (Ruggeri, Capelloni et al., 1998). Neutral lipids which constituted about 94% of the total lipids, had fatty acid composition similar to that of crude raspberry seed oil. The phospholipid fraction was richer in saturated and monounsaturated fatty acids (11 and 19% of the total fatty acid, respectively), but much lower in polyunsaturates compared to the neutral lipid fraction. The polyunsaturates of the free fatty acid fraction amounted to only 61% of the total fatty acids, while the monounsaturated and saturated fatty acids amounted to 27 and 12%, respectively. Hence, the ratio of polyunsaturates to monounsaturates to saturates varied from 84:12:4 to 61:27:12, depending on lipid fractions. The crude raspberry seed oil and the neutral lipid fraction were particularly low in palmitic acid. They contained high amounts of linolenic acid, which makes them especially prone to oxidation, but which may have favorable nutritional implications and beneficial physiological effect in the prevention of coronary heart disease and cancer (Oomah & Mazza, 1998). The free fatty acid and phospholipid fractions with lower levels of linolenic acid than the neutral fraction renders them less susceptible to oxidation. The neutral lipid fraction was characterized by the highest polyunsaturated/saturated ( $P/S$ ) ratio of 22.7, while those of free fatty acids and phospholipid fractions were 15.3 and 6.4, respectively. A high ratio of  $P/S$  is regarded favorably in the reduction of serum cholesterol and atherosclerosis and prevention of heart diseases (Rudel, Kelly, Sawyer, Shah & Wilson, 1998). Similarly, the ratio of  $n-6$  to  $n-3$  fatty acids were 1.92, 3.29 and 10.10

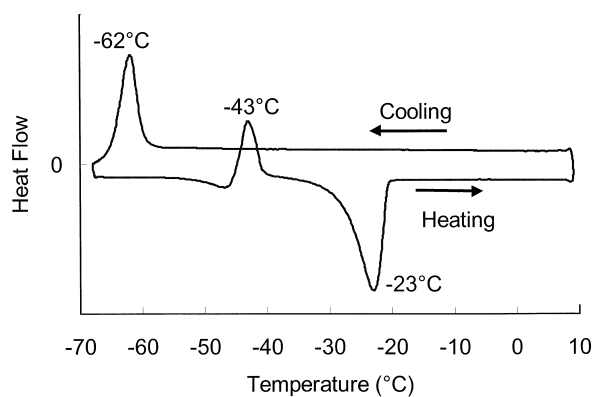


Fig. 3. DSC profile of raspberry seed oil.

for the neutral, free fatty acid and phospholipid fractions, respectively.

Raspberry seed oil has unique thermal characteristics (Fig. 3). The oil presented a crystallization peak at  $-62^{\circ}\text{C}$  with enthalpy of 38.3 J/g. Polymorphism was detected in raspberry seed oil: after melting of the low temperature modification at  $-45^{\circ}\text{C}$ , an additional modification crystallized with an exothermic peak at  $-43^{\circ}\text{C}$ . At  $-23^{\circ}\text{C}$ , peak temperature, this modification melted with an originally existing crystallite of the same kind. Similar DSC tracings were observed for grapeseed oil in this study and by Kaisersberger (1990) and safflower oil (data not presented). These polymorphic changes can be hindered by addition of emulsifiers (Kaisersberger). According to Garti, Schlichter and Sarig (1988), the first small endothermic peak at  $-45^{\circ}\text{C}$  represents the melting of the unstable  $\alpha$  crystal form followed by the crystallization of the more stable  $\beta$  form which is characterized by an exothermic peak. The melting enthalpy of raspberry seed oil was 75 J/g. The amount of melting according to DSC determinations (ratio of enthalpies) was 50.9%, i.e. the solid–liquid ratio of approximately 1:1 at  $-23^{\circ}\text{C}$ . This solid–liquid ratio and, melting and recrystallization characteristics of raspberry seed oil can impinge on its consistency, taste and texture.

The potential for production of oil as a byproduct of raspberry seed appears to be excellent. The unique fatty acid composition, high tocopherol content and quality and hence high protection against oxidative stress, relatively good shelf life, and other desirable physicochemical characteristics indicate potential uses of raspberry seed oil in food, pharmaceuticals, cosmetics, and other nonfood industries. The microconstituents of raspberry seed oil with its rich array of phytochemicals, especially the omega-3 fatty acids and tocopherols suggest that it is a nutraceutical and may be marketed as a dietary supplement with a structure/function claim about healthy blood circulation. The production of oil from raspberry seed provides the use of a renewable resource, and at the same time adding value to agricultural products and improving the environment.

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