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Characteristics of hemp (*Cannabis sativa* L.) seed oil☆

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Abstract

Characteristics of oil extracted from hempseeds subjected to microwave treatments were evaluated. Microwave treatment improved oil yield, increased carotenoid and other pigment contents and decreased *p*-anisidine value without significant changes in other properties. Hempseed oil showed absorbance in the UV-B and UV-C ranges with potential for use as a broad spectrum UV protectant. β-Tocopherol concentrations increased, while the major tocopherol, γ-tocopherol, and fatty acid composition of the oil were unaffected by microwave treatment of hempseed. Hempseed oil showed high kinetic stability during heating and cooling, as characterized by differential scanning calorimetry (DSC). Microwave treatment shifted the melting range of oils to lower temperatures and increased oxidation temperatures, suggesting increased protective effect upon heating.

Keywords: Hempseed; Hempseed oil; Oil quality; Tocopherols; DSC; Microwave; Heating effect; Chemical and physical parameters

1. Introduction

Hemp (*Cannabis sativa* L.), an annual herbaceous plant, has been grown agriculturally for many centuries for its fibre and oil. Its cultivation in Canada has been prohibited since 1938 due to the presence of the phytochemical drug component δ-9-tetrahydrocannabinol (THC). A low THC form of industrial hemp is now legal to grow in Canada (a 0.3% THC standard has been established by the European Union; Blade, 1998). The global market for low THC hemp is valued at $100–200 million annually. The North American market is increasing at a rate of $8–10 million per year (Roulac, 1997).

Hempseed, in addition to its nutritional value, has demonstrated positive health benefits, including the lowering of cholesterol and high blood pressure (Jones, 1995). It has been consumed in food and folk medicinal preparations, or employed as a feed. Hempseed contains 20–25% protein, 20–30% carbohydrates, 25–35% oil and 10–15% insoluble fibre and a rich array of minerals (Deferne & Pate, 1996; Pate, 1999). The highly polyunsaturated oil of hempseed has been used for printer's ink, wood preservative, and also for detergents and soaps. Hempseed oil has been suggested to be perfectly balanced in regards to the ratio (3:1) of the two essential polyunsaturated fatty acids (linoleic and linolenic acids) for human nutrition. The oil, because of this feature and the presence of γ-linolenic acid, is ideal as an ingredient for light body oils and lipid-enriched creams, known for their high penetration into the skin (Rausch, 1995).

The availability of hempseed is expected to increase due to the renewed demand for hemp fibre for paper and clothing. The versatility of the seed lends itself to the development of numerous products for the food, cosmetic, therapeutic, functional food and nutraceutical industries. The quality of oil is currently under investigation to improve the economical and/or environmental performances of a nonconventional crop through innovative uses of its components and/or byproducts. In the processing of hemp fibres, the seed becomes an interesting byproduct. In this context, the quality of hempseed oil has to be investigated. Although the composition and quality of hempseed oil have been previously investigated, microwave conditioning, to our knowledge, has not been used for the extraction of hempseed oil.

Improvement in oil yield and positive changes in oil quality have been ascribed to microwave treatment of seeds (Oomah, Liang, Godfrey, & Mazza, 1998). Recently, microwave heating has been found to be particularly effective in releasing membrane-bound tocotrienol and

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tocotrienol-like compounds and in maximizing the stabilization of biological materials against degrading enzymes (Lane, Qureshi, & Salser, 2001). Changes occurring, as seeds are conditioned prior to oil extraction, affect the quality of oil and dictate the type of process to be used. In this regard, the quality of the oil extracted from hempseed has been investigated to improve the understanding, on a laboratory scale, of the behaviour of oil when the seed source is subjected to varying microwave conditioning. An understanding of the microwave process can also lead to optimum choice of energy-efficient processing conditions.

2. Materials and methods

2.1. General

Hemp (*Cannabis sativa* L.) seed cultivar Fasamo, grown in Manitoba in 1998, was obtained from Fisher seeds Ltd. (Dauphin, MB, Canada). The length, diameter and width of 25 randomly selected seeds were measured using a Mitutoyo Digimatic caliper. Seed samples (~50 g) were dried in a Panasonic home microwave oven, model NN-S766 WC (Matsushita Electric of Canada Ltd., Mississauga, ON) with a maximum heating power output of 950 W at 60 Hz for 12 min with intermittent cooling and mixing every min. A second treatment consisted of drying the hempseed samples continuously for 6 min in the same Panasonic oven. A third treatment (treatment 3) involved microwaving hempseed for 3 min, followed by cooling to ~50 °C, reheating for 3 min, then cooling again, followed three times by 2 min heating with intermittent cooling for a total heating time of 12 min. These treatments, selectively based on preliminary studies, were duplicated. Temperature of the seed was measured by thermocouples connected to an Omega 871A digital thermometer. All seed samples were ground in a coffee grinder. Oil from all milled hempseed samples was extracted using hexane (46 g sample in 150 ml hexane), as described by Oomah, Mazza, and Przybylski (1996), purged with nitrogen and stored at −20 °C until analysis. Extractions were performed in duplicate and analyzed separately. Two commercial cold-pressed hempseed oils (Fountain of Life, Victoria, BC; Hempola, Missisauga, ON), purchased from a local food store, were used as controls.

2.2. Analytical procedures

Official methods (American Oil Chemist's Society, AOCS, 1993) were used for the determination of *p*-anisidine value (method Cd 18-90) and conjugated dienoic acid (method Ti 1a-64) of oils. Spectroscopic indices, K_{232} and K_{270}, in the UV region, were determined as outlined in the Standard Methods for the Analysis of Oils, Fats and Derivatives (International Union of Pure and Applied Chemistry, IUPAC, 1985). Absorbancies at 670, 610, 560, and 535 nm, related to chlorophylls and absorbancies at 475, 448, and 414 nm, related to carotenoids of a 10% (v/v) solution of oil in hexane were measured with a Spectrophotometer (DU-640B, Beckman Instruments Inc., Fullerton, CA, USA). Colour of oils was also compared with colour charts and codes of the Munsell® Book of Colour (New Windsor, NY).

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 β-carotene per gram of oil, was performed using a calibration curve constructed by analyzing solutions of increasing concentration, from 0.5 to 2.5 μg/ml of β-carotene in hexane. Absorbance was recorded at 440 nm (DU-640B, Beckman Instruments Inc., Fullerton, CA, USA), using hexane as blank. Oil was diluted with hexane (100g/l) to the β-carotene standard range.

Tocopherols in hempseed oils 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 (4.6×150 mm, Primesphere 5 silica 5 μm), with guard column (4.6×30 mm) (Phenomenex, Torrance, CA, USA), was used with hexane/2-propanol/dimethyl propane (1000/5/1, v/v/v) as mobile phase. The system was operated isocratically at a flow rate of 1 ml/min. Separations were carried out at 25 °C (Waters temperature control system, TCM) 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 1.18 to 23.60, from 0.25 to 4.95, from 1.50 to 30.1, and from 0.09 to 1.71 μg/ml of reference compounds α-, δ-, and β-, γ-tocopherols, respectively (Sigma Chemical Co., St Louis, MO, USA). Prior to HPLC analysis, hempseed oil was diluted with hexane to obtain a concentration of about 38 g/l, filtered (0.20 μm, Gelman Science Inc., Ann Arbor, MI, USA) and 20 μl sample was injected. All tocopherol analyses, including the standards, were performed in a single day to eliminate daily variations. Oil content of the ground hempseed samples was determined by Soxhlet extraction with petroleum ether for 6 h. Moisture content was determined by the AOAC method (AOAC, 1984).

The lipids were esterified by the one-step methylation method of Ulberth and Henninger (1992) with modifications reported previously (Oomah, Ladet, Godfrey, Liang, & Girard, 2000). These included the omission of toluene in the reagent and centrifugation for phase

Table 1
Quality characteristics (colour) of hempseed oils[a]

Quality characteristics	Fountain of Life	Hempola	Untreated seeds	Microwaved (6 min)	Microwaved (12 min)
Munsell colour	7.5Y 8/10	7.5Y 7/12	7.5Y 8/10	7.5Y 7/12	7.5Y 8/10
K232	1.29d	2.61a	2.27ab	1.88c	1.77c
K270	0.24c	0.54a	0.31b	0.30b	0.22c
A412	0.50a	0.97a	0.47c	0.65b	0.50c
A414	0.49c	0.94a	0.46c	0.64b	0.49c
A428	0.33c	0.59a	0.28d	0.40b	0.30cd
A448	0.29b	0.40a	0.22c	0.30b	0.23c
A453	0.26b	0.33a	0.19c	0.27b	0.20c
A475	0.20c	0.26a	0.17d	0.23b	0.18d
A482	0.15c	0.21a	0.13d	0.18b	0.13cd
A535	0.36b	0.84a	0.43b	0.49b	0.41b
A560	0.16b	0.41a	0.22b	0.23b	0.19b
A610	0.27b	0.62a	0.33b	0.37b	0.31b
A670	1.42c	2.87a	1.55c	1.94b	1.59c

[a] Means in a row followed by the same letter are not significantly different by Duncan's multiple range test at the 5% level.

separation. The top layer was transferred into a small vial and dried with anhydrous Na_2SO_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 (0.25 mm i.d., Supelco, Oakville, ON). The column temperature was programmed from 140 to 240 °C at 4 °C/min, and the injector and detector temperatures were set at 260 °C. Helium was the carrier gas. Peak areas of duplicate injections and percentages were measured with a Hewlett Packard PC Integration Pack (HP 3396 Series ChemStation Version A. 03.21) using response factors. Amounts of esters formed were calculated from the peak areas obtained relative to peak areas of known amounts of internal standard.

Thermal characteristics of hempseed oil were measured using a modulated differential scanning calorimeter (Modulated DSC 2910, TA Instruments, New Castle, DE, USA). A flow of nitrogen gas (100 ml/min) was used in the cell cooled by helium (150 ml/min) in a refrigerated cooling system. The instrument was calibrated for temperature and heat flow with mercury (melting point, mp = 38.83 °C, TA Instruments standard), gallium (mp = 29.76 °C, TA Instruments standard) and indium (mp = 156.6 °C and $\Delta H = 28.71$ J/g, Aldrich Chemical Co.). Oil samples (4–5 mg) were weighed in open solid fat index (SFI) aluminium pans (T70529, TA Instruments). An empty similar pan was used as reference. The sample and reference pans were then placed inside the calorimeter and kept at 70 °C for 5 min. The temperature was lowered from 70 to −65 °C at 1 °C/min with modulation at a period of 60 s and temperature amplitude of 0.16 °C. Samples were then kept at −65 °C for 1 min, then raised again at the same rate up to 70 °C. Scans were performed at various cooling rates between 0.5 and 20 °C/min to investigate the effect on heat flow of oils. For thermal oxidation, pans were cooled to 10 °C and scanning was done by heating at 1 °C/min to 350 °C in the presence of oxygen (100 ml/min). Thermal oxidation measurements were performed in duplicate.

All assays, except thermal oxidation, were performed in triplicate. Analysis of variance by the general linear models (GLM) procedure, means comparison by Duncan's test, and Pearson correlation, were performed according to the Statistical Analysis System (SAS Institute, 1990).

3. Results and discussion

Hempseeds were 3.3–5 mm (4.28 ± 0.44) long, 2.6–3.9 mm (3.24 ± 0.35) wide, 2.1–3.2 mm (2.54 ± 0.27) in diameter, weighed 4.7–23.7 mg (14.70 ± 4.58) and had a bulk density of 0.540 g/ml. Moisture content of the original hempseed sample was 7.7 ± 0.1%. These values are within the expected range reported previously for hempseed (Theimer & Mölleken, 1995). Exposure of seeds to microwave-drying resulted in a progressive increase in weight loss that followed a highly significant logarithmic trend ($r^2 = 0.987$, $P \leqslant 0.001$; Fig. 1). The weight loss curve also fitted the power law model ($y = ax^b$, $r^2 = 0.927$) when regressed against drying time, as reported previously for oilseeds (Oomah & Mazza, 1992). Losses of 67.3 and 81.8 g/kg of the original weight were attained after 12 min of drying with 1 and 3 min of intermittent cooling, respectively. The temperature fluctuated from 62–76 °C and 73–94 °C when the seeds were dried at intervals of 1 and 3 min, respectively. The changes represented by the power law model can be successfully used by manufacturers to exercise closer control of product quality. The microwave drying

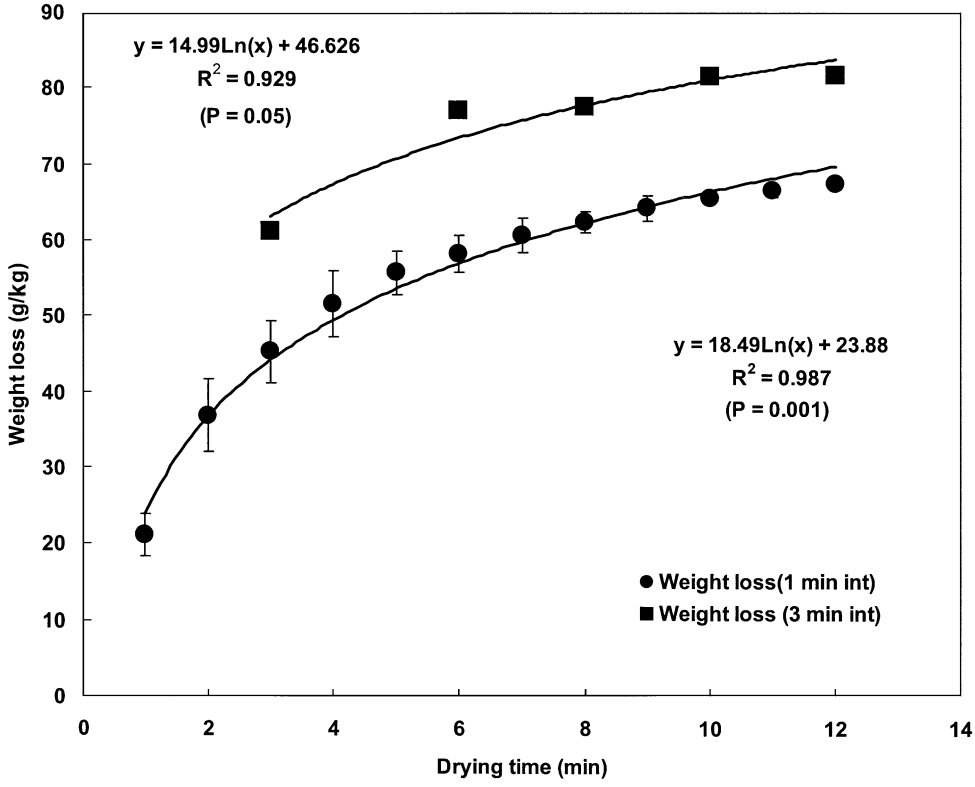

Fig. 1. Relationship between heating time and weight loss of hempseed in a microwave oven.

simulated the sterilization process (heating at 160 °F for 5 min), commonly used in the industry to ensure complete loss of seed viability. Oil contents of the seeds (30.5±0.7%) were similar to those reported earlier (Pate, 1999; Wirtshafter, 1995), but lower than the values (≈36%) reported for cultivar FIN-314 grown in Finland (Callaway & Laakkonen, 1996). Microwave drying, for 12 min at 1 min intermittent cooling, improved the yield of oil from the seeds by 15% (35.1±0.6). However, oil yields between 6 min (34.5±0.7) and 12 min (35.1±0.6) microwave treatments were not significantly different. This finding is consistent with our previous report of similar oil yield for grapeseed treated for different times (Oomah, Liang, Godfrey, & Mazza, 1998).

Hempseed oil has several characteristic UV-Vis bands centered at wavelengths 412, 453, 482 and 670 nm. The yellow colour of the oil is in accordance with strong absorbance at 412, 453, and 482 nm of the blue and violet region and as indicated by Munsell colour (Table 1). Hempseed oil absorbed strongly in the UVC (100–290 nm) and UVB (290–320 nm) range (Fig. 2). The oil had unique transmittance in both UVB and UVA (320–400 nm) regions, and can therefore be used as a UV protectant with relatively high shielding power (SPF) and protection factor (PFA) scores. Therefore, hempseed oil may provide protection against both UVA (an origin of oxidative stress to the skin) and UVB. Microwave treatment of hempseed produced an increase in chlorophyll (absorbance at 670 nm) and carotenoid (412–482 nm) pigments of the oil (Table 1), although the increase was significant ($P \leqslant 0.5$) only for seeds microwaved continuously for 6 min. Similar increases in absorbance due to darkening of oil are known to result from microwave-drying of soybean and sesame seeds (Yoshida et al., 1997; Yoshida & Takagi, 1997). Oils from the untreated and microwave (12 min)-treated seeds had colour and absorbance values similar to that of a commercial hempseed oil (Fountain of Life; Table 1). The second commercial hempseed oil (Hempola) was the darkest in colour as indicated by its high absorbance at all wavelengths.

Actual carotenoid content of hempseed oil was between 2 and 5.3 mg/100g of oil (Table 2). Carotenoid content increased significantly upon continuous microwave heating for 6 min. The commercial oils had significantly higher carotenoid contents than those extracted from the seeds, suggesting differences in seed sources. Conjugated dienes remained almost unchanged with increase in microwave exposure time, except at 12 min of heating (Table 2). Similar observations in conjugated dienes of corn oil, heated in the microwave for up to 10 min, have been previously reported (Vieira & Regitano-d'Arce, 1999). Values for oil from continuously microwaved (6 min) seeds were slightly but not significantly lower than those from the untreated seeds. The commercial hempseed oils had the extreme (lowest and highest) conjugated diene values. Conjugated triene

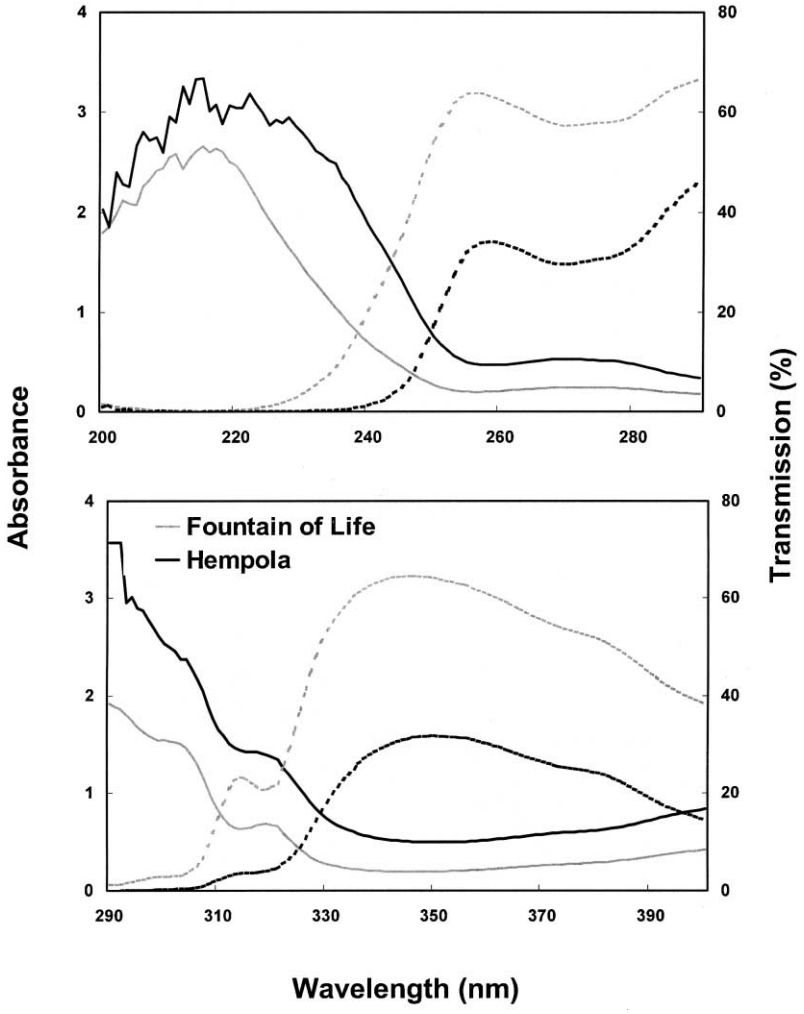

Fig. 2. Ultraviolet visible spectra of two commercial hempseed oils, Fountain of Life (grey) and Hempola (black). Figure derived from scans (λ = 200–290) of oil diluted 1:00; from scans (λ = 290–400) of oil diluted 1:10, both in hexane. Solid line is absorbance and broken line is transmission.

Table 2
Physicochemical characteristics of oils from microwave-treated hempseeds[a]

Sample	β-Carotene (mg/100 g)	Diene value (%)	Triene value (%)	*p*-Anisidine value
Fountain of Life	3.36b	0.083d	0.0017bc	0.88c
Hempola	5.34a	0.207a	0.0036a	3.41a
Untreated seed	1.99d	0.173ab	0.0020b	2.12b
Microwaved (6 min)	2.78c	0.139bc	0.0018bc	2.24b
Microwaved (12 min)	2.04d	0.129c	0.0013c	1.09c

[a] Means in a column followed by the same letter are not significantly different by Duncan's multiple range test at the 5% level.

values of oils extracted from untreated, microwave-treated for 6 min, and the commercial hempseed (Fountain of Life) sample were similar (Table 2). The similar triene values suggest very small changes in linolenate oxidation in the continuous microwave treatment that was applied. Oil from seeds microwaved for 12 min had the lowest conjugated triene value. The commercial hempseed oil (Hempola) had the highest triene value, indicating that the oil may have undergone some physicochemical refining treatment.

p-Anisidine values (AV) of oils from the continuously microwave-treated seeds were less than 10 (recommended value for fresh fully refined oil) and not significantly different from that of untreated seeds (Table 2). Microwave treatment of the seed for 12 min produced a significant decrease in AV, consistent with

Table 3
Tocopherol contents of hempseed oils (mg/100 g)[a]

	Tocopherol					Vitamin E
	α	β	γ	δ	Total	
Untreated seed	3.4c	0.6cd	73.3bc	2.5ab	79.7b	10.9d
Microwaved (treatment 3)	3.2cd	3.8b	74.9b	2.8a	84.7a	12.2c
Microwaved (6 min)	3.3cd	5.6a	74.4b	2.8a	86.0a	13.0b
Microwaved (12 min)	3.0d	0.5d	71.9cd	2.5b	77.6b	10.0c
Hempola	6.3a	0.8cd	70.5d	2.4b	79.9b	13.6a
Fountain of Life	5.2b	1.0c	79.1a	1.6c	86.8a	13.5a
Means	3.8	2.2	73.7	2.5	81.9	11.9
S.D.	1.14	2.15	2.72	0.40	3.90	1.36

[a] Means in a column followed by the same letter are not significantly different by Duncan's multiple range test at the 5% level.

Table 4
Fatty acid composition of hempseed oils

Sample	Composition (mass %)								
	16:0	18:0	18:1	18:2	18:3(n-3)	18:3(n-6)	20:0	20:2	22:0
Fountain of Life	6.4	3.2	15.6	53.4	15.1	2.7	1.0	0.9	0.4
Hempola	5.9	2.7	10.9	56.6	19.4	2.0	0.8	0.9	0.3
Untreated	6.6	2.7	10.1	54.3	19.1	3.6	0.9	1.4	0.3
Microwaved (treatment 3)	6.7	2.7	10.0	53.9	18.7	3.5	0.9	1.3	0.4
Microwaved (12 min)	6.7	2.7	10.0	54.3	19.0	3.6	0.9	1.3	0.3
Microwaved (6 min)	6.6	2.7	9.9	53.9	18.9	3.5	0.9	1.3	0.4

its low carotenoid content, and conjugated diene and triene values. These low values indicate absence of oxidative degradation of the oil and/or increased antioxidative activity when hempseed is microwave-treated intermittently. Conversely, Hempola had the highest AV values corresponding to its high levels of carotenoid and diene and triene values. The high AV of the commercial hempseed oil (Hempola) may be a reflection of a long storage period undergone by the oil.

The major tocopherol in hempseed oil was the γ isomer at 90±2.5% of the total tocopherol (Table 3). Similar results of γ-tocopherol, accounting for 90% of the total have been reported for *Cannabis ruderale* L. (Cannabinaceae; Ivanov & Aitzetmüller, 1998). Concentrations of tocopherol isomers from hempseed oil were within the range reported for four hemp cultivars grown in Alberta, Canada in 1997 (Blade, 1998). Tocopherol contents of oil differed significantly ($P<0.05$) among treatments (Table 3). β-Tocopherol levels increased significantly, resulting in higher total tocopherols and vitamin E equivalents with increased severity of heat treatment. Similar increases in total tocopherols due to heat treatment resulting in increased antioxidative activity, have been observed in sesame seed oil (Mohamed & Awatif, 1998). Concentrations of α-, γ-, and δ- tocopherols of oil extracted from the untreated seed were not significantly different from that extracted from continuously microwave treated (treatment 3 and 6 min) seeds. The commercial hempseed oil (Fountain of Life and Hempola) contained 62 and 95% higher levels of α-tocopherol, respectively, than those obtained from the seeds.

The biologically active vitamin E content relative to that of α-tocopherol, calculated by using the formula proposed by McLaughlin and Weihrauch (1979), ranged from 10.9 to 13.6 mg/100 g of oil for the untreated hempseed sample and the commercial hempseed oil, respectively. Vitamin E content of hempseed oil was similar to those of peanut oil, olive oil and soybean oil (Ensminger, Ensminger, Konlande, & Robson, 1993). The ratio of the tocopherol isomers α:β:γ:δ in hempseed oil was 5:2:90:3, and resembled that in *Melissa officinalis* L. and *Salvia officinalis* L.(Lamiaceae) at ≈6:1:91:2 (Ivanov & Aitzetmüller, 1998). The combination of high levels of γ-tocopherol with α-tocopherol in hempseed oil may offer protection against DNA damage, leading to reduced cancer risk (Elmadfa & Park, 1999).

The most abundant fatty acids of hempseed oil were linoleic, α-linolenic, and oleic acids, which together comprised 84% of the total fatty acid (Table 4). The fatty acid composition of hempseed oil was similar to that reported for four cultivars grown at Gwynne, Alberta in 1997 (Blade, 1998), for hemp cultivated in Central Europe with slightly higher linolenic acids

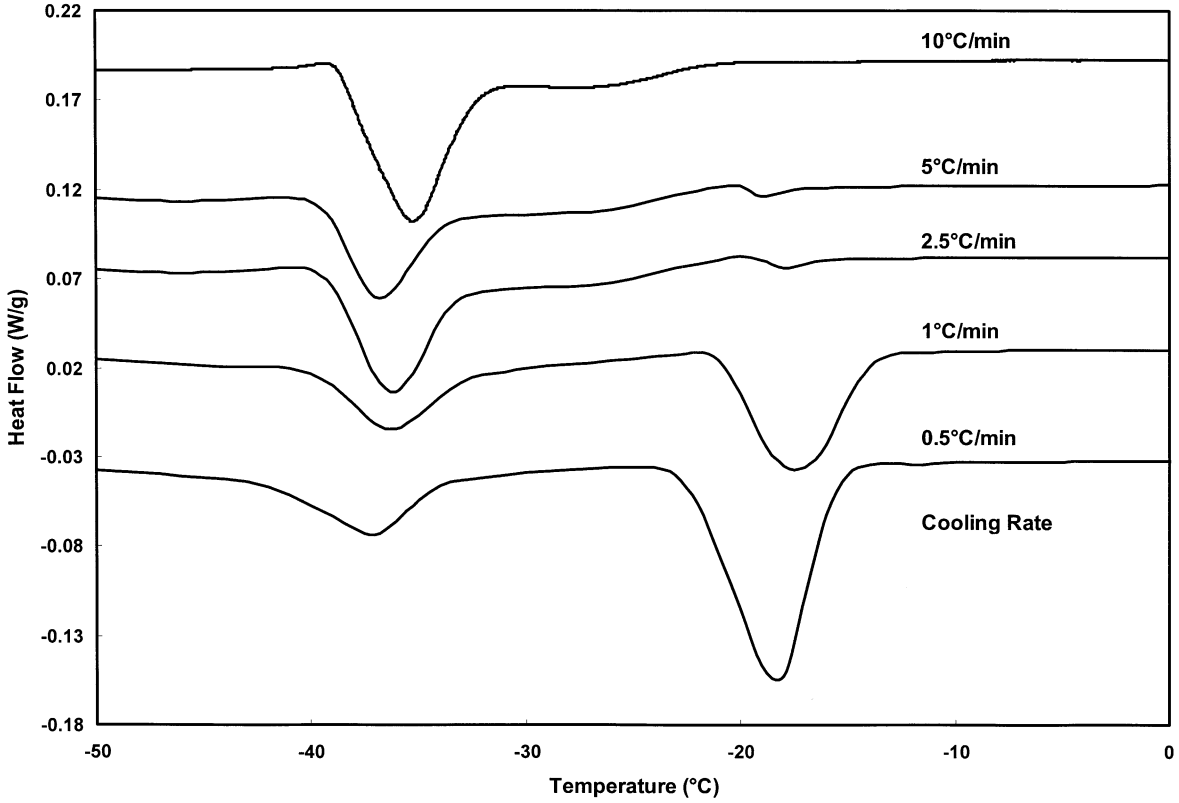

Fig. 3. Modulated Differential Scanning Colorimetry (MDSC) reversing component of a commercial hempseed oil at various cooling rates.

(Theimer & Mölleken, 1995), and for the French cultivar Futura-77 (Callaway, Tennilä, & Pate, 1996). The palmitic, stearic and oleic acid contents of hempseed oils were similar to those of evening primrose, another γ-linolenic-containing oil (Rausch, 1995). The linoleic acid content of hempseed oil was similar to that of soybean and walnut oils (56–59%; Ruggeri, Cappelloni, Gambelli, Nicoli, & Carnovale, 1998). The stearic, oleic and linoleic acid contents of hempseed oil, comprising about 70% of the total fatty acids, resembled those of cottonseed oil (Van Niekerk & Burger, 1985). The polyunsaturates of the oils amounted to 78% of the total fatty acids, while the monounsaturated and saturated fatty acids amounted to 11% each. Hence, the ratio of polyunsaturates to monounsaturates to saturates was 78:11:11. The high amounts of α-linolenic acid (18%) of hempseed oil makes it especially prone to oxidation, but may have favourable nutritional implications and beneficial physiological effects in the prevention of coronary heart disease and cancer (Oomah & Mazza, 1998). The presence of γ-linolenic acids (3.5%), characteristic of hempseed oil, provides it with a high pharmaceutical value for neurodermic diseases. The oil was characterized by a high polyunsaturated/saturated (P/S) ratio of 7.3, similar to those of walnuts (6.5–7.8; Ruggeri, Cappelloni, Gambelli, Nicoli, & carnovale, 1998). A high ratio of P/S is regarded favourably for the reduction of serum cholesterol and atherosclerosis and prevention of heart diseases (Rudel, Kelly, Sawyer, Shah, & Wilso, 1998). Similarly, the ratio of n-6 to n-3 ratio fatty acids was 2, much higher than most vegetable oils. The iodine number was estimated to be 161, which is within the range (140–170) reported for hempseed oil (Theimer & Mölleken, 1995; Wirtshafter, 1995) Microwave treatment of seeds had a negligible effect on the fatty acid composition of hempseed oil. This finding corresponds to similar observations of minimal changes in fatty acids of sesame seeds due to roasting (Mohamed & Awatif, 1998).

Commercial hempseed oil (Fountain of Life) exhibited at least three thermal structural transitions between −39 and −17 °C (Fig. 3). Two reversing transitions, indicative of crystalline melting, were observed near −36 °C and between −17 to −27 °C, corresponding to the α and β polymorphic forms, respectively. Increasing the underlying cooling rate resulted in peak-broadening of the β polymorphic form with loss of resolution especially at cooling rates greater than 5 °C/min (Fig. 3; Table 5). The reversing component of the heat flow was highly sensitive to the cooling rate, shifting the first endothermic peak (the α-form) to higher heat flow (from 10 to 27 J/g) with increasing cooling rate (Table 5). In the nonreversing component curves, to which kinetic events such as crystallization, crystal perfection and reorganization are ascribed, three endotherms were observed in the −39 to −18 °C region, at

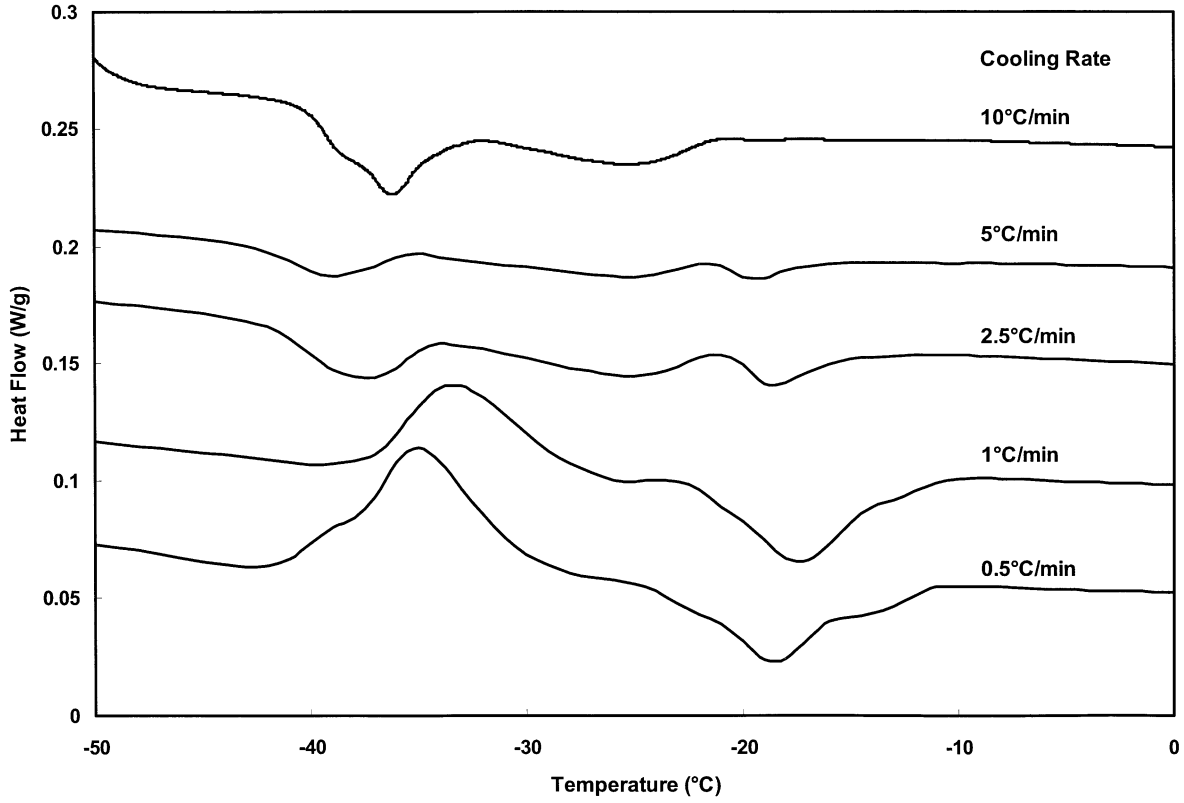

Fig. 4. Modulated Differential Scanning Colorimetry (MDSC) non-reversing component of a commercial hempseed oil at various cooling rates.

Table 5
Effect of cooling rate on thermal characteristics of a commercial hempseed oil[a]

	Non-reversing heat flow				Reversing heat flow			
Cooling rate (°C/min)	$T\alpha$	$\Delta H\alpha$	$T\beta$	$\Delta H\beta$	$T\alpha$	$\Delta H\alpha$	$T\beta$	$\Delta H\beta$
20	−37.2abc	−3.7b	−18.8a	0.0a	−35.0a	−23.9b	nd	nd
10	−37.0abc	−7.3b	−19.1a	−0.1a	−35.5a	−27.1b	nd	nd
5	−39.0c	−2.8b	−19.6a	−1.0a	−36.7a	−20.6b	−18.8a	−0.1a
2.5	−37.6bc	−5.0b	−18.5a	−2.1a	−36.0a	−24.4b	−18.1a	−0.6a
1	−33.5a	13.5a	−17.6a	−10.8b	−36.0a	−12.3a	−17.3a	−15.7ab
0.5	−35.1ab	19.3a	−18.7a	−11.5b	−37.1a	−10.0a	−18.3a	−26.9b

[a] Means in a column followed by the same letter are not significantly different by Duncan's multiple range test at the 5% level. nd, Not detected.

cooling rates above 1 °C/min (Fig. 4). These endothermic transitions are indicative of the crystallization and recrystallization of the metastable α form. The second and third peaks (where apparent) in the −25 to −18 °C region were assigned to β′ and β crystallization forms, respectively, believed to be due to the transformation of the metastable phase (α) to the more stable β form. At low cooling rates of 0.5 and 1 °C/min, the first peak appeared as an exotherm (−34.7 and −33.7 °C with high activation energies of 19.3 and 13.5 J/g, respectively) suggesting kinetic stability. The high heat content of the first transition indicates high entropy at low cooling rate, implying a first-order transition. The values of enthalpies, ΔH_α and ΔH_β, of the hempseed oil changed, with heating rate (Table 5). The ΔH_α values decreased logarithmically ($r=0.743$, $P=0.1$) for both the reversing and nonreversing heat flow as cooling rate increased (Fig. 5). The ΔH_β values for the nonreversing heat flow increased logarithmically ($r=0.839$, $P=0.05$) as cooling rate increased from 0.5 to 20 °C/min. Cooling rate above 5 °C/min completely inhibited the crystallization of the β form. The peak crystallization and melting temperatures of hempseed oil were similar to values reported for pecan and sesame oils at −37 to −30 °C and −15 to −33 °C, respectively (Tan & Che Man, 2000; Toro-Vazquez & Pérez-Briceño, 1998).

Microwave treatment had no significant effect on the first reversing and nonreversing peak temperatures, with

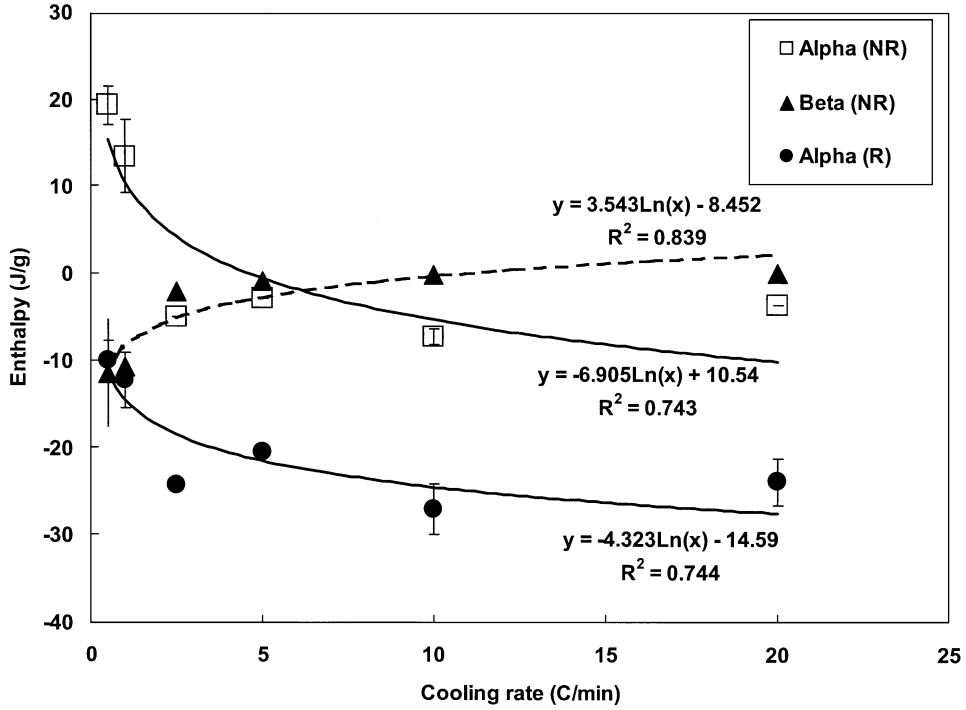

Fig. 5. Relationship between cooling rate and changes in enthalpy of hempseed oil. Alpha (N), Beta (N) and Alpha (R) denote enthalpies of the non-reversing alpha and beta and the reversing alpha peak transitions, respectively.

Table 6
Effect of microwave treatment on thermal characteristics of hempseed oils[a]

	Reversing heat flow				Non-reversing heat flow			
Sample	$T\alpha$	$\Delta H\alpha$	$T\beta$	$\Delta H\beta$	$T\alpha$	$\Delta H\alpha$	$T\beta$	$\Delta H\beta$
Fountain of Life	−34.8a	−21.0b	−18.8a	−11.4a	−32.4a	11.3c	−18.7a	−5.5a
Hempola	−38.4c	−8.0a	−20.7b	−46.8b	−36.8c	30.9ab	−20.4b	−10.5b
Untreated	−37.8bc	−13.5ab	−19.9b	−43.0b	−35.6b	33.6a	−20.2b	−1.7a
Microwaved (6 min)	−37.6b	−10.9ab	−20.4b	−33.1b	−35.4b	12.8bc	−20.7b	−2.7a
Microwaved (12 min)	−38.0bc	−7.5a	−20.3b	−48.4b	−36.1bc	21.3abc	−20.1b	−1.9a

[a] Means in a column followed by the same letter are not significantly different by Duncan's multiple range test at the 5% level.

values within the range of those of the commercial oil samples (Table 6). By contrast, the second peak transition, in both the reversing and nonreversing component curves, shifted to lower temperatures for oil extracted from seed microwaved continuously for 6 min. Microwave treatment induced small insignificant changes in enthalpies of the reversing peaks while significant reduction was observed in enthalpies of the first nonreversing peak. This reduced nonreversing enthalpy magnified the difference between the two polymorphic forms expressed as the ratio of ΔH_α and ΔH_β values for the oil extracted from seed microwaved continuously for 6 min. Similar magnifications in H_α/H_β were observed in the presence of the synthetic antioxidant, butylated hydroxy toluene (BHT) (data not shown), suggesting production of antioxidant components upon microwave heating.

Hempseed oil exhibited three maxima on the DSC oxidation curves, indicating that thermoxidation can be characterized by at least a two step exothermic effect (Fig. 6). These peaks could be considered as an indication of the level of cross-linking. Oxidation of hempseed oil started at 132 to 140 °C, well within the temperatures reported for edible oils (130–180 °C) (Litwinienko, Daniluk, & Kasprzycka-Guttman, 1999) and peaked at 151–155 °C, depending on the microwave treatment of the seeds (Fig. 6; Table 7). The commercial hempseed oil (Hempola) had the lowest onset, oxidation and peak temperatures. Continuous microwave drying of the seed resulted in significant increase in oxidation temperature. This increase in oxidation temperature is consistent with the presence of higher levels of natural constituents, such as tocopherol and carotenoids, capable of providing a protective antioxidant effect in the continuously microwaved seed (Yen, Shao, Chen, & Duh, 1997). The temperature of the first peak (151–155 °C) was not significantly affected by the microwave treatment,

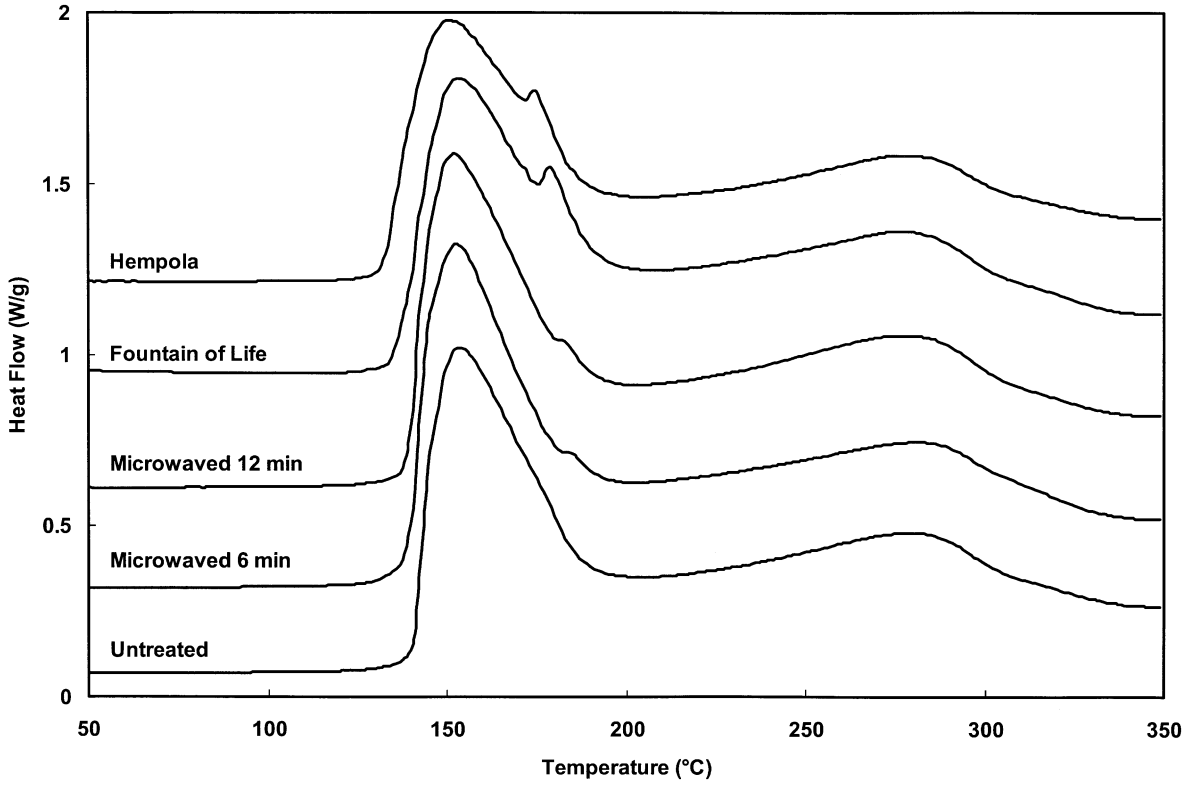

Fig. 6. Differential Scanning Colorimety (DSC) of the thermo-oxidation profiles of hempseed oils.

Table 7
Thermoxidation temperatures (°C) of oils from microwave-treated hempseeds[a]

Sample	Onset	Oxidation temperature	Peak 1	Peak 2	Peak 3
Fountain of Life	126.0b	135.8b	153.9a	178.9b	278.7
Hempola	121.6c	131.8c	151.0c	174.2c	277.2
Untreated seeds	128.8ab	137.9b	153.1ab	nd	282.3
Microwaved (6 min)	129.5a	140.2a	154.5a	184.4a	282.3
Microwaved (12 min)	128.2ab	136.8b	151.6bc	182.7a	276.8

[a] Means in a column followed by the same letter are not significantly different by Duncan's multiple range test at the 5% level. nd, Not detected.

although the peak shifted to a higher temperature with continuous microwave treatment. The oxidation temperature of the first peak was similar to those of the flash (141 °C) and smoke (165 °C) points of hempseed oil (Wirtshafter, 1995), sunflower seed oil (154–157 °C) (Wendlandt, 1986), and sesame oil (165 °C; Deshpande, Deshpande, & Salunkhe, 1996). The second peak, in the range of 174–184 °C was absent in the untreated hempseed oil for unknown reasons and was unaffected by microwave treatment. The third peak at 277–282 °C indicates inability of oxygen uptake, resulting in complete thermal polymerization.

The data presented indicate that microwave treatment of hempseed produces positive beneficial changes in the quality of its oil. The elevated tocopherol concentration, and the changes observed in the DSC, suggest an improvement in hempseed oil quality that can become an economically and environmentally sound resource for the functional food and nutraceutical industries. The production of oil from hempseed improves alternative crop utilization by adding significant financial value, and is likely to lead to more diverse and novel applications in the food, pharmaceutical, cosmetic and other nonfood industries.

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References

Association of Official Analytical Chemists. (1984). *Official methods of analysis* (14th ed.). Washington, DC: Association of Official Analytical Chemists.

Association of Official Analytical Chemists. (1990). *Official methods of analysis* (15th ed.). Washington, DC: Association of Official Analytical Chemists.

American Oil Chemists Society. (1993). *Official methods and recommended practices of the American Oil Chemists' Society* (4th ed.). Champaign, IL: American Oil Chemists' Society.

Blade, S. F. (1998). Industrial hemp in Alberta. In S. Blade (Ed.), *Alberta hemp symposia proceedings* (pp. 2–11). Red Deer, Alberta: Alberta Agriculture, Food and Rural Development.

Callaway, J. C., & Laakkonen, T. T. (1996). Cultivation of cannabis oil seed varieties in Finland. *Journal of the International Hemp Association*, *3*, 32–34.

Callaway, J. C., Tennilä, T., & Pate, D. W. (1996). Occurrence of "*omega-3*" stearidonic acid (*cis*-6,9,12,15- octadecatetraenoic acid) in hemp (*Cannabis sativa* L.) seed. *Journal of the International Hemp Association*, *3*, 61–63.

Deferne, J. L., & Pate, D. W. (1996). Hemp seed oil: a source of valuable essential fatty acids. *Journal of the International Hemp Association*, *3*, 4–7.

Deshpande, S. S., Deshpande, U. S., & Salunkhe, D. K. (1996). Sesame oil. In Y. H. Hui (Ed.), *Bailey's industrial oil and fat products* (5th ed.), (Vol. 2) *Edible oil and fat products: oil and oilseeds* (pp. 457–495). New York: Wiley.

Ensminger, A. H., Ensminger, M. E., Konlande, J. E., & Robson, J. R. K. (1993). *Foods & nutrition encyclopedia* (2nd ed.). Boca Raton, FL: CRC Press (Vol. 2).

Elmadfa, I., & Park, E. (1999). Impact of diets with corn oil or olive/sunflower oils on DNA damage in healthy young men. *European Journal of Nutrition*, *38*, 286–292.

International Union of Pure and Applied Chemists. (1985). *Standard methods for the analysis of oils, fats and derivatives* (7th ed.). Oxford, UK: International Union of Pure and Applied Chemistry.

Ivanov, S. A., & Aitzetmüller, K. (1998). Tocopherol and tocotrienol composition of the seed lipids of a number of species representing the Bulgarian flora. *Fett/Lipid*, *100*, 348–352.

Jones, K. (1995). *Nutritional and medicinal guide to hemp seed*. Gibsons, BC, Canada: Rainforest Botanical Laboratory.

Lane, R. H., Qureshi, A. A., & Salser, W. A. (2001). Tocotrienols and tocotrienol-like compounds and methods for their use. *US Patent*, 6204290.

Litwinienko, G., Daniluk, A., & Kasprzycka-Guttman, T. (1999). A differential scanning calorimetry study on the oxidation of C_{12}-C_{18} saturated fatty acids and their esters. *Journal of the American Oil Chemists' Society*, *76*, 655–657.

McLaughlin, P. J., & Weihrauch, J. L. (1979). Vitamin E content of foods. *Journal of the American Dietetic Association*, *75*, 647–665.

Mohamed, H. M. A., & Awatif, I. I. (1998). The use of sesame oil unsaponifiable matter as a natural antioxidant. *Food Chemistry*, *62*, 269–276.

Oomah, B. D., Ladet, S., Godfrey, D. V., Liang, J., & Girard, B. (2000). Characteristics of raspberry (*Rubus idaeus* L.) seed oil. *Food Chemistry*, *69*, 187–193.

Oomah, B. D., Liang, J., Godfrey, D., & Mazza, G. (1998). Microwave heating of grapeseed: effect on oil quality. *Journal of Agricultural and Food Chemistry*, *46*, 4017–4021.

Oomah, B. D., & Mazza, G. (1998). Flaxseed products for disease prevention. In G. Mazza (Ed.), *Functional foods biochemical and processing aspects* (pp. 91–138). Lancaster, PA: Technomic Publishing Co.

Oomah, B. D., & Mazza, G. (1992). Microwave oven drying for moisture determination in flax, canola and yellow mustard seeds. *Lebensmittel-Wissenschaft und Technologie*, *25*, 523–526.

Oomah, B. D., Mazza, G., & Przybylski, R. (1996). Comparison of flaxseed meal lipids extracted with different solvents. *Lebensmittel-Wissenschaft und Technologie*, *29*, 654–658.

Pate, D. W. (1999). Hemp seed: a valuable food source. In P. Ranali (Ed.), *Advances in hemp research* (pp. 243–255). Binghamton, New York: The Haworth Press.

Rausch, P. (1995). Verwendung von hanfsamenöl in der kosmetik. In *Bioresource hemp* (2nd ed.; pp. 556–561). Cologne, Germany: Nova-Institute.

Roulac, J. W. (1997). *Hemp horizon*. Canada: Chelsea Green Publishing Co.

Rudel, L. L., Kelly, K., Sawyer, J. K., Shah, R., & Wilso, M. D. (1998). Dietary monounsaturated fatty acids promote aorti atherosclerosis in LDL receptor-null ApoB100-overexpressing transgenic mice. *Arteriosclerosis, Thrombosis, and Vascular Biology*, *18*, 1818–1827.

Ruggeri, S., Cappelloni, M., Gambelli, L., Nicoli, S., & Carnovale, E. (1998). Chemical composition and nutritive value of nuts grown in Italy. *Italian Journal of Food Science*, *10*, 243–252.

SAS Institute. (1990). *SAS/STAT user's guide, version 6* (4th ed.). Cary, NC: SAS Institute.

Tan, C. P., & Che Man, Y. B. (2000). Differential scanning calorimetry analysis of edible oils: comparison of thermal properties and chemical composition. *Journal of the American Oil Chemists' Society*, *77*, 143–155.

Theimer, R. R., & Mölleken, H. (1995). Analysis of the oils from different hemp (*Cannabis sativa* L.) cultivars-perspective for economic utilization. In *Bioresource hemp* (2nd ed.; pp. 536–545). Cologne, Germany: Nova-Institute.

Toro-Vazquez, J. F., & Pérez-Briceño, F. (1998). Chemical and physicochemical characteristics of pecan (*Carya illinoensis*) oil native of the central region of Mexico. *Journal of Food Lipids*, *5*, 211–231.

Ulberth, F., & Henninger, M. (1992). One-step extraction/methylation method for determining the fatty acid composition of processed foods. *Journal of the American Oil Chemists' Society*, *69*, 174–177.

Van Niekerk, P. J., & Burger, A. E. C. (1985). The estimation of the composition of edible oil mixtures. *Journal of the American Oil Chemists' Society*, *62*, 531–538.

Vieira, T. M. F. S., & Regitano-d'Arce, M. A. B. (1999). Ultraviolet spectrophotometric evaluation of corn oil oxidative stability during microwave heating and oven test. *Journal of Agricultural and Food Chemistry*, *47*, 2203–2206.

Wendlandt, W. WM. (1986). Applications of differential thermal analysis and differential scanning calorimetry. In *Thermal analysis* (3rd ed.; pp. 359). New York: John Wiley.

Wirtshafter, D. (1995). Nutrition of hemp seeds and hemp seed oil. In *Bioresource hemp* (2nd ed.; pp. 546–555). Cologne, Germany: Nova-Institute.

Yen, G-C., Shao, C-H., Chen, C-J., & Duh, P-D. (1997). Effects of antioxidant and cholesterol on smoke point of oils. *Lebensmittel-Wissenschaft und Technologie*, *30*, 648–652.