Chemical Composition and Physicochemical and Hydrogenation Characteristics of High-Palmitic Acid Solin (low-linolenic acid flaxseed) Oil

F.S. Hosseinian[a,*] G.G. Rowland[b], P.R. Bhirud[c], J.H. Dyck[d], and R.T. Tyler[c]

[a]College of Pharmacy and Nutrition, [b]Crop Development Centre, and [c]Department of Applied Microbiology and Food Science, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, and [d]CanAmera Foods, Saskatchewan, S0K 3A0, Canada

ABSTRACT: The physicochemical characteristics and FA compositions were determined for refined-bleached-deodorized (RBD) high-palmitic acid solin (HPS) oil, RBD solin oil, and degummed linseed oil. The predominant FA in HPS oil were palmitic (16.6%), palmitoleic (1.4%), stearic (2.5%), oleic (11.3%), linoleic (63.7%), and linolenic (3.4%). HPS oil was substantially higher in palmitic acid than either solin oil or linseed oil, and similar to solin oil in linolenic acid content. HPS, solin, and linseed oils exhibited similar sterol and tocopherol profiles. The physicochemical characteristics of the three oils (iodine value, saponification value, m.p., density, specific gravity, viscosity, PV, FFA content, color) reflected their FA profiles and degree of refinement. During hydrogenation of HPS oil, the proportion of saturated FA (palmitic and stearic) increased, and that of unsaturated FA (oleic, linoleic, and linolenic) decreased as the iodine value declined. This resulted in an inverse linear relationship between m.p. and iodine value. Hydrogenation also generated *trans* FA. The proportion of *trans* FA was inversely related to iodine value in partially hydrogenated samples. Fully hydrogenated HPS oil (i.e., HPS stearine, iodine value <5) was devoid of *trans* FA.

Paper no. J10721 in *JAOCS 81*, 185–188 (February 2004).

KEY WORDS: Flax, high-palmitic acid solin oil, linseed oil, solin, solin oil.

Flax (*Linum usitatissimum* L.) is grown either as an oil crop or as a fiber crop, with fiber (linen) derived from the stem of fiber varieties and oil from the seed of linseed varieties (1). Canada is the world's largest producer of flaxseed (about 38% of the total production), where it is grown annually on approximately 1.3 million hectares of land and harvested primarily for its seed oil (2). Most Canadian flax is grown in the prairie provinces of Saskatchewan (70%), Manitoba (26%), and Alberta (4%) (3).

Linseed oil is seldom used for edible purposes because of flavor reversion problems (rapid oxidation, offensive odor, and rancidity) associated with its high-linolenic acid content. Therefore, to make traditional linseed oil more stable and, as a result, competitive as a salad and cooking oil, the linolenic acid content must be eliminated or at least greatly reduced (to ≤5%). Such modification of linseed oil was first reported by Green (1), and later by Rowland and Bhatty (4). The Flax Council of Canada has adopted the generic name "solin" for cultivars of flax containing oil with a linolenic acid content of 5% or less (5). Linola™ is a jointly registered trademark for solin varieties developed and marketed by the Commonwealth Scientific and Industrial Research Organization (CSIRO) of Canberra, Australia, and Agricore United of Winnipeg, Manitoba, Canada (6,7).

A solin line with a high-palmitic–high-palmitoleic character was crossed with a low-linolenic acid line to produce lines having oil that was high in palmitic and palmitoleic acids and low in linolenic acid [i.e., high-palmitic acid solin (HPS) oil] (8). It was suggested that this oil might be particularly suitable for the manufacture of margarines and shortenings. The objective of this paper was to determine, for the first time, the chemical composition and physicochemical and hydrogenation characteristics of HPS oil.

EXPERIMENTAL PROCEDURES

Materials. HPS oil and solin oil (both were refined-bleached-deodorized), crude degummed linseed oil, and partially hydrogenated high-palmitic acid solin (PHHPS) oils having a variety of iodine values (IV) were provided by POS Pilot Plant Corporation (Saskatoon, Canada). Solin oil and HPS oil were extracted from seed grown by the Crop Development Centre, University of Saskatchewan (Saskatoon, Canada). Hydrogenation conditions were: reaction temperature, 185°C; hydrogenation pressure, 25 psig; agitator speed, 585 rpm; catalyst, 0.3% Nysosel 655 (with nickel); hydrogenation time, 11.6 to 42.8 min. In all experiments, samples were analyzed in duplicate. SD and SE were calculated by using Excel (Office 10; Microsoft Corp., Redmond, WA).

Solvents. Solvents were ACS grade (BDH Chemicals, Toronto, Canada). FAME standards were obtained from Nu-Chek-Prep Inc. (Elysian, MN).

Color, specific gravity, and density. Color was measured with a Lovibond Auto Tintometer (model AFX 990; Hull, United Kingdom), according to AOCS method Cc 13-92 (9). Specific gravity was determined according to AOCS method Cc 10a-25 (9). Density was determined from specific gravity.

FFA, chlorophyll, tocopherols, and sterols. FFA were determined by AOCS method Ca 5a-40 (9). Chlorophyll was

*To whom correspondence should be addressed at College of Pharmacy and Nutrition, University of Saskatchewan, 110 Science Pl., Saskatoon, Saskatchewan, S7N 5C9, Canada. E-mail: farah.h@usask.ca

measured with a Lovibond Auto Tintometer according to AOCS method Cc 13e-92 (9). Tocopherols and sterols were measured by capillary GC according to the method of Slover *et al.* (10).

FA composition. FA composition was determined by GC (Model 3400; Varian, Sunnyvale, CA) using an FID. A fused-silica capillary column, 30 m in length, 0.25 mm i.d., with a 0.25 μm film of stationary phase (SUPELCOWAX™ 10; Supelco Canada, Ltd., Oakville, Ontario) was used with helium, at a flow rate of 3 mL/min, as the carrier gas. The column, injector, and detector were maintained at 200, 200, and 260°C, respectively. FAME were prepared according to the method of Hitchock and Hammond (11).

Capillary m.p. Capillary m.p. were measured by AOCS method Cc 1-25 (9). A capillary tube was stabbed into the melted and filtered oil sample, forming a fat column approximately 10 mm high. One end of the capillary tube was sealed using a small flame, and the tube was then stored (tempered) in a freezer (−20°C) for 24 h. For nonhydrogenated samples, the capillary tube containing tempered oil was secured to a thermometer (±0.01°C) and heated in a thermostatically controlled, circulating water bath (Model G; Haake, Berlin, Germany). The water bath (0.0 to −30.0°C) was filled with a 50:50 (vol/vol) water/ethylene glycol mixture. A 500-mL glass beaker containing deionized water was used for heating the capillary tubes containing hydrogenated samples; the beaker was heated with an electric hot plate. A small magnetic stir bar was used to mix the water in the beaker. The temperature at which the fat turned completely clear was recorded as the capillary m.p.

IV, PV, and saponification values. IV was measured by AOCS method Cd 1-25, PV by method Cd 8-53, and saponification value by method Cd 3-25 (9). IV were also calculated by AOCS method Cd 1c-85 (9).

Trans *FA. Trans* isomers were determined by the POS Pilot Plant Corporation using IR spectroscopy according to AOCS method Cd 14-61 (9).

Solid fat index (SFI). SFI was determined by dilatometry according to AOCS method Cd 10-57 (9). A circulating water bath (Model G; Haake) was used to control the temperature (±0.1°C).

RESULTS AND DISCUSSION

FA compositions. The FA compositions (wt% of total FA detected) of HPS oil, solin oil, and linseed oil are presented in Table 1. The predominant FA in HPS oil were palmitic (16.6%), oleic (11.3%), and linoleic (63.7%) acids. Like solin oil, HPS oil was low in linolenic acid (3.4%) relative to linseed oil. HPS oil was substantially higher in palmitic acid than either solin (6.3%) or linseed (7.0%) oil and contained approximately 19% of saturated FA, compared with approximately 10% in both solin and linseed oils. HPS oil also contained 1.4% palmitoleic acid; solin and linseed oils were essentially devoid of this FA.

TABLE 1
FA and Physicochemical Properties of High-Palmitic Acid Solin (HPS) Oil, Solin Oil, and Linseed Oil

	HPS[a]	Solin[a,b]	Linseed[c]
FA (wt% of total FA)			
C16:0 (palmitic)	16.6 ± 0.0	6.3 ± 0.0	7.0 ± 0.0
C16:1 (palmitoleic)	1.4 ± 0.0	0.1 ± 0.0	0.0 ± 0.0
C18:0 (stearic)	2.5 ± 0.0	3.6 ± 0.1	2.9 ± 0.0
C18:1 (oleic)	11.3 ± 0.0	14.6 ± 0.1	16.1 ± 0.2
C18:2 (linoleic)	63.7 ± 0.2	72.9 ± 0.1	14.7 ± 0.0
C18:3 (linolenic)	3.4 ± 0.2	2.4 ± 0.4	58.5 ± 0.1
Iodine value (cg/g, Wijs method)	126 ± 0.4	144 ± 0.2	187 ± 0.4
Iodine value (calculated)	129 ± 0.1	144 ± 0.2	190 ± 0.3
Saponification value (mL/g)	179 ± 0.1	184 ± 0.1	190 ± 0.3
PV (meq/kg)	0.6 ± 0.1	0.7 ± 0.4	0.9 ± 0.1
FFA (%)	0.01 ± 0.01	0.02 ± 0.01	0.25 ± 0.01
m.p. (°C)	−13.3 ± 0.0	−15.1 ± 0.2	−20.0 ± 0.2
Density (g/mL) at 25°C	0.9175 ± 0.0	0.9185 ± 0.0	0.9261 ± 0.1
Specific gravity at 25°C/25°C	0.9202 ± 0.0	0.9200 ± 0.1	0.9288 ± 0.0
Viscosity (cP) at 25°C	45.0 ± 0.2	42.0 ± 0.2	39.0 ± 0.4
Color	7.0Y1.0R	4.7Y0.9R	70.0Y8.6R
Chlorophyll (ppm)	0.05 ± 0.00	0.04 ± 0.01	0.10 ± 0.01
Sterols (ppm)			
Brassicasterol	16.0 ± 0.1	ND[d]	24.0 ± 0.2
Campesterol	847.0 ± 0.5	1162.0 ± 0.2	1306.0 ± 0.6
Stigmasterol	152.0 ± 0.0	178.0 ± 0.4	352.0 ± 0.1
β-Sitosterol	2234.0 ± 0.5	2393.0 ± 0.3	2725.0 ± 0.1
Tocopherols (ppm)			
γ	425.0 ± 0.4	447.0 ± 0.1	471.0 ± 0.1
α	20.0 ± 0.3	39.0 ± 0.4	28.0 ± 0.1

[a]Values are for refined, bleached, and deodorized oil.
[b]Values from DeClercq (5).
[c]Values are for crude oil.
[d]Not detected.

The contents of palmitic and palmitoleic acids in HPS oil suggest that it might contribute desirable functionality to margarines and shortenings, in that 16-carbon FA induce improved crystallization characteristics (i.e., the formation of β′- rather than β-crystals) in basestocks containing predominantly 18-carbon FA. Fats forming β crystals tend to contain a relatively low level (10% or less) of palmitic acid, whereas those forming β′-crystals contain at least twice this amount (12). The level of 16-carbon FA in HPS oil was lower than that in palm or cottonseed oil (which contain approximately 43 and 24% of palmitic acid, respectively), but higher than that in soybean oil (approximately 11% palmitic acid) (13,14). Both palm and cottonseed oils tend to exhibit β′-crystallization, whereas soybean oil is β-tending (12,15,16). The content of saturated FA in HPS oil (approximately 19%) also suggests a fit for HPS oil in margarines and shortenings, as tub margarines generally contain 6–12% saturated FA, stick margarines 20–25%, and shortenings 20–30% (13,17).

Physicochemical characteristics. The physicochemical characteristics of HPS, solin, and linseed oils are presented in Table 1. The relatively high level of saturated FA in HPS oil was reflected in its IV (126 cg/g), saponification value (179 mL/g), and m.p. (−13.3°C). Although similar in PV, crude degummed linseed oil was higher in FFA and chlorophyll, and darker in color, than the more highly refined HPS and solin oils. Differences in density and viscosity among the three oils also were consistent with differences in their respective FA profiles and the unrefined nature of the linseed oil sample. The three oils exhibited similar sterol and tocopherol profiles. The lower levels of the predominant sterols (β-sitosterol, campesterol, and stigmasterol) in HPS oil and solin oil were attributed to losses incurred during refining, the deodorization step in particular (18).

Hydrogenation of HPS oil. The FA profiles of a series of PHHPS oil samples (Table 2) exhibited the expected progressive conversion of unsaturated FA to less unsaturated or saturated FA, with lower levels of unsaturation associated with lower IV. A linear relationship existed between the m.p. of PHHPS oils and their IV (Fig. 1). The m.p. of PHHPS oils ranged from 50.0 (IV = 54) to 26.5°C (IV = 105). The m.p. of fully hydrogenated HPS oil (IV < 5) was 63°C. The proportion of *trans* FA was inversely related to IV in the partially hydrogenated samples. Fully hydrogenated HPS oil was devoid of *trans* FA. Similar values for *trans* FA concentrations were obtained with the two analytical methods employed (IR and GC). Measured and calculated IV also showed good agreement. The conversion of *cis* to *trans* isomers during hydrogenation has been shown to improve (with respect to many end uses) the physical characteristics of oils, particularly m.p. and crystal polymorphism (15,19). Oils with lower IV had higher SFI over a wider range of temperatures (Fig. 2). Samples with IV of 54, 65, 69, and 71 might have application in formulations for stick margarines and all-purpose shortenings (20), whereas samples with IV of 79, 90, 97, and 105 might have application in formulations for tub margarines and pourable frying shortenings (16,20).

The levels of palmitic acid, palmitoleic acid, and saturated FA in HPS oil may be sufficiently high to make this oil attractive to manufacturers of margarines and shortenings. Incorporation of HPS oil into basestocks would reduce the requirement for addition of palm, cottonseed, or other oils to enhance palmitic acid content. The level of saturated FA in HPS oil would likely preclude its use as a salad oil, although its relatively low content of linolenic acid would afford it excellent stability, and the m.p. of −13°C would not be problematic with respect to refrigerated storage.

Hydrogenation generated PHHPS oils with IV, m.p., and SFI of potential value in margarine and shortening basestocks. Samples with IV of 54–71 might find application in stick margarines

TABLE 2
FA Composition (wt% of total FA detected) of Partially Hydrogenated High-Palmitic Acid Solin oils

		FA							
IV[a] (measured)	IV[a] (calculated)	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	*Trans* (IR)[b]	*Trans* (GC)[c]
105	112	16.9 ± 0.0[d]	1.6 ± 0.0	3.5 ± 0.0	23.6 ± 0.3	30.8 ± 0.0	1.0 ± 0.0	23.5 ± 0.0	22.0 ± 0.0
97	102	17.1 ± 0.0	1.5 ± 0.0	4.1 ± 0.0	22.7 ± 0.0	27.7 ± 0.0	0.6 ± 0.1	26.6 ± 0.1	26.2 ± 0.1
90	93	17.2 ± 0.1	1.4 ± 0.0	4.2 ± 0.1	22.6 ± 0.0	16.3 ± 0.1	0.2 ± 0.0	36.0 ± 0.0	36.0 ± 0.1
79	78	17.3 ± 0.0	1.3 ± 0.1	4.5 ± 0.0	22.5 ± 0.1	8.9 ± 0.0	0.1 ± 0.0	43.4 ± 0.0	44.2 ± 0.2
71	74	17.5 ± 0.0	1.2 ± 0.0	6.7 ± 0.0	22.2 ± 0.3	3.2 ± 0.2	0.1 ± 0.1	45.5 ± 0.1	46.8 ± 0.4
69	72	17.7 ± 0.1	1.1 ± 0.0	9.4 ± 0.0	21.1 ± 0.1	1.5 ± 0.1	0.1 ± 0.0	46.2 ± 0.0	47.5 ± 0.3
65	68	17.7 ± 0.0	0.9 ± 0.0	11.3 ± 0.1	19.9 ± 0.1	0.5 ± 0.0	0.0 ± 0.0	47.5 ± 0.1	48.4 ± 0.1
54	50	17.8 ± 0.1	0.4 ± 0.0	21.5 ± 0.1	8.2 ± 0.0	0.4 ± 0.1	0.0 ± 0.0	49.6 ± 0.0	50.7 ± 0.2
<5	2	17.8 ± 0.0	0.1 ± 0.0	81.5 ± 0.1	0.5 ± 0.1	0.1 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

[a]IV, iodine value (cg/g).
[b]Measured by IR spectroscopy (9).
[c]Measured by GC (11).
[d]Mean ± SD. For FA names, see Table 1.

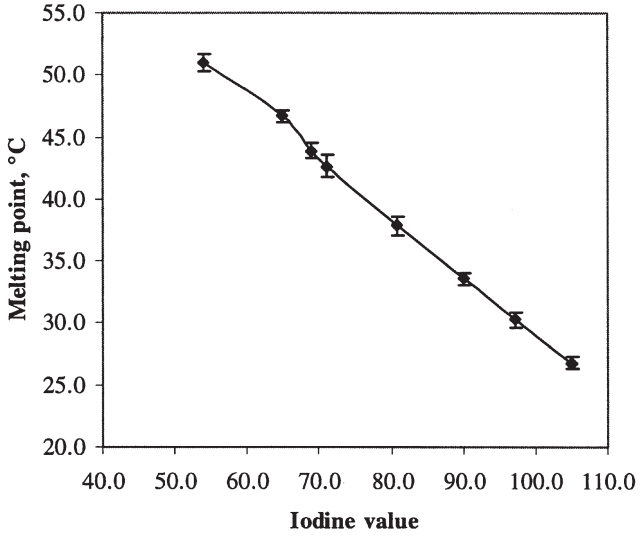

FIG. 1. Melting points of partially hydrogenated high-palmitic acid solin (PHHPS) oil samples. Error bars represent SE of the means.

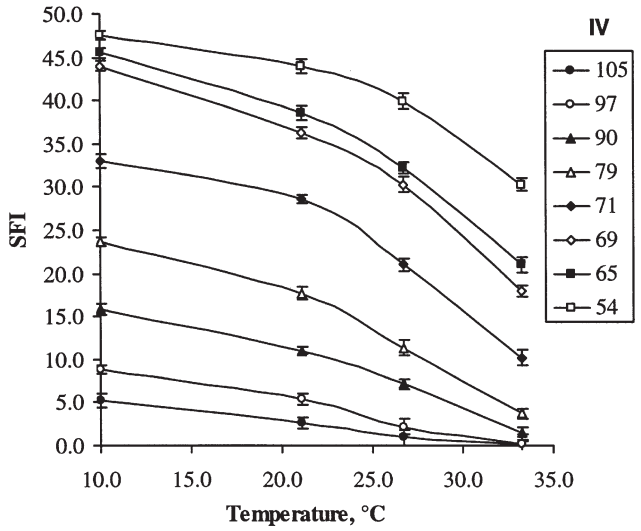

FIG. 2. Solid fat index (SFI) profiles of PHHPS oil samples. For other abbreviation see Figure 1. Error bars represent SE of the mean.

or all-purpose shortenings, whereas samples with IV of 79–105 might be of value in tub margarines and pourable frying shortenings.

REFERENCES

1. Green, A.G., A Mutant Genotype of Flax (*Linum usitatissimum* L.) Containing Very Low Levels of Linolenic Acid in Its Seed Oil, *Can. J. Plant Sci. 66*:499–503 (1986).
2. Oil World Statistics Update, *Oil World 31*:9–10 (2000).
3. DeClercq, D.R., and J.K. Daun, *Quality of Western Canadian Flaxseed*, Canadian Grain Commission, Winnipeg, 1999, 11 pp.
4. Rowland, G.G., and R.S. Bhatty, Ethyl Methanesulfonate Induced Fatty Acid Mutation in Flax, *J. Am. Oil Chem. Soc. 67*:213–214 (1990).
5. DeClercq, D.R., *Quality of Western Canadian Solin*, Canadian Grain Commission, Winnipeg, 1999, 9 pp.
6. DeClercq, D.R., and J.K. Daun, *Quality of Western Canadian Canola*, Canadian Grain Commission, Winnipeg, 1999, 17 pp.
7. Green, A.G., Linola™ '947' Low Linolenic Acid Flax, *Can. J. Plant Sci. 75*:201–202 (1994).
8. Rowland, G.G., A. McHughen, L.V. Gusta, R.S. Bhatty, S.L. MacKenzie, and D.C. Taylor, The Application of Chemical Mutagenesis and Biotechnology to the Modification of Linseed (*Linum usitatissimum* L.), *Euphytica 85*:317–321 (1995).
9. *Official Methods and Recommended Practices of the AOCS*, 5th edn., AOCS Press, Champaign, 1997, Methods Cc 13e-92, Ca 5a-40, Cc 10a-25, Cc 1-25, Cd 1-25, Cd 8-53, Cd 3-25, Cd 1c-85, Cd 14-61, Cd 10-57.
10. Slover, H.T., R.H. Thompson, C.S. Davis, and G.V. Merola, Lipids in Margarines and Margarine-like Foods, *J. Am. Oil Chem. Soc. 62*:775–786 (1985).
11. Hitchcock, C., and E.V. Hammond, The Determination of Lipids in Foods, in *Developments in Food Analysis Techniques—2*, edited by R.D. King, Applied Science, London, 1978, pp. 185–224.
12. Wiedermann, L.H., Margarine and Margarine Oils: Finished Product Quality, *J. Am. Oil Chem. Soc. 49*:478–480 (1978).
13. deMan, L., C.F. Shen, and J.M. deMan, Composition, Physical and Textural Characteristics of Soft (tub) Margarines, *Ibid. 68*:70–73 (1991).
14. Gunstone, F.D., Chemical Properties, in *The Lipid Handbook*, edited by F.D. Gunstone, J.L. Hardwood, and F.B. Padley, Chapman & Hall, London, 1994, pp. 35–105.
15. Bell, R.J., Shortening and Margarine Products, in *Introduction to Fats and Oils Technology*, edited by P.G. Wan, American Oil Chemists' Society, Champaign, 1991, pp. 183–210.
16. Stauffer, C.E., Fats and Oils, in *Egan Press Handbooks Series*, AOCS Press, Champaign, 1996, pp. 1–81.
17. Postmus, E., L. deMan, and J.M. deMan, Composition and Physical Properties of North American Stick Margarines, *J. Food Sci. Technol. 22*:481–486 (1989).
18. Hodgson, A.S., Refining and Bleaching, in *Bailey's Industrial Oil and Fat Products*, 5th edn., edited by Y.H. Hui, John Wiley & Sons, New York, 1996, Vol. 4, p. 163.
19. Grothues, B.G.M., Hydrogenation of Palm and Lauric Oils, *J. Am. Oil Chem. Soc. 62*:390–399 (1994).
20. Hastert, R.C., Hydrogenation, in *Bailey's Industrial Oil and Fat Products*, 5th edn., edited by Y.H. Hui, John Wiley & Sons, New York, 1996, Vol. 4, pp. 213–300.

[Received August 21, 2003; accepted December 9, 2003]