Margarine and Shortening Oils by Interesterification of Liquid and Trisaturated Triglycerides[1]

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ABSTRACT: Liquid vegetable oils (VO), including cottonseed, peanut, soybean, corn, and canola, were randomly interesterified with completely hydrogenated soybean or cottonseed hardstocks (vegetable oil trisaturate; VOTS) in ratios of four parts VO and one part VOTS. Analysis of the reaction products by high-performance liquid chromatography showed that at 70°C and vigorous agitation, with 0.5% sodium methoxide catalyst, the reactions were complete after 15 min. Solid-fat index (SFI) measurements made at 50, 70, 80, 92, and 104°F, along with drop melting points, indicated that the interesterified fats possess plasticity curves in the range of commercial soft tub margarine oils prepared by blending hydrogenated stocks. Shortening basestocks were prepared by randomly interesterifying palm or soybean oil with VOTS in ratios of 1:1 or 3:1 or 4:1, respectively. Blending of the interesterified basestocks with additional liquid VO yielded products having SFI curves very similar to commercial all purpose-type shortening oils made by blending hydrogenated stocks. Other studies show that fluid-type shortening oils can be prepared through blending of interesterified basestocks with liquid VO. X-ray diffraction studies showed that the desirable β′ crystal structure is achieved through interesterification and blending.
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KEY WORDS: Drop melting points, interesterification, margarine oils, shortening oils, solid-fat index, triglycerides, vegetable oils.

Interesterification is an old process whereby fats and oils can be randomized to improve plasticity, crystal habit or functional properties (1–3). Indeed, the patent literature contains many references to the preparation of margarine and shortening oils by interesterification of a wide variety of naturally occurring and hydrogenated products (4–6). Nonetheless, hydrogenation remains the technology of choice for commercial production of margarines and shortening products.

Previous reports (7,8) from our laboratory have described preparation of potential margarine and shortening through interesterification of liquid and completely hydrogenated soybean oil. The present report extends these studies to include other vegetable oils (VO) and stearines.

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EXPERIMENTAL PROCEDURES

VO and hard stocks. The liquid VO were commercially refined, bleached, and deodorized products obtained from P.V.O. Foods (Granite City, IL). The fully saturated cottonseed and soybeans flakes were commercial preparations obtained from Riceland Foods (Stuttgart, AR) or Bunge Foods (Bradley, IL).

Interesterifications. Liquid oils and hardstocks were blended and dried by heating them under a water aspirator vacuum. Dried oil (1600 g) was charged into a stirred, stainless-steel autoclave and brought to 70°C. Dry sodium methoxide (catalyst-grade; Amspec Co., Gloucester City, NJ) –8 g 0.5% by weight was added and vigorous stirring was continued for 30 min at a temperature of 70°C. The catalyst was inactivated by the addition of 2% aqueous 20% citric acid. The reaction was stirred for an additional 15 min; filter aid was stirred into the fat and it was filtered under vacuum to remove soaps.

Analytical methods. The high-performance liquid chromatography (HPLC) analytical methods for the analysis of interesterified oils have been described in detail elsewhere (9). Fatty acid composition was determined by capillary gas–liquid chromatography (GLC) after transmethylation of the fats (9). Solid-fat indexes (SFIs) were determined by the AOCS method (10). Drop melting points were determined with a Mettler drop point instrument (10).

X-ray diffraction. Approximately 300 mg of sample was applied to a microscope slide to infinite thickness. The samples were analyzed using a GE Diano (Charlotte, NC) XRD-7 powder diffractometer with copper K-Alpha radiation at 40 Kv 24 ma. Temperature and humidity were kept constant at 21°C and 40%, respectively. Percentages of β crystals were calculated based on the total peak heights of the β and β′ crystals according to Yap *et al.* (11). The margarine oils could not be analyzed by the procedure since they were too soft.

RESULTS AND DISCUSSION

The fatty acid and triglyceride composition for the starting materials are presented in Table 1. The structure and physical properties of interesterified VO-SBOTS (soybean oil triunsaturate) and VO-CSOTS (cottonseed oil) blends are shown

TABLE 1
Composition of Vegetable Oils and Stearines[a]

	Fatty acid (%)									Triglycerides						
Oil or stearine	C16	C18	C18:1	C18:2	C18:3	Calc. IV	Sat.%	Unsat.%	U/S	UUU	SUU	SSU	SSS	%Sat.	%Unsat.	U/S
Soybean	9.9	4.1	24.9	52.8	7.2	131.7	14.0	86.0	6.1	58.9	28.5	12.7	1.8	41.1	58.9	1.43
Corn	10.0	2.2	25.9	59.5	0.9	127.7	13.1	86.9	6.6	62.1	34.8	2.9	0.2	37.9	62.1	1.64
Cottonseed	21.7	2.3	15.6	58.9	0.2	116.0	24.0	76	3.2	58.9	36.8	3.7	0.5	41.1	58.9	1.43
Canola	5.6	1.9	54.6	26.0	9.9	117.8	7.5	92.5	12.3	75.4	21.0	1.6	0.5	24.6	75.4	3.06
Peanut	9.9	2.5	41.1	31.9	0.3	96.0	12.4	87.6	7.1	56.0	28.5	12.7	1.8	44.0	56.0	1.27
Palm	42.8	4.6	46.5	9.9	0.2	53.0	47.4	52.6	1.1	3.8	14.1	72.8	8.7	96.2	3.2	0.03
Soyflakes	10	90	0	0	0	0	100	0	—	0	0	0	100	100	0	—
Cottonseed flakes	18.8	70.5	7.1	1.8	0	9.2	89.3	10.7	0.12	0.7	2.7	24.7	70.7	97.8	0.7	.01

[a]U, unsaturated; S, saturated; calculated (Calc.) iodine value (IV); saturation (Sat.); unsaturation (Unsat.).

in Table 2. Glyceride types are summarized according to unsaturation as blends and, after randomization, the results are compared to that predicted by strict random theory (1,7).

Generally, excellent agreement was found between the experimental values and that calculated from strict random distributions, which shows that under the conditions employed, complete randomization of the glyceride structure occurred. As blends, high proportions of SSS glycerides (S is saturated acids) are present, which, after interesterification, are reduced to nearly the theoretical values with the possible exception of the canola/CSOTS blend (Run 10).

SFI measurement for the ten blends are also presented in Table 2 and indicate that nearly all possess SFI curves closely matching those obtained when hydrogenated stocks are blended for soft tub margarine (7,12). Typically, such hydrogenated stocks show SFI values at 50, 70, and 92° in the range of 8–10, 4–5, and 1–2, respectively, and have drop melting points of about 90–96°F. The interesterified products are all in these ranges except the canola/CSOTS blend (Run 10), which would possibly be too soft for tub margarine formulations and the cottonseed/SBOTS blend (Run 4), which possibly has a high SFI value at 92°F.

Our previous report indicated that randomized mixtures of VO and SBOTS (50:50) produced a basestock suitable for shortening oil formulations. SFI curves for the 50:50 randomized basestock and blends with liquid soybean oil are shown in Figure 1. Although low proportions (5–10%) of basestock in the blends possess sufficient solids at the 92°F SFI temperature to qualify as margarine oils, the SFI at 50 and 70°F are too low. Additional basestocks were prepared by randomizing palm oil with SBOTS and CSOTS. The properties and structures of these products are shown in Table 3. The slopes of the SFI curves are such that, without additional liquid oil, both the 50 and 104°F SFI are too high for incorporation into all purpose-type shortening oil. Increasing the amount of interesterified basestock raises the 50 and 70°F SFI, but when sufficient solids are present at these temperatures, the 92°F value becomes too high. Thus, margarine oil formulations are not practical by blending the 50:50 VO/SBOTS basestock with liquid oil.

TABLE 2
Structure and Physical Properties of Interesterified Vegetable Oil–Stearine Blends[a]

			Glyceride class (%)												Solid-fat index (@ temp. °F)					Drop m.p.
			UUU			UUS			SSU			SSS								
No.	Liquid oil (%)	Stearine (%)	B	I	Calc.	B	I	Calc.	B	I	Calc.	B	I	Calc.	50	70	80	92	104	°F
1	Peanut (80)	Soy (20)	41.7	26.1	26.9	23.1	46.9	44.3	2.8	21.4	24.3	26.6	5.0	4.4	11.8	6.7	5.5	3.6	0.8	101.6
2	Corn (80)	Soy (20)	47.0	26.9	32.9	28.4	52.4	44.4	2.6	20.1	19.8	20.6	1.6	2.9	6.4	4.1	3.4	2.2	0.3	90.7
3	Soy (80)	Soy (20)	45.3	28.9	30.1	27.4	46.9	44.4	2.5	20.4	21.8	23.3	3.3	3.6	8.4	4.5	3.7	2.7	1.1	96.0
4	Cotton (80)	Soy (20)	28.4	19.4	20.3	46.5	53.1	44.3	2.2	22.2	29.9	21.8	5.3	7.0	11.6	8.3	7.2	5.4	1.4	102.9
5	Canola (80)	Soy (20)	54.6	37.0	38.7	20.6	42.2	43.2	1.8	15.8	16.1	21.9	4.1	1.9	8.7	5.4	4.5	3.9	3.0	99.9
6	Palm (80)	Soy (20)	3.0	3.6	5.6	26.8	26.0	27.1	37.1	45.5	43.5	30.7	23.4	23.6	43.7	33.1	30.5	31.3	21.3	118.9
7	Peanut (80)	Cotton (20)	40.9	27.7	27.9	24.2	44.6	44.4	4.5	12.9	23.6	28.5	4.7	4.2	10.1	5.5	4.1	2.6	0	98.7
8	Corn (80)	Cotton (20)	47.2	31.7	34.6	29.6	47.3	44.1	28.0	18.5	18.1	14.8	2.3	2.6	7.1	4.7	3.8	2.7	0.9	97.7
9	Soy (80)	Cotton (20)	46.4	29.6	33.9	32.7	47.7	44.2	4.4	19.2	19.1	16.1	2.3	2.8	8.5	3.9	3.3	1.9	0.2	90.0
10	Cotton (80)	Cotton (20)	28.9	20.5	23.5	39.9	48.8	43.8	11.5	24.9	27.7	19.9	5.1	5.6	11.5	7.9	6.7	4.5	0.5	99.5
11	Canola (80)	Cotton (20)	57.6	36.2	41.2	19.9	46.0	42.5	1.4	11.9	14.6	20.8	4.1	1.7	4.0	2.3	1.4	0.7	0.2	83.1
12	Palm (75)	Cotton (25)	2.6	2.8	2.7	28.8	24.3	30.3	39.2	46.2	42.5	28.6	25.1	19.8	45.7	35.8	30.9	25.2	15.3	114.4

[a]U, S, determined by reversed-phase high-performance liquid chromatography. B = Blend, I = interesterified, calculated (Calc.) from random theory, m.p. = melting point. See Table 1 for other abbreviations.

TABLE 3
Properties of Interesterified Shortening Basestocks and Blends

	Basestock—interesterified		Solid-fat index, At temperature (°F)					Drop melt	%β′
	Liquid oil (%)	Hardstock (%)	50	70	80	92	104	°F	Crystal
A	Palm (75)	Soybean (25)	45.7	37.9	35.3	31.3	21.3	118.1	64.0
B	Palm (80)	Soybean (20)	43.7	33.1	30.5	26.4	16.9	116.1	59.8
C	Palm (80)	Cotton (20)	42.4	32.7	30.9	25.3	15.3	114 4	61.2
D	Palm (75)	Cotton (25)	45.7	35.8	32.8	26.6	18.6	117.3	62.5
E	Soybean (50)	Soybean (50)	40.0	28.9	—	26.6	20.1	125.9	43.6
	Blended oils								
	Basestock (%)	Liquid oil (%)							
F	A (65)	Soybean (35)	27.6	21.3	20.1	16.4	9.5	110.8	55.2
G	B (65)	Soybean (35)	26.1	20.3	19.3	15.8	8.7	109.1	54.0
H	C (65)	Soybean (35)	24.6	18.8	17.4	14.4	7.3	118.5	52.5
I	D (65)	Soybean (35)	28.4	22.6	21.7	18.2	11.3	113.4	55.6
J	E (50)	Soybean (50)	19.7	15.2	14.1	11.4	5.8	107.9	53.8
K	B (50)	Soybean (50)	19.0	14.4	13.7	10.8	4.9	103.5	51.0
L	C (50)	Soybean (50)	17.6	13.6	12.4	9.7	4.0	105.4	50.0
M	D (50)	Soybean (50)	20.6	16.3	15.4	12.6	7.2	109.3	53.4
N	E (50)	Cotton (50)	18.0	12.6	12.4	11.6	10.0	100.8	45.2
O	E (50)	Corn (50)	17.2	12.5	12.2	11.9	9.8	73.1	—
P	E (50)	Peanut (50)	18.0	12.4	12.2	11.5	9.6	103.1	49.2
Q	E (50)	Canola (50)	17.3	12.6	12.2	11.5	9.6	103.4	51.7
R	E (50)	Soybean (50)	17.6	12.5	12.3	11.7	9.8	100.5	44.6
S	E (35)	Soybean (65)	9.5	6.9	6.8	6.7	5.5	104.3	51.0
T	E (35)	Cotton (65)	15.5	7.8	7.6	7.2	5.9	99.0	0
U	E (35)	Corn (65)	10.4	7.9	7.7	7.3	5.9	75.3	41.7
V	E (35)	Peanut (65)	11.1	7.0	7.4	7.0	5.8	10.4	45.3
W	E (35)	Canola (65)	9.5	7.6	7.4	7.2	5.9	102.6	44.6
X[a]	Commercial all-purpose		23–26	19	—	14	11	—	—
Y[a]	Fluid shortening		8	8	—	7	6	—	—

[a]Reference 12.

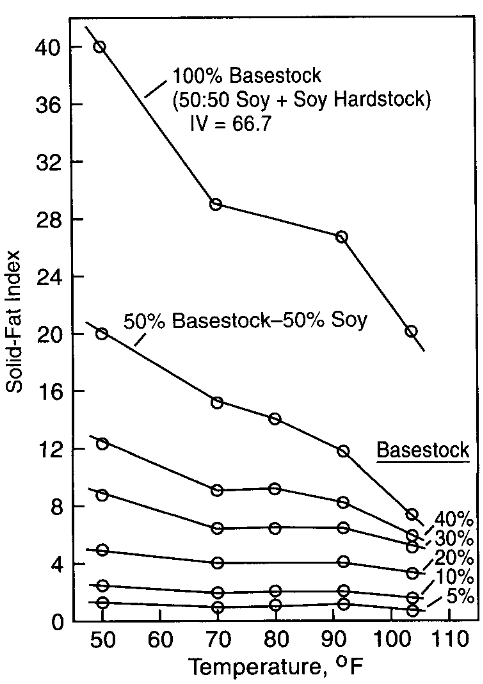

FIG. 1. Effect of liquid soybean oil on the solid-fat index of an interesterified (50:50 soy oil–soybean oil trisaturates) blend; IV, iodine value.

Typically, all purpose-type shortening oils prepared by blending hydrogenated stocks show SFI values at 50, 70, 80, 92, and 104°F of 18–23, 14–19, 13–14, 12–13, and 7–11, respectively. The blends of 50% basestock and 50% liquid oil have an SFI curve which closely matches these values. Commercial oils show drop melting points of 113–118°F, while the 50:50 blend value of 108°F is slightly lower. Thus, the concept of formulating shortening oils by blending interesterified basestocks with liquid oil appears valid.

Additional data for interesterified palm oil–SBOTS and CSOTS–blends are given in Table 3. Blends of 50–65% basestock and 35–50% soybean oil show SFI curves which closely match all purpose-type shortening oils. Additional data for other basestocks and blends are given in Table 3.

Results shown in Table 3 indicated that blends of 50% basestock E and 50% corn, peanut, canola, and cottonseed oils also possess SFI curves nearly identical to those when soybean oil is present as the liquid component.

Additional basestocks A–D were prepared by randomizing palm oil with SBOTS or CSOTS (Table 3) in ratios of 4:1 or 5:1. Blending 35–50% of these basestocks with 50–65% liquid oil yields products (F–M) whose SFI curves closely match those obtained from commercial all purpose-type shortening oils (X).

Fluid-type shortenings represent products with low flat SFI curves ranging from 8 at 50°F to about 6 at 104°F (12). Oils S–W represent products prepared by blending 35% of basestock E with 65% liquid corn, peanut, cottonseed, canola, and soybean oil. Most of these blends possess SFI curves closely matching those obtained from commercial fluid-type shortening oil (Y).

Texture hardness and spreadability of margarine depend on two dominating factors, including the SFI of the oil blend and processing conditions during chilling and crystallization of the emulsion (13).

While the studies reported here show that it is possible to control the SFI through interesterification and blending, the crystallization of the product during margarine or shortening manufacture may differ from that of hydrogenated oil. Preliminary work in the pilot plant has shown that soft margarines prepared from an 80:20 interesterified soybean–soy trisaturate blend are somewhat harder than expected from their SFI profile. These studies will be reported elsewhere.

Penetration studies made on commercial margarines made from hydrogenated soybean oil or blends of hydrogenated and liquid oil showed the following yield values: soft tub 200–550 g/cm^2, soft stick 960–1360 g/cm^2, stick 1680–2800 g/cm^2. Haighton (14) has correlated yield values with spreadability and the range of good spreadability is 200–800 g/cm^2.

Although the randomized oils shown in Table 2 appear to have ample solids for soft margarine, products made from oil 3 (80:20 soy–soy trisaturate) showed a yield value of 1961 g/cm^2, which is more in line with stick products. Thus, additional liquid oil may be required to produce products of sufficient softness This may be accomplished by either blending liquid oil with interesterified basestocks or incorporating less trisaturated triglycerides in the blend prior to interesterification.

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