Physical and Chemical Properties of *trans*-Free Fats Produced by Chemical Interesterification of Vegetable Oil Blends[1]

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ABSTRACT: Fat blends, formulated by mixing a highly saturated fat (palm stearin or fully hydrogenated soybean oil) with a native vegetable oil (soybean oil) in different ratios from 10:90 to 75:25 (wt%), were subjected to chemical interesterification reactions on laboratory scale (0.2% sodium methoxide catalyst, time = 90 min, temperature = 90°C). Starting and interesterified blends were investigated for triglyceride composition, solid fat content, free fatty acid content, and *trans* fatty acid (TFA) levels. Obtained values were compared to those of low- and high-*trans* commercial food fats. The interesterified blends with 30–50% of hard stock had plasticity curves in the range of commercial shortenings and stick-type margarines, while interesterified blends with 20% hard stock were suitable for use in soft tub-type margarines. Confectionery fat basestocks could be prepared from interesterified fat blends with 40% palm stearin or 25% fully hydrogenated soybean oil. TFA levels of interesterified blends were low (0.1%) compared to 1.3–12.1% in commercial food fats.

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KEY WORDS: Fat blends, interesterification, margarines, shortenings, *trans* fatty acids, vegetable oil.

Most native vegetable oils have only limited applications in their original forms due to their specific chemical compositions. To widen their use, vegetable oils are modified either chemically by hydrogenation or interesterification or physically by fractionation (1–4). Normally, hydrogenation is only done partially, depending upon required end-product quality. However, during partial hydrogenation, part of the *cis* double bonds are isomerized into their *trans* form. In the past, formation of *trans* isomers [*trans* fatty acids (TFA)] was considered an advantageous side-reaction because TFA have higher melting points and greater stability than *cis* fatty acids (5). Basestocks used for formulation of margarines in the United Kingdom contain 11–39% TFA, those in Western and Eastern Europe contain 7–32%, and those in North America contain 22–45% TFA (1,6,7).

In the past few years, several nutritional studies have suggested a direct relationship between TFA and increased risk for coronary heart disease (8–11). As a consequence of this controversy about TFA, a trend is observed in the food industry to replace partially hydrogenated oils by other fat sources with lower *trans* contents. Recent literature data show that fully hydrogenated oils are used for the manufacture of low- to zero-*trans* commercial fats (12).

Interesterification is one of the alternatives to the partial hydrogenation process that can be used to give fats and oils desired functionality. It has been applied for many years to modify the physical properties of lard (13). Interesterification of blends of fully hydrogenated vegetable oil with a liquid oil has been used to produce a zero-*trans* solid fat with the desired physical properties (14–17).

The aim of this study was to assist in the proper choice of oils to produce a zero-*trans* hard fat phase with melting characteristics similar to commercial fats. Changes in triglyceride (TAG) composition and melting behavior during the interesterification of blends of a highly saturated fat (palm stearin or fully hydrogenated soybean oil) with a native vegetable oil (soybean oil) are presented. Interesterified hard stocks can be further fractionated to obtain the required products with low- to zero-*trans* isomer content.

EXPERIMENTAL PROCEDURES

Materials. Neutralized bleached soybean oil (SBO), fully hydrogenated soybean oil (FHSBO), and palm stearin (Pst) were obtained from De Smet Group, Edegem, Belgium. Sodium methoxide was provided by HULS, Halle, Belgium. Commercial tub and stick margarines were purchased locally. All fats and oils were stored below 0°C until analysis.

TAG standards were purchased from Sigma Chemical, Bornem, Belgium. Acetonitrile and acetone were high-performance liquid chromatography (HPLC)-grade. Before use, they were filtered through a 0.45-μm filter.

Interesterification procedure. The fat blend (200 g), neutralized with 50% caustic soda solution, was dried for 40 min

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at 110°C and *ca.* 50 mbar. After lowering the temperature to 90°C, 0.2% sodium methoxide (powdered form) as catalyst was added. After 90 min of stirring, the mixture was cooled below 80°C. Vacuum was broken, and 20% citric acid solution was added to inactivate the catalyst, while the mixture was stirred mechanically for 15 min. Postbleaching was performed with 0.5% of bleaching earth (Tonsil 210 FF) under vacuum for 30 min at 90°C.

Analytical procedures. Solid fat content (SFC) was determined with a Brucker Minispec pulsed nuclear magnetic resonance (pNMR) analyzer Model No. 20 (Karlsruhe-Forchheim, Germany). The fat was melted at 80°C and placed in an ice-bath (0°C) for 60 min before the first SFC measurement. Before measuring, the samples were conditioned for 30 min at the desired temperature. The capillary melting point was determined by AOCS Official Method Cc 1-25 (18). Fatty acid methyl esters (FAME) were prepared and subsequently analyzed with a Carlo Erba 5160 gas–liquid chromatograph, equipped with a flame-ionization detector and a split injector (Carlo Erba, Milano, Italy), as described in AOCS Official Methods Ce 1-62 and Ce 2-66 (18). A fused-silica capillary column, coated with 100% cyanopropyl polysiloxane (CP™-Sil 88, 50 m × 0.25 mm internal diameter; 0.25 µm film thickness; Chrompack, Bergen op Zoom, The Netherlands), was used with helium as a carrier gas. For TFA determination, temperature was programmed as described in AOCS Official Method Ce 1c-89 (18). Initial oven temperature was set at 150°C and increased at a rate of 1.3°C/min to 200°C, where it was held until completion of the analysis. Injector and detector were maintained at 250°C. Identification of the individual *trans* isomers was realized with pure TAG standards and elaidinized linseed oil FAME, prepared as described elsewhere (19), as reference compounds. Quantitative analyses were performed with a Shimadzu RC3A (Kyoto, Japan). Iodine values (IV) were determined directly from the fatty acid (FA) compositions by AOCS Official Method Cd 1c-85 (18). Free fatty acids (FFA) were determined by AOCS Official Method Ca 5a-40 (18).

The TAG composition was analyzed in a reversed-phase high-performance liquid chromatograph (RP-HPLC) (Gilson, France) on an Allsphere ODS-2 column (3 µm, 150 × 4.6 mm; Alltech, Laarne, Belgium) with acetonitrile–acetone (37:63, vol/vol) as the eluent at a flow rate of 1 mL/min, and a refractive index detector. The equivalent carbon number (ECN) method was used to predict the elution order of TAG on RP-HPLC. Individual peaks were identified by comparing the retention time with that of reference TAG. Vegetable oils were solubilized in solvent mixture at 20 mg/mL and injected in the quantity of 20 µL. Random TAG distributions were calculated from FA compositional data [AOCS Official Method Ce 5b-89 (18)].

RESULTS AND DISCUSSION

The physical and chemical characteristics of the starting materials are presented in Table 1. Pst and FHSBO were both used as hard stocks. Pst, compared to FHSBO, had a lower melting point and higher IV. Small amounts of TFA (0.1%) were detected. According to literature data, starting materials can contain up to 2.1% of TFA (16). TFA in SBO and Pst are formed during deodorization or physical refining. TFA in FHSBO are minor side components formed during hydrogenation.

TABLE 1
Physical and Chemical Characteristics of Palm Stearin, Fully Hydrogenated Soybean Oil, and Soybean Oil[a]

Feedstock	m.p. (°C)	IV ($g\ I_2/100\ g$)	PUFA/SFA	TFA (%)
SBO	—	134.3	5.5	0.1
Pst	56.5	26.0	0.4	0.1
FHSBO	71.0	0.8	—	0.1

[a] m.p., melting point; IV, iodine value; PUFA/SFA, ratio of polyunsaturated and saturated fatty acids; TFA, *trans* fatty acids; SBO, soybean oil; Pst, palm stearin; FHSBO, fully hydrogenated soybean oil.

Good catalyst activity results in a clear increase in FFA. Theoretically, addition of 0.2% catalyst leads to the formation of 1.0% soap and 1.0% FAME. The soaps are converted to FFA during catalyst inactivation, while the FAME remain unchanged. Both volatile compounds are removed during deodorization and are effective losses. An increase in acidity from 0.1 to 1.0% was observed in all interesterified fat blends.

Randomization induced changes in TAG composition of the fat blends. In Tables 2 and 3, experimentally determined TAG compositions of Pst/SBO and FHSBO/SBO blends are compared with the calculated random distribution. TAG types are summarized according to the degree of unsaturation: U_3, U_2S, and S_3 (U_3 = triunsaturated, U_2S = diunsaturated, S_3 = trisaturated). Monounsaturated (S_2U) can be calculated by subtraction ($S_2U = 100 - U_3 - U_2S - S_3$). After interesterification, the high proportions of S_3 present in the starting blends were reduced 73–89%. Furthermore, interesterification resulted in a decrease of U_3 and formation of U_2S. The greatest changes were observed for the blends with 40–50% hard stock (a relative decrease of U_3 of 38–40% and 54–64%

TABLE 2
Triacylglycerol Class[a] of Fat Blends of Palm Stearin and Soybean Oil Before (B) and After (I) Interesterification and Calculated (C) According to Random Distribution Hypothesis

Fat blend (Pst/SBO[c] wt%)	Triacylglycerol[b] (mol %)								
	U_3			U_2S			S_3		
	B	I	C	B	I	C	B	I	C
10:90	51.9	51.1	49.5	27.1	30.9	39.2	8.2	0.9	0.9
20:80	49.8	39.4	37.0	25.8	33.3	43.6	21.9	3.7	2.3
30:70	45.5	33.1	28.3	24.0	34.2	44.4	30.7	4.3	4.1
40:60	37.2	23.0	21.0	19.3	33.6	43.0	38.5	6.3	6.7
50:50	35.0	21.0	14.3	18.4	29.3	39.2	47.7	10.4	10.9

[a] Determined by reversed-phase high-performance liquid chromatography with refractive index detector.
[b] Fatty acids in triacylglycerol: U, unsaturated; S, saturated.
[c] Pst/SBO, blend of palm stearin and soybean oil.

TABLE 3
Triacylglycerol Class of Fat Blends of Fully Hydrogenated Soybean Oil and Soybean Oil Before (B) and After (I) Interesterification and Calculated (C) According to Random Distribution Hypothesis

Fat blend (FHSBO/ SBO[a] wt%)	Triacylglycerol[b] (mol%)								
	U_3			U_2S			S_3		
	B	I	C	B	I	C	B	I	C
10:90	58.3	50.9	43.9	28.0	40.5	41.6	8.4	1.5	1.4
20:80	45.3	37.0	32.1	27.4	42.4	44.4	23.3	3.3	3.2
30:70	40.5	26.0	21.2	21.6	51.0	43.1	32.5	8.5	6.6
40:60	37.0	17.1	14.2	17.4	40.0	39.1	40.7	11.0	11.0
50:50	31.0	11.1	9.0	15.1	28.4	33.2	50.4	13.1	16.9

[a] FHSBO/SBO, blend of fully hydrogenated soybean oil and soybean oil. Other abbreviations as in Table 2.

and a relative increase of U_2S of 59–74% and 88–130%, respectively, for Pst/SBO and FHSBO/SBO blends). Generally, interesterification altered the experimental TAG compositions so that the composition was close to that of the calculated random distribution.

The altered TAG composition of the randomized fat blends was also reflected in the capillary melting point and SFC. After interesterification, an absolute decrease in the melting point, ranging from 7–25 and 9–31°C, respectively, was detected for the different Pst/SBO and FHSBO/SBO blends. This decrease in the melting points can be explained by the decrease of the higher-melting S_3 proportion.

SFC curves of the randomized fat blends were changed completely (Figs. 1 and 2). Interesterified blends tended to have lower SFC values than starting blends. At a lower temperature (10°C), large changes in SFC were observed for the blends with 20–30% hard stock. At a higher temperature (40°C), the largest changes in SFC for the blends with 40–50% of hard stock were noticed.

Interesterified blends of 10:90 hard stock/SBO had low SFC values at all analyzed temperatures. Therefore, their plasticity is poor. This can be explained by low levels (20–23%) of saturated fatty acids (SFA), which should be at least 25–30% to have good plasticity.

Interesterification of fat blends with large amounts of hard stock (75%) produced little change in the melting point. Changes in SFC were observed only at temperatures greater than 35°C.

Interesterification of pure SBO did not change SFC. Therefore, to improve its plastic range, SBO was blended with a hard stock and interesterified. The interesterified blend, consisting of 20% hard stock, had a SFC profile that is suitable for soft tub margarine oil (Table 4).

Interesterified blends of 25:75 FHSBO/SBO and 40:60 Pst/SBO with melting points of, respectively, 38 and 41°C are suitable for use as confectionery fats (15), and would be especially rich in polyunsaturated fatty acids (PUFA) (63.8 and 53.9%, respectively) (Table 4).

Randomized mixtures of FHSBO and SBO (30:70) or Pst and SBO (40:60) produced basestocks that are suitable for shortening oil formulations (Table 4). According to Kheiri (20), shortening oils prepared by blending hydrogenated stocks show SFC values at 20, 30, and 40°C of 18.8–22.0, 7.8–11.0, and 1.7–5.0%, respectively. The interesterified blends of 40% Pst and 30% FHSBO had SFC curves that closely match these values. Commercial shortenings showed melting points of 37.0–41.0°C, while the interesterified 30:70 blend value of 47.0°C was slightly higher.

The interesterified blends of 40% FHSBO and 50% Pst possessed SFC curves that closely matched those obtained by blending hydrogenated stocks for stick-type margarines (Table 4).

PUFA/SFA for experimental blends with 10–50% hard

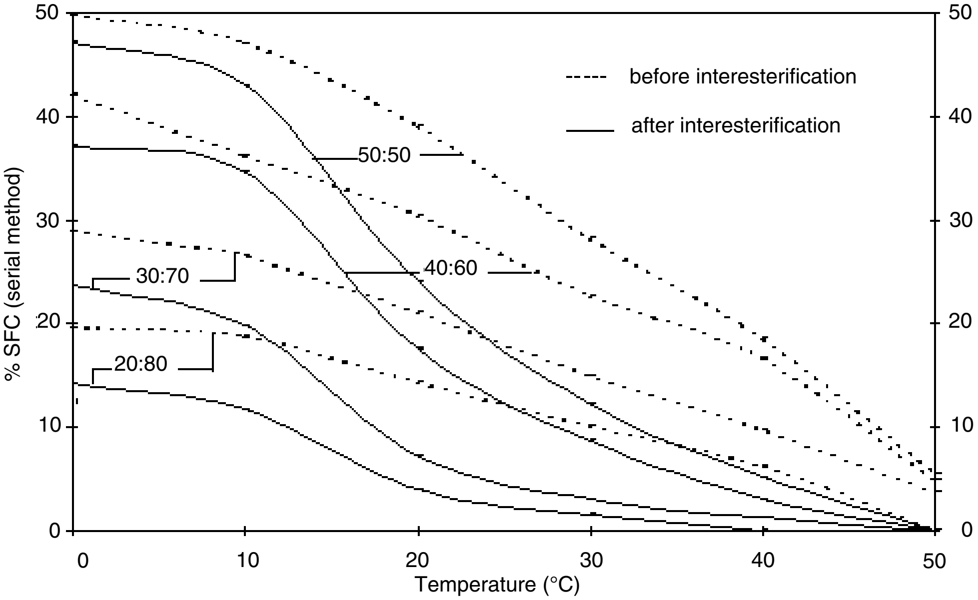

FIG. 1. Solid fat content (SFC) profiles of blends of palm stearin and of soybean oil before and after chemical interesterification.

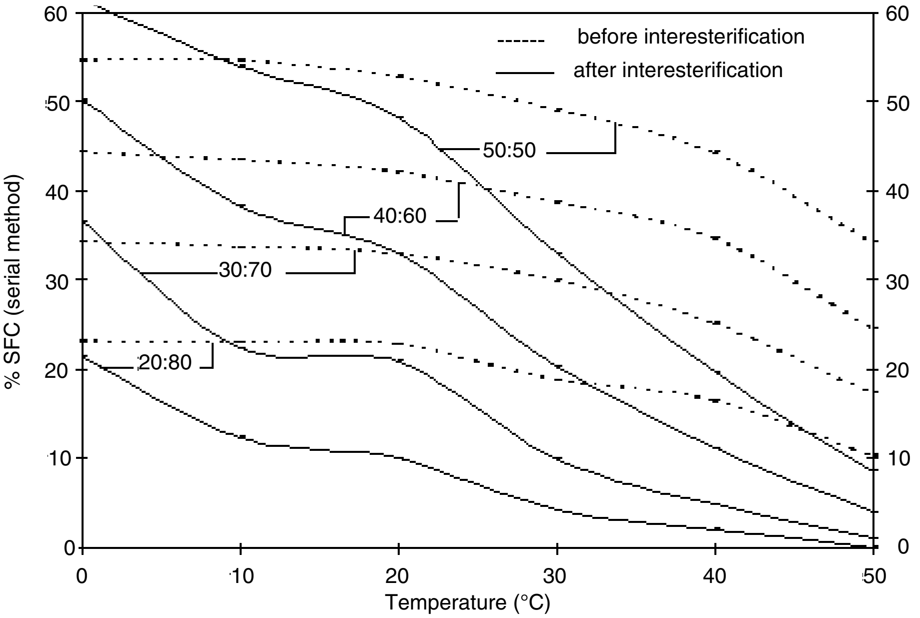

FIG. 2. SFC profiles of fat blends of fully hydrogenated soybean oil and soybean oil before and after chemical interesterification. See Figure 1 for abbreviation.

stock were higher than 1 and conformed to the recommendation of the Food and Agricultural Organization/World Health Organzation (FAO/WHO) and European Union Committee (EUC) for a minimal PUFA/SFA ratio.

Randomization did not produce *trans* isomers of unsaturated fatty acids. Therefore, TFA levels of interesterified blends were low (0.1%) compared to 1.3–12.1% in commercial food fats (Table 4).

In general, chemical randomization of 20–50% highly saturated fat (Pst or FHSBO) with a soft vegetable oil (SBO) can be used as an alternative to partial hydrogenation to produce a plastic fat phase that is suitable for manufacture of shortenings, stick or tub-type margarines, and confectionery fats. The final products had comparable physical properties and acceptable fatty acid compositions. Interesterified hard stocks can be further fractionated to

TABLE 4
Comparison of Interesterified Fat Blends with Commercial Fats

	SFC[a] (%) at °C						
Sample	10	20	30	IV	m.p. (°C)	PUFA/ SFA	TFA (%)
20:80 FHSBO/SBO	12.3	10.0	4.2	107.4	31.0	2.2	0.1
20:80 Pst/SBO	11.7	3.9	1.5	113.0	21.2	2.7	0.1
Tub margarine	11.7	8.1	4.6	125.3	32.5	3.8	1.3
25:75 FHSBO/SBO	19.4	16.6	7.3	100.6	38.0	1.8	0.1
40:60 Pst/SBO	34.6	17.5	8.7	92.3	41.0	1.6	0.1
Confectionery fat A[b]	20.4	9.9	5.9	87.3	38.9	1.8	N.A.[c]
Confectionery fat B[b]	22.7	10.7	6.6	85.1	40.6	1.6	N.A.
30:70 FHSBO/SBO	22.4	20.9	9.9	93.8	47.0	1.5	0.1
40:60 Pst/SBO	34.6	17.5	8.7	92.3	41.0	1.6	0.1
Shortening A[d]	N.A.	22.0	11.0	71.0	41.0	1.2	—
Shortening B[d]	N.A.	18.8	7.8	89.9	37.0	N.A.	11.6
40:60 FHSBO/SBO	38.3	33.0	20.3	81.5	53.0	1.1	0.1
50:50 Pst/SBO	43.0	24.1	12.2	78.4	44.5	1.2	0.1
Stick margarine A	50.8	29.9	11.3	50.3	37.9	0.7	12.1
Stick margarine B	44.2	25.4	8.9	55.4	36.8	0.8	5.7
Stick margarine C	49.1	29.0	10.3	47.7	37.6	0.7	1.5
Stick margarine D	43.0	32.8	21.4	73.2	45.5	0.9	4.0

[a] SFC, solid fat content (serial method).
[b] Reference 15.
[c] N.A., data not available.
[d] Reference 20. Other abbreviations as in Tables 1 and 2.

obtain the required products with low to zero *trans* isomer contents.

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REFERENCES

1. Hauman, B.F., Tools: Hydrogenation, Interesterification, *INFORM 5*:668-670, 672, 675–678 (1994).
2. Anderson, D., A Primer on Oils Processing Technology, in *Bailey's Industrial Oil and Fat Products,* 5th edn., edited by Y.H. Hui, Wiley-Interscience, New York, 1996, Vol. 4, pp. 1–60.
3. Hoffmann, G., The Chemistry and Technology of Edible Oils and Fats and Their High Fat Products, Academic Press, New York, 1989, pp. 201–277.
4. Kellens, M., Developments in Fat Modification Technology: Interesterification of Oils and Fats, Presented at Workshop on Oils Interesterification*,* Texas A&M University, 1996, pp. 1–2.
5. Thomas, L.M., and B.J. Holub, Nutritional Aspects of Fats and Oils, in *Technological Advances in Improved and Alternative Sources of Lipids,* edited by B.S. Kamel and Y. Kakuda, Blackie Academic and Professional, New York, 1994, pp. 16–49.
6. Berger, K., Food Product Formulation to Minimize the Content of Hydrogenated Fats, *Lipid Technol. 3*:37–40 (1993).
7. D'Souza, V., L. deMan, and J.M. deMan, Chemical and Physical Properties of the High Melting Glyceride Fractions of Commercial Margarines, *J. Am. Oil Chem. Soc. 68*:153–162 (1991).
8. Mensink, R.P., and M.B. Katan, Effect of Dietary *Trans* Fatty Acids on High-Density and Low-Density Lipoprotein Cholesterol Levels in Healthy Subjects, *N. Engl. J. Med. 323*:439–445 (1990).
9. Enig, M.G., *Trans* Fatty Acids in Diets and Databases, *Cereal Foods World 41*:58–63 (1996).
10. Gurr, M., *Trans* Fatty Acids and Health—An Update, *Lipid Technol. 2*:105–107 (1990).
11. Lichtenstein, A., *Trans* Fatty Acids, Blood Lipids and Cardiovascular Risk: Where Do We Stand, *Nutr. Rev. 51*:340–343 (1993).
12. De Greyt, W., O. Radanyi, M. Kellens, and A. Huyghebaert, Contribution of *Trans*-Fatty Acids from Vegetable Oils and Margarines to the Belgian Diet, *Fett/Lipid 98*:30–33 (1996).
13. Sreenivasan, B., Interesterification of Fats, *J. Am. Oil Chem. Soc. 55*:796–805 (1978).
14. Zeitoun, M.A.M., W.E. Neff, G.R. List, and T.L. Mounts, Physical Properties of Interesterified Fat Blends, *Ibid. 70*:467–471 (1993).
15. Hurtova, S., S. Schmidt, J. Zemanovic, P. Simon, and S. Sekretar, Random Interesterification of Fat Blends with Alkali Catalysts, *Fett/Lipid 98*:60–65 (1996).
16. List, G.R., E.A. Emken, W.F. Kwolek, T.D. Simpson, and H.J. Dutton, "Zero *Trans*" Margarines: Preparation, Structure and Properties of Interesterified Soybean Oil-Soy Trisaturate Blends, *J. Am. Oil Chem. Soc. 54*:408–413 (1977).
17. List, G.R., T.L. Mounts, F. Orthoefer, and W.E. Neff, Margarine and Shortening Oils by Interesterification of Liquid and Trisaturated Triglycerides, *Ibid. 72*:379–382 (1995).
18. *Official Methods and Recommended Practices of the American Oil Chemists' Society,* 4th edn., edited by D. Firestone, American Oil Chemists' Society, Champaign, 1989, Vol. 1, Methods Ca 5a-40, Cc 1-25, Cd 1c-85, Ce 1-62, Ce 1c-89, Ce 2-66, Ce 5b-89.
19. Grandgirard, A., F. Julliard, J. Prevost, and J.L. Sebedio, Preparation of Geometrical Isomers of Linolenic Acid, *J. Am. Oil Chem. Soc. 64*:1434–1440 (1987).
20. Kheiri, M.S.A., Palm Oil Products in Cooking Fats, *Ibid. 62*:410–416 (1985).

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