Physical and Chemical Properties of Randomly Interesterified Blends of Soybean Oil and Tallow for Use as Margarine Oils[1,2]

Y.C. LO and A.P. HANDEL, Department of Food Science and Technology, University of Nebraska, Lincoln, NE 68583-0919

ABSTRACT

Refined, unhydrogenated soybean oil and edible beef tallow were interesterified with sodium methoxide. This was done as an alternative to hydrogenation for the production of plastic fats for use as margarine oils. Using 0.5% sodium methoxide at 80 C, interesterification was complete in 30 min as determined by lipase hydrolysis. A blend of 60% soybean oil and 40% edible beef tallow was found to have physical characteristics (melting point, solid fat index) similar to those of commercial tub margarine oils. The level of polyunsaturated fatty acids was slightly lower and the level of saturated fatty acids slightly higher than the commercial margarine oils. Iodine value and *trans* fatty acid determinations indicated no discernible effect on the degree of unsaturation or the level of isomeric fatty acids by the interesterification process. The interesterified blend did contain 3.0% *trans* fatty acids which were originally present in the tallow. Oxidative stability of the interesterified oils was estimated by peroxide value determinations over several days on samples stored at 60 C. Experimental blends treated with 0.1% citric acid had poorer stability than the partially hydrogenated margarine oils; however, 0.01% BHA significantly delayed oxidation of the experimental samples.

INTRODUCTION

Margarines in the United States are generally produced from vegetable oils that have been modified by hydrogenation, which reduces double bonds to single bonds, thereby increasing both the melting point and stability of the oil (1). However, hydrogenation also results in the formation of positional isomers with double bonds in positions other than the 9-, 12- and 15-positions, and geometric isomers in the *trans* rather than *cis* configuration found in most vegetable oils (1,2). From a physical and chemical standpoint, formation of *trans* isomers is advantageous because *trans* isomers have higher melting points and greater stability than their *cis* counterparts. Stick-type margarines have been found to contain 9.9-28.7 g *trans* fatty acids per 100 g of margarine and tub-type margarines have 10.5-21.4 g per 100 g of margarine (3).

Several reports have been published on the metabolic effects of *trans* fatty acids, since margarines containing hydrogenated vegetable oils are a major source of *trans* fatty acids in the diet and consumption of these margarines has increased. Based on a review of the literature from 1920 to 1976, the Federation of American Societies for Experimental Biology (FASEB) found no reason to suspect hydrogenated soybean oil of being a hazard to the public (4). Their report concluded that there is no difference between *trans* and *cis* isomers in digestion or excretion and, although *trans* fatty acids have no essential fatty acid activity, they also have no antimetabolic activity. In a review of the effect of *trans* fatty acids on the physiological functions of fatty acids, Houtsmuller (5) concluded that *trans* fatty acids from hydrogenated vegetable oils cause no adverse effects in humans, provided adequate amounts of linoleic acid are present. These conclusions were reiterated by Applewhite (6) in a more recent review. However, other workers have reported that *trans* fatty acids in rats affect heart mitochondrial enzymes (7), decrease prostaglandin formation (8), decrease kidney size, impair growth and aggravate essential fatty acid deficiency (9,10). Hopkins and West (11) reported that *trans* fatty acids may be involved in carcinogenesis because of their influence on membrane fluidity. Results of investigations of the effect of *trans* fatty acids on plasma cholesterol levels, triacylglycerol levels and coronary heart disease have been equivocal (12,13). Obviously, the metabolism of *trans* fatty acids must be further elucidated before recommendations are made on their use. If *trans* fatty acids are found to have adverse effects on health, alternatives to partial hydrogenation should be available for use in the production of plastic fats.

One alternative to partial hydrogenation is interesterification of liquid vegetable oils with a hard fat. Interesterification has been used for many years to modify the physical properties of lard to produce a smooth, noncrystalline consistency (14,15). Recently, List and coworkers (16) interesterified soybean oil with completely hydrogenated soybean oil to produce a plastic fat suitable for use in margarines. Chobanov and Chobanova (17) interesterified sunflower oil with lard and tallow as the solid fraction. In the experiments reported here, soybean oil was interesterified with edible beef tallow to produce a plastic fat suitable for use in making tub-type margarines.

EXPERIMENTAL PROCEDURES

Fats and Oils

The soybean oil used was commercially refined, bleached and deodorized edible oil. Edible beef tallow was obtained from a local beef packer. Commercial tub and stick margarines were purchased locally. All fats and oils were stored below 0 C until used.

Interesterification Procedures

Interesterification procedures were based on those of Sreenivasan (18) and Chobanov and Chobanova (17). Appropriate proportions (w/w) of beef tallow and soybean oil were placed into a clean, dry 250 mL suction flask and, using a hot plate-stirrer, heated to 95 C under vacuum for 30 min with vigorous stirring to remove any water present. After lowering the temperature to 80 C, 0.5% sodium methoxide (Fisher Scientific Co., Fair Lawn, NJ) was added and interesterification was allowed to proceed for 30 min under a nitrogen atmosphere while agitation and temperature

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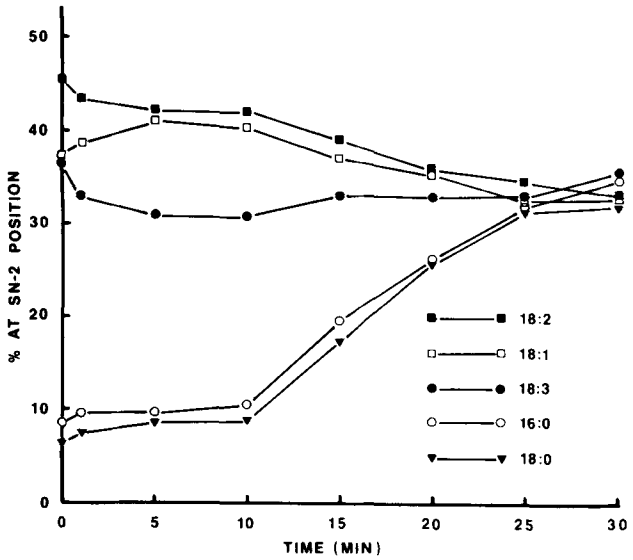

FIG. 1. Changes in the fatty acid distribution at the sn-2 position during interesterification of 60:40 soybean oil:beef tallow.

were maintained. The reaction was then stopped by the addition of an equal volume of distilled water. The interesterified blend was washed five times with equal amounts of lukewarm distilled water and dried under vacuum at 50 C. When blends were to be used for oxidative stability determinations, 0.01% citric acid as a 50% aqueous solution and 0.01% powdered BHA were added, where necessary, prior to drying.

For comparison purposes, uninteresterified mixtures of soybean oil and edible beef tallow were prepared in the same way and carried through the same heating and washing sequence except that no interesterification catalyst was added.

Melting Point

Melting points were determined by the closed capillary AOCS Official Method Cc 1-25 (19). Melting points were calculated by averaging the readings from four samples.

Solid Fat Index

Solid fat indices (SFI) were determined by dilatometry according to the AOCS Official Method Cd 10-57 (19). Two determinations were made for each sample.

Acid Value

Acid values were determined by the AOCS Official Method Cd 3a-63 (19).

Iodine Value

Iodine values were determined by the AOCS Official Method Cd 1-25 (19).

Fatty Acid Composition

Methyl esters of fatty acids were formed by the boron trifluoride/methanol procedure of Metcalfe et al. (20). Methyl esters were injected into a Varian Aerograph (Palo Alto, CA) Model 1200 gas chromatograph equipped with a flame ionization detector. A 1/8 in. × 12 ft aluminum column packed with 14% stabilized DEGS on Anakrom A, 90/100 mesh was used. The chromatograph was operated isothermally at 180 C with a nitrogen carrier gas flow of 30 mL/min. Quantitation was accomplished by means of peak areas. The fatty acid profile was also used to determine polyunsaturated fatty acid content.

Analysis of sn-2 Position

Analysis of fatty acids at the sn-2 position was used to determine completion of randomization. The methods of Lands et al. (21) were used for lipase hydrolysis of oil blends. After hydrolysis, the lipids were extracted with chloroform/methanol (2:1, v/v) and applied in a band on a TLC plate coated with 0.5 mm of Adsorbosil-5 (Applied Science Laboratories, State College, PA) that had been activated at 110 C for at least one hour. The plate was developed in petroleum ether/diethyl ether/acetic acid (70:20:4, v/v/v). Separated bands were visualized by exposing the developed plate to iodine vapors. The sn-2 monoacylglycerol band was scraped off the plate into a small funnel plugged with glass wool. The lipid was eluted from the silica gel with 5 mL of 10% methanol in petroleum ether into a test tube where it was transesterified with sodium methoxide into methyl esters. Methyl esters were separated by gas chromatography as described previously.

Trans Fatty Acids

Quantitation of *trans* fatty acids was conducted by the AOCS Official Method Dc 14-61 (19) using methyl elaidate as a standard.

Accelerated Storage and Oxidative Stability

Twenty mL oil samples were placed in 120 mL glass jars (60 mm od × 70 mm) and capped, then stored at rest in an incubator at 60 C. Oxidative stability was determined on sample aliquots by the peroxide value (PV) as determined by the AOCS Official Method Cd 8-53 (19). Storage was discontinued after the most stable sample reached a PV of 100.

RESULTS AND DISCUSSION

An important consideration in the preparation of margarine oils by means of interesterification is the choice of hard fat to be used. Edible beef tallow was used in this study because of its high melting point, availability and desirable buttery flavor. It was determined that lard was not as suitable as beef tallow since a greater proportion of lard than tallow would be needed to achieve the desired physical properties. It was our aim to maximize the proportion of soybean oil because of its high polyunsaturated fatty acid content. Some workers have used lard as the hard fraction (17) and others have used fully hydrogenated vegetable oils (16).

Change in Glyceride Structure

Determination of the percentage of fatty acids at the sn-2 position of triacylglycerols provides a means to follow the progress of interesterification in an oil blend. Fully randomized blends have a theoretical value of 33.3% of each fatty acid esterified to each of the three hydroxyl groups of the glycerol moiety. Figure 1 illustrates the change in the percentages of the major fatty acids at the sn-2 position during interesterification of a blend of 60% soybean oil and 40% edible tallow (60 SBO:40 T) by weight. It took 10-15 min

TABLE I

Properties of Soybean Oil, Beef Tallow and Margarine Oils

Oil	Melting point[a] (C)	Acid value (mg KOH/g)	Iodine value (g I_2/100 g)	P/S ratio[b]	*trans* (%)
Soybean	–	0.05	133.8	5.15	nd[c]
Tallow	47.0	0.46	48.6	0.03	7.3
60 SBO:40 T mixture[d]	42.0	0.05	99.7	1.57	2.9
60 SBO:40 T interesterified[d]	39.8	0.11	99.7	1.57	3.0
Tub margarine A	38.5	0.03	105.3	3.43	15.5
Tub margarine B	36.3	0.03	112.0	2.11	27.8

[a]Capillary method.
[b]Calculated from fatty acid data.
[c]nd = not detected.
[d]SBO = soybean oil, T = beef tallow.

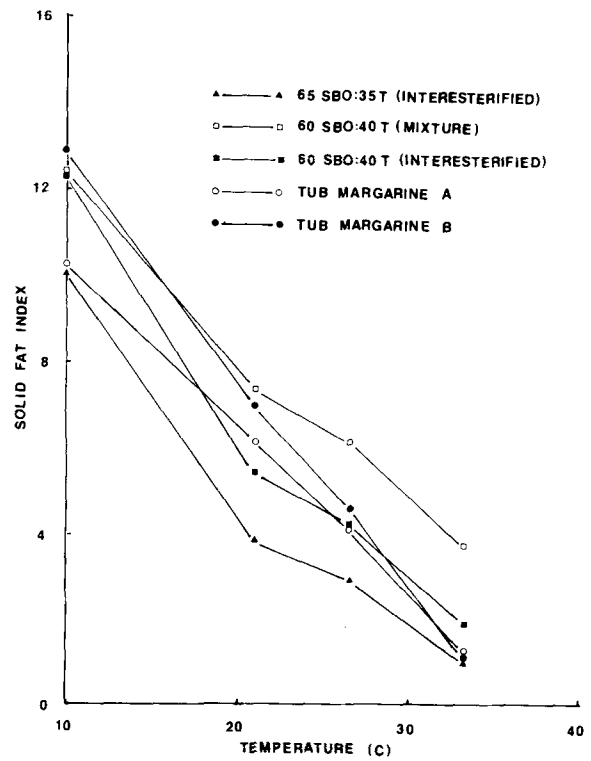

FIG. 2. Solid fat indices of margarine oils.

for interesterification to be initiated, indicated by formation of a brown color (14), and 25-30 min for the reaction to be completed. Thus, a relatively short time (10-20 min) is required for actual interchange of fatty acids among the triacylglycerols.

Physical Properties

Melting points of the interesterified blends, noninteresterified mixtures and commercial margarine oils are shown in Table I. Randomized blends tended to melt at lower temperatures than their corresponding mixtures. Sreenivasan (14) reported a similar change due to interesterification of other fats and oils.

Solid fat indices of the above samples are shown in Figure 2. As was the case with the melting point, interesterification caused a decrease in SFI. These decreases in melting point and SFI are due to a decrease in the proportion of higher melting triacylglycerols (S_3 and S_2U) as a result of interesterification.

On the basis of the melting point and SFI, an interesterified blend of 60% soybean oil and 40% tallow was chosen for further investigation, since this blend came closest to the melting points and SFI curves of the commercial margarine oils.

Chemical Properties

The levels of fatty acids in the various oil samples are listed in Table I. The commercial margarine oils and soybean oil-tallow mixture were well refined and maintained at very low levels of fatty acids. Interesterification increased the fatty acid level slightly from 0.05 to 0.11%, probably due to soap formation during acyl interchange. Refining and deodorization can be used to reduce the acid level.

The degree of unsaturation of the fat blends was not affected by interesterification as indicated by iodine values of the experimental oils before and after interesterification (Table I). The commercial margarine oils had slightly higher iodine values.

Fatty acid profiles of the various samples are shown in Table II, along with the starting materials. Interesterification did not alter the fatty acid profile of the blend. The interesterified blend had a substantial linoleic acid content of 35.8%; however, the commercial samples had higher linoleic acid contents of 37.6 and 45.5%. Oleic acid content of the interesterified blend was similar to that of the two commercial samples (31.1 vs 32.6 and 39.6%). Saturated fatty acid content of the blend was higher than that of the commercial samples due to the use of tallow in the blend.

The *trans* fatty acid content of the soybean oil-tallow blend was not affected by interesterification (Table I). The low level (3.0%) of *trans* fatty acids in the blend was derived from the tallow fraction which contained 7.3% *trans* fatty acids. The *trans* fatty acids in tallow result from microbial hydrogenation in the rumen (22). The *trans* fatty acid content of the commercial samples (15.5 and 27.8%) was substantially higher than the blend due to the use of partially hydrogenated soybean oil in their formulations.

Polyunsaturated to saturated (P/S) fatty acid ratios are reported in Table I. The P/S ratio for the experimental blend was 1.57 which was lower than for the commercial oils (2.11 and 3.43). However, the experimental blend did conform to the recommendation of the American Medical Association (16) of a minimum P/S ratio of 1.2. The blend also met the requirement of a minimum of 25% polyunsaturates by having 40.9% polyunsaturates. The blend

TABLE II

Fatty Acid Composition of Soybean Oil, Beef Tallow and Margarine Oils

Oil	Fatty acid composition (mole %)						
	14:0	16:0	16:1	18:0	18:1	18:2	18:3
Soybean	0.1	9.5	nd[a]	3.0	22.5	56.8	8.1
Tallow	3.4	25.8	3.0	20.2	45.9	1.7	nd
60 SBO:40 T[b]	1.3	15.5	1.2	9.3	31.8	36.3	4.6
Tub margarine A	0.1	10.2	nd	4.9	32.6	45.5	6.7
Tub margarine B	0.2	14.4	nd	4.8	39.6	37.6	3.4

[a]nd = not detected.

[b]SBO = soybean oil, T = beef tallow.

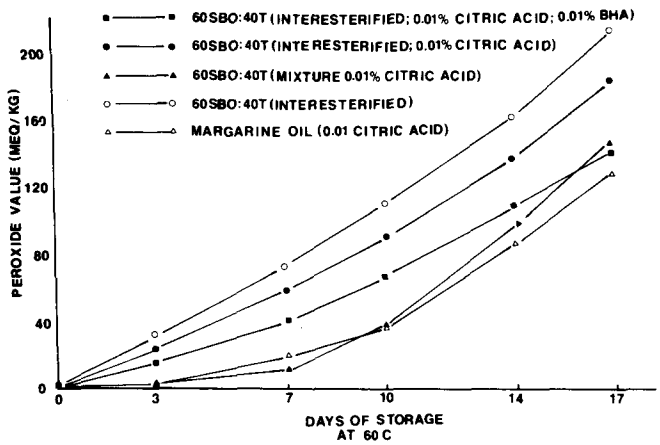

FIG. 3. Oxidative stabilities of margarine oils.

contained 27.9% saturates which was slightly over the maximum of 25% recommended by the AMA.

Oxidative Stability

Oxidative stability of the various experimental samples and a commercial margarine oil are shown in Figure 3. The interesterified blend without citric acid or BHA was the least stable. Addition of citric acid increased the stability of this blend and BHA with citric acid enhanced the stability even further. The mixture was more stable than the interesterified blend and exhibited a similar stability to the commercial margarine oil. Interesterification has been shown to lower the oxidative stability of corn oil, although the reasons for this are not clear (23). The lower stability of the interesterified blend could also be due to residual soaps, methyl esters formed during randomization and/or loss of tocopherols by reaction with sodium methoxide.

This study has shown that interesterification of soybean oil and edible tallow can be used as an alternative to hydrogenation to produce a plastic fat suitable for manufacture of tub-type margarines with low levels of *trans* fatty acids. The final product has comparable physical properties and acceptable fatty acid composition and oxidative stability.

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