"Zero *trans*" Margarines: Preparation, Structure, and Properties of Interesterified Soybean Oil-Soy Trisaturate Blends[1]

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ABSTRACT AND SUMMARY

The sodium methoxide-catalyzed random interesterification of liquid soybean oil-soy trisaturate blends was explored as a possible route to zero *trans* margarine oils. Lipase hydrolysis of the rearranged fats showed that with 0.2% catalyst, interesterification is complete within 30 min at 75-80 C. The glyceride structures of natural and randomized soybean oil-soy trisaturate blends are presented, and relationships between their structure and physical properties are discussed. Organoleptic evaluations showed that randomization of the glyceride structure had no adverse effects on flavor and oxidative stability. Flavor evaluations made against a commercially hardened tub margarine oil showed that interesterified oil had comparable initial and aged flavor scores. X-ray diffraction studies demonstrated that randomized soybean oil-soy trisaturate blends possess the beta-prime crystal structure desirable for use in margarine production. Dilatometric data indicate that random interesterification of 20% by weight of soy trisaturate into the glyceride structure of soybean oil provides a product having a solid fat index suitable for use in a soft tub margarine.

INTRODUCTION

The margarines and shortenings we consume contain isomeric fatty acids with double bonds in other than the 9-, 12-, and 15-positions and in the *trans* rather than the *cis* configuration (1-3). Hydrogenation not only reduces double bonds to single bonds, but it also isomerizes the double bonds up and down the alkyl chain and from *cis* to *trans* configuration. The metabolism of these isomeric fats have been investigated by in vitro and whole animal studies. In vitro experiments with rat liver acyl coenzyme A phospholipid acyl transferase (4), cholesterol hydrolase from rat liver (5,6), and porcine pancreatic lipase (7) show selectivities and reaction rates which are dependent on the double bond configuration or position. Results from studies with swine fed hydrogenated vegetable oil have been somewhat contradictory and controversial (8,9).

Recently, high polyunsaturated dietetic margarines have appeared in European markets which contain no *trans* fatty acids. It should be pointed out that these margarines are formulated, in part, for economic reasons in European countries. In these countires fats of high saturated content and oils of low saturated content are available and therefore interesterification rather than hydrogenation may be the processing technology of economic choice to obtain hardened fats, i.e., margarine oils. In the United States, where vegetable fats of high saturated content are generally lacking, hydrogenation of liquid oils to desired solid fat index (SFI) characteristics is necessarily the processing procedure of choice and interesterification does not present an attractive alternative to hydrogenation.

However, should the need for zero *trans* margarines present itself it would be well to have an alternative to partial hydrogenation of liquid oils at hand. The following experiments have consisted simply of applying prior state of the art processing treatments (10-16). These experiments involve completely hydrogenating one portion of soybean oil to soybean trisaturate for the solid component. It is then interesterified with liquid soybean oil to give a margarine oil with desired compositional and plasticity properties.

EXPERIMENTAL PROCEDURES

Oils

The soybean oil and soybean trisaturate (completely hydrogenated soybean oil) were commercially refined, bleached, and deodorized edible-grade fats. The hydrogenated soybean oil stocks were commercial products blended for stick or tub margarine manufacture. The tub margarine oil used in the flavor evaluations had the following weight composition by gas liquid chromatography (GLC): palmitic 10.5%, stearic 5.9%, monoene 44.3%, diene 34.8%, triene 4.4%. The soy-trisaturate composition by GLC was 11.4 and 88.6 mole% of palmitic and stearic acids, respectively. The compositions of the other fats are given elsewhere.

GLC Analyses

Fatty acid compositions of natural and randomized fats were determined as methyl esters after sodium methoxide catalyzed transesterification of the triglycerides. An Aerograph Model 1800 fitted with a flame ionization detector was used. The column, a 6 ft x 1/8 in. stainless steel tube packed with 15% EGSS-X, was operated isothermally at 185 C with nitrogen as the carrier gas.

Fatty acid GLC data were processed by an on-line computer system described previously (17).

Lipase Cleavage and Glyceride Structure Studies

Lipase hydrolyses of natural and randomized triglyceride were carried out according to Mattson and Volpenhein (18). Monoglycerides were isolated from the lipolysis mixture by adsorption chromatography on silicic acid (19). The column consisted of 16% by weight of methanol on silicic acid as the stationary phase. Methanol (2%) in benzene served as the mobile phase. The 300-500 ml eluate was taken as the monoglyceride fraction (20). After sodium methoxide catalyzed transesterification, fatty acid compositional analyses of the monoglyceride fractions were determined by GLC as described above.

Glyceride structures of natural and interesterified fats were calculated from lipase hydrolysis data and the 1,3-random-2-random theory advanced by Vanderwal (21) and Coleman (22). Strict random triglyceride distributions were calculated from fatty acid compositional data and the laws of probability. These equations may be found in Bailey's book (23). To aid in analysis of the data, a computer program was used to calculate both strict random and 1,3-random-2-random triglyceride distributions. A more

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TABLE I

Lipase Hydrolysis of Natural and Interesterified Soybean Triglycerides

Fraction	Fatty acid composition (mole %)				
	(16:0)	(18:0)	(18:1)	(18:2)	(18:3)
Natural soybean triglycerides	11.8	3.9	20.0	55.7	8.5
2-Monoglycerides	0.9	0.3	16.7	74.2	7.9
Proportion 2-position[a]	2.5	2.6	27.8	44.4	31.0
Random proportion 2-position	33.3	33.3	33.3	33.3	33.3
Interesterified					
90% Soy-10% soy trisaturate triglycerides	11.6	12.2	18.1	50.6	7.5
2-Monoglycerides	13.8	11.5	16.8	50.4	7.5
Proportion 2-position	39.3	31.4	30.9	33.2	33.3
85% Soy-15% soy trisaturate triglycerides	11.7	16.8	17.1	47.7	7.1
2-Monoglycerides	14.4	14.5	15.3	48.2	7.4
Proportion 2-position	41.0	28.8	29.8	33.7	35.1
80% Soy-20% soy trisaturate triglycerides	11.8	20.4	16.4	44.8	6.7
2-Monoglycerides	13.5	19.1	15.2	45.3	7.0
Proportion 2-position	38.1	31.2	30.9	33.7	34.8

[a]Proportion 2-position = $\frac{\text{Mole \% 2-monoglyceride}}{\text{Mole \% triglyceride x 3}}$ x 100.

detailed description and further applications of this program will be presented elsewhere.

Flavor Evaluations

Deodorizations were carried out in an all-glass system described previously (24). Where required, stabilizers (citric acid, 0.01% and Tenox 6, 0.076% by weight) were added on the cooling side of deodorization. Organoleptic evaluations were conducted by methods described by Moser et al. (25,26). Flavor data were supplied by a 16-member taste panel. Peroxide values were determined by modification of the Wheeler method (27). Active oxygen determinations were carried out according to the AOCS Official Method (28).

Interesterification Procedures

A typical nondirected interesterification of soybean oil-soy trisaturate was conducted on 300 g fat as follows. The required amounts of soybean oil and soybean trisaturate were charged into a 1-liter round-bottomed flask. The contents were placed on a rotating evaporator and heated for 1/2 hr at 90 C under 30-in. water vacuum to solubilize the tristearin portion and to remove traces of moisture from the oil. The fat was transferred to a 500-ml round-bottomed flask fitted with a thermometer, a stirring shaft fitted with a teflon blade driven by a 5000 rpm stirring motor. After flushing the flask with nitrogen, the stirring motor was then started (near maximum speed) and the sodium methoxide catalyst (0.6 g, 0.2% by wt) was added. After vigorously stirring the fat at 75-80 C for 30 min, 3 ml of distilled water was added to inactivate the catalyst. Stirring was maintained for another 3 min after which the rearranged fat was filtered under vacuum through a bed of Celite filter aid. The filtration served to remove soaps and color bodies formed during rearrangement (16).

Preparation of Fats for Flavor Evaluation

The procedure outlined above was scaled up to 1200 g fat except that the rearrangement was accomplished by stirring for 1 hr at 65 C. As a control, a simple mixture of soybean oil-soy trisaturate was processed identically except that no interesterification catalyst was added. The fats were steam deodorized for 3 hr at 210 C under less than 1 mm Hg.

Catalyst Preparation

Sodium methoxide was prepared by the reaction of freshly cut metallic sodium with anhydrous methanol according to the following procedure. After the reaction between the sodium and methanol subsided, the methanol was removed under vacuum with a rotating evaporator, and the dry product was finely ground with a porcelain pestle and mortar just prior to use in the interesterification reactions.

X-Ray Diffraction

Samples were prepared for X-ray diffraction studies by absorbing the fat on filter paper under vacuum. The sample was then placed in a thin-walled (0.3 mm ID) glass capillary and sealed with a torch. The capillary was placed in the X-ray beam (copper source Kα wavelength; nickel filter). Photographs were made with an evacuated camera 5 cm from the sample. Exposures varied from 4 to 24 hr.

Melting Points

Melting points were determined by differential scanning calorimetry (DSC). The instrument used was a Perkin Elmer Model 1B. The sample (ca. 10 mg) was heated to and held for 2 min at 60 C, cooled to -97 C, and then heated at 20 C per min until the end of melt was reached. The end of melting range was taken as the point where a steady baseline was achieved on the strip chart recorder.

Solid Fat Indexes

Solid fat indexes were determined by dilatometry according to AOCS Official Method Cd 10-57 (28).

Trans Acids

Trans isomers were determined either as methyl esters by infrared spectroscopy using methyl elaidate as a standard (28) or by GLC on a 7 m x 4 mm glass column packed with Silar 10C operated isothermally at 200 C.

RESULTS AND DISCUSSION

Glyceride Structure of Interesterified Fats

Other workers (29-31) have concluded that interesterified fats approach a random distribution based on their trisaturated glyceride content obtained by fractional crystallization. Our approach to the analysis of randomly interesterified fats involved cleavage of the triglyceride with pancreatic lipase (18) followed by isolation of the 2-monoglycerides. After fatty acid compositional analyses are made (GLC) of the original triglycerides and the 2-monoglycerides, the fatty acids are distributed on the 2-position in the

TABLE II

Glyceride Structure of Natural and Interesterified Soybean Oil-Soy Trisaturate Blends

	100% Soy[a]		% Soy oil: % soy trisaturate in blend, by weight					
			90:10		85:15		80:20	
			Mole %					
Glyceride class[b]	Random	Found[c]	Random	Found	Random	Found	Random	Found
SSS	0.4	0.07	1.3	1.3	2.3	2.3	3.3	3.3
SUS	2.1	5.2	4.3	4.0	5.8	5.7	7.0	6.9
USS	4.2	0.4	8.6	9.0	11.7	11.8	14.1	14.2
USU	11.2	0.7	13.8	15.0	14.7	15.1	14.8	15.0
UUS	22.4	35.0	27.7	26.5	29.4	29.1	29.6	29.4
UUU	59.7	58.4	44.3	44.3	37.1	37.1	31.2	31.2

[a]Natural soy triglycerides.

[b]S = saturated, either palmitic or stearic; U = unsaturated, oleic, linoleic, or linolenic.

[c]Determined from lipase hydrolysis data.

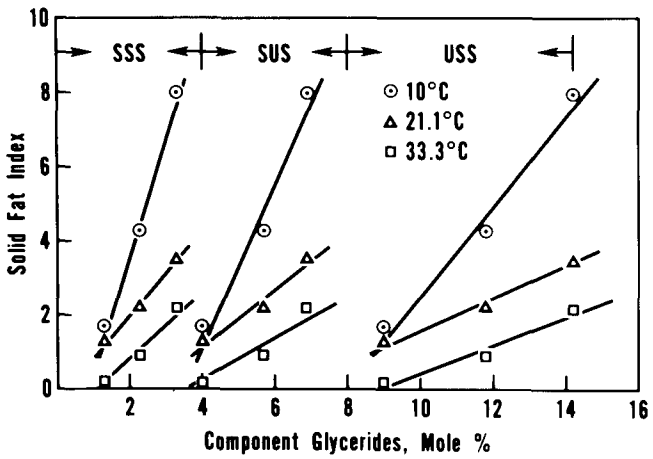

FIG. 1. Relationship between solid fat indexes and component glycerides of interesterified soy-soy trisaturate blends.

amounts determined experimentally. The remainder are distributed on the 1- and 3-positions at random and are considered equivalent (21,22). This approach, while having been extensively applied to natural triglycerides (32-38), has not been extended to interesterified fats.

Lipase hydrolysis data of soybean triglycerides (Table I) show the unique features of its glyceride structure. It will be noted that under a strict random distribution, the proportion of fatty acids at the 2- (or any other) position will be 33-1/3%. The distinguishing features of soybean oil's triglyceride structure include the virtual absence of the saturated palmitic and stearic acids in the 2-position of the triglycerides. The proportions of oleic and linolenic acids of 27.8 and 31.0% closely match the 33-1/3% predicted by random theory and may, within experimental error, be considered randomly distributed. Linoleic acid shows a high specificity for the beta position in soybean oil triglycerides. The experimentally determined proportion (44.4%) is considerably higher than the 33-1/3% predicted by random theory. Thus, natural soybean oil triglycerides are characterized by the occurrence of saturated acids at the 1- and 3-positions, random distributions of oleic and linolenic, and a high specificity of linoleic acid for the beta position. These results are in excellent agreement with previous investigations (38).

Application of the lipase hydrolysis technique to analysis of interesterified soybean oil-soybean trisaturate blends is also shown in Table I. Included are data for 90:10, 85:15, and 80:20 interesterified mixtures of liquid soybean oil and soybean trisaturate. The results show that the lipase hydrolysis technique may be successfully applied to the analysis of interesterified soybean oil fats. Although some discrepancies are noted, the proportions of fatty acids in the beta position of the randomized triglycerides correspond closely to the 33-1/3% calculated from strict random theory. Further evidence that the interesterification reactions have gone to equilibrium stems from the observations that whereas in natural soybean oil triglycerides, palmitic acid, and stearic acid are virtually absent in the 2-position, nearly the theoretical proportions (33-1/3%0 have been incorporated into the beta position of the interesterified triglycerides. In addition, linoleic acid showing a high specificity for the 2-position (44.0%) in natural oil has been reduced to the 33-1/3% random proportion by interesterification.

Table II compares the distribution of glycerides determined experimentally with strict random theory. Grouping of glycerides with respect to unsaturation (SSS, SUS, USS, USU, UUS, UUU; where S = saturated, U = unsaturated) as suggested by Hilditch (39) has been followed. It will be noted that despite minor discrepancies between the lipase hydrolysis data (Table I), the results when considered by glyceride class are in excellent agreement with a strict random distribution. Small amounts of diglycerides present in the interesterified mixtures have been ignored in these calculations.

The changes in glyceride structure after randomizing soybean oil and soy trisaturate are reflected in Table II. Unmodified soybean oil consists of over 93% triunsaturated and diunaturated glycerides according to the 1,3-random-2-random theory. The low proportions of saturated acids in the beta position of soybean triglycerides limit the amounts of SSS, USS, and USU classes to about 1.2%. The remainder is composed of about 5% SUS glycerides.

As the soy trisaturate percentage is increased, triunsaturated (UUU) glycerides show a progressive decrease while the proportions of UUS glycerides remain relatively unchanged. The most marked changes in glyceride structure occur in the amounts of trisaturated (SSS) and disaturated USS) glycerides.

Functional properties such as melting point and solid fat indices of corandomized soybean oil-trisaturate blends are determined by the relative proportions of the component glycerides. Thus, the glyceride structure of these fats is of both practical and theoretical interest.

It is expected that a relationship exists between the solid fat indices of the interesterified fats and the molar percentages of the tri- and disaturated glycerides. Figure 1 depicts the relationship between the solid fat indices and the molar percentage of SSS, SUS, and SSU glycerides of corandomized soybean oil-soy trisaturate blends (Table II). The results clearly show that at 10, 21.1, and 33.3 C, the amount of solid fat correlates well with the molar amounts

TABLE III

Flavor and Oxidative Stability of Interesterified and Hydrogenated Soybean Fats

Days storage, 60 C	Flavor scores and significance[a]				
	Simple mixture[b]		Interesterified	Interesterified[c]	Hydrogenated[d]
0	4.1 (1.3)	**	6.9 (0.9)	8.0 (0.6) +	7.7 (0.3)
4	4.1 (10.2)	**	6.0 (8.8)	5.6 (2.2) +	6.0 (1.9)
AOM[e] peroxide value, 8 hr	56.8		87.8	5.1	1.9
Initial flavors	Metallic, grassy, painty		Buttery	Buttery	Buttery, rancid
Storage flavors	Rancid, painty, grassy		Rancid, grassy, buttery	Rancid, buttery, beany	Rancid, buttery
Triene, %	7.5		7.5	7.5	4.4

[a]** Denotes significance at 1% confidence level, + denotes no statistical significance. Values in parentheses are peroxide values at time of tasting.

[b]Liquid soybean oil (90%), 10% soy trisaturate by weight; simple mixture and interesterified samples contained no antioxidants or metal scavengers.

[c]Liquid soybean (90%), 10% soy trisaturate by weight, sample treated with 0.01% citric acid and 0.076% Tenox 6 during deodorization.

[d]Commercial tub margarine oil, sample treated with 0.01% citric acid and 0.076% Tenox 6 during deodorization.

[e]AOM = active oxygen method.

of the aforementioned glycerides.

Although it is not known whether the linear relationships between solid fat indices and component glycerides hold for higher soy-soy trisaturate ratios, the results suggest that "tailor-made" fats having the desired plasticity could be prepared by proper blending of liquid and hard fats prior to random interesterification.

Flavor and Oxidative Stability

Flavor and oxidative stability are prime considerations in the use of interesterified fats in margarine manufacture because their high polyunsaturated acid content increases their susceptibility to autoxidation. Accordingly, some evaluations were made to determine the effect of interesterification on flavor stability and to compare the performance of an interesterified soybean oil-soy trisaturate blend against a commercially processed hydrogenated soybean oil blend used in tub margarine.

The left portion of Table III presents evaluations of blends of soybean oil and soybean trisaturate (90:10 by weight) as a simple mixture and after random interesterification. These fats contained no metal scavengers or antioxidants.

Quite surprisingly, initial flavor scores were highly significant in favor of the interesterified oil. Similarly, after 4 days' storage at 60 C, the difference favoring the interesterified fat was highly significant. These observations can be accounted for by their flavor descriptions. Initially, the simple mixture was described as metallic, grassy, and painty while the randomized fat had the more desirable buttery flavor. After storage, the flavor descriptions were qualitatively the same—rancid, painty, and grassy but less intense in the interesterified fat. The poor quality of the simple mixture may be attributed to the trisaturate portion. Some panel members described it as rubbery, hydrogenated, weeds, tallow, and sewer gas. Since no metal inactivators or antioxidants were added to the fats, the high AOM and storage peroxide values are to be expected.

Flavor and oxidative stability of a commercial margarine oil and a randomized soybean oil-soy trisaturate blend (90:10 by wt) stabilized with citric acid and antioxidants are shown in the right portion of Table III. Initial flavor scores were high and equal with no significant differences evident between the two oils. Accelerated storage data showed that the two oils deteriorated to the same extent. The slight difference favoring the hydrogenated oil is not statistically significant. From the predominant flavor descriptions, it may be concluded that during accelerated storage, no unusual flavors developed in the interesterified fat. The value of antioxidants and metal scavengers is apparent in the lower AOM and storage peroxide values.

These preliminary results indicate that interesterification is not harmful to the flavor and oxidative stability of soybean oil-soy trisaturate blends and, in view of the evaluations shown in Table III, margarines prepared from them would not pose any flavor problems despite their high levels of polyunsaturates.

Composition and Physical Properties

Table IV compares the physical properties and composition of commercially hardened margarine fats (oils A, B, C) with interesterified soy-soy trisaturate blends (oils D, E, F).

The functional properties of margarine are determined to a great extent by the solid fat index (SFI) of the oil phase (40). Spreadability, holding together at room temperature, and melting characteristics either in the mouth or on foods are largely influenced by the SFI values at 10, 21.1, and 33.3C. The SFI values of oils A and B are in good agreement with published values for U.S. stick and tub margarines (40) while oil C was apparently blended for a somewhat softer product.

None of the interesterified blends has enough solids at any temperature to qualify as a stick margarine oil. The 90:10 blend lacks sufficient solids at any temperature to quality as a tub margarine oil. The 85:15 blend, while having about the same solids at 33.3 C as hydrogenated oil B (0.9 vs. 1.3), probably would not qualify as a margarine oil because of the low 10 and 21.1 C SFI values. Of the three candidates evaluated, 80:20 interesterified blend shows the most promise as a zero *trans* margarine oil since the SFI values at 10, 21.1, and 33.3 C of this blend closely approximate those of tub margarine oil C.

The results show that by increasing the soy-trisaturate component, the SFI values at 10, 21.1, and 33.3 C increase and that for each 5% increase in soy trisaturate, the SFI values roughly double. Thus, the 10 and 21.1 C SFIs could be raised by increasing the amount of soy trisaturate prior to random interesterification. However, the 33.3 C SFI of 2.2 seems optimum for mouth feel at 80 parts liquid soy and 20 parts soy trisaturate.

The melting points of the interesterified fats compare quite well with the commercially hardened margarine oils.

The American Medical Association has recommended that a diet margarine contain a polyunsaturated to saturated (P:S) ratio of 1.2, a minimum of 25% polyunsaturates, and a maximum of 25% saturated acids (41). The results (Table IV) show that while containing slightly more

TABLE IV

Composition and Properties of Hydrogenated and Interesterified Margarine Oils

Oil	Type	Solid fat index[a]			Melting point (C)[c]	Fatty acid composition (wt %)[b]				P:S ratio	*trans* (%)	I.V. (calc)
		10 C	21.1 C	33.3 C		S	M	D	T			
A. Hydrogenated	Stick margarine	28.6	18.9	5.3	46	23.1	49.9	24.4	2.6	1.17	31.0	92.1
B. Hydrogenated	Tub margarine	15.6	8.8	1.3	46	18.8	42.9	33.8	4.8	2.05	23.2	108.0
C. Hydrogenated	Tub margarine	7.1	4.5	2.0	46	17.9	30.1	45.5	6.5	2.90	12.9	121.8
D. Interesterified	90:10[d]	1.7	1.3	0.2	40	23.2	18.4	51.0	7.5	2.52	1.7[e]	123.8
E. Interesterified	85:15	4.3	2.2	0.9	46	27.6	17.3	48.0	7.1	2.00	2.1	116.6
F. Interesterified	80:20	8.0	3.5	2.2	47	31.7	16.6	44.8	6.7	1.62	1.6	109.4

[a]By dilatometry.
[b]S. = satuarated, M = monoene, D = diene, T = triene.
[c]By differential scanning calorimetry.
[d]Parts soybean oil:parts soy trisaturate by weight.
[e]As simple mixtures the soy-soy trisaturate blends contained 1.5% *trans* by gas liquid chromatography (see text).

TABLE V

Effect of Interesterification on X-Ray Diffraction Patterns of Soy-Soy Trisaturate Blends

80% Soy-20% soy trisaturate			
Mixture		Interesterified	
d(Å)	I/Io	d(Å)	I/Io
		SS	
3.69	S	3.8	S
3.85	S	4.2	S
4.6	VS	4.6	W
5.37	L-M		
		LS	
14.9	L		
22.3	L	22.0	L

than the recommended amount of saturated acids, the interesterified fats far exceed the minimum P:S and polyunsaturated acid content outlined above.

The P:S ratios (calculated from GLC data) of the interesterified fats represent true values, while the values shown for the hydrogenated fats are probably high. Nazir et al. (42) recently determined the P:S ratios of 86 margarine oils by GLC and lipoxidase. Invariably, lower P:S ratios were obtained by the latter procedure which estimates true *cis-cis* polyunsaturation. Alfin-Slater et al. (43) reported a nutritional evaluation of interesterified fats where it was concluded that they are at least nutritionally equal to other similar fats of equivalent essential fatty acid content.

Other workers (43) have reported that interesterified fats contain small amounts (1.5-1.8% of *trans* acids. Our results (Table IV) indicate that interesterified soy-soy trisaturate blends contained similar levels (1.6-2.1% of *trans* acids, but this can be attributed to contaminants present in the starting materials. The simple mixtures of soy-soy trisaturate contained an average of 1.5% *trans* which could arise from oxidation or contamination from hydrogenated stocks during processing. The results clearly show that interesterification does not produce *trans* isomers. Although UV analysis showed about 0.6% conjugated diene in the starting material, no further increase was detected after random interesterification.

Crystal Structure

The crystal habits of margarine oils are often classified as either beta or beta prime, with the latter the desirable form (41). Finished product characteristics are, in part, dictated by the crystal structure of the oil phase. Margarine oils possessing the beta form impart an undesirable characteristic to margarine known as "graininess." Struble (44), in an early review, stated that graininess is caused by high melting glycerides already present in the fat or their formation during plasticizing. Later, Merker et al. (45) provided experimental evidence showing that "graininess" results from higher melting beta polymorphs formed during the tempering or the crystal formation step in margarine manufacture. Thus, a margarine fat should possess the beta prime crystal structure and show no tendency to revert to the beta form during manufacture into the finished product.

The effect of random interesterification on the X-ray diffraction patterns of soy-soy trisaturate blends is shown in Table V. As simple mixtures, the soy-soy trisaturate blends exist as the beta form as evidenced by the strong short spacings at 3.69 and 3.85 Å. The very strong short spacing at 4.6 Å further characterizes these fats as the beta form (46). The long spacing at 14.9 Å agrees well with published values for beta-type fats (46).

After random interesterification of soybean trisaturate into the glyceride structure of soybean oil, the strong short spacings appearing at 3.8 and 4.2 Å characterize these fats

as beta prime (46). Thus, random interesterification of soy-trisaturate blends affects the transition from the undesirable beta form to the desirable beta prime form required to avoid graininess in finished margarine products. However, it should be pointed out that certain beta-type fats, notably lard, can be plasticized to a beta prime form only to revert to a coarse grained beta crystal structure within a short time (46).

As shown, saturated glycerides derived from soybean oil may be interesterified with liquid soybean oil to give a zero *trans* hardened fat having acceptable flavor stability plasticity and crystal structure. It is therefore apparent that should the need for zero *trans* margarines present itself, an alternative to partial hydrogenation of liquid oils is at hand.

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REFERENCES

1. Scholfield, C.R., V.L. Davison, and H.J. Dutton, JAOCS 44:648 (1967).
2. Jones, E.P., C.R. Scholfield, V.L. Davison, and H.J. Dutton, Ibid. 42:727 (1965).
3. Carpenter, D.L., and H.T. Slover, Ibid. 50:372 (1973).
4. Okuyama, H.W., E.M. Lands, F.D. Gunstone, and J.A. Barves, Biochemistry 11:4392 (1972).
5. Sgoutas, D., Biochim. Biophys. Acta 164:317 (1968).
6. Goller, H.J., D.S. Sgoutas, I.A. Ismail, and F.D. Gunstone, Biochemistry 9:3072 (1970).
7. Heimermann, W.H., R.T. Holman, D. Gordan, D.E. Kowalyshyn, and R.G. Jensen, Lipids 8:45 (1973).
8. Kummerow, F., Abstract 124, 65th Annual AOCS Meeting, Mexico City, April 1974.
9. Lohman, T.G., and F.E. Romack, "Proceedings of the World Soybean Research Conference," Edited by Lowell D. Hill, Interstate Publishers, Danville, IL, 1976, pp. 883-891.
10. Gillies, M.T., "Shortenings, Margarines, and Food Oils," Noyes-Data Corporation, NJ, 1974, p. 143.
11. Melnick, D., and F.H. Luckmann, U.S. Patent 2,955,039.
12. Sreenivason, B., U.S. Patent 3,859,447 (1975).
13. Thompson, J.E., U.S. Patent 3,392,031.
14. Eckey, E.W., U.S. Patent 2,442,531.
15. Van Akkeren, L.A., U.S. Patent 2,872,463.
16. Vanderwal, R.J., and L.A. Van Akkeren, U.S. Patent 2,751,315.
17. Dutton, H.J., JAOCS 45:4A (1968).
18. Mattson, F.H., and R.A. Volpenhein, J. Lipid Res. 2:58 (1961).
19. McConnell, D.G., R.L. Hoffmann, G.J. Elman, and C.D. Evans, JAOCS 44:641 (1967).
20. Evans, C.D., E. Panek, and D.G. McConnell, Abstract 74, 385h Annual AOCS Meeting, Chicago, IL, October, 1964.
21. Vanderwal, R.J., Advances in Lipid Research, Vol. 2, Academic Press, New York, NY, 1964, pp. 1-16.
22. Coleman, M.H., JAOCS 38:684 (1961).
23. Bailey, A.E., "Industrial Oil and Fat Products," Edited by D. Swern, 3rd Edition, Interscience, New York, NY, 1964, pp. 965.
24. Schwab, A.W., and H.J. Dutton, JAOCS 25:57 (1948).
25. Moser, H.A., H.J. Dutton, C.D. Evans, and J.C. Cowan, Food Technol. 4(3):105 (1950).
26. Moser, Helen A., Carol M. Jaeger, J.C. Cowan, and H.J. Dutton, JAOCS 24:291 (1947).
27. Wheeler, D.H., Oil Soap 9:89 (1932).
28. "Official and Tentative Methods of the American Oil Chemists' Society," 3rd Edition, AOCS, Champaign, IL, 1972, Method Nos. Cd 12-57, Cd 10-57, Cd 14-61.
29. Bhattacharya, R., and T.P. Hilditch, Proc. Roy. Soc. (London) A 129:468 (1930).
30. Desnuelle, P., and M. Naudet, Bull. Soc. Chim. 13:90 (1946).
31. Norris, F.A., and K.F. Matill, Oil Soap 23:289 (1946).
32. Mattson, R.H., and L.W. Beck, J. Biol. Chem. 219:735 (1956).
33. Mattson, F.H., and R.A. Volpenhein, Ibid. 236:1891 (1961).
34. Coleman, M.H., and W.C. Fulton, "Enzymes of Lipid Metabolism," Pergamon Press, New York, NY, 1961, pp. 127-137.
35. Vanderwal, R.J., JAOCS 40:242 (1963).
36. Gunstone, F.D., R.J. Hamilton, and M. Ilyas Qureshi, J. Chem. Soc. 319 (1965).
37. Jurriens, G., and A.C.J. Knoesen, JAOCS 42:9-14 (1965).
38. Evans, C.D., D.G. McConnell, C.R. Scholfield, and H.J. Dutton, Ibid. 43:345 (1966).
39. Hilditch, T.P., "Chemical Constitution of Natural Fats," 4th Edition, Wiley and Sons, New York, NY, 1964, p. 364.
40. Weis, T.J., "Food Oils and Their Uses," AVI Publishing Co., Westport, CT, 1970, pp. 130-144.
41. Wiedermann, L.H., JAOCS 45:519A-522A, 560A (1968).
42. Nazir, D.J., B. Moorecroft, and M.A. Mishkel, Am. J. Clin. Nutr. 29:331 (1976).
43. Alfin-Slater, R.B., L. Aftergood, H. Hansen, R. Morris, D. Melnick, and C. Gooding, JAOCS 43:110 (1966).
44. Struble, C.H., Ibid. 31:34 (1954).
45. Merker, D.R., L.C. Brown, and L.H. Wiedermann, Ibid. 35:130 (1958).
46. Wiedermann, L.H., T.J. Weiss, G.A. Jacobson, and K.F. Mattill, Ibid. 38:389 (1961).

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