

Effect of Interesterification on the Structure and Physical Properties of High-Stearic Acid Soybean Oils

G.R. List^{a,*}, T.L. Mounts^a, F. Orthoefer^b, and W.E. Neff^a

^aUSDA, Agricultural Research Service, Food Quality and Safety Research, NCAUR, Peoria, Illinois 61604, and ^bRiceland Foods, Stuttgart, Arkansas 72160

ABSTRACT: Triglyceride structures of genetically modified soybean oils high in stearic acid were determined by high-pressure liquid chromatography, and their physical properties were assessed by dilatometry and dropping point. In their natural state, these oils lack sufficient solids at 10–33°C to qualify as margarine oils. However, after random interesterification, soybean oil containing 17% stearic acid shows a solid fat index (SFI) profile and dropping point closely matching those of a liquid margarine oil. Other oils, with stearic acid contents in the range of 20–33%, showed appreciable SFI values at 10°C but lacked sufficient solids at 21.1–33.3°C. After random interesterification, these oils also exhibited SFI profiles suitable for soft tub margarine, and their drop points increased from 18–19°C to 36–38°C.

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KEY WORDS: Dropping point, genetically modified soybean oil, interesterification, margarine oils, palm oil, solid fat index, stearic acid, triglycerides.

Intesterification of liquid oils and hardstocks has been shown to be a versatile tool for the preparation of margarine and shortening oils (1–7). Within the past decade, a number of genetically modified soybean varieties have been introduced that contain varying amounts of palmitic and stearic acids (8–10). In their natural states, genetically modified soybean oils that contain 30–40% of saturated acids lack sufficient solids over the temperature range required for margarine oils. However, after blending with harder components, their solid fat index (SFI) profiles and dropping points qualify them as potential margarine oil (11). Additional studies on the effect of interesterification on the physical properties of genetically modified soybean oils are reported here.

EXPERIMENTAL PROCEDURES

Soybean (*Glycine max* L. Merr.) germplasm exhibiting a high-stearic acid trait was obtained from the following sources: A6, Iowa State University (Ames, IA); HS-1, Jacob

Hartz Seed Co. (Stuttgart, AR); and A90-143073, Pioneer Hi-Bred International, Inc. (Waterloo, IA).

Seed preparation, oil extraction, and processing were carried out as described previously (12). Refined, bleached, and deodorized palm oil (PO) was obtained from PVO International (Granite City, IL). Interesterifications were conducted as described previously (2). Fatty acid compositions were determined in duplicate by capillary gas–liquid chromatography (13). Triacylglycerols (TAG) were determined, in duplicate, by reversed-phase high-performance liquid chromatography (13). Solid fat index (SFI) and dropping points were determined by the American Oil Chemists' Society official methods (14). Dropping points are the means of duplicate determinations. Lipase hydrolysis of TAG was carried out as described previously (15). SFI determinations were conducted in triplicate, and values reported are the means.

RESULTS AND DISCUSSION

The effect of interesterification on the physical properties of genetically modified soybean oils high in stearic acid are shown in Table 1. The three samples of A6 oil had stearic acid contents ranging from about 24 to 33%, while the Pioneer and Hartz varieties contained about 17 and 20%, respectively. In their natural states, most of these oils possessed enough solid fat at 10°C for soft tub or perhaps stick margarine, but beyond 10–21.1°C they lacked sufficient solids. However, after random interesterification, nearly all candidates examined possessed sufficient solids over the entire temperature range (10–40°C) to qualify as soft tub margarine oils. The Pioneer A90 143073, while unsuitable for tub margarine, possesses an SFI profile that is similar to liquid margarine oil. The means of SFI determinations were in the ranges reported as acceptable by the SFI method. Dropping points of the unmodified oil ranged from about 14–20°C, and they increased after random interesterification to 22–38°C. Typical dropping points for commercial soft tub margarine oil, obtained by hydrogenation, showed dropping points from 32–34°C (1). The means of dropping point determinations were in the ranges reported as acceptable by the dropping point method. Thus, random interesterification of genetically modified soybean oils high in stearic

*To whom correspondence should be addressed at USDA, ARS, NCAUR, Food Quality and Safety, 1815 N. University St., Peoria, IL 61604.

TABLE 1
Effect of Interesterification on Physical Properties and Component Glycerides of Genetically Modified Soybeans That Are High in Stearic Acid

Variety	State	Stearic (%)	Solid fat index @ temp. (°C) ^a					Drop point (°C) ^c	Component glycerides (%) ^b			
			10.0	21.1	26.7	33.3	40.0		UUU	SUU and USU	USS and SUS	SSS
A6	Natural	23.9	11.2	0.0	0.0	0.0	0.0	19.7	22.1	47.8	26.3	2.3
A6	Natural	27.1	22.8	12.1	0.0	0.0	0.0	18.7	15.9	39.5	40.8	2.5
A6	Natural	33.0	18.7	7.9	0.0	0.0	0.0	19.9	18.1	41.0	37.5	4.3
A6	Interest	23.9	6.8	3.3	2.8	1.5	0.6	23.2	24.9	46.1	23.8	2.2
A6	Interest	27.1	13.7	4.5	3.8	2.6	1.5	38.2	19.9	42.7	30.0	4.3
A6	Interest	33.0	13.5	5.5	4.7	3.5	1.7	36.4	18.2	40.8	35.2	3.2
HS-1	Natural	20.6	12.6	1.5	0.0	0.0	0.0	17.6	25.8	42.6	23.9	2.5
HS-1	Interest	20.6	7.8	4.4	3.4	2.6	1.2	36.8	26.6	45.1	21.1	2.9
A90	Natural	17.2	6.0	0.0	0.0	0.0	0.0	14.2	36.0	45.1	17.2	1.5
A90	Interest	17.2	3.8	2.7	1.7	1.1	0.4	30.4	37.8	44.6	14.5	2.1

^aBy AOCS method (14); interest., interesterification; U, unsaturated; S, saturated.

^bBy AOCS method (14).

^cBy HPLC (13), % of total triglycerides; A6 (Iowa State University (Ames, IA); HS-1, Jacob Hartz Seed Co. (Stuttgart, AR); A-90, Pioneer Hi-Bred International Inc. (Waterloo, IA).

acid offers an alternative approach to hydrogenation or blending natural oils with harder components for the formulation of margarine oil.

The effect of random interesterification on the glyceride structures of genetically modified soybean oils is shown in Table 1. The reversed-phase high-performance liquid chromatography method unfortunately will not resolve isomeric mono- and disaturated glycerides. Thus, the values for UUS include USU, and SUS include SSU, where S = saturated and U = unsaturated fatty acids. When considered as classes with respect to unsaturation, little differences exist, yet marked changes in physical properties such as SFI and dropping point are evident.

We have previously reported lipase hydrolysis data for naturally occurring high-stearic soybean oils (11). In general, the glyceride structure of genetically modified soybean oil is similar to ordinary soybean oil, with saturated acids (palmitic and stearic) occurring primarily at the outer *sn*-1-3 positions of the glycerol. Oleic and linolenic acids were distributed essentially at random in all three positions, and linoleic showed high preference for the *sn*-2 position. Because palmitic and stearic acids are distributed mainly at the outer *sn*-1 and -3 positions, most of the mono- and disaturated triglycerides consist of the SUU and SUS species. However, after randomization, substantially more of the USU and SSU types are formed, which may account for the marked differences shown in the SFI and dropping point data between the natural and rearranged oils.

Common vegetable oils, including soybean, cottonseed, palm, cocoa butter, kokum butter, and coconut oil, show increased melting points after interesterification, while animal fats, including oleo stock, tallow, and butter, remain essentially unaltered or are only slightly changed (16). This in part can be accounted for in terms of the intrapositional distribution of the fatty acids within the triglycerides. In vegetable oils, palmitic and stearic acids are distributed primarily in the outer *sn*-1 and -3 positions, thereby resulting in the symmetrical SUS types (1,11). On the other hand, animal fats show different distribution patterns because saturated acids (palmitic and stearic) are

distributed on all three *sn* positions, resulting in both SUS and SSU isomers. These ratios remain virtually unchanged by interesterification.

Differences between the SFI profiles of natural and randomized PO have been reported (11). Natural PO consists of about 50% S and 50% U fatty acids. The triglycerides consist of 47% disaturated and trisaturated triglyceride, which after interesterification only increase to about 51%. However, above 21.1°C, the SFI profile of the randomized oil is markedly higher. Natural PO consists of about 32% of the symmetrical SUS-type triglycerides and 7.5% of the SSU type, whereas after randomization, symmetrical SUS decreases to 7.6% and SSU increases to 26.5%.

Little has been published on the melting points of isomeric disaturated SUS and SSU triglycerides. Daubert and Clarke (17) and Daubert *et al.* (18) reported that SOS (S = stearic; O = oleic) shows four transitional forms that melt from 41.6 to 22.3°C, whereas SSO shows only two forms, which melt from 38.5 to 26.7°C. POP also shows four forms that melt from 35.2 to 12.0°C, whereas PPO shows three forms that melt from 34.5 to 18.5°C. Thus, it appears that unsymmetrical triglycerides, which predominate in natural oils, melt at lower temperature than their unsymmetrical counterparts formed during interesterification.

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