



Effect of Triacylglycerol Composition on Functionality of Margarine Basestocks

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The triacylglycerol compositions of several margarine basestocks, including blends and interesterified blends of corn and soybean oils with cottonseed oil stearine, randomized corn oil and randomized soybean oil, were determined. Quantitative results obtained by reversed-phase high performance liquid chromatography for samples of known composition (randomized and interesterified samples) exhibited low average absolute errors (0.6–1.8%) for the fatty acid composition calculated from the triacylglycerol composition compared to the fatty acid composition determined by gas chromatography. The evaporative light scattering detector did not give accurate quantitation with average absolute errors greater than 3%, for the noninteresterified blends, however. Accurate determination of the triacylglycerol composition allowed the study of both melting and solid fat indices with respect to the influence of unsaturated to saturated triacylglycerol groups.

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Introduction

The triacylglycerol fraction of a margarine or shortening basestock is responsible for most of the physical properties of a product that affect lubricity (pourability, holding together at room temperature or melting in the mouth to give a pleasant cooling effect). Lubricity is dependent on melting temperature, solid fat index and texture. The relationship between triacylglycerol structure and lubricity has been reviewed previously (1). Triacylglycerols with fatty acids designated by U for unsaturated fatty acid and S for saturated fatty acid were grouped into four sets. Group 1 triacylglycerols consisted of UUU/SUU (1:1 ratio) types, the melting points of which ranged from –13 to 1°C. Group 1 triacylglycerols served to promote pourability and ease of handling when taken directly from a refrigerator. Common vegetable oils such as soybean, corn, cottonseed, peanut and canola contained 56–75%

Group 1 triacylglycerols. These oils remained liquid at 5°C, refrigerator temperature. Group 2 triacylglycerols mainly consisted of SUU types that melt at 6–23°C. These products furnished appropriate lubricity at 25°C. The aforementioned oils showed Group 2 concentrations, ranging from 21 to 37%. Corn, cottonseed, soybean, peanut and canola oils were all easy to handle and pour over temperatures ranging from 5 to 25°C due to their high proportions of Group 1 and 2 triacylglycerols. The functional properties of margarine oils, such as holding together at room temperature and mouth melting characteristics, are influenced by Groups 3 and 4 triacylglycerols. Groups 3 and 4 consisted of di- and trisaturated triacylglycerols, which melted at 27–42°C and 56–65°C, respectively. Research has been directed towards improvement of the triacylglycerol composition and structure of vegetable oils (2–6) that may then be used as basestocks or components of basestocks (7–11). Improvements in margarine have been accomplished by altering the percentages of fatty acids and triacylglycerols to produce oils with a wide range of elements compositions (12). Basestocks have been prepared from either the randomization of a single oil or the interesterification of the oil and hard stock blend. Oil blends with hard stocks produced triacylglycerol mixtures which exhibited more solids at higher temperatures. Interesterification of the product that may be chemically (8,9) or enzymatically (7)

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catalysed after blending, changed the triacylglycerol composition even further to provide improved food components (12,13).

The ability to characterize the triacylglycerol composition of a potential fat or oil food product is thus integral to the formulation of a desirable end product of appropriate lubricity. Reversed-phase high performance liquid chromatography (RP-HPLC) with a detector such as a flame ionization detector (FID) refractive index (14–18), or evaporative light scattering detector (ELSD) (17, 18) has become common in triacylglycerol analysis. The flame ionization and evaporative light scattering detectors have been used to provide satisfactory qualitative and quantitative composition information for triacylglycerols from a variety of sources without the need for response factors (14–18) and were not adversely affected by gradient runs. These detectors were also useful for triacylglycerol analyses in which chromatographic standards were available for the triacylglycerol, in which structures could be identified by theoretical carbon number or equivalent carbon length. They were also useful for the identification of triacylglycerol by atmospheric pressure chemical ionization mass spectrometry (19, 20). As more is learned about how specific molecular species affect the lubricity and other characteristics of a fat or oil (21–24), it becomes increasingly important to be able to determine the quantitative composition of all individual triacylglycerols accurately.

In this study, we determined triacylglycerol composition, using FIDs or ELSDs, for normal and randomized corn and soybean oil. Blends were made from 80% (by weight) corn and soybean oils with 20% cottonseed oil stearine, and interesterified corn and soybean oils with cottonseed oil stearine. The FID and ELSD methodology for triacylglycerol composition was correlated with data on the solid fat index and the dropping point to relate composition to functional properties.

Materials and Methods

Materials

The commercially refined, bleached and deodorized corn and soybean oils were obtained from PVO Foods (Granite City, IL, U.S.A.). The fully saturated cottonseed oil stearine (hard stock) was a commercial preparation obtained from Riceland Foods (Stuttgart, AR, U.S.A.) or Bunge Foods (Bradley, IL, U.S.A.). Acetonitrile and dichloromethane were HPLC grade.

Blends, interesterification and randomization of vegetable oil samples

The liquid oils and cottonseed oil were blended and dried by heating under a water aspirator vacuum. The two blends produced were corn–cottonseed oil stearine (80:20 ratio) and soybean–cottonseed oil stearine (80:20 ratio). The interesterification of the blends and the randomization of the corn and soybean oils, in the presence of the catalyst sodium methoxide, were performed as previously described (25).

High performance liquid chromatography

RP-HPLC was performed with a Thermo Separation Products Model SP 8800 ternary solvent system (Schau-mburg, IL, U.S.A.), which was equipped with two in series RP-HPLC columns, 25 × 0.46 cm, with bonded silyl (CT8) octadecylsilyl, 5 μm particle size, Inertsil octadecylsilyl-80A (GL Sciences, Keystone Scientific Bellefonte Park, PA, U.S.A.). The mobile phase involved a gradient program of acetonitrile (ACN) 80% and dichloromethane (DCM) 20% to ACN 20% and DCM 80% over 120 min. The mobile phase flow rate was 0.6 mL/min throughout the gradient program. The triacylglycerol solution sample (25 μg) injected was 10 μL of 25 mg solute/mL DCM.

Evaporative light scattering detector

This detector was a Sedex Model 55 (Sedone Altontville, France). The drift tube was set at 32 °C. The gas flow was set at a pressure of 168 N/m². The photomultiplier gain was × 5. High purity N₂ was used as the nebulizer gas.

Flame ionization detector

This detector was a Tracor Model 945 HPLC detector (Finnigan, Inc., Austin, TX, U.S.A.). The detector operating conditions were: block temperature of 130 °C; 140 mL/min hydrogen detector gas; 250 mL/min hydrogen cleaning flame gas; 175 mL/min oxygen and 0.1 cubic meter/min air. The detector electronic noise filter was set on high.

Triacylglycerol identification

The triacylglycerol HPLC chromatogram peaks were identified based on earlier analyses of the basestock products by RP-HPLC coupled with an atmospheric pressure chemical ionization mass spectrometer (19,20).

Data processing

The data output from the ELSD or FID was processed or integrated by a Star Chromatography Workstation, with version 4.0 software (Varian Associates, Inc., Walnut Creek, CA, U.S.A.). The ELSD, a mass detector, gave triacylglycerol composition in mole percent. The HPLC and GC FID gave triacylglycerol composition in weight percent, which was converted by calculation to mole percent to allow comparison of the triacylglycerol composition obtained by both detectors.

Physical properties

The solid fat index was determined by pulsed NMR spectrometry using the AOCS Method Cd 10–57. The drop melting point was determined by AOCS Method Cc 18–80.

Gas chromatography

The fatty acid methyl esters were prepared by potassium hydroxide catalysed transmethylation of the triacylglycerol

Table 1 Physical properties of interesterified corn and soybean oil blends with cottonseed oil stearine^a

Base stock	Solid fat index ^b					Melting point (°C) ^c
	10.0	21.1	26.7	33.3	40.0 (°C)	
Corn	7.1	4.7	3.8	2.7	0.9	36.5
Soybean	8.5	3.9	3.3	1.9	0.2	32.2

^a Triacylglycerol basestock from interesterified vegetable oil – cottonseed oil stearine blend (9)

^b AOCS method Cd 10–57

^c AOCS method Cc 18–80

mixtures. The fatty acid methyl esters were analysed using calibrated gas chromatography with FID (18).

Results and Discussion

The melting points and solid fat indices of the basestocks of interesterified corn oil and soybean–cottonseed oil stearine products are given in **Table 1**. The triacylglycerol

quantitative compositions obtained by the ELSD and FID for the corn and soybean oil products are presented in **Tables 2** and **3**. The FID is considered a quantitative detector without the need for triacylglycerol quantitation adjustment by response factors (14–17). The Sedex, one of the newer generation of ELSDs, has also recently been found to be a quantitative detector without the need for triacylglycerol quantitation adjustment by response factors (18). The triacylglycerols were previously identified by RP-HPLC coupled with a mass spectrometer with an atmospheric pressure chemical ionization source (20). **Tables 4** and **5** present the fatty acid compositions calculated from each of the triacylglycerol compositions, along with the fatty acid composition determined as the fatty acid methyl esters, using calibrated gas chromatography with flame ionization to check the accuracy of the triacylglycerol quantitation (18). **Tables 6** and **7** give the simplified triacylglycerol composition in terms of the saturated (S) and unsaturated (U) fatty acid of the triacylglycerol. This designation was commonly used in previous reports on margarine base stocks (8–11) and is derived from the triacylglycerol composition shown in **Tables 2** and **3**. **Tables 8** and **9** give a simplified

Table 2 Triacylglycerol (TAG) composition of corn oil (CO) products by reversed phase HPLC with evaporative light scattering detection (EV) and flame ionization detection (FID)^a (mol per mol of oil)

TAG ^b	CO		Randomized CO			Blend		Interesterified blend		
	EV	FID	EV	FID	PRE ^c	EV	FID	EV	FID	PRE
LLO	23.8	22.8	26.5	24.6	27.0	17.6	17.2	16.0	15.2	14.9
LLL	23.3	22.4	22.9	21.4	20.0	17.0	19.4	11.5	11.4	11.4
LLP	15.5	15.5	15.0	14.5	12.8	11.1	14.3	10.0	10.3	9.8
OOL	11.7	10.5	12.2	10.5	12.2	8.1	8.0	6.8	6.1	6.6
PLO	10.1	10.6	11.1	10.5	11.4	7.3	9.2	8.9	10.3	8.6
PPL	1.7	1.8	1.8	2.2	2.7	1.3	1.9	2.3	2.8	2.8
OOP	2.4	2.5	2.3	2.4	2.6	2.0	2.4	1.5	2.0	1.9
LLS	1.9	1.8	1.6	1.8	2.2	1.4	1.6	11.3	10.0	11.0
LOS	1.3	1.3	1.2	1.4	2.0	1.1	1.3	10.0	8.9	9.7
OOO	4.7	3.2	3.1	2.8	1.8	2.7	2.3	1.3	1.3	1.0
PPO	0.6	0.4	0.6	0.6	1.3	0.4	0.3	0.9	1.1	1.2
PLS	0.4	0.4	0.4	0.5	0.9	0.4	0.4	5.8	6.0	6.3
LLL _n	0.5	0.8	0.5	1.1	0.8	0.0	0.6	0.3	0.4	0.5
LnLO	0.5	2.3	0.4	2.0	0.7	0.4	0.2	0.3	1.2	0.4
OOS	0.4	0.5	0.3	0.4	0.4	0.7	0.4	2.1	1.6	2.1
POS	0.2	0.3	0.2	0.3	0.4	0.2	0.2	2.4	2.6	2.8
PLnL	0.2	0.5	0.2	0.6	0.3	0.0	0.1	0.1	0.6	0.3
PPP	0.1	0.1	0.1	0.1	0.0	0.0	0.2	0.2	0.4	0.4
OOL _n	0.2	1.0	0.1	1.1	0.2	0.1	0.0	0.1	0.8	0.1
PLnO	0.1	0.5	0.0	0.8	0.2	0.1	0.0	0.1	0.0	0.1
PPS	0.1	0.1	0.1	0.1	0.1	3.7	2.4	0.5	0.7	0.9
SSL	0.1	0.3	0.1	0.2	0.1	0.1	0.1	3.6	3.2	3.6
SSO	0.0	0.0	0.0	0.1	0.0	0.1	0.0	1.4	1.4	1.6
PPL _n	0.1	0.2	0.1	0.2	0.0	0.0	0.0	0.0	0.1	0.0
SSP	0.0	0.1	0.1	0.0	0.0	10.6	7.4	0.7	1.0	1.0
SSS	0.0	0.1	0.0	0.0	0.0	13.8	10.0	0.3	0.6	0.4
AAE ^d			0.5	0.6				0.3	0.4	

^a See experimental section for chromatography and detector operating conditions, TAG identification and TAG quantitation accuracy check procedures. HPLC peak area standard deviation was + –0.1 – 0.7% for triplicate analyses

^b TAG fatty acids: Ln, linolenic; L, linoleic; O, oleic; S, stearic; P, palmitic

^c Predicted TAG composition from statistical distribution of fatty acids among the glycerol moiety carbons during chemical randomization or interesterification

^d AAE is the average absolute error = sum of the difference between experimental and predicted TAG for all the TAG detected divided by the total number of TAG detected

Table 3 Triacylglycerol (TAG) composition of soybean oil (SBO) products by reversed phase HPLC with evaporative light scattering detection (EV) and flame ionization detection (FID)^a (mol per mol of oil)

TAG	SBO		Randomized SBO			Blend		Interesterified blend		
	EV	FID	EV	FID	PRE	EV	FID	EV	FID	PRE
LLO	18.7	17.0	22.6	20.7	20.6	17.8	12.8	12.0	10.6	12.1
LLL	18.3	17.3	16.2	14.3	14.8	17.2	12.1	7.8	8.2	8.4
LLP	13.7	13.1	11.1	10.8	10.0	12.1	9.8	10.4	10.4	7.6
OOL	9.6	7.0	10.4	9.2	9.6	8.6	6.7	5.4	4.4	5.8
PLO	8.7	8.9	9.4	9.8	9.4	7.8	7.7	8.6	9.0	7.3
LLLn	6.1	7.2	5.2	4.9	5.9	5.0	4.8	2.3	2.3	3.4
LnLO	3.8	6.9	4.8	6.9	5.5	3.1	4.7	2.4	2.5	3.2
LLS	3.3	3.1	3.0	2.8	3.3	2.7	2.6	11.2	10.5	10.3
LOS	2.6	2.2	2.6	2.6	3.1	2.1	2.7	10.6	9.5	9.9
PLnL	2.4	3.3	1.8	2.8	2.7	1.7	2.6	1.5	2.2	2.0
PPL	1.9	1.8	1.7	1.9	2.3	1.3	1.7	2.7	3.3	2.2
OOP	2.3	1.7	1.5	1.7	2.2	1.9	2.2	1.3	1.5	1.7
OOO	3.3	2.2	1.7	1.7	1.5	2.7	2.4	0.8	0.8	1.0
PLS	1.0	0.9	0.8	1.0	1.5	0.7	1.2	6.6	6.4	6.3
OOLn	0.3	1.5	0.9	1.9	1.3	0.3	1.3	0.6	0.8	0.8
PLnO	0.2	1.7	0.8	1.7	1.2	0.2	1.2	0.7	1.4	1.0
PPO	0.7	0.5	0.7	0.7	1.0	0.4	0.5	0.9	1.2	1.1
LnLnL	0.5	1.0	0.5	0.7	0.8	0.4	0.8	0.3	1.0	0.4
OOS	0.9	0.6	0.6	0.6	0.7	0.8	0.8	2.1	1.8	2.4
POS	0.5	0.3	0.4	0.6	0.7	0.3	0.4	2.6	3.0	3.0
LnLnO	0.1	0.5	0.3	1.1	0.4	0.1	0.5	0.2	0.1	0.2
PPLn	0.0	0.1	0.1	0.2	0.3	0.0	0.2	0.1	0.3	0.3
SSL	0.2	0.3	0.2	0.2	0.2	0.1	0.3	4.1	3.7	4.4
LnLnP	0.1	0.3	0.1	0.3	0.2	0.0	0.3	0.1	0.1	0.1
PPS	0.2	0.1	0.1	0.2	0.2	1.4	2.2	0.6	1.8	1.0
PPP	0.2	0.1	0.1	0.2	0.2	0.1	0.2	0.1	0.4	0.2
SSO	0.2	0.2	0.0	0.2	0.1	0.2	0.3	1.7	1.2	2.0
SSP	0.0	0.1	0.1	0.2	0.1	4.6	7.0	0.7	0.9	1.3
SSS	0.0	0.1	0.0	0.1	0.0	6.1	10.1	0.3	0.9	0.6
AAE			0.4	0.3				0.5	0.6	

^aSee footnotes in **Table 2** for definitions and experimental details

triacylglycerol composition in terms of triacylglycerol, containing saturated fatty acids. (S = palmitic + stearic), monoene (M = oleic), diene (D = linoleic) and triene (T = linolenic). These data were also obtained from the triacylglycerol composition in **Tables 2** and **3**. The S, M, D and T TAG designation has been previously used for triacylglycerols resolved by silver ion HPLC (16). The S, M, D and T TAG designation more precisely correlated triacylglycerol compositions with melting points, solid fat indices and a possible increased oxidative stability, than the extremely simplified triacylglycerol composition listed in **Tables 6** and **7**. The S, M, D and T designation is more simplified, however, than the exact triacylglycerol quantitation and identification given in **Tables 2** and **3**.

Comparison of the quantitative triacylglycerol data between the ELSD and FID for the corn oil products indicated that data from both detectors agreed with predicted triacylglycerol composition for the randomized and interesterified corn oil products (**Table 2**). The data given in percent produced by the ELSD showed an average absolute error of 0.5% for randomized corn oil and 0.3% for interesterified corn-cottonseed oil compared to the predicted triacylglycerol composition. The data in percent produced by the FID showed an average absolute error of 0.6% for randomized corn oil and 0.4%

for interesterified corn-cottonseed oil stearine, compared to the predicted triacylglycerol composition. The ELSD and FID were in agreement for the triacylglycerol composition of corn oil. They yielded different triacylglycerol compositions for the noninteresterified corn-cottonseed oil blend, however. The blend contained 20% cottonseed oil stearine, mainly comprising dipalmitoylstearyl, palmitoyldistearoyl and tristearoyl glycerols. The triacylglycerol composition obtained by the FID was 19.8% and the triacylglycerol composition obtained by the ELSD was 28.3% cottonseed oil stearine triacylglycerols, respectively. The calculated fatty acid compositions, compared to the experimental fatty acid compositions, were also in agreement for both the ELSD and the FID for corn oil, randomized corn oil and interesterified corn-cottonseed oil stearine products (**Table 4**). The calculated and experimental fatty acid compositions of the non-interesterified blend were in agreement for the triacylglycerol composition obtained by the FID, but not for the triacylglycerol composition obtained by the ELSD. This had a large average absolute error three times greater than the average absolute error obtained by the FID for the blend triacylglycerols. The ELSD also gave large absolute errors compared to experimental linoleic and stearic acid compositions (**Table 4**). Changes in operating conditions did not improve the quantitative

Table 4 Fatty acid (FA) composition of corn oil products obtained experimentally by GC-FID and calculated from TAG composition listed for LC-EV and LC-FID in **Table 2^a** (mol per mol of oil)

FA	Corn oil					Randomized corn oil				
	EV	AE ^b	FID	AE ^b	GC	EV	AE ^b	FID	AE ^b	GC
P	11.4	0.3	12.7	1.0	11.7	11.5	0.6	13.0	0.9	12.1
Ln	0.7	0.2	1.4	0.5	0.9	0.4	0.4	1.2	0.4	0.8
L	59.8	0.4	59.7	0.5	60.2	60.7	2.1	59.2	0.6	58.6
O	26.7	1.5	24.5	0.7	25.2	26.1	0.3	24.3	2.1	26.4
S	1.5	0.5	1.8	0.2	2.0	1.3	0.8	2.3	0.2	2.1
AAE ^c		0.6		0.6			0.8		0.8	
FA	Corn oil blend					Interesterified corn oil blend				
	EV	AE ^b	FID	AE ^b	GC	EV	AE ^b	FID	AE ^b	GC
P	14.1	0.2	14.1	0.2	13.9	12.7	1.2	13.8	0.1	13.9
Ln	0.4	0.3	0.3	0.4	0.7	0.4	0.3	0.9	0.2	0.7
L	43.2	5.2	48.7	0.3	48.4	49.8	1.0	48.7	0.1	48.8
O	18.9	2.3	19.3	1.9	21.2	22.1	0.9	22.1	0.9	21.2
S	23.4	7.7	17.7	2.0	15.7	15.0	0.5	14.5	1.0	15.5
AAE ^c		3.1		1.0			0.8		0.5	

^a See Experimental section for analytical conditions and TAG accuracy check procedures. GC precision $\pm 0.0 - 0.1\%$

^b AE, absolute error = absolute value of the error compared to GC for each FA

^c AAE, average absolute error = sum of the absolute error compared to GC for each FA divided by the number of FAs ($n = 5$)

Table 5 Fatty acid composition (FA) composition of soybean oil (SBO) products obtained experimentally by GC-FID and calculated from TAG composition listed for LC-EV and LC-FID in **Table 3^a** (mol per mol of oil)

FA	Soybean oil					Randomized soybean oil				
	EV	AE	FID	AE	GC	EV	AE	FID	AE	GC
P	11.7	0.8	11.8	0.9	10.9	10.7	0.9	11.1	0.5	11.6
Ln	4.7	2.6	8.3	1.0	7.3	5.2	1.8	7.3	0.3	7.0
L	56.6	3.6	54.8	1.8	53.0	56.2	3.5	52.8	0.1	52.7
O	23.9	0.9	22.2	2.6	24.8	25.1	0.5	25.7	1.1	24.6
S	3.1	1.0	2.9	1.2	4.1	2.8	1.1	3.1	0.8	3.9
AAE		1.8		1.5			1.6		0.6	
FA	Soybean oil blend					Interesterified soybean oil blend				
	EV	AE	FID	AE	GC	EV	AE	FID	AE	GC
P	11.9	1.0	13.0	1.0	12.9	14.0	1.2	14.9	2.1	12.8
Ln	3.8	2.0	6.4	3.4	5.8	3.0	2.6	3.5	2.1	5.6
L	51.1	7.6	43.5	2.9	43.5	46.4	3.1	44.1	0.8	43.3
O	21.1	0.8	20.1	0.4	20.3	20.5	0.1	21.9	1.3	20.6
S	12.1	5.3	17.0	0.9	17.4	16.1	1.5	15.6	2.0	17.6
AAE		3.3		1.7			1.7		1.7	

^a See footnote in **Table 4** for definitions and experimental conditions

triacylglycerol composition obtained by the ELSD for the noninteresterified blend. This was not suitable for blends with higher amounts of saturated triacylglycerols. The FID was suitable for triacylglycerol compositions of all the corn oil products.

In the study of the corn oil products for margarine basestocks (9), only the interesterified corn-cottonseed oil stearine blend had sufficient solids for the solid fat index and melting point of soft tub margarines. Commercial soft tub margarines had solid fat index values at 10, 21 and 33.3°C of 8–10, 4–5, and 1–2, respectively. The

soft tub margarines also had melting points of 32.2–36.6°C (9). The interesterified blend had many more of the following triacylglycerols compared to the natural corn oil (L, O, P, S = linoleic, oleic, palmitic and stearic acids, respectively): LLS, LOS, PLS; and slightly more of the following triacylglycerols: OOS, POS, PPS, SOS, PSS and SSS. This change in triacylglycerol composition improved the normal corn oil, which was liquid at 5°C, to a margarine product, with a melting point 36.5°C and solid fat index of 10, 21.1 and 33.3°C of 7.1, 4.7 and 2.7, respectively (**Table 1**).

Table 6 Classification of triacylglycerols based on unsaturation/saturation in the fatty acyl chains for corn oil products in **Table 2^a** (mol per mol of oil)

	Normal CO		Randomized CO			CO/CSOS blend		Interesterified CO/CSOS blend		
	ELSD	FID	ELSD	FID	PRE	ELSD	FID	ELSD	FID	PRE
UUU	64.6	63.6	65.7	64.1	63.2	45.9	48.2	36.3	36.8	34.9
UUS	32.1	32.7	30.8	31.7	31.3	23.7	28.9	44.0	43.6	44.0
SUS	3.1	3.3	3.2	4.0	5.2	2.5	2.8	17.2	16.9	18.5
SSS	0.2	0.4	0.3	0.2	0.3	28.1	20.1	1.7	2.7	2.6

^a Calculated by assigning U to unsaturated fatty acids and S to saturated fatty acids. For example, LLO is UUU, LLS is UUS, PLP is SUS and PSS is SSS. Thus, UUU is obtained by the summation of all TAG with three unsaturated fatty acids, UUS, all TAG with one saturated and two unsaturated fatty acids, SUS all TAG with two saturated and one unsaturated fatty acid, and SSS all TAG with three saturated fatty acids

Table 7 Classification of triacylglycerols based on unsaturation/saturation in the fatty acyl chains for SBO products in **Table 3^a** (mol per mol of oil)

	Normal SBO		Randomized SBO			SBO/CSOS blend		Interesterified SBO/CSOS blend		
	ELSD	FID	ELSD	FID	PRE	ELSD	FID	ELSD	FID	PRE
UUU	60.4	61.1	62.9	61.9	60.2	55.2	46.5	31.8	31.0	33.7
UUS	34.2	34.4	30.4	32.6	33.3	29.3	29.4	46.5	46.3	44.2
SUS	4.5	4.0	3.9	4.7	6.1	3.0	4.5	18.7	18.7	19.3
SSS	0.4	0.4	0.3	0.7	0.4	12.1	19.6	1.7	3.9	2.8

^a See footnote to **Table 6**

The triacylglycerol compositions for corn oil, randomized corn oil, the blend and interesterified corn-cottonseed oil stearine in regard to triacylglycerol effect on basestock physical properties have usually been simplified by summation into four classes based on the number of saturated and unsaturated fatty acids per triacylglycerol (1, 8–11). These data are given in **Table 6** for the corn oil products. The interesterification of corn oil with cottonseed oil stearine improved the quantity of UUS, SUS and SSS and reduced the quantity of UUU triacylglycerols compared to natural corn oil and randomized corn oil (**Table 6**). Triacylglycerols represented by SSD, SMD, SDD also increased and MMD, DDM and DDD decreased after interesterification (**Table 8**). While the increase in SUS and SSS species is known to increase the solid fat index and melting point and to improve the basestock with respect to a margarine oil (1, 8–11), this triacylglycerol designation was not precise enough. The S, M, D, and T (**Tables 8** and **9**) proved a more useful triacylglycerol designation for basestock candidates. For example, the triacylglycerols LOP and LLP in **Table 2** were both UUS triacylglycerols in **Table 6**. LOP and LLP had very different melting points, however, and thus exerted different effects on oil lubricity (1). These triacylglycerols were better distinguished by the classes SMD and SDD, respectively, in **Table 8**. The latter designation not only showed more precisely how the triacylglycerols of corn oil could be changed to produce a margarine basestock, through the addition of saturated fatty acids in regard to the number of fatty acid unsaturation sites (**Tables 1** and **8**), but also indicated the basestock oxidative stability. Thus, while an increase in SSD, SMD and SDD assisted the production of the necessary melting range and solid fat index range (9), the change in

triacylglycerol composition through an increase in saturated fatty acids and a decrease in dienoic fatty acid, would be expected to improve basestock oxidative stability (3, 26).

The comparison of the quantitative triacylglycerol data between the ELSD and FID for the soybean oil products, showed that the detectors were in agreement with predicted triacylglycerol composition for the randomized and interesterified soybean oil products (**Table 3**). The ELSD had an average absolute error of 0.5% for randomized soybean oil and interesterified soybean-cottonseed oil stearine, compared to the predicted triacylglycerol composition. The FID had an average absolute error of 0.4% for randomized soybean oil and 0.6% for the interesterified soybean oil-cottonseed oil stearine, compared to predicted triacylglycerol composition. The detectors were in agreement for the triacylglycerol composition of soybean oil, although they gave different triacylglycerol compositions for the noninteresterified soybean-cottonseed oil stearine blend. The blend contained 20% of cottonseed oil stearine. The triacylglycerol composition obtained by the FID was 19.3% and the triacylglycerol composition obtained by the ELSD was 12.1% cottonseed oil stearine triacylglycerols. Also, the calculated fatty acid compositions compared to the experimental fatty acid compositions were in agreement as determined by the average absolute error for both the evaporative light scattering and flame ionization detectors for the soybean oil, randomized soybean oil and interesterified soybean-cottonseed oil stearine products (**Table 5**). The average absolute error for soybean oil was greater than the average absolute error for the corresponding corn oil products. The difference between the average absolute error for corn and soybean oils may be

Table 8 Classification of triacylglycerols based on the degree of unsaturation in the fatty acyl chains for corn oil products in **Table 2^a** (mol per mol of oil)

TAG	Number of sites	Normal CO		Randomized CO			Blend CO/CSOS		Interesterified blend CO/CSOS		
		EV	FID	EV	FID	PRE ^b	EV	FID	EV	FID	PRE
SSS	0	0.2	0.4	0.3	0.2	0.3	28.1	19.8	1.6	2.7	2.6
SSM	1	0.8	0.7	0.8	1.0	1.6	0.7	0.5	4.7	4.9	5.6
SSD	2	2.2	2.4	2.3	2.8	3.5	1.8	2.3	12.5	11.6	12.7
SMM	2	2.8	2.9	2.6	2.5	3.0	2.9	2.7	4.4	3.5	4.0
SMD	3	11.4	11.6	12.3	11.7	13.2	8.4	10.2	18.9	18.9	18.3
MMM	3	4.7	3.2	3.1	2.8	1.9	2.7	2.3	1.3	1.3	1.0
SST	3	0.1	0.2	0.1	0.2	0.0	0.0	0.0	0.0	0.1	0.2
SDD	4	17.4	16.9	16.6	15.9	14.6	12.5	15.4	21.3	19.9	20.8
MMD	4	11.7	10.5	12.2	10.7	12.3	8.1	8.1	6.8	6.2	6.6
SMT	4	0.1	0.5	0.0	0.8	0.2	0.1	0.0	0.1	0.0	0.1
TMM	5	0.2	1.0	0.1	1.1	0.2	0.1	0.0	0.1	0.8	0.1
DDM	5	23.8	23.0	26.5	24.9	27.2	17.6	17.4	16.0	15.4	15.0
TDS	5	0.5	2.3	0.4	2.0	0.7	0.4	0.2	0.3	1.2	0.4
DDD	6	23.3	22.6	22.9	21.5	20.1	17.0	19.5	11.5	11.5	11.4
TDM	6	0.5	2.3	0.4	2.0	0.7	0.4	0.2	0.3	1.2	0.4
TTS	6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TDD	7	0.5	0.8	0.5	1.1	0.8	0.0	0.6	0.3	0.4	0.5
TTM	7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TTD	8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
TTT	9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

^a S, saturated (stearic, palmitic) M, monenoic (oleic) D, dienoic (linoleic) and T, trienoic (linolenic) TAG fatty acids. For example, SMT is POLn, DDD is LLL and MMM is OOO. Calculations: SSS = tristearin + SSP + PPS + Tripalmitin; SSM = SSO + POS + PPO; SSD = PPL + PLS + SSL; SMM = SOO + OOP; SDD = LLP + LLS. The remaining TAG designations are for one TAG only. For example, TMM is OOLn; LnLO is TDM, etc

^b Predicted TAG composition from statistical distribution of fatty acids during chemical randomization

Table 9 Classification of triacylglycerols based on the degree of unsaturation in the fatty acyl chains for soybean oil products in **Table 3^a**

TAG	Number of sites	Normal SBO		Randomized SBO			Blend SBO/CSOS		Interesterified blend SBO/CSOS SOS		
		EV	FID	EV	FID	PRE	EV	FID	EV	FID	PRE
SSS	0	0.4	0.4	0.3	0.7	0.4	12.1	19.4	1.7	3.9	2.8
SSM	1	1.4	1.0	1.1	1.5	1.8	0.9	1.2	5.2	5.2	5.7
SSD	2	3.1	2.9	2.7	3.0	3.9	2.1	3.1	13.4	13.1	12.1
SMM	2	3.2	2.3	2.1	2.3	2.8	2.7	2.9	3.4	3.3	4.4
SMD	3	11.3	10.9	12.0	12.2	12.2	9.9	10.3	19.2	18.6	16.4
MMM	3	3.3	2.2	1.7	1.7	1.5	2.7	2.4	0.8	0.8	0.9
SST	3	0.0	0.1	0.1	0.2	0.3	0.0	0.2	0.1	0.3	0.3
SDD	4	17.0	16.0	14.1	13.3	13.0	14.8	12.2	21.6	20.9	21.8
MMD	4	9.6	7.1	10.4	9.3	9.6	8.6	6.8	5.4	4.4	5.5
SMT	4	0.2	1.7	0.8	1.7	1.2	0.2	1.2	0.7	1.4	0.9
TMM	5	0.3	1.5	0.9	1.9	1.3	0.3	1.3	0.6	0.8	0.7
DDM	5	18.7	17.2	22.6	20.9	20.6	17.8	12.9	12.0	10.8	11.6
TDS	5	2.4	3.2	1.8	2.7	2.6	1.7	2.5	1.5	2.1	1.9
DDD	6	18.3	17.5	16.2	14.5	14.7	17.2	12.2	7.8	8.3	8.1
TDM	6	3.8	6.9	4.8	6.9	5.5	3.1	4.7	2.4	2.5	3.0
TTS	6	0.1	0.3	0.1	0.3	0.2	0.0	0.3	0.1	0.1	0.1
TDD	7	6.1	7.2	5.2	4.9	5.9	5.0	4.8	2.3	2.3	3.2
TTM	7	0.1	0.5	0.3	1.1	0.4	0.1	0.5	0.2	0.1	0.2
TTD	8	0.5	1.0	0.5	0.7	0.8	0.4	0.8	0.3	1.0	0.4
TTT	9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

^a See footnote to **Table 8**

as a result of the detection by the atmospheric pressure chemical ionization-mass spectrometry of minor amounts (less than 0.1–1%) of linolenic containing triacylglycerols, enclosed in brackets, which coelute via RP-HPLC with the following triacylglycerols: (LnLnS)

with LnLP, (LnLS) with LLP, (LnOS) with POL, (PSLn) with PLP and (LnSS) with SLP (20). These coeluting triacylglycerols did not occur for corn oil products (20). For the noninteresterified soybean-cottonseed oil triacylglycerol blend, the calculated and experimental

fatty acid compositions were in agreement for the triacylglycerol composition obtained by the FID, but not for the triacylglycerol composition obtained by the ELSD. The latter showed a large average absolute error of 3.3% for this blend. It also gave a large absolute error for calculated compared to experimental linoleic and stearic compositions (**Table 5**). As was the case for the noninteresterified corn-cottonseed oil stearine blend, changes in operating conditions did not improve the triacylglycerol quantitation obtained by the ELSD. The FID was suitable for quantitation of all the soybean oil products.

In the study of soybean oil products for potential margarine basestocks, only the interesterified soybean oil-cottonseed oil stearine blend contained sufficient solids for an appropriate solid fat index and melting point of soft tub margarines. The interesterified blend compared to the natural soybean oil contained many more of the following triacylglycerols: LLS, LOS, PLS and slightly more of the following triacylglycerols: OOS, POS, PPS, SOS, PSS and SSS. This assisted the improvement of the normal soybean oil, which is liquid at 5°C, to a margarine product, which has a melting point of 32.2°C with solid fat at 10.0, 21.1 and 33.3°C of 8.5, 3.9 and 1.9, respectively (**Table 1**).

The interesterification of soybean oil with cottonseed oil stearine improved the quantity of UUS, SUS and SSS and reduced the quantity of UUU triacylglycerols, compared to the natural soybean oil and randomized soybean oil (**Table 7**). Triacylglycerols represented by the classification of triacylglycerols based on the degree of unsaturation in the fatty acyl chains by SSS, SSD, SSM, SMD and SSD increased and DDD, DDM, MMD, TDM and TDS decreased after interesterification (**Table 9**). The latter designation gave more precise information on which of the triacylglycerols needed to be increased and which needed to be decreased to produce a suitable soybean oil based margarine basestock. Also, reduction in triacylglycerols such as DDD, TDM and TDS would be expected to increase the oxidative stability of the soybean oil-based product (26).

Knowledge of accurate triacylglycerol compositions of margarine basestocks is important in order to understand the triacylglycerol compositions that are responsible for certain important physical properties of margarines. Lubricity, for example, is an important physical property related to triacylglycerol species and quantity (10). Normal corn and soybean oil blends with cottonseed oil stearine hard stock showed high concentrations of trisaturated triacylglycerols such as PPS, PSS and SSS. Interesterified blends showed higher concentrations of saturated triacylglycerols than the original liquid oils. Selection of basestock products with these triacylglycerol types may assist the development of margarines with good lubricity. Similarly, spreadability, tub stability and other important characteristics depend on the presence of specific triacylglycerol species. The efforts to link texture, sensation and flavour characteristics with structural properties continue and the ability to predict the triacylglycerol composition of a product will be central to understanding the relationship between triacylglycerol

form and function better. Accurate knowledge of the basestock triacylglycerol composition in **Tables 2–4** allowed the calculation of UUU, SUU, SSU and SSS classes (**Tables 6** and **7**), and classes of triacylglycerols represented S, M, D, and T compositions (**Tables 8** and **9**). It also allowed the study of the effect of triacylglycerol classes on the solid fat index and melting points of some interesterified vegetable and soybean stearine blends and randomized high stearic soybean oils (**Table 1**). The triacylglycerol distributions of the interesterified blends with regard to degree of unsaturation were similar. The solid fat index data for these blends were also similar over the temperature range of 10–33.3°C, providing evidence that melting profiles of the blends are influenced by the relative proportions of the component triacylglycerols, which in turn provide information on functional properties, such as holding together at room temperature and mouth melt. The relatively high proportion of groups with saturated fatty acid triacylglycerols should lend themselves well to incorporation into margarine formulations (1).

Analytical tools are now available to provide the necessary information for more thorough characterization of oil products than ever before. For natural oils and interesterified or randomized oils, evaporative light scattering and flame ionization detectors were both shown to provide good quantitation for use in routine triacylglycerol analysis. As the FID is no longer commercially available, however, the ELSD is presently one of the suitable detectors for quantitative triacylglycerol analysis.

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