Alterations in Glyceride Composition During Interesterification of Mixtures of Sunflower Oil with Lard and Tallow

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ABSTRACT AND SUMMARY

An analytical approach is presented for the study of one-phase interesterification of mixtures of sunflowerseed oil with fully hydrogenated lard, natural lard, and tallow, based on triglyceride group analysis by argentation thin layer chromatography. The curves for the changes of each of ten triglyceride groups, differing in unsaturation, are reported. These are used to establish the conversion of the initial composition to the random limits in the mixtures cited. The alterations in the differential dilatation curves are explained in part by the changes in the triglyceride composition.

INTRODUCTION

With the progress in the triglyceride analysis it became possible to prove experimentally that the one-phase interesterification of fats conforms to a pattern of random distribution of the acyl groups. Naudet et al. (1) demonstrated that random composition of the four triglyceride types is reached at equilibrium when starting from model mixtures of triolein and tristearin. Many workers found that to be valid for interesterified fats as well. To this end the triglycerides (TGs) of natural and randomized fats have been compared using the enzymatic deacylation (2-9), argentation thin layer (9-14) and gas liquid chromatography (15-17), mass-spectrometry (18), and stereospecific analysis (19). These methods have been applied for several rearranged fats: lard (2,6,10,16), olive oil (3,11,12), rapeseed oil (4,16), tallow (5,18), cocoa butter (14,18), margarine fat (7), butter fat (16,19), whale oil highly unsaturated TGs (8), Moringa concanensis seed fat (9), palm kernel oil (17), and some fat mixtures (15,16). The importance of knowing the glyceride composition of the interesterified fats was emphasized in four recent reviews (20-23). But although the above end products were studied, very little is known regarding the course of interesterification with respect to the changes of the individual TG groups (13,14).

TABLE I

Calculated and Found Fatty Acid Group Composition of the Fat Mixtures

Acid group	Relative % by wt S60-FHL40 Calc.	S60-FHL40 Found	S60-T40 Calc.	S60-T40 Found	S50-L50 Calc.	S50-L50 Found
S[a]	40.4[b]	41.0[c]	28.6	29.1	28.8	27.9
M	14.8	14.7	25.2	24.0	39.8	41.2
D	44.5	44.3	46.1	46.9	31.3	30.8

[a] Acyl groups in the TGs: S–saturated, M–cis-monoene, D–all-cis-diene.

[b] Mean values calculated from the triglyceride group composition, e.g., Table II.

[c] Found by argentation thin layer chromatographic methyl ester analysis.

In this study the curves representing the changes in the amount of each of ten TG groups, differing in their degrees of unsaturation, were established. This enabled us to prove experimentally that in complex fat mixtures the TG composition changes towards the random values of the four TG types, containing different number of unsaturated acyls. The results were used to explain the differential dilatations of both the initial mixtures and their randomized products.

EXPERIMENTAL PROCEDURES

The fats and oils were commercial samples, neutralized, washed, and dried prior to use. Sodium methoxide and silica gel G were purchased from E. Merck (Darmstadt, GFR). Redistilled reagent grade solvents were used for thin

TABLE II

Changes in Triglyceride Group Composition of Mixture S60-FHL40

Triglyceride group	No. of double bonds	Minutes after start 0	20	40	60	Difference
		Relative % by wt				
S_3[a]	0	37.7[b]	32.0	17.1	6.7	–31.0[c]
S_2M	1	–	0.7	3.7	9.2	+ 9.2
SM_2	2	0.5	1.6	3.1	5.4	+ 4.9
S_2D	2	0.5	2.9	12.7	20.9	+20.4
M_3	3	0.7	1.1	–	–	– 0.7
SMD	3	4.7	5.2	11.2	14.0	+ 9.3
M_2D	4	4.8	4.8	5.1	2.5	– 2.3
SD_2	4	11.4	11.8	16.2	20.2	+ 8.8
MD_2	5	20.3	20.2	16.5	9.5	–10.8
D_3	6	19.2	19.4	14.3	11.6	– 7.6

[a] Acyl groups in the triglycerides: S–saturated, M–cis-monoene, D–all-cis-diene. The order of the letters is not concenred with positional isomers.

[b] Composition of the initial mixture.

[c] Difference between the value for the randomized and initial mixture: + increase, – decrease.

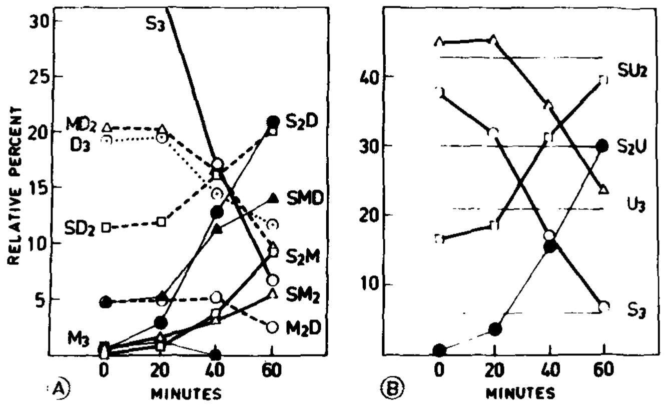

FIG. 1. Changes in triglyceride composition of mixture S60-FHL40 during randomization: A. Triglyceride groups–S saturated, M monoene, and D diene acyls; B. Triglyceride types–S saturated, and U unsaturated acyls.

layer chromatography (TLC) of TGs.

The fat mixtures (50 g) were interesterified with the aid of sodium methoxide (0.2% w/w) at 70-90 C by vigorous stirring in a glass flask under nitrogen. Samples (500 mg) were taken at timed intervals after adding the catalyst. They were dissolved in ether, washed, and dried. The TGs were purified by preparative TLC, using plates (20 x 20 cm) coated 0.5 mm thick with silica gel G. Approximately 50 mg of the sample in heptane were streaked as a 19 cm long band on each plate and developed with petroleum ether-acetone 100:8 v/v. The TGs were located under ultraviolet light after spraying with 0.05% of 2,7-dichlorofluorescein alcoholic solution at three points of the band. The indicator-free pure TGs were then extracted with diethyl ether. After evaporating the solvent in vacuo at 20 C, a 0.1% solution in heptane was prepared. It was used for quantitative analysis of the TG groups, differing in their degrees of unsaturation. A new argentation TLC method (24) was applied, which is based on densitometric measurement of the charred bands. A Carl Zeiss Densitometer (Model ERI 65m; Jena, GDR) was used. With its aid, quantitative analysis of ten TG groups was made with a standard deviation of three analyses not exceeding ± 1.5% for a group. Almost the same procedure was applied for TLC quantitative determination of the methyl ester groups of the fat mixtures. The esters were prepared after the method of Hartman et al. (25). The differential dilatation curves were established by the method of Jasperson et al. (26).

RESULTS AND DISCUSSION

The interesterification was studied on many fat mixtures, the three examples here reported being most illustrative from a theoretical point of view. In two mixtures the fatty acid distribution among the TG types was far enough from the statistical. The acids of the third mixture were randomly distributed among the TG types. Their fatty acid group composition is given in Table I.

The mixture S60-FHL40, composed of sunflowerseed oil and fully hydrogenated lard (60:40 w/w), was chosen in order to study in a comparatively simple case the saturated fatty acids distribution among the mixed TGs. Four samples, taken at 20 min intervals during the process, were analyzed. The resulting changes are presented in Table II. The last column shows the increase (plus) and the decrease (minus) of each TG group. The fatty acid group composition, calculated from the TGs, remained almost constant, and this well known fact was used for accuracy control. When a calculated amount of an acid group exceeded ± 2.5% of its known value the TG analysis of the respective sample was repeated. The mean and found values are compared in Table I for all fat mixtures.

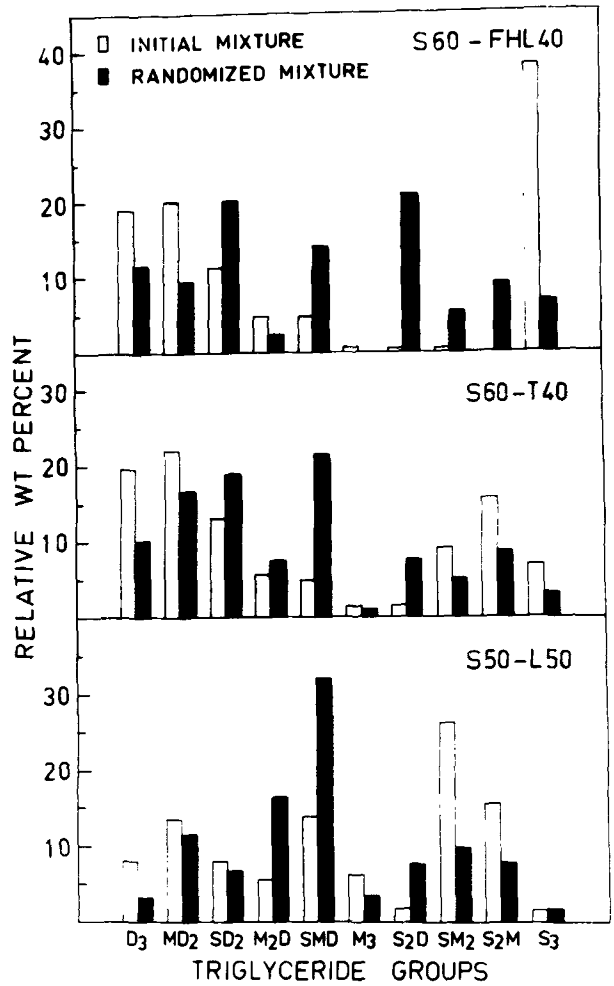

FIG. 2. Overall changes in the triglyceride group composition of the mixtures, caused by randomization.

The changes of the TGs are more clearly illustrated in Figure 1A, the curves of which are obtained by plotting the data of Table II. Using diagrams of this type one can find the alterations of each TG group during the process. In this particular case the saturated acyls of S_3 are rearranged to a great extent intermolecularly given rise to formation of mixed TGs, especially of S_2D and SD_2. The increase of their total amount is greater than that of S_2M and SM_2. This was expected because of the preponderance of diene over monoene acyls in the mixture.

The experimental values for the groups (Table II) were then used to calculate the TG type compositions. By plotting the respective values against time, the curves representing the changes of the types were obtained and these are shown in Figure 1B. The random values of the types, which correspond to 40% saturated acids present, were found by interpolation from the theoretical diagram (27). These are presented as straight lines, parallel to the abscissa. It can be seen that the curve of each type converges to its random value.

The overall change that has occurred during the process is more clearly seen in Figure 2, where the compositions of the initial and random mixtures are compared. After a careful examination of the diagram it can be noted that only the percentages of the saturated acid containing TGs increase, while the reverse is true for the remaining groups. This is to be expected, since tristearin is a source of saturated acyl groups, and its amount exceeds by far the random quantity in the mixture.

In this simple case of rearrangement the formation of

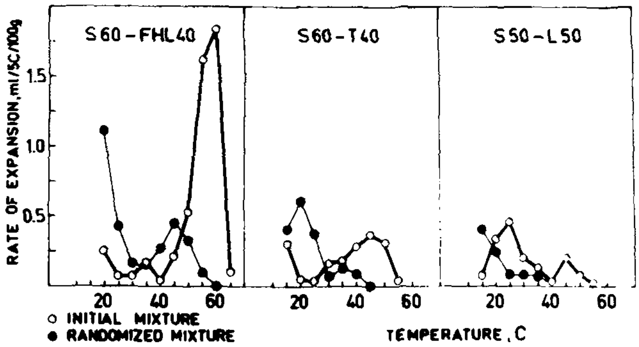

FIG. 3. Comparison between the differential dilatation curves of the initial and randomized mixtures.

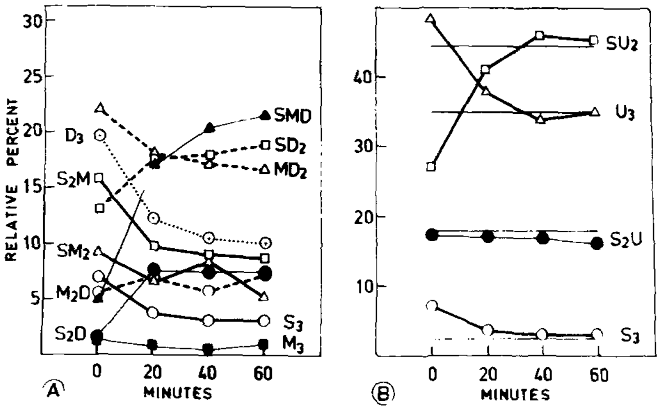

FIG. 4. Changes in triglyceride group (A) and type (B) composition of mixture S60-T40 during randomization.

lower melting TGs was observed, and this was proved by the differential dilatation curves of both the initial mixture and its product, shown in Figure 3. The large peak at 40-65 C caused by S_3 decreased to a great extent after randomization. The peak of the product in the region 25-55 C is much smaller which is due to the presence of S_3, S_2M, and S_2D. Their total amount is comparable with that of S_3 in the starting mixture. However, S_2M and S_2D are lower melting groups. For that reason, the latter peak is considerably smaller, its maximum being displaced with 15 C accordingly.

The interesterification was studied in the same manner on the more complex mixture S60-T40 composed of sunflower oil and beef tallow (60:40 w/w). The alterations of the TG groups were followed again by analysis of four samples (Fig. 4A). Each curve illustrates the way of reaching the random value of the respective group. The same is valid for the types (Fig. 4B) which converge to the random limits, corresponding to 29% of saturated acids present. In this case it is interesting to note that the relative S_2U percentage remains near the theoretical level all the time. Since S_2M and S_2D are the only components in S_2U, their mutual compensation is responsible for the type S_2U to remain almost constant (Fig. 4A & B). The changes in SU_2 and U_3 are more complex because these types contain many groups.

The initial mixture is compared with the final product in the respective diagram of Figure 2. The compositions of sunflower oil and tallow are clearly seen from the white profile. The randomization had led to a new fat (black profile) which is enriched on TGs with an intermediate unsaturation, especially SMD. For that reason the melting characteristics of the product were displaced to a lower temperature range in comparison with the initial mixture. This was supported by the results from the dilatation measurements (Fig. 3). The total decrease of 11% for S_3 and S_2M has led to the small peak found in the 30-45 C range of the product's dilatation curve.

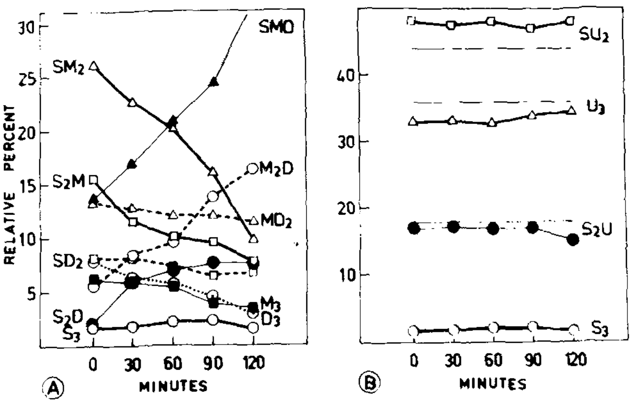

FIG. 5. Changes in triglyceride group (A) and type (B) composition of mixture S50-L50 during randomization.

Analogous results were obtained for the interesterification of mixture S50-L50, composed of equal parts of sunflower oil and lard (Fig. 5A). It was chosen as an example illustrating the rearrangement of a mixture whose initial TG type composition is closely related to a random pattern. In this particular case, the types retained their chance values during the process as shown in Figure 5B. In spite of this, many of the TG groups underwent considerable alterations. It is clear, therefore, that the determination of the four TG types is not always sufficient to follow the course of interesterification.

The overall change is seen from the profiles depicted for comparison in the diagram of Figure 2. Considerable increase of the TGs with two to four double bonds was again established. Lowering of the melting range (Fig. 3) resulted from these structural changes.

The more detailed study here presented has experimentally proved the chance rearrangement of complex fat mixtures. The one-phase interesterification leads to an increase of the TGs with intermediate degrees of unsaturation provided the initial group composition is not quite close to the random levels. These structural changes are responsible for shifting the melting range of the product to lower temperatures.

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