Alterations in Glyceride Composition during Directed Interesterification of Lard

D.G. CHOBANOV and **M.R. TOPALOVA**, Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

ABSTRACT

A detailed study on directed interesterification is presented based on triglyceride group analysis by argentation thin layer chromatography. The process is illustrated by the curves for the changes of six triglyceride groups with different unsaturation using lard as a suitable model fat. The deviation of the triglyceride types away from their theoretical change levels is presented. The influence of the temperature on the rearrangement is examined towards trisaturated and disaturated triglycerides, respectively. Appropriate conditions are shown which can be used by analogy for other fats and triglyceride mixtures.

INTRODUCTION

The possibility of rearranging the fatty acids among triglycerides (TGs) of a fat was extended by Eckey (1,2) who discovered the two phase or directed interesterification. The process is conducted at sufficiently low temperatures at which part of the TGs crystallize, thus causing the fatty acids to be redistributed away from the statistical endpoint. Only the trisaturated and disaturated TGs can crystallize at temperatures above 0 C for which active catalysts are available. The process has been examined for production of plastic shortenings (3-6), confectionery hard butters (3,7), salad oils (3,8), drying oils (9) and margarine oils (10,11), using mainly the physical characteristics of the products for control (12,13). The TG type composition has been determined only in some cases (6,14-17). However, the directed interesterification could be better elucidated by determining the TG groups with different unsaturation in a manner already shown for random interesterification (18).

In this study the directing effect of crystallization was examined by the changes of six TG groups during rearrangement using lard as a proper model fat. These data were used to establish the change in the TG type composition away from random distribution. Attempts were made to direct the process to maximize formation of trisaturated and disaturated TG types, respectively. The dilatation behavior of the products also was examined.

EXPERIMENTAL PROCEDURES

Lard was a commercial sample, neutralized, washed and dried. Sodium-potassium alloy was prepared (19) by heating equal parts of the metals (total 5 g) in xylene (100 ml) at 115 C in a round-bottomed flask connected with a reflux-condenser and equipped with a mechanical stirrer. Initially, the molten metals were carefully mixed with the aid of a glass rod until a large globule of the alloy formed which then was finely dispersed by vigorous stirring at 40 C under nitrogen.

In all experiments lard (100 g) was randomized in a glass flask under nitrogen with a suspension of Na-K alloy (0.2% w/w) in xylene at 70-80 C by vigorous stirring until a dark brown coloration appeared. Samples (1 ml) were transferred into test tubes and set aside without stirring for different periods of time at definite constant temperatures in a thermostated water bath. Then each charge was immediately treated with diluted aqueous acetic acid solution (6% w/w) to destroy the catalyst, dissolved in ether, washed and dried.

Preparative thin layer chromatographic (TLC) plates (20 x 20 cm) coated 0.5 mm thick with silica gel G were used to purify the TGs. This was accomplished with ca. 50 mg of sample in heptane streaked as a 19 cm long band and developed with petroleum ether/acetone 100:8 v/v as described (18). A 0.5% solution in heptane was prepared with the pure TGs which was used for quantitative analysis of the TG groups with different number of double bonds by a TLC method (20) using a Carl Zeiss Densitometer (Model ERI 65 m, Jena, GDR). The results of triplicate analyses are reported. Analogous method of TLC analysis of the methyl ester groups, which will be published elsewhere, was applied for control of the TG determinations by comparing the calculated and directly found methyl esters. The latter were prepared after Hartman et al. (21). The method of Jasperson et al. (22) was applied for differential dilatometry.

RESULTS AND DISCUSSION

The directed interesterification was studied on lard with the following fatty acid composition (in rel. wt %): 14:0

TABLE I

Triglyceride Group Composition of the Final Products

Sample	Conditions of directed interesterification	Relative % by wt[a]					
		M_2D[b]	SMD[c]	M_3[d]	SM_2	S_2M	S_3
1A	Natural lard	6.8	15.9	16.8[d]	30.8	23.5	3.7
1B	Randomized lard (70 C)	7.9	13.0	12.6	29.0	26.0	8.0
2	Isothermal (38 C) for S_3, 5 days	7.5	9.4	17.5	21.0	19.0	18.5
3	Isothermal (28 C) for S_3, 3 days	10.1	7.4	16.3	19.0	18.1	24.1
4	Isothermal (20 C) for S_3, 3 days	8.3	9.2	16.3	19.8	21.4	19.8
5	Stepwise[e] (38, 28, 20 C) for S_3, 24 hours	9.7	6.7	19.5	14.9	15.0	27.0
6	Isothermal (10 C) for S_2U, 5 days	12.7	5.9	19.4	14.0	27.0	16.0
7	Isothermal (0 C) for S_2U, 12 days	11.4	8.0	19.7	18.4	32.8	7.6

[a]Small amounts of linoleic acid containing TG groups, varying from 2.2 to 7.1%, are not included, but are taken into account.

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

[c]The order of the letters is not concerned with positional isomers.

[d]The sum of M_3 and S_2D (9.7 and 7.1%, respectively in natural lard), the latter greatly decreasing during the process.

[e]See Figure 2.

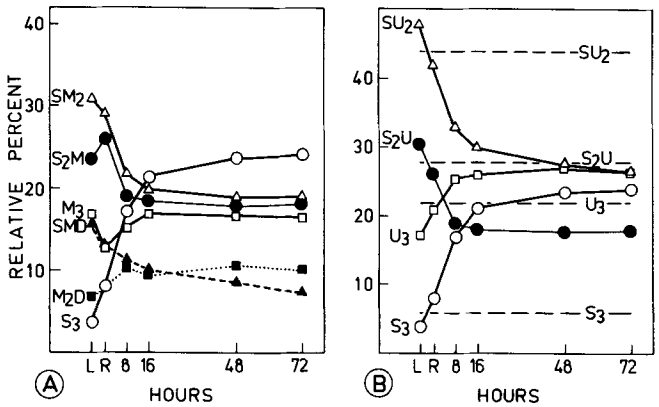

FIG. 1. Changes in triglyceride composition of lard during isothermal, directed interesterification at 28 C: A. Triglyceride groups – S saturated, M monoene, and S diene acyls; B. Triglyceride types – S saturated, and U unsaturated acyls.

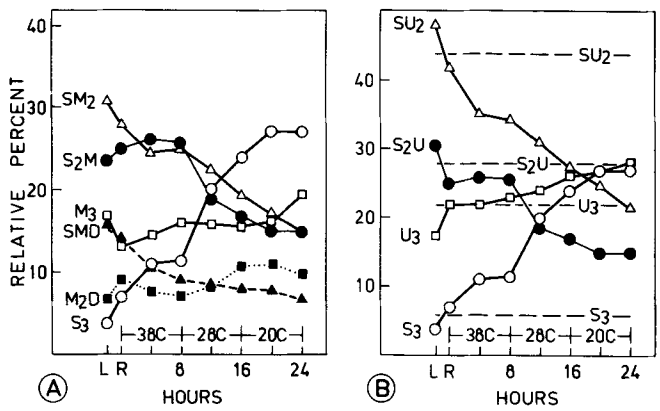

FIG. 2. Changes in triglyceride group (A) and type (B) composition of lard during directed interesterification with a stepwise temperature schedule.

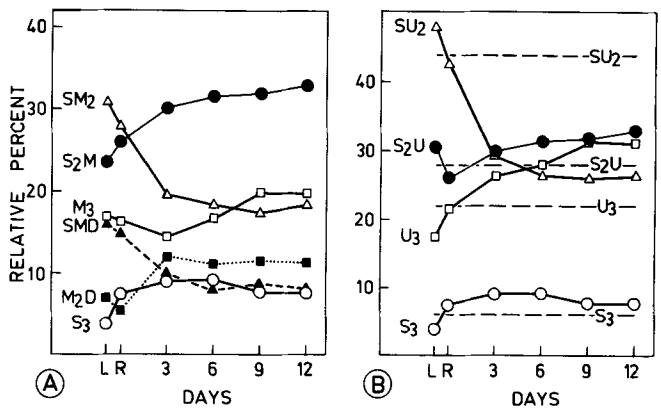

FIG. 3. Changes in triglyceride group (A) and type (B) composition of lard during isothermal directed interesterification at 0 C towards enrichment of S_2M molecules.

1.3, 16:0 22.9, 17:0 0.3, 18:0 13.3, 20:0 0.9, 16:1 1.8, 17:1 0.2, 18:1 46.1, 18:2 13.1, 18:3 0.2, or saturated (S) 38.7, monoenoic (M) 48.1 and dienoic (D) 13.1. Its TG group composition is presented in Table I. The groups MD_2 and S_2D were neglected.

Two sets of experiments were carried out in order to observe the formation of trisaturated (S_3) and disaturated (S_2U) TGs, respectively. The alteration of six TG groups was followed in each case in the temperature range of 0 to 38 C. It was of interest to find conditions for maximum formation of these TGs in as short as possible a period of time. In this respect, the recommendation of Eckey (1) for a step-wise reduction of temperature was taken into account. However, for this purpose it was necessary to know the intervals at which to change the temperature. This problem was solved by first studying the isothermal directed interesterification at 38, 28, and 20 C during sufficiently long periods. The TG group composition of the final products is shown in Table I.

The curves for the isothermal changes of each group against time are of the same kind and are best illustrated by the experiment at 28 C as shown in Fig. 1,A. The random composition obtained at 70 C and denoted by R on the abscissa (Table I, 1B) is close to that of natural lard (point L). It is almost equal to that recently reported by Peredi et al. (23). At that moment the sample is immediately chilled at 28 C and crystallization of S_3 begins. In 16 hours this group reaches ca. 21%. At the same time a statistical redistribution of the fatty acids is caused by the decrease of saturated acid content in the liquid phase. This is clearly seen from the curves of the other five TG groups. After 72 hours an equilibrium between the solid and liquid phases occurs. As a result directed interesterification practically stops. The main sources for the formation of S_3 are the S-containing TG groups, namely SMD, SM_2, and especially S_2M and S_2D, the contents of which decrease. In accordance with the theory, the amounts of M_2D and M_3 gradually increase.

This is more clearly illustrated in Figure 1,B where the changes of the four TG types are plotted. They are recalculated by summing the respective TG groups in A of the same Figure. The chance levels of the TG types for 39% of saturated fatty acids in lard are found from the theoretical statistical diagram of the types (24). They are represented in Fig. 1,B as dotted straight lines parallel to the abscissa. The deviations of S_3 and SU_2 from their random values is greater than those of S_2U and U_3. Irrespective of the greater quantity of unsaturated acids in lard, the triunsaturated glycerides U_3 were not the predominating type of the product as was expected. This was observed in all the experiments in this study. The same curves show that the deviations of this type are in the opposite directions to those observed in one phase interesterification (18).

The TG groups M_2D, SD_2 and eventually D_3 were not included in the analysis. Their total amount in lard was 2.5% which increased during the reaction to some extent but did not exceed 7%. However, their sum as found from their peaks on the densitogram was taken into account when calculating the relative percentages of the other six TG groups. Thus, the difference from 100 in the reported figures is due to the former TGs. Since their composition was not accurately known, some differences were observed between the fatty acid composition calculated from the TGs and that found directly by TLC analysis of the methyl esters. These differences, however, were not as high as to require a substantial correction of the data reported here.

Analogous results were obtained by the isothermally directed interestierification of lard at 38 C (Table I). At this temperature the amount of S_3 increased to ca. 18% in 5 days without any crystallization of S_2M. This shows that in spite of the high activity of the catalyst at 38 C the process is governed in this case almost exclusively by the rate of crystallization of S_3. However, this temperature is too high to obtain more crystals of these TGs.

Two factors suppress the rate of isothermal directed interesterification of lard at 20 C towards formation of S_3: (a) the catalyst activity is lowered, and (b) part of S_2M glycerides leave the reaction area. Thus, at 20 C in 16 hr, 12% S_3 and 24% of S_2M were obtained as compared with 21% and 18%, respectively, for the same period of time at

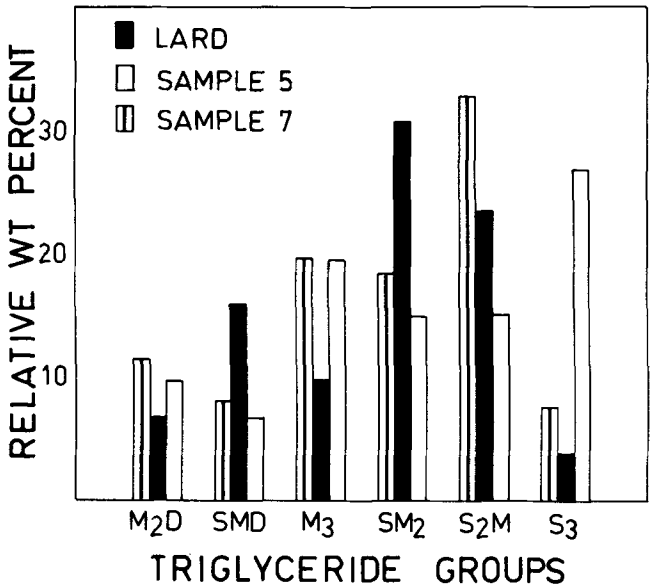

FIG. 4. Overall changes in the triglyceride group composition of directed interesterified products as compared with lard.

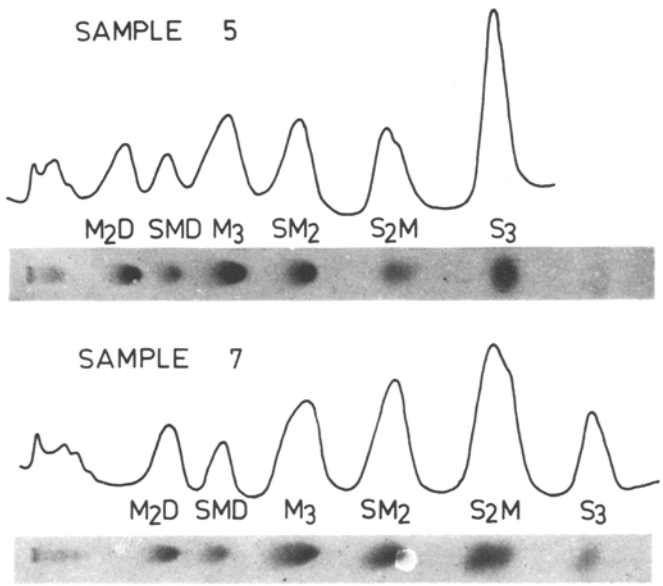

FIG. 5. Examples of the original thin layer chromatograms and the respective densitograms for the triglyceride group analysis.

28 C. Consequently, 20 C is not a suitable temperature for fats with comparatively high saturated acid content (16) as shown in Table I, sample 4.

Using the data from the isothermal interesterification, a stepwise reduction of temperature was examined following the schedule presented in Fig. 2. This changes the character of the curves. Actually, each curve is now composed of threee separate isothermal sections corresponding to the respective temperatures. This is best seen for the S_3 group curve. The final product (Table I, sample 5) contains the maximum proportion of 27% S_3 reached in ca. 24 hr.

The accelerating effect of the stepwise temperature reduction as recommended by Eckey (2) can be explained by the gradual disappearance of the saturated fatty acids from the liquid reaction area. When their concentration is considerable, then higher temperatures are needed to suppress the crystallization of S_2M group and to enrich the solid phase with S_3 group. On the other hand, when the concentration of S_2M is lowered in a liquid phase with low saturated acid content, then this phase is not saturated with respect to S_2M group at 20 C due to the solubility of the latter group. This circumstance favors the crystallization of the newly formed least soluble S_3 molecules from the liquid phase. This conclusion was confirmed by the curves of Figure 2,A,B for the 20 C interval. Under this condition the amounts of S_2M and SM_2 groups gradually decrease to 15% each. Briefly said, the stepwise temperature reduction favors directed interesterification towards S_3 group because the S_2M molecules remain mainly in the liquid phase.

If the curves of Fig. 2 are examined carefully, it can be noticed that the same final composition of directed interesterified lard can be reached in a shorter period of time. Thus, Fig. 1 clearly shows that 28 C is a more suitable temperature than 38 C for starting crystallization. This was proved to be valid by the results of an experiment conducted according to the temperature schedule of 8 hr at 28 C and 8 hr at 20 C. In this way a product with almost the same TG composition as that of sample 5 (Table I) was obtained in 16 hr only.

A second set of experiments was carried out to direct the rearrangement of lard towards formation of S_2M glycerides. When the process was conducted isothermally at 10 C, only a slight increase of S_2M group occured, as shown in Table I, sample 6, while at the same time the content of S_3 increase to 16%. Therefore, it was possible to suppress the formation of greater quantities of the latter at not higher than 0 C. Figure 3,A and Table I, sample 7, clearly show the increase of S_2M. These molecules are mainly formed from SM_2 and SMD while the proportion of S_3 remains at almost constant level. However, about 12 days were needed to reach the above composition. This is due to a significant decrease in catalyst activity at 0 C.

The TG composition of the most important products in this study is compared for the sake of clarity with that of lard in the diagram of Fig. 4. The overall change is quite clearly shown from these profiles. In all the experiments, the percent of M_3 remains almost constant in spite of the total increase of the triunsaturated type U_3. This is due to the presence of linoleic acid (D). Since its concentration in the liquid phase gradually increases, this acid recombines

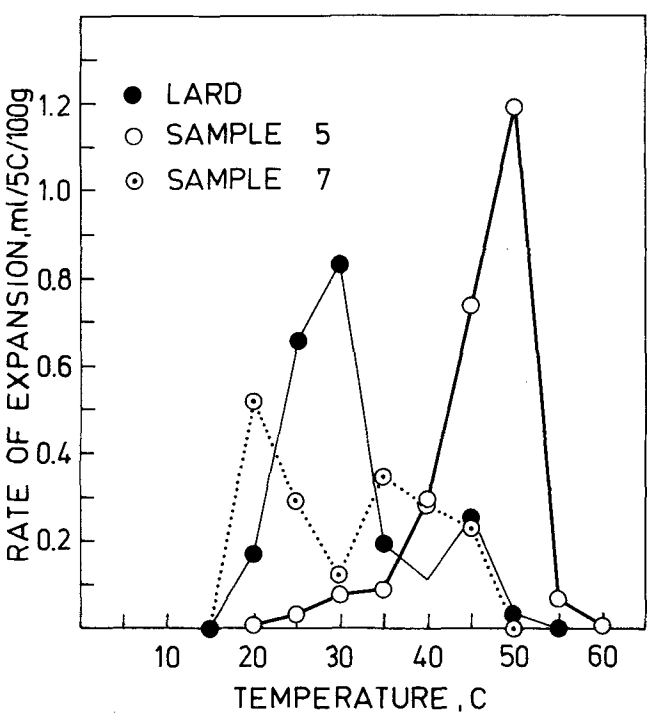

FIG. 6. Comparison between the differential dilatation curves of the initial lard and its directed interesterified products.

into mixed TGs with oleic acid (M) as MD_2 and M_2D groups of U_3 type. It is illustrated by the M_2D increase in the diagram. If this acid is present in negligible amounts of a fat, say beef tallow, then a greater enrichment in M_3 molecules may be expected.

Original thin layer chromatograms and the respective densitograms of the same products are given in Fig. 5 in order to illustrate the method used. The small amounts of linoleic acid containing TGs near the start line were not included in the above study. The S_2M group is partially separated into positional isomers. The smaller peak of these corresponds to the symmetrical TGs of SMS.

The differential dilatation curves of the same lard products are compared with that of the initial lard in Fig. 6. They can be considered in connection with the overall change of the TG composition presented in Fig. 4. These alterations towards higher melting TGs are responsible for shifting the melting range of the products to higher temperatures.

With the aid of the above analytical approach for a more detailed study on directed interesterification of fats, it became possible to experimentally confirm any conclusions of other workers in this area. The results presented here for lard can be of some use by analogy for studying this process for other fats and oils.

REFERENCES

1. Eckey, E.W., Ind. Eng. Chem. 48:1183 (1948).
2. Eckey, E.W., U.S. Pat. 2,442,531, 1948.
3. Eckey, E.W., U.S. Pat. 2,442,532, 1948.
4. Hawley, H.K., and G.W. Holman, JAOCS 33:29 (1956).
5. Placek, G., and G.W. Holman, Ind. Eng. Chem. 49:162 (1957).
6. Martin, D., Grasas Aceites (Sevile) 17:177 (1966).
7. Eckey, E.W., U.S. Pat. 2,442,536, 1948.
8. Martin, D., Grasas Aceites (Sevile) 18:20 (1967).
9. Eckey, E.W., U.S. Pat. 2,442,533, 1948.
10. Eckey, E.W., U.S. Pat. 2,442,535, 1948.
11. Abbott, A.D., U.S. Pat, 2,442,538, 1948.
12. Anon., Fette Seifen Anstrichm. 75:467,587,663 (1973).
13. Duterte, R., Rev. Fr. Corps Gras. 23:547 (1976).
14. Rost, H.E., Fette Seifen Anstrichm. 62:1078 (1960).
15. Amat Guerri, F., and R.M. Utrilla, Grasas Aceites (Sevile) 23:117 (1972).
16. Kattenberg, H.R., Fette Seifen Anstrichm. 76:79 (1974).
17. Neito, F.J., and A. Madarro, Grasas Aceites (Sevile) 28:409 (1977).
18. Chobanov, D., and R. Chobanova, JAOCS 54:47 (1977).
19. Gilman, H., and R.V. Young, J. Org. Chem. 1:315 (1936).
20. Chobanov, D., R. Tarandjiska, and R. Chobanova, JOACS 53:48 (1976).
21. Hartman, L., and R.C.A. Lago, Lab. Pract. 22:475 (1973).
22. Jasperson, K.S., and A.A. McKerrigan, J. Sci. Food Agric. 8:46 (1957).
23. Perédi, J., M. Szungyi, and M. Jeránek, Olaj, Szappan, Kosmetika, 26:11 (1977).
24. Markley, K.S., "Fatty Acids," Part 2, Interscience Publishers Inc., New York, 1961, p. 895.

[Received September, 7, 1978]