Effect of Catalytic Treatment with Sodium Methylate on Glycerine Composition and Properties of Lard and Tallow[1]

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THE APPLICATION of interesterification reactions to triglycerides was first described in 1924 by Van Loon (24). The following year Norman (16) and Grün (9) published further observations on this type of reaction. Thus it was early recognized that the physical character of a fat could be altered by a reshuffling or rearrangement of the fatty acids on the glyceride molecules. The rearrangement, as carried out by the early investigators, required extremes of time and temperature and was often accompanied by breakdown of the treated fat. Since that time many patents and publications have appeared which describe more favorable conditions and improved catalysts. The later contributions of Van Loon (25), Gooding (8), Eckey (4, 5), Bailey (1), and Vander Wal (23) typify the advances in this field.

In the absence of a catalyst, rearrangement occurs slowly, requiring more than 8 hours at 270°C. to reach equilibrium for a mixture of beef stearine and soybean oil (25). The addition of certain catalysts greatly reduces the time required and permits the use of much lower temperatures. Tin, stannous hydroxide, and sodium ethylate were originally proposed as effective catalysts by Van Loon (24). Desnuelle and Naudet (3) reported that sodium methylate was more active than sodium ethylate, tin, or powdered zinc and that temperatures of 200°C. or slightly less could be used successfully. Eckey (4) later showed however that alkali metal alkoxides are effective catalysts even at 50°C. when dispersed rapidly through dry neutral glycerides. Based on changes in amounts of trisaturated glycerides produced in the treatment, his evidence indicated that extensive randomization of the glycerides' structures had occurred. Evidence for randomization had previously been presented by Naudet and Desnuelle (15) and Norris and Mattil (17) under other conditions of treatment.

The recent applications of ester interchange reactions to natural fats have been evaluated largely on the basis of changes in physical properties. For example, Vander Wal (23) described a process for treating lard with sodium methylate to produce a product with creaming properties far superior to those of the original lard as judged by cake volume studies. Bailey (1) utilized a rearrangement process to change the crystal habit of lard, thus improving the fat for baking purposes. Hoerr *et al.* (12) have shown that rearranged lard differs from ordinary lard not only in cake-making properties but also in X-ray diffraction spectra and in microscopic appearance of the crystallized fat.

Aside from its value in improving the physical character of certain fats, rearrangement is also of interest in connection with attempts to answer the controversial question of pattern of glyceride distribution in natural fats. Riemenschneider *et al.* (21) recognized that the glyceride distribution in lard was significantly different from random but thought these differences could be attributed to metabolic changes occurring after the glycerides were formed and suggested that the formation (synthesis) by the animal probably followed a random pattern. In later work (14) by two independent methods they confirmed the finding that lard glycerides are non-random in character. In this same report however there was evidence that some fats may have a random pattern. Chicken fat, for example, based on percentage composition of the four principal types of glycerides, conformed to a random pattern. Norris and Mattil (17), on the other hand, concluded that animal fats, unlike seed fats, have a random pattern of glyceride distribution. Eckey (4) has shown that beef tallow, unlike lard, is almost unchanged by catalytic interesterification treatment with sodium methylate and attributed this to the already random nature of the fat. Quimby *et al.* (20) however, from fractional crystallization, X-ray, and thermal data on lard, tallow, and mutton fat, concluded that animal fats are non-random in glyceride distribution.

The present paper is a report on the glyceride compositions and properties of a lard and an edible beef tallow before and after treatment with sodium methylate under mild conditions. The term "rearranged" in this paper is used in its broadest sense to include any type of "reshuffling" of fatty acids either within the same glyceride molecule or between different molecules and any configurational changes which at present may not be well defined.

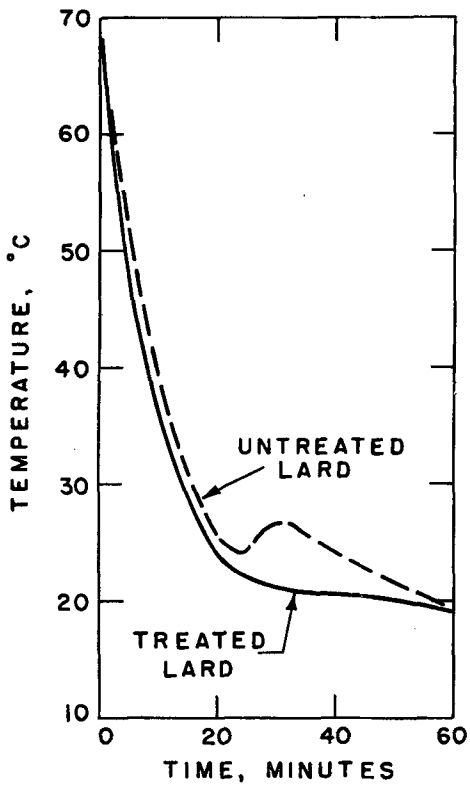

FIG. 1. Cooling curves. Untreated and treated lards.

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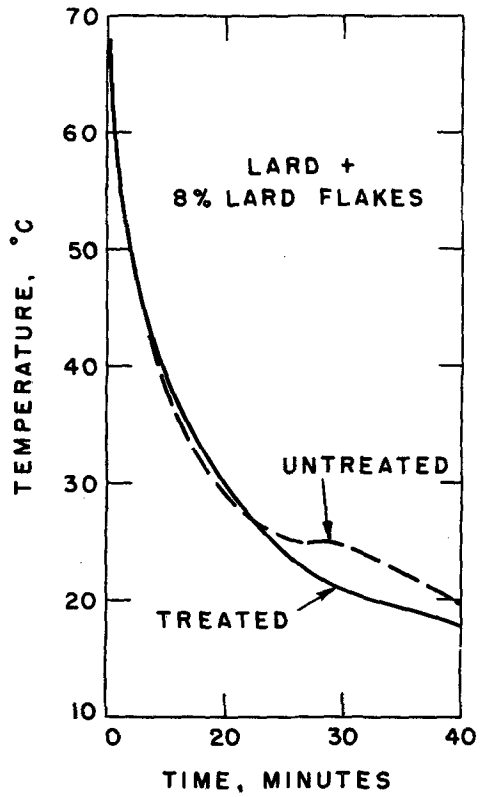

FIG. 2. Cooling curves. Untreated and treated lards plus 8% lard flakes.

Experimental

A commercial, steam-rendered lard of high quality was used in this investigation. The lard was composed of 25% killing fats and 75% cutting fats. The tallow was rendered in the laboratory from fresh edible beef ruffle tissue.

Catalytic Treatment. The catalytic treatment was carried out in a 2-l., 3-neck round-bottom, glass flask, equipped with standard taper joints, a stirrer, thermometer, gas inlet and outlet tubes for nitrogen, and an inlet for admitting catalyst. The fats were thoroughly dried by heating under vacuum at 95°C. under a stream of purified nitrogen.

Approximately 600 g. of the dried fat were introduced into the flask, nitrogen was passed through, and the fat was heated with stirring to 55°C. The catalyst in the form of finely divided sodium methylate 0.5% was added while the fat was being vigorously stirred. Stirring was continued at this temperature for 1 hr., following which a small quantity of water (11 ml.) was added to the reaction. The temperature of the mixture was increased to 70°C., and the contents of the flask were then filtered through a Buchner funnel containing a bed of filter-aid, ¼ in. in thickness. The filtered fat was then redried at 95° C. in a stream of nitrogen at a pressure of approximately 5 mm. Hg. Deodorization of a 235-g. sample of such rearranged lard at 170°C. for 2 hrs. at 1 mm. of Hg. pressure, yielded only 0.12 g. of ethyl ether-soluble material in the dry ice trap. The free fatty acid content of the material was equal to 11% as oleic acid.

Analytical Characteristics. Values for the iodine number, saponification equivalent, hydroxyl values, capillary melting points, and Wiley melting points were obtained by official A.O.C.S. methods.

The fats were analyzed for monoglyceride content by the modified periodic acid method of Pohle and Mehlenbacher (19).

Consistency numbers were obtained by using an apparatus and procedure similar to that described by Harrington (10). However, for the beef tallow, the cooling bath was maintained at 20°C. instead of the usual 11°C.

Fatty Acid Composition. The content of polyunsaturated acids of the lard and of the tallow, before and after treatment, was determined spectrophotometrically by the method of Herb and Riemenschneider (11). The oleic acid content was calculated from the spectrophotometric data and the iodine value. No significant changes in fatty acid composition were produced in either the lard or tallow by the sodium methylate treatment. The fatty acid composition of the lard was typical of those reported in the literature, having 37.8% of saturated acids and 62.2% of unsaturated acids (50.2% oleic, 10.9% linoleic, 0.8% linolenic, 0.3% arachidonic, and 0.1% pentaenoic acids). The tallow consisted of 59.4% saturated acids and 40.6% unsaturated acids (38.0% oleic, 2.0% linoleic, and 0.6% linolenic acids).

Glyceride Composition. The glyceride compositions of the treated and untreated fats were estimated by Kartha's acetone-permanganate method (13). The percentages of trisaturated glycerides were determined by an independent crystallization method (14).

Penetration Data. The penetration values were obtained over a range of temperatures by the method of Feuge and Bailey (6).

Dilatometric Data. The dilatometric measurements were made with dilatometers of the type described

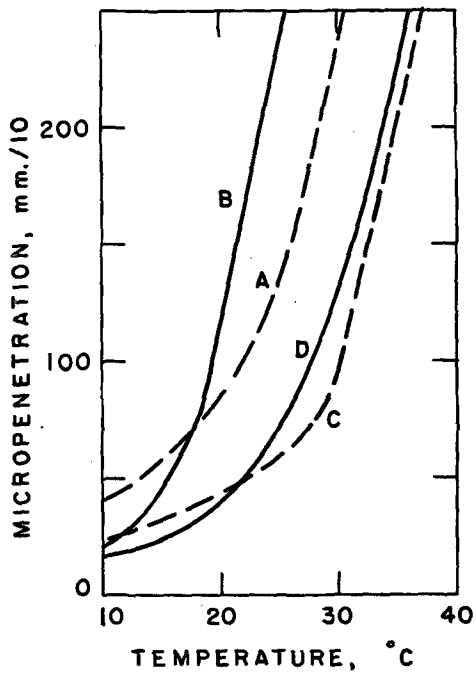

FIG. 3. Micropenetration curves. Untreated and treated lards with and without lard flakes.
A—Untreated lard.
B—Treated lard.
C—Untreated lard + 8% lard flakes.
D—Treated lard + 8% lard flakes.

by Schroeder (22). The percentage of solids in the fats were calculated from these data according to the method of Fulton *et al.* (7).

Cooling Curves. The cooling curves of the original and treated fats were obtained by recording temperature and time when 20-g. samples of the melted fats (70°C.) were cooled in air at 15.0°C. without stirring.

TABLE I

Analytical Characteristics of Lard and Tallow Before and After Treatment with Sodium Methylate

	Lard		Tallow	
	Untreated	Treated	Untreated	Treated
Iodine Number	66.0	64.9	37.8	37.6
Sapon. Equivalent	287.1	284.8	284.2	286.7
% Monoglycerides	0.9	2.0	1.2	0.9
Hydroxyl Value	4.1	4.6	3.5	12.1
Capillary M.P. °C.	35.2–38.8	36.0–37.8	46.0–48.4	46.0–48.5
Wiley M.P. °C.	36.7	37.8	47.4	47.4

Results and Discussion

The iodine values, saponification equivalents, hydroxyl values, percentages of monoglycerides, and melting points (Table I) show no significant difference between the treated and untreated fats. The treated tallow had a higher hydroxyl value than the untreated, but this does not show up in an increase in monoglycerides.

The consistency numbers (Table II) show that the physical character of lard was greatly changed by the treatment. The addition of lard flakes to "rearranged" lard produced a much greater change in this measurement than did similar addition to untreated lard. The tallow appeared to be unaffected by the sodium methylate treatment. Consistency numbers, although strictly empirical, are obtained under carefully controlled conditions of cooling and mixing and are readily reproducible for a given sample of fat. Hence the difference in values for the treated and untreated lard undoubtedly reflects considerable changes in glyceride structures or composition.

TABLE II

Effect of Sodium Methylate Treatment on Consistency Numbers of Lard and Tallow

Substrate	"C" No. (°C.)
Untreated Lard	17.2
Untreated Lard + 8% Lard Flakes	24.8
Treated Lard	12.1
Treated Lard + 8% Lard Flakes	30.4
Untreated Tallow	33.6
Treated Tallow	33.4

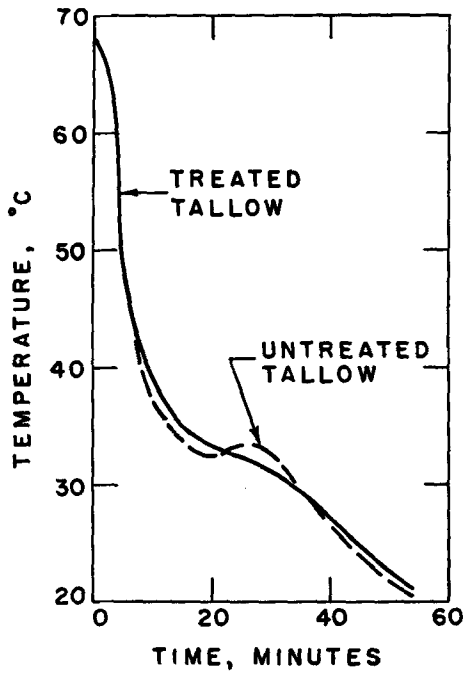

FIG. 4. Cooling curves. Untreated and treated tallows.

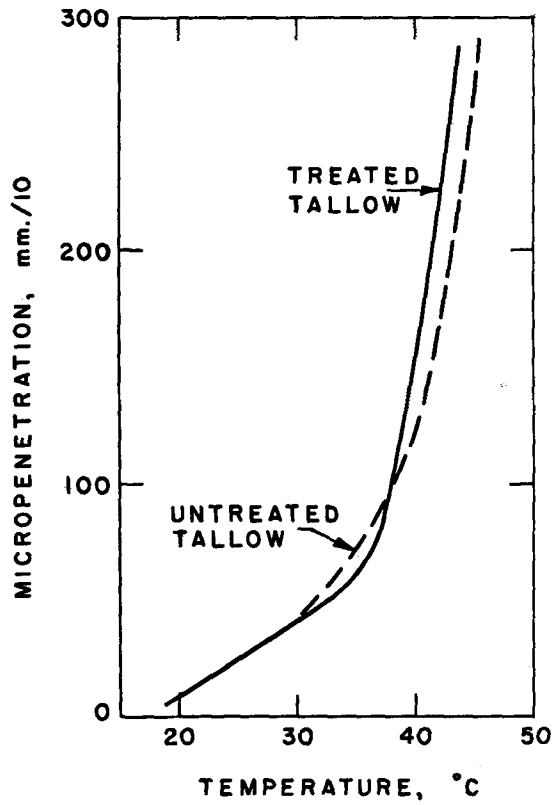

FIG. 5. Micropenetration curves. Untreated and treated tallows.

The glyceride compositions of the untreated and treated fats in terms of the four types as found experimentally are shown in Table III along with values calculated for random distribution. The composition of the untreated lard is significantly different from random whereas the treated lard shows that extensive interchange of fatty acids has taken place. The glyceride compositions determined for tallow and treated tallow however are probably not significantly different. The values calculated for random distri-

TABLE III

Glyceride Compositions of Lard and Tallow (% mol) before and after Treatment with Sodium Methylate

	GS_2	GS_2U	GSU_2	GU_3
Lard				
Untreated	2.9	25.3	53.3	18.5
Treated	4.3	27.3	45.5	22.9
Random[a]	5.3	26.5	43.9	24.3
Tallow				
Untreated	18.2	46.6	30.3	4.9
Treated	18.5	48.4	28.0	5.1
Random[b]	21.4	43.1	29.0	6.5

[a] Saturated Acid Content, 37.65% (mol) used in calculation of random distribution.
[b] Saturated Acid Content, 59.75% (mol) used in calculation of random distribution.

bution are in reasonably good agreement with those found experimentally. It should be pointed out that the determination of the four types of glycerides does not take into account the actual position a given fatty acid occupies on the glyceride molecule, as discussed by Quimby *et al.* (20).

The percentages of solid glycerides estimated from dilatometric measurements (Table IV) show further evidence of the effect of the sodium methylate treatment on lard. The lard containing lard flakes showed little difference in content of solids above 30°C., but below that temperature the effect of the treatment was still considerable. Tallow did not show any appreciable change.

Cooling curves and micropenetration measurements (Figures 1-5) present additional evidence of change in character of lard. A slight but apparently significant change in tallow was observed in the cooling curves. Despite the apparent increase in solid glyceride content of treated lard at 30°C. or higher temperatures (Table IV), the micropenetrations were

TABLE IV

Dilatometric Data—Estimated Percentages of Solids in Lard and Tallow before and after Treatment with Sodium Methylate

Temp. °C.	Lard				Tallow	
	Untreated	Treated	Untreated + 8% lard flakes	Treated + 8% lard flakes	Untreated	Treated
10	27.0	28.7	33.6	31.9	58.0	57.1
15	24.2	21.3	31.1	27.6	56.7	55.9
20	20.4	14.2	27.7	22.7	51.6	50.0
25	14.3	12.5	22.4	19.1	43.6	43.1
30	4.2	9.5	15.1	16.4	34.6	34.7
35	3.0	6.7	14.0	14.2	26.7	26.7
40	1.6	3.4	12.0	11.6	19.1	18.4
45	0.0	2.0	7.7	6.9	9.4	8.8
50	....	....	0.2	0.2	....	....

greater at these temperatures than those for the untreated lard (Figure 3). The addition of lard flakes greatly lessened the differences in micropenetrations between the treated and untreated lard.

Cake volume tests were conducted with the lard and treated lard to which 8% lard flakes had been added. In a typical test with pound cake formulation the treated lard yielded a cake volume of 225 cc. per 100 g. of cake compared to 190 cc. per 100 g. of cake for the untreated.

Summary

Treatment of lard with sodium methylate did not affect fatty acid composition nor the usual chemical constants and melting points. The glyceride composition however was altered considerably and showed close agreement with values calculated for random distribution. This change in glyceride composition was accompanied by significant changes in physical character as shown by consistency numbers, dilatometric and micropenetration measurements, and cooling curves.

Beef tallow remained almost unaffected by the sodium methylate treatment. The glyceride composition before and after treatment as determined by Kartha's method agreed well with values calculated for random distribution. Only the cooling curves indicated any change induced by the treatment.

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An Investigation of the Oil of Laemonema Morosum Matsubara. I. Research on the Docosenol Fraction

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THE FISH *Laemonema Morosum* Matsubara is native to the Pacific ocean near the northern part of Japan and is caught by a depth drag-net at 300–350 m. below the surface in deep sea areas. The flesh of this fish is used as food, and the oil is used in the leather industry. In this investigation it was found that the oil of this fish contains a large amount of unsaponifiable matter, consisting of the esters of higher alcohols and fatty acids instead of glycerides. Except for toothed whale oil, such an animal oil has not been reported before. The main component of the unsaponifiable matter of this oil is a new alcohol, 11-docosen-1-ol. Toyama has reported (6) the existence of docosenol in the oil of a bottle nose whale, but the structure of this alcohol was not determined because its content was very small. The docosenol in whale oil is liquid at room temperature while 11-docosen-1-ol is solid, m.p. 31.5–32.1°C. In the vegetable kingdom the existence of 13-docosen-1-ol has been confirmed in the seed wax of *simmondsia californica* (1).