acetone, and dried. Care was taken to prevent acetone entering the flask. Thus, the glycol in the boiling flask could be used for several analyses simply by adding 10 g additional 40% NaOH for each succeeding test.

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Preparation of Glycerides by Controlled Esterification[1]

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Abstract

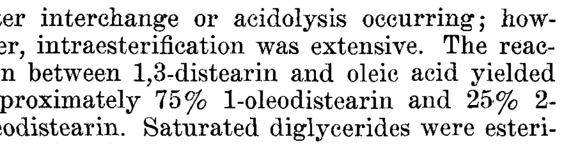
A simple procedure for esterifying glycerides without interesterification occurring would be highly useful for preparing on a large scale a number of tailor-made fats, including cocoa butter-like fats. Such esterifications were carried out by employing *p*-toluenesulfonic acid as catalyst and continuously removing the water of esterification by azeotropic distillation with aliphatic hydrocarbons or by stripping with vaporized hydrocarbons. Even though *p*-toluenesulfonic acid rapidly disproportionated 1-monostearin, even at 120C, apparently esterification was faster and only a moderate amount of ester-ester interchange and acidolysis occurred. Diacid glycerides might be prepared from monoglycerides by the procedure which was employed. Saturated diglycerides were esterified with oleic acid with little ester-ester interchange or acidolysis occurring; however, intraesterification was extensive. The reaction between 1,3-distearin and oleic acid yielded approximately 75% 1-oleodistearin and 25% 2-oleodistearin. Saturated diglycerides were esterified wtih sebacic acid, again with little or no interesterification occurring.

Introduction

VARIOUS FAT and fat-type products which are actually or potentially of considerable economic importance cannot be produced readily on a large scale. Cocoa butter-like fats belong in this category. Much effort has been devoted by research workers toward devising a process for making a fat product resembling closely the mixture of 2-oleodisaturated glycerides of palmitic and stearic acids predominating in cocoa butter. The problem of preparing by a simple procedure a di- or triacid triglyceride of reasonably high purity has not been solved satisfactorily.

In this laboratory a series of dibasic acid-containing glycerides as exemplified by

BIS/1-(STEAROYLOXYMETHYL)-2-(STEAROYLOXY)ETHYL/ADIPATE,



have been prepared and found to have potentially useful properties (9,10,25). The compounds cannot be readily prepared on a large scale by presently available processes.

A number of other new-type fat products, including the acetoglycerides (8), could be mentioned as examples of products whose preparation by a simplified procedure would be desirable.

A survey of the literature reveals that the catalysts commonly used to promote esterification also promote one or more types of interesterification, which includes acidolysis, alcoholysis, and ester interchange (2,18).

Various metals or compounds of these metals have been claimed to be esterification catalysts. Stannous chloride and zinc chloride have been found to be particularly effective (7). Again many of these compounds have been found to promote interesterifications.

Hydrochloric, sulfuric, and sulfonic acids are among the most widely used esterification catalysts, but they also are recognized as alcoholysis and ester interchange catalysts. Van Loon (24) patented the use of aromatic sulfonic acids to bring about ester interchange in triglyceride mixtures. Normann (20) carried out an ester interchange between tristearin and coconut oil by adding 1% of β-naphthalenesulfonic acid and heating the mixture for 2.5 hr at 250C.

Despite the evidence that esterification is accompanied by interesterification, and that some catalysts are good for both types of reactions, there are indications that esterification without interesterification should be possible. Even though acid catalysts are used in interesterification reactions, their activity is far below that of equivalent amounts of sodium alkoxides, at least in some systems. The methanolysis of a highly refined vegetable oil in boiling methanol under anhydrous conditions has been found by the authors to proceed quite slowly in the presence of small amounts of anhydrous hydrochloric or sulfuric acids. Presumably when interesterification occurs in some acid-catalyzed esterifications, it is caused by the water which is formed. Water in small amounts is a good interesterification catalyst (22). By continuously distilling water and some acetic acid out of the reacting mixture Grummitt and Fleming (12) succeeded in repressing the hydrolysis of castor oil during acetylation with acetic acid in the presence of *p*-toluenesulfonic acid.

While evidence is available that strong acids are generally poor interesterification catalysts and that triglycerides in the absence of water are relatively unaffected by such acids, it has not been shown heretofore that acid-catalyzed esterifications of mono- and

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diglycerides can be carried out without substantial interesterification occurring. Mono- and diglycerides are much more reactive than triglycerides. Some ester interchange reactions have been shown to be greatly assisted by the presence of small amounts of mono- and diglycerides or free glycerol (11).

The objective of the present report is to show how well interesterification can be repressed during the esterification of mono- and diglycerides when an acid or acid-type catalyst is employed and the water formed during the reaction is removed continuously.

Procedure and Discussion

Fatty Materials

The oleic acid employed was derived from olive oil by way of methanolysis, fractional crystallization of the methyl esters essentially according to the procedure of Wheeler and Riemenschneider (26), saponification under mild conditions, and acidulation. The final oleic acid had an iodine value (I.V.) of 91.5 and an acid value of 195.6. It contained 3.04% linoleic acid, 0.41% linolenic acid, and no *trans* isomers.

The technical grade oleic acid was purchased from Distillation Products Industries. The following fatty acids were present in the percentages indicated: oleic, 73.6; myristic, 3.8; palmitic, 3.7; pentadecanoic, 2.4; linoleic, 1.6; stearic, 0.5; and unidentified fatty acids, 13.8 by GLC analysis. The acid value was 207.6.

The sebacic acid was Eastman grade obtained from Distillation Products Industries (DPI).

The 1-monostearin was prepared by repeated fractional crystallization of molecularly distilled monoglycerides (Myverol 18-06, DPI) derived from complete hydrogenated soybean oil. The distilled monoglycerides were crystallized first from commercial hexane, then three times from 70% isopropyl alcohol, and then from commercial hexane. The ratio of solvent to monoglycerides was 6:1 by weight, based on the weight of the monoglycerides at the start of the series of crystallizations. All crystallizations were carried out by cooling the solutions to 25C. The final product contained 99.0% 1-monostearin, according to a periodic acid analysis, and had a melting point of 81.7C.

The mixed diglycerides of palmitic and stearic acids were obtained from DPI as molecularly distilled diglycerides prepared from completely hydrogenated lard. Before being used, the product was dissolved in hexane and washed with water to remove any free glycerol. The washed product analyzed:

Hydroxyl value	97.8
I.V.	0.5
Content of 1-monoglycerides, average molecular weight of 349.6	3.5%
Content of free fatty acids, average molecular weight of 275.5	2.3%
Average molecular weight of component fatty acids	275.5

Pure 1,3-distearin was synthesized by a modification of a procedure described by Porck and Craig (21). 1,3-Benzylideneglycerol was prepared according to Hibbert and Carter (13), except that the reaction product was fractionally crystallized at −20C from the dried solution of diethyl ether. The 1,3-benzylideneglycerol was converted into 1,3-benzylidene-2-benzylglycerol by the procedure Howe and Malkin (14) used to make 1,2-isopropylidene-3-benzylglycerol. The 2-benzylglycerol obtained on hydrolysis was acylated with stearoyl chloride in the presence of pyridine. The 1,3-stearoyl-3-benzyl-glycerol was dissolved in glacial acetic acid and hydrogenated at 50C with the aid of a palladium-on-carbon catalyst. After purification by fractional crystallization, first from chloroform and then from commercial hexane, the 1,3-distearin had a hydroxyl value of 88.8 and a melting point of 79.5C.

TABLE I

Effect of Catalysts on the Stability of Diglycerides and of 1-Monostearin in Mineral Spirits at 180C

Catalyst	1-Monostearin after 3 hr[a]		Diglycerides of palmitic and stearic acids after 4 hr[b]	
	Cat. concn,[c] %	1-Monostearin content, %	Cat. concn,[d] %	Hydroxyl value
None	0.0	37.5	0.00	92.6
Acetic anhydride	0.5	34.3	0.51	88.2
Phosphoric acid	0.5	22.7[e]	0.49	76.7
p-Toluenesulfonic acid	0.4	24.6	0.86	72.2
	0.4	6.3[f]	....	....
Stannous chloride dolydrate	0.5	33.6	1.13	64.9
Stannous stearate	....	....	3.43	62.2
Sodium hydroxide	....	....	0.20	49.8
Sulfuric acid	0.5	4.4[e]	0.49	23.6

Purity of 1-monostearin, 99.0%. Hydroxyl value of diglycerides, 97.8.

[a] Ratio of monostearin to solvent, 1:10 by wt.

[b] Ratio of diglycerides to solvent, 1:1.7 by wt.

[c] Calculated on monostearin basis.

[d] Equal to 0.005 mole per 100 g diglycerides.

[e] Gum formed in bottom of flask.

[f] No solvent used. Mixture flushed continuously with dry nitrogen.

Selection of Catalyst

The stabilities of 1-monostearin, and the diglycerides of palmitic and stearic acids in the presence of several catalysts, were determined. Dry nitrogen was blown through the solutions and reactants in mineral spirits (bp 200–210C) at the beginning and during the early stages of heating, so as to remove any traces of moisture. At the completion of the heating period the monostearin product was removed from the mineral spirits by low temperature crystallization and filtration, including a crystallization from hexane. The product then was dissolved in ethyl acetate and washed with water, or dilute acetic acid and water, to remove free glycerol and catalyst. After removal of the ethyl acetate, the content of 1-monostearin was determined with periodic acid.

In the case of the diglyceride experiments the solution of mineral spirits was washed to remove free glycerol and catalyst, and the mineral spirits were then removed by stripping with dry nitrogen while under a vacuum and at a low temperature.

As is evident from the data recorded in Table I, the 1-monostearin was unstable under all conditions. If the disproportionation had been merely an ester-ester interchange with all of the reactants remaining in solution at equilibrium, the 1-monostearin content should have been about 44% (6). Obviously, the insolubility of glycerol in mineral spirits and other factors were involved.

The diglycerides, on the other hand, were relatively stable, at least in the presence of the weaker acids.

Preliminary esterification experiments with stannous chloride indicated that this catalyst always promoted ester-ester interchange. While metal salt catalysis probably is similar to acid catalysis (5,23), differences were encountered. *p*-Toluenesulfonic acid was selected as the catalyst in the work which will be reported here.

Esterification of 1-Monostearin

Reactions between 1-monostearin and technical grade oleic acid were carried out at 100, 120, 150, and 200C. For each reaction the following proportions of materials were employed:

1-Monostearin	36.2 g
Technical grade oleic acid	59.4 g (10% excess)
p-Toluenesulfonic acid	0.39 g (0.4%)
Dry hexane	120 g/hr

The technical grade oleic acid was placed in the reaction flask immersed in a hot oil bath. With the hexane flowing at the proper rate into the bottom of the flask, vaporizing, passing through the oleic acid, and distilling off, the temperature of the oil bath was adjusted. Then the 1-monostearin was added and the temperature was adjusted to exactly that desired. Finally, the catalyst was added. Samples were withdrawn at given time intervals, quickly solidified, and later titrated for content of free fatty acids. These contents were corrected for the presence of *p*-toluenesulfonic acid. During one reaction samples also were withdrawn for a determination of monoglyceride content. Calculations made with data from these samples are recorded in Figure 1.

A portion of the reaction product obtained after 3 hr at 120C was washed with a solution of potassium hydroxide according to the Wesson loss procedure (15) to remove the free fatty acids as soaps, which were converted to methyl esters and analyzed by gas chromatography. According to these analyses, the 19.1% of free fatty acids in the reaction product consisted of 3.32% stearic acid from the 1-monostearin, and 15.78% fatty acids from the technical grade oleic acid. Subsequently, the Wesson procedure was found to either saponify a large proportion of any monoglycerides present or to force them into the aqueous phase. Therefore, at least a portion of the 3.32% of stearic acid which was found came from monostearin in the reaction product.

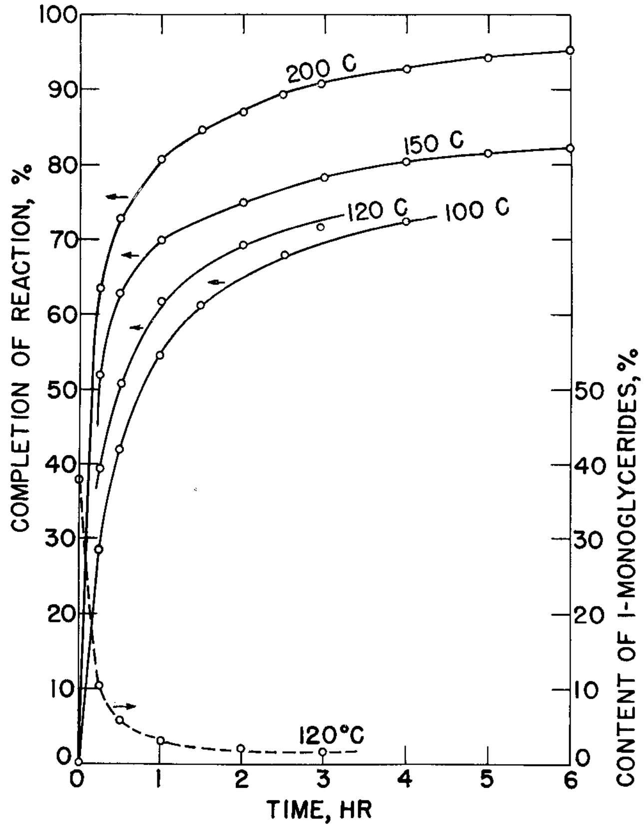

FIG. 1. Esterification of 1-monostearin with technical grade oleic acid (10% excess). Reaction catalyzed with *p*-toluenesulfonic acid (0.4%), and water removed continuously by stripping with vaporized hexane.

Free fatty acids were removed from portions of the reaction products obtained at 150C and 200C after 6 hr (Fig. 1). The acid-free glycerides in both instances melted at 45C.

A test of the stability of the 1-monostearin at 120C in the presence of *p*-toluenesulfonic acid was made. The apparatus and conditions employed in the esterifications with technical grade oleic acid were used, except that the addition of the technical grade oleic acid was omitted. Samples were withdrawn after 1 and 3 hr and without further purification were analyzed for content of 1-monostearin (1). That withdrawn after 1 hr contained 34.1% and that withdrawn after 3 hr, 28.7%.

On the basis of the data obtained, one can conclude that while 1-monostearin disproportionates rapidly in the presence of *p*-toluenesulfonic acid, probably to distearin by way of ester-ester interchange, esterification with oleic acid also is rapid. Apparently, the latter is the faster reaction because the glycerides which were obtained from two of the reaction products melted at 45C. This melting point is fairly close to that of 1-oleo-3-stearin (52C) and far from that of 1,3-distearin (79.5C).

During the esterification of 1-monostearin with oleic acid apparently some acidolysis occurred. The extent to which this acidolysis produced the effect of interesterification, that is, decreased the proportion of oleostearin and dioleostearin, has not been determined. Certainly acidolysis never came to an equilibrium based on the total amount of free and combined fatty acids.

One can conclude that the esterification of a monoglyceride with a fatty acid under the reported conditions should be suitable for making single acid and diacid diglycerides for technical use. For example, oleostearin produced by this procedure might be further esterified with palmitic acid, using a procedure to be described below to produce a cocoa butter-like fat.

Esterification of Saturated Diglycerides with Oleic Acid

Numerous experiments in esterifying oleic acid and the mixed diglycerides of palmitic and stearic acid were carried out. The most satisfactory procedure consisted of preparing a solution of diglycerides, oleic acid, and *p*-toluenesulfonic acid in mineral spirits and introducing this solution dropwise into the bottom of the reaction flask by means of a glass tube. The flask was kept at a temperature high enough to distill off mineral spirits continuously, but not high enough to remove all of it. At the end of the reaction period the reaction product was stripped with dry nitrogen.

The dropwise addition controlled the rate of esterification and provided a steady stripping action to remove water as it was formed. Also, with this procedure fresh catalyst was always being added, and the possibility of the catalyst vaporizing and thus being lost was minimized.

In one fairly typical esterification a solution containing the following proportions of materials was prepared:

Diglycerides of palmitic and stearic acids	60.0 g
Oleic acid (technical)	36.0 g (20% excess)
p-Toluenesulfonic acid	0.19 g (0.2%)
Dry mineral spirits (bp 200–210C)	900 g

TABLE II

Analysis of Product Obtained by Reaction Between Oleic Acid and Diglycerides of Palmitic and Stearic Acids[a]

Fraction	Yield, %	I.V.	Hydroxyl value	Free fatty acids,[b] %
Unfractionated product	100	32.5	14.0	10.1
Ppt from pet. ether at 25C	9.1	2.9	22.6	0.6
Ppt from ethanol at —17C	77.7	30.4	4.6	1.2
Filtrate from ethanol ppt	13.2	69.7	10.1	56.6

[a] Reaction catalyzed by *p*-toluenesulfonic acid and reactants continuously stripped by boiling mineral spirits.

[b] Calculated as oleic acid.

This solution was run dropwise into the reaction flask over a period of 4.5 hr while the temperature was maintained at 211–233C. The reaction was continued for 0.25 hr after the solution had been added. Then the reaction product was stripped with dry nitrogen for about 0.3 hr.

A portion of the product, 60 g, was dissolved in an equal weight of petroleum ether, cooled to 25C, and filtered to obtain a high-melting fraction consisting mostly of saturated di- and triglycerides. The fraction recovered by stripping the filtrate of solvent was dissolved in 350 g of absolute ethanol and cooled to −16C to precipitate a main fraction. The fatty material remaining in solution also was recovered. Analyses of the original product and the three fractions are recorded in Table II.

A gas chromatographic analysis of the free fatty acids in the fraction remaining in ethanol solution indicated the following percentages, calculated on a free fatty acid basis: myristic, 0.3; palmitic, 1.8; stearic, 6.7; oleic, 90.1; and linoleic, 0.9. Apparently very little acidolysis occurred during the esterification.

The fraction insoluble in petroleum ether at 25C (Table II) is relatively large in this particular esterification, probably because the reaction was stopped about 0.5 hr after the last drops of reactants had been added, and a larger than usual proportion of unreacted diglycerides remained. In other similar reactions about half this percentage of high-melting glycerides was obtained.

Fractionation from petroleum ether was quite effective in removing completely saturated di- and triglycerides. In model experiments with cocoa butter, a mixture containing 10% diglycerides of palmitic and stearic acids and a mixture containing 10% completely hydrogenated cottonseed oil were dissolved in equal weights of petroleum ether, cooled to 25C, and filtered. Approximately 85% of the diglycerides and 93% of the completely hydrogenated cottonseed oil were filtered out.

The fraction precipitated from ethanol (Table II), as well as similar products obtained by purifying crude reaction products by the petroleum ether treatment and refining with alkali to remove free fatty acids, were compared with a product made by acylating the diglycerides of palmitic and stearic acids with oleoyl chloride. The I.V., cooling curves, and melting ranges were similar. However, the product made with the oleoyl chloride had a slightly higher melting point.

TABLE III

Composition of Fatty Acids Removed by Lipase Hydrolysis from Oleodisaturated Glycerides Prepared by Catalyzed Esterification with Oleic Acid and by Reaction with Oleoyl Chloride

Type of fatty acid	Percentage in mixed acids from	
	Product prepared by catalyzed esterification	Product prepared with oleoyl chloride
Myrisitc	1.1	1.9
Palmitic	15.6	24.6
Palmitoleic	0.3	3.3
Stearic	24.3	41.2
Oleic	57.1	25.8
Linoleic	1.6	3.2

When the product made with oleoyl chloride and the main fraction of the esterified product represented in Table II were subjected to lipase hydrolysis (19) to remove some of the fatty acid groups in the 1- and 3-positions of the glycerides and their fatty acids were analyzed, marked differences appeared, as shown in Table III.

To obtain further evidence for the suspected explanation of these differences, oleodistearin was prepared using a solution of the following composition:

1,3-Distearin	16.48 g
Oleic acid	9.00 g (20% excess)
p-Toluenesulfonic acid	0.075 g
Mineral spirits (bp 200–210C)	75 ml

The solution was run dropwise into the reaction flask over a period of 3 hr while the temperature was maintained at 210–220C. Then mineral spirits alone was added at the same rate over a period of 1 hr. The reaction product was stripped to remove the residual mineral spirits, dissolved in diethyl ether, and washed with a dilute solution of potassium hydroxide. The free fatty acids, which were removed as soaps, were found on analysis to consist of 9.2% stearic and 90.8% oleic and associated fatty acids. After removal of the diethyl ether from the acid-free glycerides, 21.72 g of the glycerides were dissolved in an equal weight of

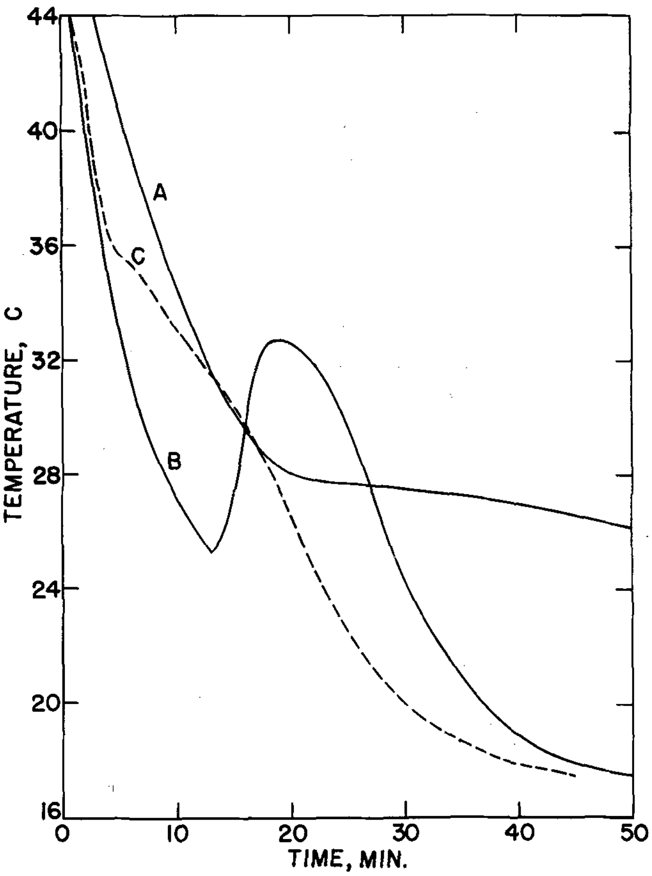

FIG. 2. Cooling curves: *A*, oleodistearin prepared by esterification of 1,3-distearin with oleic acid; *B;* 2-oleodistearin, and *C*, 1-oleodistearin.

petroleum ether, cooled at 25C, and 2.14 g of precipitate consisting mostly of distearin was removed. The purified oleodistearin had an I.V. of 29.8. Nearly all melted slightly below 40C, and the last traces of solids disappeared at 43C.

The polymorphs of 2-oleodistearin melt at 22.8, 30.0, 37.7, and 42.8C (16); and those of 1-oleodistearin melt at 30.3 and 42.1C (17).

Lipase hydrolysis of the purified oleodistearin product to remove a portion of the fatty acid groups in the 1- and 3-positions yielded a mixture of 37.4% stearic acid and 62.6% oleic acid and the other acids associated with it. These percentages probably are affected by the fact that some of the possible products of hydrolysis melt above the temperature at which the hydrolysis had to be conducted. These data indicate that a large amount of the purified oleodistearin product was not 2-oleodistearin.

Cooling curves were obtained for the purified oleodistearin product and for pure 2-oleodistearin and 1-oleodistearin. These curves, Figure 2, definitely indicate that the oleodistearin product consisted of a mixture containing a large proportion of 1-oleodistearin.

X-ray diffraction patterns of the purified oleodistearin product were obtained. When these were compared with patterns of known mixtures of 2-oleodistearin and 1-oleodistearin subjected to the same thermal treatment, it appeared that the oleodistearin product consisted of about 75% 1-oleodistearin and 25% 2-oleodistearin.

At this point some recent observations made by others become pertinent. Crossley et al. (4) found that under the influence of heat alone 1,3-distearin readily isomerizes or intraesterifies to an equilibrium mixture consisting of 58.1% 1,3-distearin and 41.9% 1,2-distearin. *p*-Toluenesulfonic acid increases the rate of isomerization. Brandner and Birkmeier (3) concluded that the equilibrium constant favoring esterification of the primary hydroxyl of glycerol over the secondary hydroxyl is about 2.3 at 200C and increases as the temperature decreases.

One can conclude that in our esterification of the diglycerides with oleic acid, isomerization or intraesterification occurred at a more rapid rate than did esterification, and the more reactive primary hydroxyls were preferentially esterified. Interesterification occurred to only a very limited degree.

Esterification of Saturated Diglycerides with Dibasic Acid

The diglycerides of palmitic and stearic acids were esterified with sebacic acid by the general procedure used with oleic acid. A solution of the following composition was employed:

Diglycerides of palmitic and stearic acids	60.70 g (0.1 mole)
Sebacic acid	10.11 g (0.05 mole)
p-Toluenesulfonic acid	0.17 g (0.001 mole)
Mineral spirits (bp 200–210C)	1000 ml

The solution was run into the reaction flask over a period of 4.5 hr, and the reaction temperature was about 220C. The reaction product was purified by dissolving it in 5 times its weight of petroleum ether, cooling the solution to 25C, removing about 1 g of precipitate (mp 72.5C), and then crystallizing the bulk of the reaction product from the solution by cooling to −18C and filtering.

The crystallization at −18C was repeated twice. The purified reaction product, 57.8 g, analyzed as follows:

Melting point	44.3C
Hydroxyl value	14.7
Free acids, as sebacic	3.9%
Number average molecular weight	1128 (theoretical, 1380)

A similar product prepared by acylating the diglycerides of palmitic and stearic acids with sebacyl chloride and purified by successive washings with dilute acid, alkali, and acid, had about the same number average molecular weight but the mp was about 10C higher.

Another product was made by esterifying the diglycerides of palmitic and stearic acids with a slight excess of sebacic acid. When the free acids in the reaction product were removed by alkali washing and analyzed, only sebacic acid was found.

The dibasic acids sublime at higher temperatures, and a tendency for sublimation to occur under the reaction conditions was noted, particularly in experiments carried out with adipic acid. The problem with adipic acid was solved by first making the half ester by a reaction between 0.18 mole adipic acid and 0.1 mole diglycerides. The excess adipic acid was removed by dissolving the reaction product in isoöctane and washing with hot water. The washed product had the following properties: number average molecular weight, 690 (theoretical, 735); melting range, 39.5–50.0C; hydroxyl value, 4.3; and free acids, calculated as the half-ester, 98.1%.

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