

# Lectures of the 1962 Short Course on Developments in Fat Chemistry

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Part III

## Derivatives of Fats for Use as Foods

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BY DEFINITION, any modification of a fat produces a derivative. Therefore, the present discussion might involve most of the edible fat and oil products which are produced, including hydrogenated oils and rearranged lard. Obviously, limits must be set and selections made. Not only is the possible subject matter very broad, but certain aspects, including hydrogenation, will be discussed by others. The present discussion will be confined mostly to the chemistry of those edible products which are derivatives by connotation as well as definition; that is, derivatives which generally are not regarded by oil chemists as being fats and oils.

Usually, such derivatives are prepared by procedures in which esterification or interesterification are important reactions. The objectives may be any one of the following:

- (1) Removing a portion of the fatty acid groups from triglycerides.
- (2) Inserting new acid groups into glycerides.
- (3) Substituting other polyhydric compounds for glycerol.

In a few instances the fatty acid chains of fats are modified by the introduction of new groups, though generally this produces derivatives which are viewed with suspicion by nutritionists.

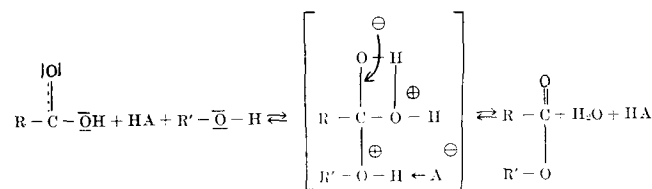
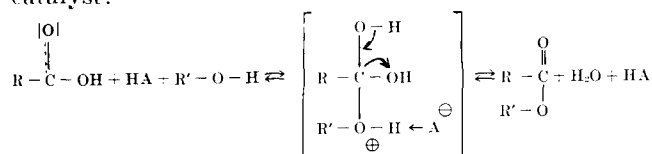
Predominantly, the edible derivatives of fats and oils have been surface active agents, such as the monoglycerides, lactoglycerides, and polyglycerol esters of the fatty acids. A few products are being marketed which are not primarily valued for their surface activity; these include the acetoglycerides and brominated oils. A number of fatty derivatives of great potential utility probably would be manufactured if economically feasible methods of preparation could be developed and if approval for use with foods could be obtained with moderate effort and expense.

Because esterification and interesterification are so important in the preparation of fat derivatives, the mechanism and various aspects of these reactions will be emphasized.

### Esterification and Interesterification

*Esterification.* Three different esterification mechanisms have been observed, according to Gould (1). Two of these are rarely encountered in the preparation of fat derivatives. One is the mechanism observed in some esterifications in concentrated solutions of very strong acids, and the other is observed in the esterification of tertiary alcohols and those secondary alcohols, such as benzhydrol and *α*-methylallyl alcohol, which yield the most stable carbonium ions. The third mechanism, which apparently is almost invariably encountered in acid-catalyzed esterification of fatty acids with primary and secondary alcohols, is bimolecular and involves cleavage of the acyl-to-oxygen bond.

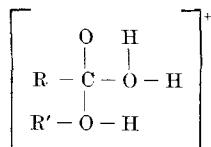
The third mechanism may be written in two ways (2), depending on which oxygen of the carboxyl group acts as a base toward the acid (HA) used as catalyst:



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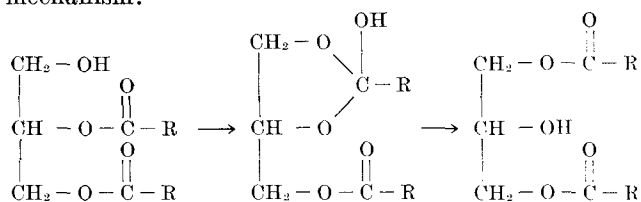
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This mechanism is a slightly abbreviated version of one of three suggested by Roberts and Urey (3). The function of the acid catalyst is to increase the positive charge on the already slightly positive carboxyl carbon and thereby increase the reaction rate of the carboxyl group with the alcohol. The formation of the complex,



is the rate-determining step. It involves reducing the bond angle about the acyl carbon from near 120 degrees to near 109 degrees, which means that steric crowding is a factor in the reaction rate. Other steric effects, including the polarity of the solvent or substrate, also are factors.

The esterification of glycerol is further complicated by the presence of primary and secondary hydroxyl groups and the isomerization or migration of the acyl groups of mono- and diglycerides. This migration is believed to occur according to the following mechanism:



Acids, alkali, and heat increase this rate of migration. According to Martin (4), monoglycerides at equilibrium contain about 90% 1-monoglycerides. Crossley et al. (5) found that diglycerides at equilibrium contain about 58% 1,3-diglycerides.

The esterification of glycerol will probably always involve the simultaneous addition of acyl groups at the 1- and 2-positions, whose reactivity differs appreciably. Brandner and Birkmeier (6) in an investigation of the interesterification of glycerides came to the conclusion that the relative esterifiability of the primary hydroxyl over the secondary was about 2.3 at a reaction temp of 200C and that the ratio increased to between 6 and 10 at room temp. Thus, the composition of the final product in the esterification of mono- and diglycerides can be expected to be temp dependent under at least some conditions. However, under most conditions interesterification proceeds rapidly during esterification, and the effects of differences in relative esterifiability are eliminated or at least minimized.

All esterifications occur in neutral or acidic media, none are observed in basic media. The very strong acids are about equally effective as catalysts while the organic acids are generally poorer catalysts. Their relative efficiencies are indicated by the relative rates at which they catalyze the hydrolysis of methyl acetate (2):

Acid	Relative rate of hydrolysis
Hydrochloric	100.0
Hydrobromic	89.3
Sulfuric	54.7
Ethylsulfuric	98.7
Ethanesulfonic	97.9
Benzenesulfonic	99.0
Oxalic	17.46
Succinic	0.496
Formic	1.31
Acetic	0.345
Chloroacetic	4.3
Trichloroacetic	68.2

The validity of using rates of hydrolysis to indicate rates of esterification is based on the fact that hydrolysis is the reverse reaction of esterification and the two reactions can be made to come to an equilibrium. For a hydrolysis-esterification to come to equilibrium, the total number of molecular systems participating in a given step per unit of time must be the same as the total number of systems participating in the reverse of this step.

Metal salts also are used as esterification catalysts. They probably function in the same manner as acids, but under most conditions are not as efficient as the best acids. In an investigation of the efficiency of a number of metal salts in catalyzing the esterification of peanut oil fatty acids and glycerol it was found that stannous chloride and zinc chloride were best (7). Dunlap and Heckles (8) investigated the efficiency of certain divalent metal salts and found that for the Group II B series the efficiency was inversely proportional to their ionic volume.

The rate at which an acid is esterified in a catalyzed reaction is dependent upon the structure of the acid. Many investigations of this factor have been conducted and not all of the investigators came to the same conclusion, as might be expected. Variations in the type of alcohol employed, the proportion of alcohol (which could, in effect, change the reaction order), and the amount and type of catalyst can minimize or emphasize differences. Generally, the reaction rates for most of the fat-forming acids have been found to be similar. In Table I are recorded some velocity constants based on data obtained by J. J. Sudborough and coworkers (9) and reported by them in a number of articles.

Formic acid has a far higher velocity constant than do the other homologous acids. In the range of butyric to stearic acid the const is practically independent of chain length. Oleic and elaidic acid have almost identical velocity const. Apparently the position of a double bond in a long-chain fatty acid has little effect on the velocity const when the double bond is well inside the chain, but a double bond adjacent to the carboxyl carbon greatly decreases the value of the const. The latter effect is due to steric hindrance in the approach of the carboxyl group to the alcohol group.

Side chains and other types of structures also create steric hindrance. In Table II are shown esterification rates of various acids with isobutyl alcohol (10). The equilibrium const, *K*, for the reaction also is included in Table II. This const, which is defined by the equation,

$$K = \frac{\text{Ester} \times \text{Water}}{\text{Acid} \times \text{Alcohol}}$$

is of particular interest when experimental conditions are to be designed for preparing derivatives

TABLE I  
Rate of Esterification of Various Fatty Acids and Methyl Alcohol  
Catalyzed by Hydrochloric Acid (9)<sup>a</sup>

Acid	Velocity constant, <i>k</i>	Acid	Velocity constant, <i>k</i>
Formic.....	2568.0	Lauric.....	121.9
Acetic.....	239.0	Myristic.....	120.9
Propionic.....	211.7	Palmitic.....	114.4
Butyric.....	115.2	Stearic.....	123.7
Caproic.....	118.7	Oleic.....	54.4
Caprylic.....	125.8	Elaidic.....	54.4
Nonanoic.....	123.5	Erucic.....	51.2
Capric.....	119.3	2-Octadecenoic.....	1.3

<sup>a</sup> Calculated according to the equation for monomolecular reactions. Corrected to a normality of one for hydrochloric acid.

TABLE II  
Esterification of Various Acids with Isobutyl Alcohol at 155C (10)

Acid	Conversion in 1 hr, %	Equilibrium constant, k
Formic.....	61.7	3.22
Acetic.....	44.4	4.27
Propionic.....	41.2	4.82
Butyric.....	33.2	5.20
Isobutyric.....	29.0	5.20
Trimethylacetic.....	8.28	7.06
Phenylacetic.....	48.8	7.99
Benzoic.....	8.62	7.00
p-Toluic.....	6.64	10.62

of fat. It shows that the lower the esterification rate of one fatty acid compared to another the higher will be the limit to which the reaction will proceed if the by-product water is not removed.

The structure of the alcohol likewise has a marked influence on the rate of esterification. As a rule, a primary alcohol has a higher rate than a secondary alcohol, which has a higher rate than a tertiary alcohol. Some conversion rates, together with the equilibrium const determined by Menshutkin (10), are recorded in Table III. The conversion rates and equilibrium const of the alcohols are unlike those of the acids in that the const of the alcohols decreases as the conversion rate decreases.

More recently Dunlap and Heckles (8) determined the rate of esterification of oleic acid with various alcohols. Their data, which are recorded in Table IV, indicate that under the conditions and with the compounds frequently used to make fat derivatives, the rates of esterification are similar.

In the actual practice of making fat derivatives, the rate at which an esterification proceeds often is not as important as the degree to which it goes to completion. If only a moderate excess of one of the reactants is employed, the rate in percentage conversion/hr decreases greatly as the concentration of reactive groups decreases. If the alcohol is polyhydric and is to be esterified completely, its mol wt increases, in effect. If the alcohol contains both primary and secondary hydroxyl groups, the proportion of the latter increases toward the end of the reaction. Both the increase in mol wt and the increase in the proportion of secondary hydroxyl groups slow the rate of esterification.

TABLE III  
Esterification of Various Alcohols with Acetic Acid at 155C (10)

Alcohol	Conversion in 1 hr, %	Equilibrium constant, k
Methyl.....	55.6	5.24
Ethyl.....	47.0	3.96
Propyl.....	46.9	4.07
Butyl.....	46.8	4.24
Allyl.....	35.7	2.18
Benzyl.....	38.6	2.39
Diethylcarbinol.....	16.9	2.01
Diallylcarbinol.....	10.3	1.01
Menthol.....	15.3	2.55
Trimethylcarbinol.....	1.43	0.0049
Phenol.....	1.45	0.0089

That the rate of esterification can decrease markedly as the mol wt of one of the reactants increases was demonstrated by experiments in the preparation of polyester by esterifying mixtures of fatty acids, short-chain dibasic acids, and glycerol (11). Stannous chloride was used as catalyst (0.226 g/100 g of total acids) and the reactants were heated for 2 hr at 175C plus 2 hr at 200C while under a partial vacuum of 200 mm of mercury. None of the prod-

ucts possessed a number-average mol wt higher than about 1650. Carothers and Hill (12) were unable to obtain mol wt above 5000 on heating compounds like hexamethylene glycol and adipic acid at temp up to 250C.

In spite of the difficulties mentioned, it has been the author's experience that the catalyzed esterification of glycerol with fat-forming acids could readily be brought to the stage where no mono- and a relatively small proportion of diglycerides remained. To accomplish this, one of the better catalysts had to be employed, fatty acids had to be present in a 5-20% excess, and the reaction had to be continued for 3-6 hr at a temp of 180-230C while under subatmospheric pressure or while being stripped with an inert gas.

Increasing the temp to increase the esterification rate of long-chain fatty acids is a useful technique, but the maximum temp should not exceed about 240C. In a recent investigation by Crossley et al. (13) it was found that in the absence of air even a

TABLE IV  
Esterification Rate of Oleic Acid at 180C (8)<sup>a</sup>

Alcohol	Rate constant, % 1 hr
1,4-Butanediol.....	0.050
Dodecanol.....	0.048
Octadecanol.....	0.047
1,10-Decanediol.....	0.041
1,5-Pentanediol.....	0.040
1,3-Propanediol.....	0.038
Ethylene glycol.....	0.033
Pentaerythritol.....	0.035
Trimethylol ethane.....	0.033
Diethylene glycol.....	0.032
Triethylene glycol.....	0.025
Glycerol.....	0.023

<sup>a</sup> Equivalent amounts of oleic acid and alcohol used and 0.005 M zinc acetate per 100 g oleic acid employed as catalyst. Rate constant calculated on basis of second order reaction.

fully saturated triglyceride has only a limited resistance to deterioration by heat. The first important degradation product, the component fatty acid, appears at 240-260C.

*Interesterification.* Three types of reactions comprise the area of interest; namely, alcoholysis, acidolysis, and ester interchange. They consist of reactions between an ester and an alcohol, an acid, and another ester.

Much that has been said about acid-catalyzed esterification applies to acid-catalyzed alcoholysis and acidolysis. The mechanism of acid-catalyzed alcoholysis is similar to that of acid-catalyzed esterification; the only difference is that an R'OH group replaces the HOH group. Alcoholysis equilibrium constants can be calculated from the esterification equilibrium const (2). Therefore, it can be predicted that a tertiary alcohol will not replace a primary alcohol, and a secondary alcohol will replace a primary alcohol to only a small extent.

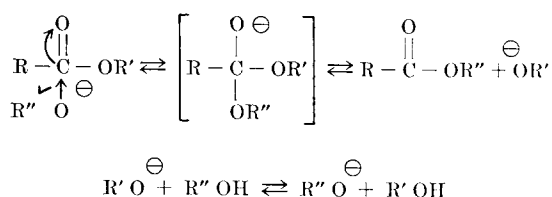
Acid-catalyzed acidolysis may be considered to be the counterpart of alcoholysis. So far it has not attained the technical importance of alcoholysis, and fewer details concerning specific reactions have been reported.

Acid-catalyzed ester interchange is regarded as an old and well-known reaction for modifying fats (14). Presumably, the reaction mechanism is similar to that for other types of interesterification; and in common with these other types, the reaction rate can be very slow when fats are involved and temp below 180C.

are employed. It is suspected that in at least some instances the presence of a small proportion of hydroxyl groups contributed by water or monoglycerides is necessary to increase the reaction rate to a useful level (15).

The preferred catalysts for alcoholysis and ester interchange are basic compounds such as sodium hydroxide and sodium methoxide. Basic compounds cannot, of course, be used in acidolysis reactions because these catalysts react with the acids. The rate of an interesterification catalyzed by a basic compound may be several thousand times that obtained when the same reaction is catalyzed with an equivalent amount of hydrochloric acid.

The effect of basic compounds in increasing the rate of alcoholysis is explained by saying that the basicity of the alcohol oxygen is increased and that this facilitates the attack on the positive carbonyl carbon according to the following mechanism (2):



Ester interchange reactions catalyzed by compounds like sodium hydroxide and calcium hydroxide may proceed in a somewhat analogous manner. The rate of these reactions can be greatly increased by the presence of small proportions of hydroxyl groups supplied by glycerol or monoglycerides (16), which could function according to the mechanism represented above.

Weiss et al. (17) postulated a different mechanism for ester interchange catalyzed by sodium methoxide. The function of the sodium methoxide was said to be the production of an enolate ion which was the true

catalyst. For the intraesterification of a triglyceride molecule the reaction was represented as shown in Figure 1.

The enolate ion (I) reacts with another ester group in the same triglyceride molecule to form a *beta*-keto ester (III) which will react further by either path *a* or *b*. Path *a* gives another *beta*-keto ester intermediate (IV) which then goes to the intramolecularly esterified product (V).

Interesterification occurs when the enolate ion reacts with an ester group in another triglyceride molecule. According to the investigators, intraesterification predominates in the initial stages of the reaction.

Evidence that the proposed mechanism is the correct one is supplied by the fact that the presence of *beta*-keto groups was detected in the infrared spectra of the reaction mixtures, but not in the original fat.

*Esterification Without Interesterification.* If the esterification of fatty acids with mono- and diglycerides and other partial esters could be readily accomplished without interesterification occurring, a large number of tailor-made fats, including cocoa butter-like fats, might be prepared on a commercial scale by simple esterification. Because acid-catalyzed esterification and interesterification are such closely related reactions and are catalyzed by the same acids, it has generally been assumed that esterification without interesterification occurring was impossible. Yet, the two types of reactions should be sufficiently different so that under some conditions uncomplicated esterification should be possible. Recently it has been shown that the esterification of diglycerides could indeed be carried out without interesterification occurring (15). The necessary conditions were the use of *p*-toluenesulfonic acid as catalyst and the continuous removal of the water of esterification by azeotropic distillation with a dry hydrocarbon. Under these conditions it was found possible to esterify 1,3-distearin with oleic acid and obtain an approximately 90%

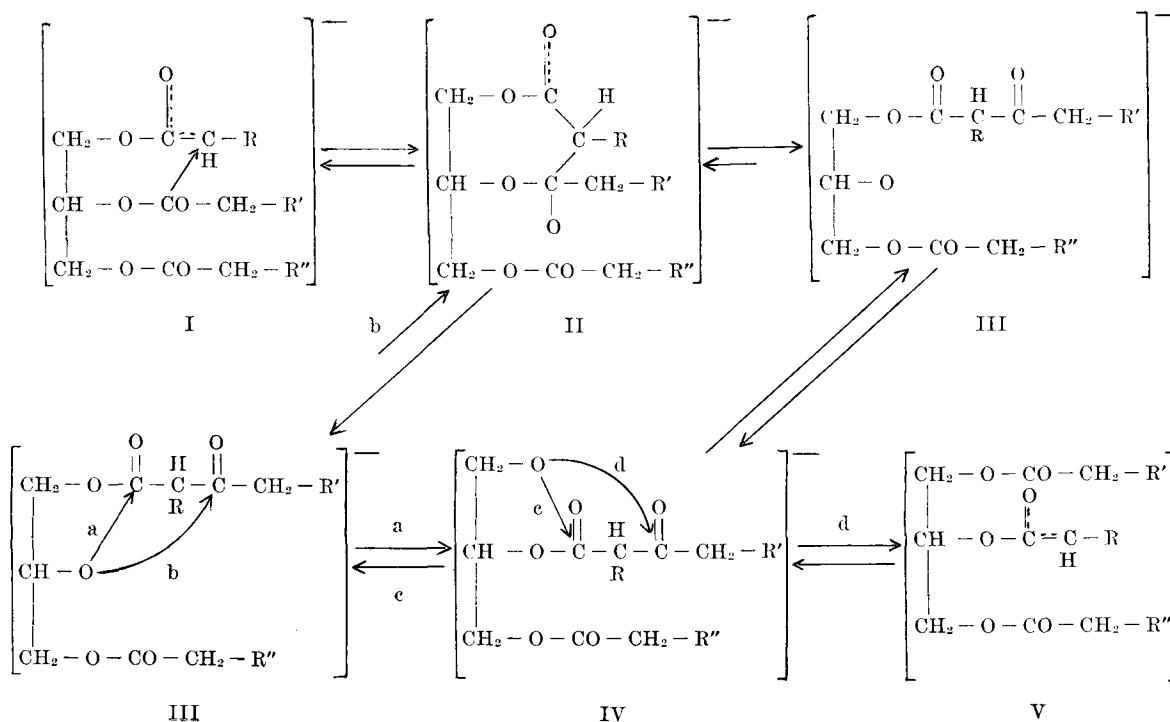


Fig. 1.

yield of oleodistearin. However, intraesterification did occur during the reaction, and it was estimated that the final product consisted of approximately 75% 1-oleodistearin and 25% 2-oleodistearin.

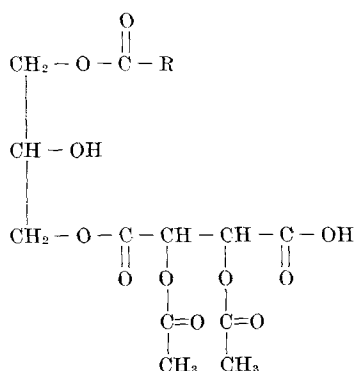
### Some Surface Active Derivatives

The monoglycerides are among the oldest of the fat derivatives used as emulsifiers. They usually are prepared by the glycerolysis of a natural or a hydrogenated fat using about 0.1% sodium hydroxide or calcium hydroxide as catalyst. The reaction product at equilibrium consists of a mixture of glycerol and mono-, di-, and triglycerides. The proportion of each component can be calculated on the assumption that the esterified hydroxyl groups are distributed in a random pattern (18). This assumption serves very well for practical purposes even though it has subsequently been shown that the esterifiabilities of the primary and secondary hydroxyl groups of glycerol differ (6).

The concentration of monoglycerides in the glycerol-free reaction product prepared from a hydrogenated C<sub>18</sub>-acid oil will be approx 60% when the reaction is carried out by heating a mixture of 100 parts fat and 40 parts glycerol for a few min at 250C and then destroying the catalyst before cooling the reaction mixture. The upper limit of about 60% monoglycerides is set by the proportion of glycerol miscible with the glycerides, which in turn is set by the maximum permissible temp, about 250C. At temp higher than this, polyglycerols and other unwanted products form rapidly. Oils composed of oleic-linoleic acid glycerides are miscible with glycerol to a somewhat greater degree than are stearic-palmitic acid fats, but their sensitivity to heat is also greater. Lauric acid oils also are relatively miscible with glycerol.

Monoglyceride mixtures can be and are molecularly distilled to obtain monoglycerides of well over 90% purity. In the laboratory the distillation of monostearin can be carried out at 100-130C. The molecular distillation of the monoglycerides of lauric acid oils can be carried out at even lower temp.

Monoglycerides not only are used as such in and with foods, but they also are modified to produce other surface-active products suitable for use with foods. Among these are the diacetyl tartaric acid esters of mono- and diglycerides. A major compound in these products is claimed to be 1-acyl-3-(diacetyl tartaroyl) glycerol,



The preparation of the technical grade product is very simple (19). Approx 2 moles of monoglycerides, usually molecularly distilled monoglycerides, and 1

mole of diacetyl tartaric anhydride are mixed and heated for 5-10 min at 100-160C. The lower temp is used for a monoglyceride of relatively low mol wt such as monolaurin. No catalyst is required. The reaction product may or may not be neutralized in whole or in part.

The preparation of the intermediate also is relatively simple (20). Dry tartaric acid and acetic anhydride are heated to 115-120C and vacuum is applied gradually to remove acetic acid by distillation. The residue of diacetyl tartaric anhydride solidifies on cooling. If desired, the diacetyl tartaric anhydride can be distilled without decomposition at 230-250C and atmospheric pressure.

The lactoglycerides comprise another important series of edible emulsifiers which are derived from monoglycerides or mixtures of mono- and diglycerides. According to an early patent (21) a suitable lactostearin can be prepared by gradually heating to 150C a mixture of stearic acid (1 mole), lactic acid (1 mole), and glycerol ( $\frac{2}{3}$  mole), and then maintaining the mixture at this temp and under vacuum for 6-12 hr, after which the mixture is cooled and washed with water to remove a small proportion of bitter-tasting triglycerides of lactic acid.

Currently, lactostearin which meets the standards of the Food and Drug Administration is made by subjecting hydrogenated soybean oil to glycerolysis, using sodium hydroxide as catalyst, and then esterifying this mixture directly with lactic acid. The resulting product is identified as "glyceryl lactostearate and mono- and diglycerides," and its specifications under the Food, Drug, and Cosmetic Act are as follows: Total lactic acid content, not to exceed 16%; acid number, not to exceed 14; and the total free and combined lactic acid of the finished shortening, not to exceed 1.75% (22).

The lactoglycerides of the technical grade products consist of a variety of compounds, and undoubtedly in some of these compounds both the hydroxyl and carboxyl groups of lactic acid are esterified, though the extent of polymer formation should be small. To prepare in the pure form a compound like 2-lactoyl-1,3-dipalmitin, the hydroxy group of lactic acid must be blocked while the esterification is carried out. This can be accomplished by the reaction of 1,3-dipalmitin with the benzyl ether of lactoyl chloride followed by hydrogenolysis of the benzyl group (23).

Another type of surface active product is prepared by the partial esterification of polyglycerols with fat-forming acids. The esterification is carried out in the usual manner. The sodium hydroxide or other alkali used in the formation of the polyglycerol may also serve to form the esterification catalyst when the fatty acids are added.

The polyglycerol, which is formed by the dehydration of glycerol, varies in composition depending upon the reaction conditions employed and whether or not the reaction product has been fractionated. Even the fractionated products are mixtures, and the designation of a product as a diglycerol, triglycerol, or polyglycerol is based on its average composition. The polyglycerols include open-chain and cyclic ethers formed by intermolecular dehydration and epoxy ethers formed by intramolecular dehydration.

According to Minor and Dalton (24) the commercial production of polyglycerol typically involves heating glycerol with an alkaline catalyst (about

0.3% sodium hydroxide or sodium acetate) at a temp between 200 and 275C over a period of hr while the water of dehydration is removed.

Products of the same general nature as the polyglycerol esters are being prepared by the esterification of fatty acids or the interesterification of fatty esters with dehydrated hexitols. The latter form a number of hexitans and hexides.

Among the new types of surface active agents which are just beginning to appear on the market are the sucrose esters of the fat-forming acids. Potentially they are of great importance. The first compounds of this type were prepared and characterized many years ago, but commercialization was impossible because no suitable method of large-scale preparation was available. Sucrose is insoluble in fat and the common fat solvents, and it degrades readily when heated and when put into contact with strong acids.

Relatively recently, a method of preparing mono- and diesters of sucrose on a large scale was developed (25). It involves dissolving the sucrose in dimethylformamide, adding the methyl ester of the fatty acid, adding potassium carbonate as catalyst (0.14 mole/mole of methyl ester), and heating the mixture to 90-95C and maintaining it at this temp for 9-12 hr, while under a pressure of 80-100 mm of mercury. To produce sucrose monostearate, a 3:1 molar ratio of sucrose to methyl stearate is employed. To produce sucrose distearate, this ratio is changed to 1:2.

The major disadvantages of this method of preparation are that a large amount of expensive solvent is required and that the solvent reacts with a small proportion of stearate to form toxic compounds.

More recently an adaptation (26) of the Schotten-Bauman reaction (27,28) has been proposed for the preparation of sucrose esters. In this procedure the sucrose is dissolved or suspended in an aqueous alkaline medium (pH 9-11) and the chloride of the fatty acid is added slowly and with vigorous mixing. The reaction is carried out preferably below 45C but above the freezing point of the acid chloride.

### Some Specialty Fats

*Cocoa Butter-Like Fats.* Many investigators have attempted the development of economically feasible procedures for making cocoa butter-like fats on a large scale. In essence the problem has been the development of a process for preparing 2-oleo disaturated glycerides of palmitic and stearic acids, which comprise about 80% of cocoa butter. Up to now the different investigators have succeeded only in approaching to various degrees the glyceride composition of cocoa butter. A full review of the subject it not possible here. Only two or three approaches to the problem can be outlined.

In one approach (29,30) completely hydrogenated cottonseed oil (75 parts) and olive oil (25 parts) were interesterified with sodium methoxide as catalyst, and the randomly interesterified product was fractionated by crystallization from acetone. The fraction crystallizing out of solution between 1C and 20C was retained as the cocoa butter-like fat. Yield was approx 30%, based on the total wt of fat.

When the percentage of liquid content of well-tempered samples of the cocoa butter-like fat and cocoa butter were determined at various temp, the results recorded in Table V were obtained. The cocoa butter-like fat had as short a melting range as did co-

coa butter, and all of the fat melted below body temp.

However, the cocoa butter-like fat on being solidified in molds did not contract as well nor become as hard as did cocoa butter. The difference was attributed to the presence of a large proportion, about 66%, of 1-oleoglycerides.

TABLE V  
Liquid Content of Cocoa Butter-Like Fat and Cocoa Butter After Tempering

Temp, C	Liquid content, %	
	Cocoa butter	Cocoa butter-like fat
15	6.8	.....
20	10.8	6.0
25	16.7	10.7
30	36.1	19.3
35	100.0	93.3
36.1	.....	100.0

Using the technique mentioned under "Esterification without Interesterification," cocoa butter-like fats resembling to a reasonable degree the product just described were obtained. While the physical properties were not improved, the process was deemed to be potentially cheaper and the yield was about three times that obtained by the interesterification technique. Also, improvements in the esterification technique may be possible.

Alsop and Bell (31) used a novel approach to the preparation of a cocoa butter substitute. Instead of attempting to duplicate the structure of cocoa butter, they attempted to simulate only the melting characteristics. They prepared a cocoa butter substitute by esterifying propylene glycol with a mixture of oleic, palmitic, and stearic acids. This approach seems to have merit. With the three acids only six chemically different esters of propylene glycol are possible, but these same three acids can form 18 chemically different triglycerides. The problem of obtaining a fat of the desired characteristics should be simplified.

Possibly the idea of Alsop and Bell might be extended to the preparation of diglyceride mixtures having properties similar to those of cocoa butter.

*Acetoglyceride Products.* Another group of specialty fats suitable for use as foods are the acetoglyceride products (32,33). They are produced by substituting acetic acid for a portion of the fatty acids occurring in ordinary fats and oils to obtain predominately either diaceto triglycerides or monoaceto diglycerides or combinations of these. The acetostearins are unique in that they solidify in a crystal structure which is quite plastic; thus, flexible films of solid fat can be formed. While the plastic crystals are not thermodynamically stable, they are stable for all practical purposes. The technical grade products will remain plastic for years when stored at room temp. Other acetoglycerides can be produced which are relatively stable to oxidation and solidify at temp far below those of other fats of the same degree of unsaturation.

Originally, the acetoglycerides were prepared by acetylating pure monoglycerides or monoglyceride products with acetic anhydride. This reaction proceeds readily at 110C. After completion of the reaction, the residual acetic anhydride can be hydrolyzed by boiling the product with water for 30 minutes, and the acetic acid can be removed by water washing. Contrary to what might be expected, acetic anhydride and acetic acid apparently do not promote interesterification during the esterification.

