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Modification of Vegetable Oils. VIII. Conversion of Monoesters of Peanut Oil Fatty Acids to Triglycerides[1]

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RELATIVELY few investigations have been made of the reactions involved in the conversion of monoesters to polyesters, principally because in the past this type of reaction has been of little practical importance. However increasing demand for special products derived from fatty acids imparts a potential value to this conversion. Fatty acids to be incorporated in special products are obtained conveniently in the form of monoesters and are preferred to the free acids in purification and fractionation processes. The tailor-made fatty products into which the monoesters can be transformed are numerous and varied, including, for example, the simple and mixed triglycerides of pure fatty acids. The techniques used in the manufacture of triglycerides from monoesters can be employed with little or no modification in the manufacture of alkyd resins and esters of pentaerythritol and other polyhydroxy alcohols.

The preparation of triglycerides from monoesters can be accomplished by several different methods, some of which are principally valuable in laboratory work. Indirect methods include those in which the monoesters are first converted to free acids, acid anhydrides, or acid chlorides before being reacted with glycerol. Processes involving only alcoholysis or ester-ester interchange can be considered as being direct methods and therefore more desirable from the standpoint of cost and simplicity.

The present investigation was undertaken to determine and compare the effectiveness of the various known catalysts for the alcoholysis reaction and to establish the conditions most favorable for the production of triglycerides by alcoholysis. Also certain aspects of the production of triglycerides by the ester-ester interchange were investigated.

Materials, Equipment, and Methods of Analysis

Materials. One lot each of methyl and ethyl esters of mixed fatty acids was used for all of the experiments. Both of these types of monoesters were prepared from the same refined and bleached peanut oil by alcoholizing the oil with reagent grade alcohols to which some metallic sodium had been added. The reaction mixture was neutralized, and the resultant crude products were washed with water, dried, and distilled below 0.5 mm. pressure. The average molecular weight of the methyl esters was 293.6 and that of the ethyl esters 308.8. The glycerol (U.S.P. grade) and triacetin (reagent grade) were dehydrated before use by distilling under vacuum. Reagent grade chemicals or preparations made from them were used as catalysts. With the exception of zinc stearate all the

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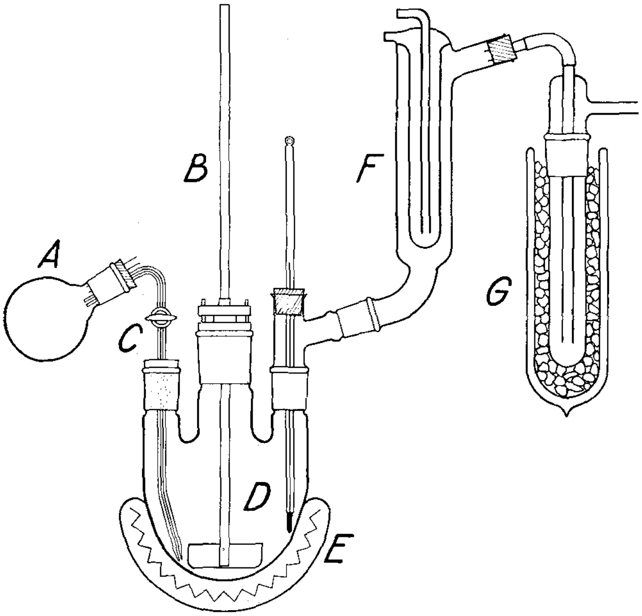

FIG. 1. Diagram of interesterification apparatus.

metallic stearates were prepared by either the fusion or precipitation method described by Elliott (4).

Equipment. All reactions were carried out in the apparatus illustrated in Figure 1. The flask, *D,* which is the reaction flask proper, is an ordinary 3-neck, 500-ml. capacity, round-bottom Pyrex flask, equipped with standard-taper, ground-glass joints. The flask was heated by the hemispherical mantle, *E,* provided with an electrical resistance winding operated through a variable transformer. This arrangement permitted raising the temperature of the reactants to the desired point in less than five minutes. The temperature of the reaction mixture was indicated by a calibrated partial immersion thermometer. The collapsible stainless steel stirrer, *B,* was operated at 400 r.p.m. through a stuffing box in a stainless steel standard-taper plug. The reflux condenser, *F,* which was heated with hot water, removed any glycerol in the vapors leaving the reaction mixture and returned them to the reaction zone. Vapors issuing from the reflux condenser were collected in the dry ice trap, *G.* The sampling tube, *C,* which was constructed of 2 mm. capillary tubing, permitted withdrawal of a sample without interrupting the reaction. The sample was transferred to flask, *A,* with the aid of a vacuum higher than that maintained over the reacting mixture.

The necessity for maintaining a constant reduced pressure in the reaction flask and at the same time protecting the contents from the air required the use of a pressure control system of special design. This pressure control system which was connected to the dry ice trap consisted of a rotary oil-sealed pump operated in conjunction with a sulfuric acid manostat and an electronically controlled gas leak of dry hydrogen or nitrogen.

Methods of analysis. The reaction products obtained by alcoholysis as well as by ester-ester interchange were neutralized with dilute acetic acid, washed with distilled water, and dried before being analyzed. Glycerol was determined by a combination of two methods; that is, a weighed portion of the reaction product was saponified according to the procedure of Smith and Matthews (9); and the aqueous portion was analyzed for free glycerol using a minor modification of the periodic acid oxidation method of Pohle, Mehlenbacher, and Cook (8) for determining monoglycerides. The washed and dried products were analyzed for monoglyceride content by a modification (6) of the method of Pohle, *et al.* Hydroxyl values were determined by the acetic anhydride-pyridine method of West, Hoagland, and Curtis (10). Free fatty acids were determined by the method prescribed by the American Oil Chemists' Society (1).

Catalysts for Alcoholysis

As mentioned previously, very few data have been published concerning the conversion of monoesters of fatty acids to triglycerides or other polyesters by catalyzed alcoholysis. Probably the best data available are those of Wright, *et al.* (11) who showed that the methyl esters of linseed oil acids could be alcoholized reasonably well with pentaerythritol when lead naphthenate was employed as catalyst at temperatures of the order of 225° to 280°C. No other catalysts for this reaction were mentioned by these workers, and, so far as could be ascertained, no evaluation and comparison of catalysts for this specific type of alcoholysis have been reported.

Chemically, the alcoholysis of monoesters with polyalcohols is analogous to the alcoholysis of polyesters with the polyhydric alcohols. In an investigation of the latter type of alcoholysis Burrell (3) compared the catalytic activity of a number of catalysts for the reaction between soybean oil and pentaerythritol. He reported that barium, cadmium, calcium, cerium, lead, lithium, strontium, and zinc catalyzed the reaction when these metals were employed as naphthenates, stearates, or abietates. Burrell also found that under the same conditions aluminum, bismuth, cobalt, chromium, copper, iron, magnesium, manganese, mercury, nickel, and thorium had no effect. Sodium methylate or ethylate appears to be the catalyst preferred by other workers for the replacement of glycerol in fats with other polyhydric alcohols.

All the catalysts mentioned above, as well as some other generally recognized interesterification catalysts, are of course also suitable for the conversion of the monoesters of fatty acids to triglycerides. How-

TABLE I

Catalytic Effect of Various Compounds in the Alcoholysis of Equivalent Amounts of Methyl Esters and Glycerol [a]

Catalyst	Catalyst per 100 g. methyl esters, g.	Glycerol combined in fatty portion,[b] %	Hydroxyl value of fatty portion
None	....	0.2	......
$Sn(OH)_2$[c]	0.305	1.8	......
$Cd(C_2H_3O_2)_2 \cdot 2H_2O$	0.533	5.1	......
$Zn(C_{18}H_{35}O_2)_2$	1.264	8.6	......
$SnCl_2 \cdot 2H_2O$	0.451	10.7	......
$Mg(C_{18}H_{35}O_2)_2$	1.182	23.1	......
$SnCl_2 \cdot 2H_2O + FFA$[d]	....	31.0	......
$Pb(C_2H_3O_2)_2$	0.651	39.1	......
$Cd(C_{18}H_{35}O_2)_2$	1.358	59.3	63.1
$Ce(C_{18}H_{35}O_2)_2$	1.413	69.8	65.6
$Ca(OH)_2$	0.148	76.5	32.0
$Pb(C_{18}H_{35}O_2)_2$	1.548	81.1	24.5
KOH	0.112	83.9	34.4
$Sr(C_{18}H_{35}O_2)_2$	1.301	85.4	37.2
NaOH	0.080	86.6	32.0
$Ba(OH)_2 \cdot 8H_2O$	0.631	87.1	22.0
$LiOH \cdot H_2O$	0.084	89.4	22.0
$NaOC_2H_5$	0.136	94.3	38.1

[a] Reactions conducted for 2 hours at 200°C. and 50 mm. pressure with 0.002 mole of compound per 100 g. of ester.

[b] Calculated as percentage of free glycerol originally present.

[c] Van Loon's catalyst prepared according to the method described by Bailey (2).

[d] Twice the amount of free fatty acids from peanut oil required to combine with the stannous chloride were dissolved in the methyl ester.

TABLE II

Comparison of the Activity of the Four Most Reactive Alcoholysis Catalysts[a]

Reaction time (minutes)	Completion of reaction,[b] %			
	$Ba(OH)_2 \cdot 8H_2O$	$LiOH \cdot H_2O$	$NaOC_2H_5$	NaOH
15	65.4	40.2	6.6	3.8
30	67.8	68.0	23.9	7.6
60	68.9	70.2	67.2	36.2
105	70.0	73.6	68.8	63.9
165	70.0	71.8	70.0	63.1

[a] Equivalent quantities of methyl esters and glycerol reacted at 180°C. and 200 mm. pressure with 0.002 mole of catalyst for 100 g. esters.

[b] Calculated as a percentage of the methyl esters converted to glycerides.

ever since the relative effectiveness of the various compounds has not heretofore been known, various potential catalysts were tested under identical conditions. In each of the tests 100 g. of methyl esters, the equivalent amount of glycerol, and 0.002 mole of the catalyst were allowed to react under a pressure of 50 mm. for 2 hours at 200°C. The pressure used was the lowest possible at the temperature (200°C.) employed. At 200°C. glycerol boils at a pressure slightly below 50 mm. The concentration of catalyst used was based on the results of preliminary experiments and was not in excess of the maximum amount soluble under the test conditions. Results of these tests are shown in Table I.

It is rather surprising that practically no reaction occurred in the control run, in which no catalyst was used. Grün and co-workers (5) showed that ethyl stearate can be alcoholized with glycerol without the assistance of a catalyst and reported that in some instances conversions of 94 to 96% were effected after reaction times of 15 hours. However they used an excess of glycerol and heated and stirred the mixture at 270°C. in an open flask under atmospheric pressure. Their reaction products were analyzed by vacuum distillation.

The data in Table I show that the activity of the catalyst is determined not only by the metallic portion of the compound but also by its anionic portion. The acetates of lead and cadmium were not nearly as reactive as the stearates of these metals, which were prepared in the laboratory from the acetates. Stannous chloride became more reactive when transformed to tin soaps by the addition of free fatty acids to the reaction mixture.

Glycerol is relatively insoluble in methyl esters and at 200°C. not more than a minor portion of the added glycerol, which amounted to 10.45 g. per 100 g. of esters, dissolved in the ester phase when no catalyst or one of the more unreactive catalysts was used. Apparently most catalysts dissolved first in the glycerol phase. In any case, the glycerol phase exhibited a tendency to discolor, and side reactions, if any, probably occurred in this medium. Van Loon's catalyst (freshly prepared stannous hydroxide) gave evidence of being insoluble in both the glycerol and ester phases. Insolubility in the ester phase may explain the relative inertness of some of the other catalysts and the difference in activity between the stearates and acetates of lead and cadmium.

The relative reactivities of the catalysts in Table I should be regarded as being close approximations. The reaction flask was partially filled during these tests and in some instances small amounts of free glycerol condensed on the cool walls of the flask above the reaction zone. A second series of tests was made to compare more precisely the four best catalysts. In the latter series the reaction temperature was lower and the pressure over the reactants was higher than in the first series, and the reaction flask was practically full at the beginning of each run. Consequently the differences in reaction rates were more marked, and there was practically no tendency for the glycerol to leave the reaction zone. The results obtained in the second series of tests are given in Table II.

The data in Table II show that barium hydroxide is the most active and lithium hydroxide the next most reactive catalyst on a mole basis. However from a practical point of view comparison of equivalent amounts of catalyst is more significant because one mole of barium hydroxide reacts with and removes two moles of fatty acids from the ester mixture while a mole of lithium hydroxide removes only one mole of fatty acids. When equivalent quantities of barium and lithium hydroxide were compared at a reaction temperature of 160°C., lithium hydroxide was found to be decidedly more active.

Effect of Conditions on the Course of Alcoholysis

Several series of interesterifications were made with the methyl esters and equivalent amounts of glycerol to determine the effect of variation of temperature, pressure, concentration of catalyst, and type of monoesters on the course of alcoholysis. The results of a series of experiments in which only the temperature of the reaction was varied are shown in Figures 2 and 3. In the curves included in these figures the term "monoesters converted" refers to the monoesters changed into glycerides, and the term "glycerol combined" refers to the glycerol found in the washed fatty portion of the reaction product and is calculated as a percentage of the free glycerol present at the start of the reaction. The curves show that under the given conditions an increase in temperature from 160° to 180°C. results in an unusual increase in the reaction rate. On the basis of the curves in Figure 2 it is evident that the reaction rate is greater than would be suspected on the basis of the increase ob-

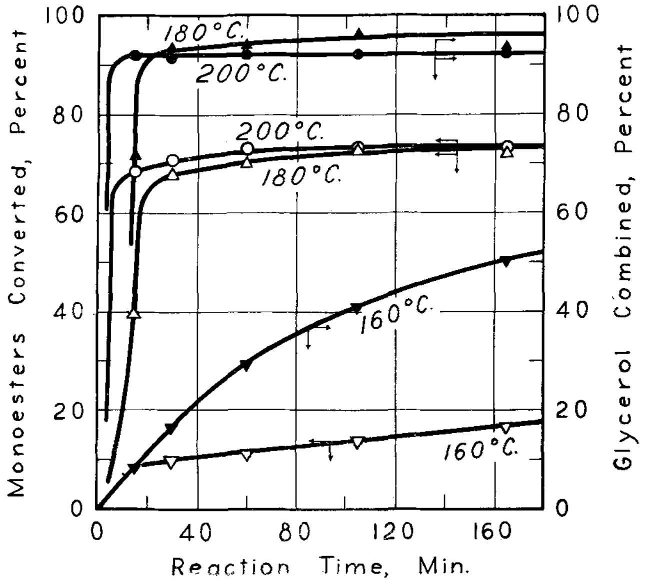

FIG. 2. Effect of temperature on the course of the reaction between equivalent quantities of methyl esters and glycerol at 200 mm. pressure. Catalyst, 0.002 mole of barium hydroxide per 100 g. of monoesters.

tained by raising the temperature from 180° to 200° C. In addition to the usual acceleration of the reaction proper, the increased temperature probably produces several secondary effects. Among other things, the initial concentration of the free glycerol in the ester phase probably is greater, and the monohydric alcohol formed may be removed at a faster rate. Apparently the temperature has no effect on the point at which these reactions cease. In these and subsequent tests no temperatures appreciably in excess of 200° C. were employed because such temperatures greatly accelerate the side reactions occurring in the fatty acid portions of the esters and in the free glycerol.

The effect of varying the pressure over the reacting mixture is shown in Figure 4. At the lower pressure the reaction comes to equilibrium after a somewhat higher percentage of conversion of monoesters to glycerides. Unfortunately the pressures over these reacting mixtures cannot be reduced below the boiling point of either the free glycerol or monoesters, and at practical reaction temperatures the boiling points occur at appreciable pressures.

The effect of varying the concentration of the catalyst is shown in Figure 5. Doubling the concentration of catalyst has an unsuspectedly marked influence on the reaction rate. Here again the unusual acceleration is probably the result of secondary effects.

The curve representing the earlier portion of the reaction when 0.004 mole of catalyst per 100 g. of methyl esters was used, is S-shaped and is typical of other curves obtained with medium rates of reaction. The "S" shape is caused by the low solubility of the free glycerol in the esters at the beginning of the reaction. As the reaction proceeds, more and more glycerol is converted to monoglycerides which enter the ester phase while the monoglycerides already in the ester phase continue to react to form di- and triglycerides. Possibly the solvent power of the ester phase for glycerol also increases as the reaction proceeds. The maximum rate of reaction probably is attained just as the system becomes homogenous, and as the reaction nears completion the rate of course decreases.

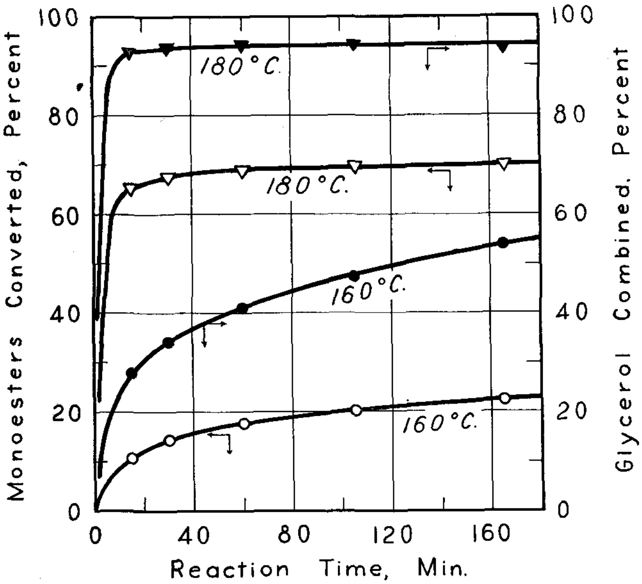

FIG. 3. Effect of temperature on the course of the reaction between equivalent quantities of methyl esters and glycerol at 200 mm. pressure. Catalyst, 0.002 mole lithium hydroxide per 100 g. of monoesters.

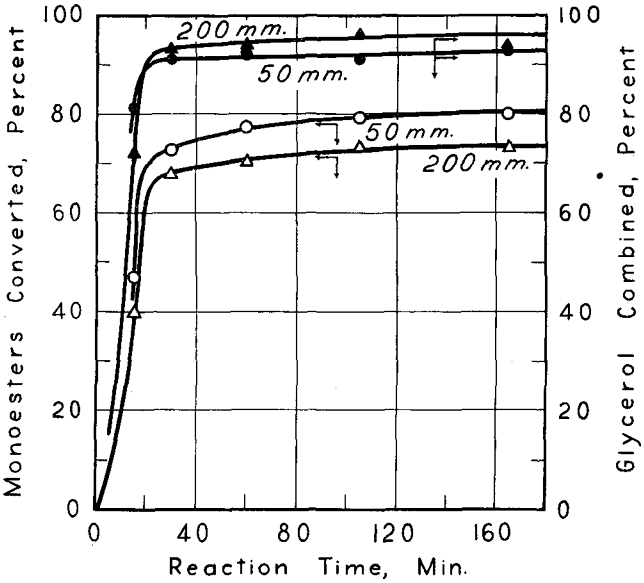

FIG. 4. Effect of pressure on the course of the reaction between equivalent quantities of methyl esters and glycerol at 180°C. Catalyst, 0.002 mole lithium hydroxide per 100 g. of monoesters.

Concentrations of catalyst which were much above 0.004 mole per 100 g. of monoesters could not be employed because the catalysts became insoluble, formed gels, or caused the reacting mixture to foam.

In Figure 6 a comparison is made of the relative reactivities of methyl and ethyl esters. As might be expected, the ethyl esters are less reactive than the corresponding methyl esters. Also with the ethyl esters the reaction comes to equilibrium at a lower percentage of completeness of the reaction.

In Table III the analyses of the fatty portions of a number of reaction products are given. It is seen that all of the possible types of compounds are present in all the products. While the reactions represented come to equilibrium at approximately 70% completion, diglycerides are not predominant in the end products, as might be supposed. No explanation is offered to explain why these reactions come to equilibrium at approximately 70% completion or why the various reaction products are produced in the ratios found.

To determine to what degree of completion the alcoholysis of methyl esters with an equivalent amount of glycerol could be carried under the most favorable conditions of temperature, pressure, and catalyst concentration, a run was made using 0.004 mole of lithium hydroxide per 100 g. of monoesters. To avoid a violent reaction and possible loss of reactants at the beginning of the run, the reactants were first mixed for 15 minutes at 150°C. and 400 mm. pressure, after which they were maintained for periods of 15 minutes at 160° and 200 mm., 170° and 100 mm., 180° and 50 mm., then for 20 minutes at 200° and 25 mm., and 20 minutes at 220° and approximately 15 mm. The unreacted methyl esters boiled at the lowest pressure. The fatty portion of the final product contained 9.62% glycerol and had an hydroxyl value of 20.3, indicating that the reaction was only 81.9% complete, and the product was only slightly better than some of those shown in the aforementioned curves.

TABLE III

Composition of Products Prepared by the Reaction of Methyl Esters With an Equivalent Quantity of Glycerol [a]

Catalyst	Reaction temp., °C.	Reaction time, min.	Composition of fatty product [b]						
			Per cent by weight					Glycerol content,[c] %	Hydroxyl value
			Monoglyc.	Diglyc.	Triglyc.	Methyl esters	Free fatty acids		
$LiOH \cdot H_2O$	160	15	......	......	......	......	......	0.86	......
		30	6.1	0.0	1.6	92.0	0.29	1.76	12.8
		60	11.2	0.0	0.9	87.6	0.37	3.01	34.8
		105	12.2	13.3	0.0	74.1	0.41	4.04	50.9
		165	13.1	22.6	0.0	63.8	0.42	4.69	62.0
$LiOH \cdot H_2O$	180	15	15.0	12.5	14.5	57.8	0.24	7.31	59.1
		30	9.2	19.8	39.7	30.8	0.46	9.55	47.4
		60	8.7	18.4	43.8	28.6	0.53	9.61	44.3
		105	7.3	21.3	45.6	25.2	0.61	9.87	42.5
		165	5.9	23.7	42.8	26.9	0.72	9.58	40.3
$NaOC_2H_5$	180	15	9.7	0.0	0.0	89.9	0.40	1.99	24.7
		30	15.5	5.2	5.5	73.6	0.35	5.37	53.8
		60	9.5	23.6	35.0	31.5	0.52	9.66	51.5
		105	7.8	26.6	35.1	29.8	0.64	9.71	49.1
		165	6.7	28.5	35.5	28.6	0.68	9.74	47.2

[a] All reactions conducted with 0.002 mole of catalyst per 100 g. methyl esters under a pressure of 200 mm.
[b] Composition of reaction product washed free of uncombined glycerol.
[c] Percentage of glycerol obtainable by hydrolyzing a given weight of product.

Methyl esters were allowed to react with 1½ equivalents of glycerol for 2 hours at 200°C. and 50 mm. pressure in an effort to produce relatively pure triglycerides from monoesters containing 0.002 mole of lithium hydroxide per 100 g. The untreated end product, which contained a fatty portion having an hydroxyl number of 137.2 and a glycerol content of 17.63%, was deodorized at 200°C. and 1½ mm. pressure. One sample was withdrawn from the deodorizer after 2 hours, and another sample after 4 hours. The sample withdrawn after 2 hours had an hydroxyl value of 14.7 and contained 10.96% glycerol; that withdrawn after 4 hours had an hydroxyl value of 9.5 and contained 10.66% glycerol. Since a pure triglyceride obtained from the original methyl esters would have had a glycerol content of 10.50% and no hydroxyl value, the sample obtained after deodorization for 4 hours can be considered to be a fairly pure triglyceride.

TABLE IV

Products Obtained by Interaction of 1.5 Equivalents of Monoesters per Equivalent of Glycerol [a]

Type of monoesters	Reaction time, min.	Analysis of fatty portion			Completion of reaction, %
		Combined glycerol,[b]	Hydroxyl value	Monoglyc. content,%	
Methyl	15	6.46	20.4	......	82.8
	30	6.55	11.7	......	90.2
	60	6.60	8.3	......	93.1
	105	6.64	7.7	2.13	93.6
	165	6.71	7.6	1.80	93.8
Ethyl	15	1.75	19.8	5.68	37.9
	60	6.24	22.1	2.01	80.1
	165	6.29	18.5	1.50	83.9

[a] All reactions conducted at 180° C. and 50 mm. pressure with 0.002 mole of lithium hydroxide for 100 g. monoesters.
[b] Percentage of glycerol obtainable by hydrolyzing a given weight of product.

In another series of experiments an attempt was made to convert monoesters into triglycerides with the aid of an excess of monoesters. The results are recorded in Table IV. Since monoesters can be separated readily from glycerides by distillation or the glycerides isolated by fractional crystallization from solvents, the preparation of triglycerides using an excess of monoesters is fairly satisfactory, at least in the case of the methyl esters. Glycerides having an hydroxyl value of about 10 could be obtained by purifying the product having an hydroxyl value of 7.6. The hydroxyl value of peanut oils is often about 5.

Ester-Ester Interchange Reaction

The ester-ester interchange reaction provides another means by which monoesters can be converted directly into glycerides. Konen, Clocker, and Cox (7) reported that they obtained pure trieleaostearate by reacting 3 moles of neutral methyl eleaostearate with 1 mole of anhydrous neutral triacetin in which 0.05% of dry sodium methylate was dissolved. The reaction was conducted under a vacuum at a temperature of 60° to 100°C. It was claimed that practically pure triglycerides were obtained after washing the end product with ethanol.

While the preparation of technical triglycerides by the ester-ester interchange reaction is not as desirable as is alcoholysis, a series of experiments was made using approximately the conditions described by Konen, *et al.* In the present experiments the monoesters and triacetin were mixed and the sodium meth-

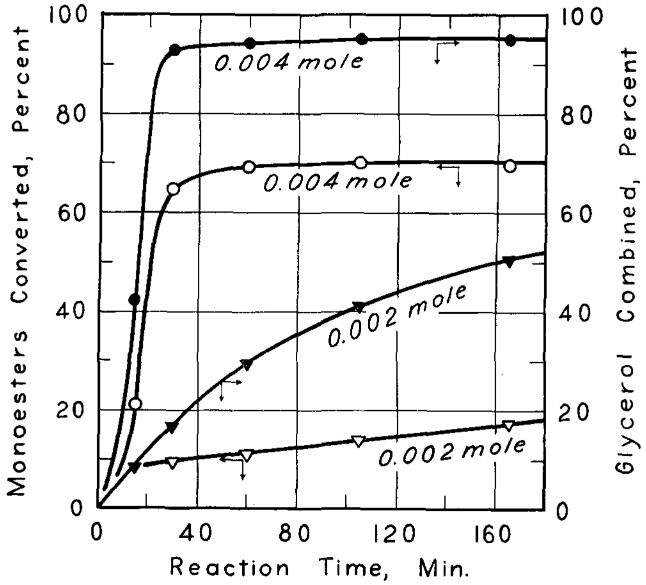

FIG. 5. Effect of concentration of catalyst on the course of the reaction between equivalent quantities of methyl esters and glycerol at 160°C. and 200 mm. pressure. Values shown represent moles of lithium hydroxide per 100 g. of monoesters.

ylate was usually added in the form of a concentrated methanol solution. Instead of washing the reaction products with ethanol they were washed first with dilute acetic acid and then with water. The results of these experiments are given in Table V.

The results show that the reaction did not go to completion under the conditions employed; also the reaction did not follow immediately upon addition of the catalyst. An induction period was noted in all of the reactions. When the vacuum was applied after addition of the catalyst, the small amount of methanol flashed off immediately, but sometimes 15 minutes elapsed before there was any visible evidence of the formation of methyl acetate vapors.

One of the objections to the practical application of the ester-ester interchange reaction is that the catalyst is readily destroyed. The reactants must be anhydrous and free of oxygen and peroxides. Such materials as lithium hydroxide or lithium stearate, which are unaffected by moisture, do not catalyze this type of reaction.

TABLE V

Products Obtained by the Interaction of Equivalent Quantities of Monoesters and Triacetin in the Presence of Sodium Methylate

Type of monoester	Catalyst conc., moles per 100 g. monoesters	Reaction temp. and pressure, °C.—mm.	Reaction time, min.	Glycerol in fatty portion,[a] %	Completion of reaction,[b] %
Methyl	0.008[c]	90-20	120	10.29	90.1
Methyl	0.006	100-25	15	3.32	......
Methyl	0.006	100-25	30	8.06	......
Methyl	0.006	100-25	60	9.60	57.6
Methyl	0.006	100-25	105	9.77	65.6
Methyl	0.006	100-25	165	9.86	69.8
Ethyl	0.006	100-25	15	4.90	......
Ethyl	0.006	100-25	30	8.01	......
Ethyl	0.006	100-25	60	9.24	48.8
Ethyl	0.006	100-25	105	9.39	54.9
Ethyl	0.006	100-25	165	9.62	64.2
Methyl	0.006	100-10	180	9.90	71.7
Methyl	0.006	100-10	360	9.92	72.6

[a] Percentage of glycerol obtainable by hydrolyzing a given weight of washed and dried product.

[b] Calculated on the assumption that at least a portion of each triacetin molecule had reacted at this stage.

[c] Catalyst added in the form of dry sodium methylate suspended in xylene.

Not many experiments were made using the ester-ester interchange reaction, principally because it was impossible to determine the amount of catalyst which is actually active under any given conditions. The greater part of the catalyst always appeared to be insoluble in the reactants. Traces of catalyst could not be used because the monoesters usually contained traces of moisture, oxygen, and peroxides.

Summary

1. Conversion of the methyl and ethyl esters of peanut oil fatty acids into triglycerides by means of alcoholysis and ester-ester interchange reactions has been investigated with the object of establishing the conditions most conducive to rapid and complete transformation of the esters.

2. Data are presented showing that the most effective catalysts for alcoholysis are barium hydroxide, lithium hydroxide, sodium ethylate, and sodium hydroxide. When the catalysts are compared on a molar basis, barium hydroxide is somewhat more effective than lithium hydroxide and sodium hydroxide is the least effective. On an equivalence basis or on a weight for weight basis, lithium hydroxide is the most effective catalyst.

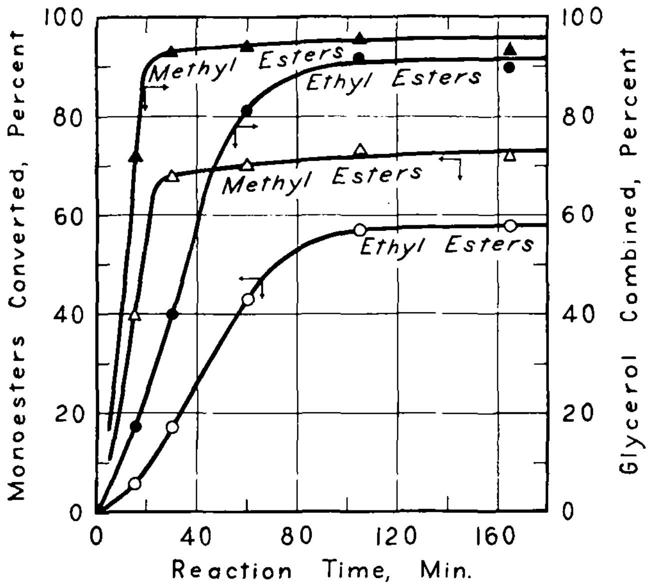

FIG. 6. Comparison of reaction rates of methyl and ethyl esters with equivalent quantities of glycerol at 180°C. and 200 mm. pressure. Catalyst, 0.002 mole lithium hydroxide per 100 g. of monoesters.

3. When equivalent quantities of monoesters are allowed to interact, the initial rate of alcoholysis is influenced markedly by the temperature and concentration of catalyst and to some extent by the pressure. All reactions, however, come to equilibrium at approximately 70% completion. For practical reasons the variations in temperature, pressure, and concentration of catalyst are somewhat limited.

4. Under identical conditions ethyl esters are alcoholized less readily than are the corresponding methyl esters. Also when ethyl esters are used, the reactions cease at a lower percentage of completion.

5. Monoesters can be converted fairly completely into triglycerides by reacting the monoesters with an excess of glycerol and then decomposing the resulting glycerides by heating and stripping with steam under low pressure.

6. The alcoholysis reaction itself can be forced to produce approximately 90% triglycerides by employing an excess of monoesters.

7. Ester-ester interchange reactions using triacetin and methyl or ethyl esters did not proceed as well as has been reported in the literature. The influence of various conditions on the reaction rate was not evaluated because only a small amount of the easily destroyed catalyst is soluble in the reactants and because the reaction was complicated by the existence of an induction period.

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