was stored at 90° F. in diffused light for a period of two months, and peroxide values were determined at periodic intervals. Average peroxide value of all atmospheric bleached and all vacuum bleached samples at each interval are shown in Figure 14.

TABLE VI

Type of Adsorbent	% Adsorbent	Average Reduction in Oil Stability in Bleaching	
		Atmospheric	Vacuum
Activated Carbon	.125-.75	24	21
Natural Clay	1	27	22
Activated Clay (1)	1	25	10
Activated Clay (2)	1	27	12

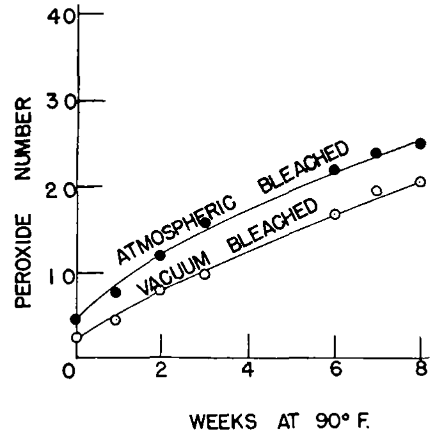

FIG. 14. Effect of vacuum bleaching on oil stability.

Averages for a relatively large number of tests show that stability of vacuum bleached oil, as determined by the Swift Stability Method, is approximately 15% greater than of atmospheric bleached oil when activated clays are used as the adsorbent. Data comparing the effects of various adsorbents in vacuum versus atmospheric bleaching on Swift Stability of a good quality refined cottonseed oil are given in Table VI.

These data substantiate previous conclusions that the effectiveness of vacuum bleaching depends on the extent to which oxidation is reduced. The activated clays, which showed greatest response to vacuum bleaching in regard to color removal, also showed the greatest improvement in oil stability due to vacuum bleaching. The activated carbon which reduced oil stability only slightly more in atmospheric than in vacuum bleaching showed no significant advantage in vacuum over atmospheric bleaching in regard to color removal.

Summary

In bleaching fatty oils an equilibrium exists between two reactions favorable and two unfavorable in respect to color reduction. Adsorption of color and oxidative decrease in color are favorable. Oxidative increase in color and oxidative stabilization against adsorption are unfavorable. Adsorbents are shown to catalyze these oxidative reactions.

Under any comparable set of conditions significantly lower colors result when bleaching is carried out under vacuum or in an inert atmosphere. Multiple stage bleaching under atmospheric conditions shows no advantage because of the adverse oxidative effect but may be advantageous under vacuum conditions.

Low pH earths respond better than high pH earths to vacuum bleaching with respect to improved color removal and oil stability.

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Directed Interesterification in Glycerides. Reaction in Presence of Added Glycerol

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WHEN triglycerides are heated to a temperature sufficiently high, a process of ester-ester interchange occurs which allows the acid radicals to change places until, at equilibrium, the composition of the triglyceride mixture approximates the composition corresponding with random distribution of the acid radicals in the esters.

At low temperature, in the presence of highly active catalysts, triglycerides can undergo a process of directed interesterification in which fractional crystallization of the triglycerides take place simultaneously with ester-ester interchange (1, 2). The simple form of this process as applied to a fat such as cottonseed oil, containing mixed glycerides of saturated and unsaturated fatty acids, consists of mixing the oil with catalyst and holding the mixture at temperatures below those at which the fully saturated triglycerides, at their equilibrium concentration, can remain in solution. Crystallization of saturated glycerides from the mixture alters the composition of the reacting phase and allows additional quantities of saturated triglycerides to form progressively from mixed saturated-unsaturated glycerides as new equilibria are approached. In this way a large proportion of the saturated fatty acids of the fat can be segregated into the fully saturated glyceride fraction. The range of triglyceride compositions attainable by interesterification of a given fat is thus greatly extended in comparison with that produced by high-temperature reaction.

This paper describes results that can be obtained when the process is applied to glyceride mixtures containing free hydroxyl groups. When these are present, as in the case when a small proportion of glycerol is added to a triglyceride mixture while it is undergoing interesterification, the process becomes a mixed process of ester-alcohol interchange together with ester-ester interchange since the same catalysts serve to accelerate both these reactions. The ester-

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TABLE I

Interesterification of Cottonseed Oil[1] in Presence of Added Glycerol, 2.5 Parts per 100 of Oil

Reaction conditions	1	2	3		4		5	6	7	8		9	
	d	b	b		b		b	c	c	c		c	
Time-temperature cycle after initial mixing:													
Time at 32.2°C. (90°F.), days	......	3	......		......		1	3	......	......		1	
Time at 26.7°C. (80°F.), days	......	......	3		......		1	......	3	......		1	
Time at 21.1°C. (70°F.), days	......	......	......		3		1	......	......	3		1	
Whole fat after reaction:													
Capillary melting point, °C	......	47.1	53.1		55.5		51.7	40.2	50.6	53.7		54.1	
Cloud-point, °C	18.5	34.1	42.0		46.3		42.9	19.2	41.1	45.8		44.4	
Drop No. of 5% solution in Primex	......	9.4	9.1		11.4		9.1	9.8	9.7	11.5		8.6	
Estimated minimum % monoglyceride[2]	......	6	5		11		5	7	7	11		4	
Crystallization from petroleum ether at 10°C.:													
Yield of crystals, %	1.2	4.3	9.3	8.0	12.0	11.7	8.6	2.8	9.1	11.1	10.8	14.4(?)	11.4
Capillary M.P. of crystals, °C	67.0	66.9	66.7	67.0	66.8	67.0	67.8	67.2	66.8	68.3	67.7	66.0	67.7
Iodine value	......	......	......	10.3	......	5.3	......	......	......	......	2.1	......	5.6
Drop No. of 1.5% solution in Primex	14.0	12.3	7.7	......	8.6	......	7.7	16.0	8.2	9.9	......	7.9	......
Estimated % monoglyceride	56	45	2	......	10	......	2	68	8	25	......	5	......
Crystallization from petroleum ether at 4.4°C.:													
Yield of crystals, %			10.9		15.2					14.5		14.3	
Capillary M.P., °C			65.7		67.3					65.8		66.1	
Iodine value			6.0		2.7					2.4		4.4	
Crystallization from petroleum ether at 0°C.:													
Yield of crystals, %			11.1		15.4					14.8		15.1	
Capillary M.P., °C			65.6		65.6					65.7		65.8	
Iodine value			......		2.3					3.6		4.1	

[1] Iodine value of the cottonseed oil: 110.4.

b. Catalyst consisting of 0.48% of sodium methoxide, in the form of a suspension in xylene (1), was stirred into the refined, dried oil at 48.9°C. (120°F.) with a high-speed stirrer. Glycerol was then added slowly from a burette, over a period of about 5 min., after which the stirring was continued for 30 minutes more at the same temperature. The mix was then chilled rapidly to 15.5°C. by surrounding the vessel with ice water while stirring was continued. The mix was then transferred to a container which was rotated continuously in constant-temperature rooms for times stated.

c. Same conditions as b, but omitting the chilling after the initial mixing.

d. Reaction stopped by neutralizing the catalyst at end of the 30-min. mixing at 48.9°C.

[2] The per cent monoglyceride estimated for the whole oil by comparing the drop numbers with those in Fig. 1 will be somewhat less than the actual value, since mono-olein and monolinolein, which may be present in the whole oil, have less effect than monopalmitin on the drop number.

alcohol interchange tends to produce an equilibrium among glycerol, monoglycerides, diglycerides, and triglycerides.

The investigation was undertaken with the expectation that selective crystallization of monoglycerides and diglycerides, in preference to triglycerides, could be obtained from such reaction mixtures. One purpose was to develop, on this basis, improved methods for the preparation of mono- and diglycerides. Another purpose was to develop a method that would be even more effective than the simple form of directed interesterification for segregating the saturated fatty acid radicals of a fat in a fully saturated glyceride fraction.

Both of these aims have been realized. The experimental results show that a strong tendency exists for mono- and diglycerides to precipitate in preference to triglycerides from glyceride mixtures in which ester-ester and ester-alcohol interchanges are occurring, and further, that with selected ratios of free hydroxyl to ester groups, the precipitated glyceride may be made to consist either of diglyceride almost free from monoglyceride, or of monoglyceride almost free from diglyceride.

Experimental

General Procedure. Cottonseed oil was chosen as the triglyceride mixture for the main series of experiments because it contains a convenient ratio of solid to liquid fatty acids, combined in the form of mixed triglycerides, and because the solid acids are principally of one kind, namely, palmitic acid.

Catalyst, consisting of a suspension of sodium methoxide in xylene, was stirred into the dry refined oil in a vessel arranged to exclude air; dried glycerol was then stirred into the mix and the whole transferred to a Mason jar, or other vessel that could be closed air-tight, and rotated continuously end-over-end in a constant-temperature room.

After this treatment, over the desired schedule of time and temperature, the mixture was treated with a small quantity of glacial acetic acid to destroy the catalyst, then melted, washed thoroughly with hot water, and given a distillation treatment at reduced pressure to remove the xylene.

The yield of solid glycerides obtained by crystallization of a sample of the product in 10 volumes of petroleum ether and the characteristics of the fraction obtained served as the principal means for determining the results of the interesterification process.

Glycerol. C. P. glycerol was mixed with xylene in a flask equipped with a motor-driven stirrer and a reflux condenser, arranged to reflux the xylene through a Bidwell-Sterling moisture trap. The mixture was boiled, with continuous stirring, until no more water was evolved. The xylene was then boiled off, and the glycerol was distilled at reduced pressure.

Catalyst. The catalyst was a suspension of sodium methoxide in xylene, prepared as described previously (1).

Estimation of monoglycerides. The interfacial tension between slightly acidified water and a solution of a given sample in triglyceride oil serves as a means for estimating the proportion of monoglyceride in the sample when the kind of fatty acid constituting the monoglyceride is known. This is so because diglycerides do not affect the interfacial tension while monoglycerides have a large effect.

The monoglyceride content of the solid glycerides crystallized from interesterified cottonseed oil was estimated[3] by determining the drop number of a

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[3] Results obtained by others in the Procter and Gamble laboratories since this work was done have shown that the percentages of monoglyceride estimated by the drop number method in mixtures consisting of mono-, di-, and triglycerides are in satisfactory agreement with the percentages found by the periodate method (10, 11). The use of the drop number method of course involves an assumption concerning the kinds of monoglyceride present in the sample, and the use of an appropriate standard curve for comparison. A few typical results with glyceride mixtures are as follows:

Mixture	Monoglyceride found by periodate method (11), %	Monoglyceride estimated from drop number, %
A	54.4	57.5
B	36.1	38.9
C	2.9	2.8
D	2.6	2.8

solution of the solid glycerides in a hydrogenated vegetable oil shortening (Primex) consisting practically entirely of triglycerides, and comparing the values obtained with those obtained with a sample of monopalmitin prepared by repeated recrystallization of crude monoglyceride obtained in directed interesterification of cottonseed oil. See Fig. 1.

Drop number. The drop number was standardized arbitrarily as the number of drops formed by 2.5 ml. of oil at 48.9° C. (120° F.) flowing slowly upward through an inverted Monel metal tip into 0.001 N aqueous HCl solution. The tip where the drops formed was the end of a cylinder 6.35 mm. (0.250 inch) in diameter.

Interesterification of cottonseed oil with added glycerol. Table I describes a series of experiments in which 2.5% of glycerol was added after the catalyst was mixed with the oil and in which different temperatures were used after the initial mixing at 48.9°C.

The temperature had a large influence on the result. At 32.2°C. (90°F.) there was little or no crystallization of solid from the oil during the three days of mixing of the unseeded sample (Col. 6, Table I), with the result that the product was not much different from the sample obtained by 30 min. mixing at 48.9°C., without subsequent storing at lower temperature. The seeded sample, Col. 2, gave some crystallization of solid during the reaction so that the product had higher cloud point and melting point and higher content of solid glycerides.

At 26.7°C. (80°F.) and at 21.1°C. (70°F.) more crystallization took place during the reaction, and the changes produced in the fat were more striking.

The solid glycerides crystallized during the reaction at 26.7°C. appear to consist principally of diglycerides since the crystals obtained from petroleum ether have melting points that are higher than that of pure tripalmitin, in spite of some contamination with unsaturated glycerides, and drop numbers that show that the proportion of monopalmitin is very small. The same is true for the experiments with stepwise reduction of the temperature during reaction to 21.1°.

The separation of solid glycerides from the reaction product by crystallization from 10 volumes of petroleum ether was more complete when the crystallization was carried out at 4.4°C. (40°F.) than when the temperature was 10°C. (50°F.).

Table II gives the results of further experiments, in which different proportions of glycerol were used, and the reaction was carried out over a long period during which the temperature was reduced in stepwise fashion to a final reaction temperature of 10°C.

Under these conditions the solid crystallized during the reaction consisted almost wholly of diglyceride when the proportion of glycerol added was 2.5% or 5%, and almost wholly of monoglyceride when the proportion was 10%. The quantity of solid glycerides formed was large enough to account for most of the saturated portion of the cottonseed oil.

Table III gives the results of other variations in the time-temperature cycle and in the proportion of glycerol used. When the proportion of glycerol was 10%, the solids formed were again practically pure monoglyceride. With 7.5% glycerol and stepwise reduction of the temperature to 10°C. a less pure monoglyceride was precipitated.

With 2.5% glycerol the solids again tended to be diglyceride, but when the temperature of reaction was 15.5°C. or lower, without a preceding period of reaction and crystallization at higher temperature, a mixture of diglycerides and monoglycerides precipitated.

The experiment given in the first column of data in Table III is noteworthy in that it shows that when a favorable set of reaction conditions is used, practically all of the saturated fatty acids of cottonseed oil can be accumulated in a saturated diglyceride fraction. The yield and characteristics of the solid and liquid fractions obtained in the petroleum ether crystallization, in comparison with the characteristics of the original oil, show that the liquid fraction contained less than 1% of saturated fatty acids.

Recrystallization of mono- and diglycerides ob-

TABLE II

Interesterification of Cottonseed Oil[1] With Different Proportions of Glycerol

	1	2	3	4	5	6
Glycerol, parts by wt., per 100 of oil	10.0	10.0	2.5	5.0	10.0	2.5
Reaction conditions:	b	c	d	d	d	e
Time at 32.2°C. (90°F.), days	......	......	3[2]	3[2]	3[2]	......
Time at 26.7°C. (80°F.), days	......	......	3	3	3	1
Time at 21.1°C. (70°F.), days	......	......	4	4	4	1
Time at 15.5°C. (60°F.), days	......	......	4	4	4	1
Time at 10.0°C. (50°F.), days	......	......	3	3	3	3
Whole fat after reaction:						
Capillary M.P., °C	......	......	55.3	55.1	61.0	54.1
Cloud point, °C	18.9	22.4	50.1	50.3	45.4	50.1
Drop No. of 5% solution in Primex	......	......	8.3	10.3	19.0	10.5
Estimated minimum % monoglyceride	......	......	3	9	25	9
Crystallization from petroleum ether:						
Temperature of crystallization, °C	10	10	4.4	4.4	4.4	4.4
Yield of crystals, %	0.8	2.9	22.6	24.8	22.4	25.3
Capillary M.P., °C	69.2	69.7	67.2	66.5	71.5	63.6
Iodine value	......	......	12.2	17.6	5.6	......
Drop No. of 1.5% solution in Primex	18.3	22.9	7.9	8.1	22.3	9.5
Estimated % monoglyceride	80	100	5	7	98	22
Hydroxyl value	......	......	99	104	313	......
Glycerin yield, %	......	......	15.48	15.53	26.27	......
Oleine fraction:						
I. V. of liberated fatty acids	......	......	......	......	......	145.5
Titer test, °C	......	......	......	......	......	6.2

[1] Iodine number, 110.4.

b. Catalyst neutralized at end of 30-min. mixing at 48.9°C., after addition of the glycerol.

c. Same as b except that mixing time was 3 hours.

d. Same method as described in Note b, Table I, except that after 1 day at 26.7°C., the end-over-end rotation was discontinued and the vessels stood without agitation for the remainder of the cycle.

e. Same as described in Note b, Table I.

[2] At the end of the 3 days at 32.2°C., the batch in Column 3 was semi-liquid, the one in Column 4 was almost solid, and the one in Column 5 was solid. Within a few hours after transfer to room at 26.7°C., all three were too stiff to be stirred by the rotation.

TABLE III

Interesterification of Cottonseed Oil[1] With Added Glycerol

	1	2	3	4	5	6
Glycerol, parts by wt. per 100 of oil	2.5	2.5	2.5	2.5	7.5	10.0
Reaction conditions[2]:						
Time at 26.7°C. (80°F.), days	......	......	......	......	......	3
Time at 21.1°C. (70°F.), days	2	7	......	......	1	......
Time at 15.5°C. (60°F.), days	3	......	7	......	1	......
Time at 10.0°C. (50°F.), days	2	......	......	7	1	......
Whole fat after reaction:						
Capillary M.P., °C	54.2	55.7	56.1	57.3	58.9	59.8
Cloud point, °C	51.1	50.6	50.5	38.9	38.0	42.2
Drop No. of 5% solution	9.1	10.3	9.2	10.2	12.4	20
Estimated % monoglyceride	5	9	6	8	13	27
Crystals from petroleum ether at 4.4°C. (40°F.):						
Yield of crystals, %	22.6	17.7	20.3	14.6	15.9[3]	17.6[4]
Capillary M.P., °C	65.2	65.1	64.9	63.7	......	71.4
Iodine number of crystals	6.4	10.9	4.8	......	......	......
Drop No. of 1.5% solution	8.5	8.3	9.9	11.4	16.9	23.6
Estimated % monoglyceride	12	10	25	38	73	103
Oleine from crystallization:						
Iodine No. of liberated fatty acids	144.4	138.8	139.4	......	......	......
Titer of liberated fatty acids, °C	6.4	15.8	9.8	......	......	......

[1] Iodine number, 109.7; thiocyanogen number, 71.3. Calculated composition: linoleic glycerides, 47%; oleic glycerides, 32%; saturated glycerides, 21%. Calculated iodine number of mixed unsaturated fatty acids, 145.

[2] See Note b, Table I.

[3] To test other methods of crystallization, a portion of this batch of oil was dissolved in 10 vols. of petroleum ether, chilled to —6.7°C., then held for 24 hrs. at 4.4°C. and filtered. Yield of crystals, 18.9%; M.P., 68.7°C.; I.V., 7.2. Another portion crystallized from 10 vols. petroleum ether at —6.7°C.(20°F.) yielded 19.4% of crystals; M.P., 67.4; I.V., 6.9.

[4] Another portion of this batch, crystallized from petroleum ether at —6.7°C., yielded 18.9% of crystals; M.P., 72°C.; I.V., 6.7.

tained by interesterification of cottonseed oil. Samples of solid glycerides obtained by crystallization of selected batches of interesterified cottonseed oil were composited to give two samples with a high content of diglyceride and monoglyceride respectively. These were recrystallized from solution in 20 volumes of commercial hexane, then from 20 volumes of ethanol, then twice again from 20 volumes of commercial hexane. The characteristics of the products obtained are given in Table IV. The monopalmitin was used in the determinations of drop number given in Fig. 1.

Discussion

The results show that the method of directed interesterification can be applied without difficulty to glyceride mixtures containing free alcohol groups over a fairly wide range of concentrations. Cottonseed oil and glycerol, in proportions such that the ratio of free alcohol groups to ester groups was between about 1 to 5 and 1 to 2, gave precipitates during reaction that consisted predominantly of diglyceride when a favorable time-temperature cycle was used; when the ratio was about 1 to 1, nearly pure monoglyceride precipitated.

This highly selective action may be accounted for by considering the probable relative concentrations of the various glycerides existing in the reaction mixture when crystallization begins. In the single-phase alcoholysis of triglycerides with glycerol Feuge and Bailey (9) have shown that the equilibrium concentrations of triglyceride, diglyceride, monoglyceride, and free glycerol approximate those calculated on the assumption that there is a completely random distribution of the acid radicals among the hydroxyl groups. Such calculated values are shown in Fig. 2.

Considering, for example, the third column of data in Table II, the ratio of free hydroxyl groups to ester groups in this experiment is 0.24. According to Fig. 2, the equilibrium composition in the alcoholysis reaction would be about 1% of glycerol, 10% of monoglyceride, 37% of diglyceride, and 52% of triglyceride. Assuming that equilibrium in the ester-ester interchange reaction also is approached, about one-fourth of the monoglyceride, one-sixteenth of the diglyceride, and one sixty-fourth of the triglyceride would be saturated glycerides (assuming about one-fourth of the fatty acids of the cottonseed oil to be saturated acids). Thus, the molar percentages of saturated mono-, di-, and triglycerides would be about 2.5, 2.3, and 0.8 respectively. On a weight basis the proportions of the three saturated glycerides to each other would be 1:1.6:0.8. Since diglyceride is the saturated constituent present in the largest proportion at equilibrium, it is not surprising that it should be the first to precipitate when the mixture is cooled. When the cycle of temperature vs. time is favorable, it appears that the preferential crystallization of diglyceride continues until practically all the saturated constituents of the fat appear in the precipitated diglyceride fraction.

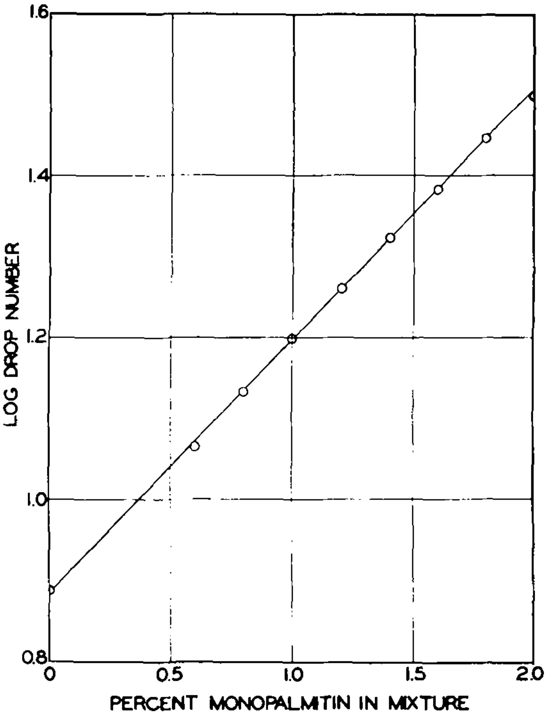

FIG. 1. Effect of monopalmitin on interfacial tension between triglyceride oil and 0.001 N aqueous HCl at 48.9°C.

TABLE IV

Monopalmitin and Dipalmitin From Interesterified Cottonseed Oil

	Recrystallized Monoglyceride Fraction	Recrystallized Diglyceride Fraction	Calculated or Published Values for Pure Glycerides					
			Monopalmitin		Dipalmitin		Tripalmitin	
			Value	Ref.	Value	Ref.	Value	Ref.
Melting point, °C	75.6	72.4	77.0[1] 68.5[3]	3 3	72.5[2]	4	65.5	5
Iodine value	1.1	0.8	0	Calc'd	0	Calc'd	0	Calc'd
Saponification value	168.8	195.3	169.9	Calc'd	197.4	Calc'd	208.6	Calc'd
Hydroxyl value	336	99	340	Calc'd	99	Calc'd	0	Calc'd
Glycerin yield, %	27.46	16.03	27.85	Calc'd	16.19	Calc'd	11.1	Calc'd
Drop No. 1.5% solution in Primex	22.6	7.4	......	......	......	......	......	......
Melting point of liberated fatty acids, °C	62.3	62.4	62.85 62.67	6 7	......	......	......	......
Saponification value of liberated fatty acids	......	219.6	218.9	Calc'd	......	......	......	......

[1] 1-isomer. [2] 1,3-isomer. [3] 2-isomer.

Similar calculations for the case shown in the 4th column of data in Table II give a calculated weight ratio of 1:0.9:0.2 for the three saturated glycerides. The preferential crystallization of diglyceride instead of monoglyceride in this reaction probably occurs because dipalmitin has a higher cloud point than monopalmitin and crystallizes more readily in spite of the fact that the capillary melting point of monopalmitin is higher than that of dipalmitin. This experiment is a striking example of the effect of the fractional crystallization upon the course of the reaction since not only were the saturated constituents almost completely segregated from unsaturated, but also they were obtained predominantly in the form of diglyceride from a mix which at equilibrium would contain as much saturated monoglyceride as saturated diglyceride.

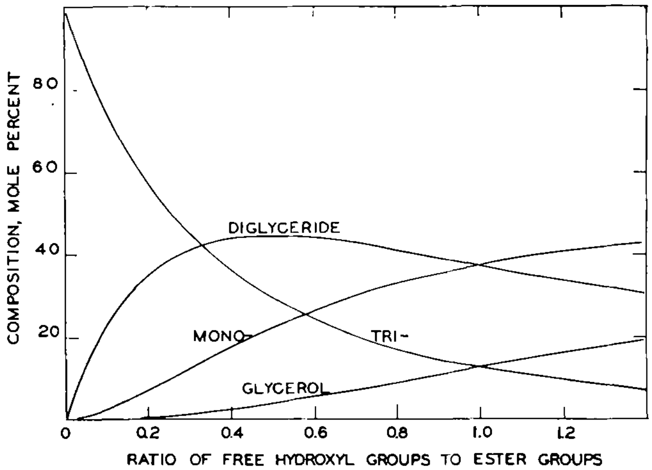

FIG. 2. Calculated composition produced at equilibrium by single-phase alcoholysis of triglycerides with glycerol.

In the case of the experiment recorded in the fifth column of Table II the calculated equilibrium weight ratio for the three saturated glycerides is about 1:0.5:0.06. With this advantage the saturated monoglyceride evidently is the first to crystallize and continues to crystallize in nearly pure form throughout the cycle.

The general method described is patented (8). Application of the method to synthetic mixtures of pure glycerides to provide a convenient way to prepare pure monoglycerides and diglycerides will be described in another paper from this laboratory.

Summary

Directed interesterification, in which ester-ester interchange is carried out in triglyceride mixtures with simultaneous crystallization of solid glycerides, has been applied to glyceride mixtures containing free hydroxyl groups. Solid glycerides precipitated from cottonseed oil with added glycerol were principally saturated diglycerides or saturated monoglycerides.

The principal variables controlling the kind and proportion of solid precipitated during reaction from glycerides of a given original composition are the proportion of free alcohol groups, the time-temperature schedule for the reaction, and the method of seeding, if any, used to start the crystallization. The method makes it possible to segregate the high-melting and low-melting fatty acids of a fat practically completely into separate ester fractions.

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