

collected on a Buchner funnel. The dry acid, 2.2 g., was crystallized twice from benzene m.p. 80° C.

Calc. for $C_{16}H_{30}O_4$ % C = 67.13 % H = 10.55.

Neutral Equiv. = 286.

Saponification Equiv. = 286.

Found % C = 66.94 % H = 10.63,

Neutral Equiv. = 289.

Saponification Equiv. = 287.

A portion of the above acid ester was saponified with alcoholic caustic potash. After a few minutes warming, a quantity of granular crystals separated. These were filtered off and washed with 95% alcohol to remove potassium myristate and recognized as potassium glycolate by conversion to the p-nitro benzyl ester m.p. 107° and comparison with a known specimen of p-nitro benzyl glycolic ester (7).

Summary

1. It has been shown that pure anhydrous glycerol and fatty triglycerides do not react appreciably below

decomposition temperatures, but that water or an alkaline material such as soap will catalyze reaction.

2. It has been shown that fatty monoglycerides when free from soap or alkaline material can be distilled in vacuum with only slight reversion in the higher members of the series.

3. The monoglycerides produced by the action of glycerol on methyl esters of fatty acids using caustic alkali as catalyst have been shown by periodic acid oxidation to have α -mono glyceride structure.

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Modification of Vegetable Oils

VI. The Practical Preparation of Mono- and Diglycerides

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TECHNICAL mono- and diglycerides are prepared by the reaction of fat or fatty acids with glycerol in the presence of an alkaline catalyst (4, 6, 8). These materials not only find wide use in such industrial applications as the manufacture of "high-ratio" shortenings and oil-modified resins, but are also potentially important as intermediates for the preparation of so-called "tailor-made" fats.

The reaction product of fatty acids or fat with an excess of glycerol consists invariably of a mixture of mono-, di-, and triglycerides with unreacted glycerol. No systematic investigation has been made of the reaction in terms of the composition of the reaction product. However, various investigators (8, 9, 11, 12, 15) have reported that the composition is dependent upon such factors as the temperature, the reaction time, and the amount and nature of the catalyst used, as well as the proportions of fatty acids and glycerol in the reaction mixture.

In the case of a fat reacted with a very small excess of glycerol and a suitable catalyst there is strong evidence (2) that the fatty acid radicals become rearranged to an ultimate state of random distribution amongst the triglyceride molecules. Since in technical mono- and diglyceride manufacture there exist conditions equally favorable to acyl interchange, it seems surprising that the composition of the product should depend upon the temperature or similar conditions of reaction. In a homogeneous material in which the reaction has been carried to equilibrium it would ap-

pear more reasonable to expect that the proportions of triglycerides, diglycerides, monoglycerides, and free glycerol would conform to a pattern of random distribution with respect to OH groups esterified.³ In such a material the composition would depend solely upon the proportions of fatty acids and glycerol reacted, and would be calculable by statistical methods (2).

The present investigation was undertaken to generally elucidate the manner of mono- and diglyceride formation and decomposition, and particularly to test the above-mentioned hypothesis of random distribution.

Experimental

The fat used in the experiments consisted of refined cottonseed oil which had been hydrogenated to an iodine value of 0.7. The average molecular weight of the (tri-) glycerides, calculated from the neutralization value of the fatty acids, was 876.2. This corresponds to a molecular weight of 614.9 for the diglycerides and 353.5 for the monoglycerides. Calculated glycerol contents for the tri-, di-, and monoglycerides were 10.51%, 14.98%, and 26.05%, respectively.

Reaction between the fat and glycerol was carried out in the stirred glass vessel described previously (7), under an atmosphere of hydrogen. In all cases sodium hydroxide equivalent to 0.1% of the weight of the fat was used as a catalyst.

The reaction product was analyzed for total content of free and combined glycerol by the official A. O. C. S. bichromate method (1), after alcoholic

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³This expectation was first called to the attention of the authors by Mr. E. W. Eckey of the Proctor and Gamble Laboratories.

saponification and removal of the alcohol by the procedure of Smith and Matthews (14). After being freed of uncombined glycerol by washing with 20% sodium sulfate solution, the fatty portion of the product was analyzed for combined glycerol by the above-mentioned method and for monoglyceride content by the periodic acid oxidation method of Pohle, Mehlenbacher, and Cook (13). From these data the composition of the product was calculated, in terms of free glycerol, mono-, di-, and triglycerides. In making the calculations, it was assumed that sodium soap equivalent to the sodium hydroxide catalyst was present in the unwashed but not in the washed product. The glycerol used was a U. S. P. product which contained 95.4% anhydrous glycerol by analysis. In all succeeding tabulations of data amounts of glycerol are given in terms of anhydrous material.

In some cases, in order to obtain a homogeneous reaction product at a relatively low temperature, the reaction was conducted in the presence of phenol or cresol as a solvent as recommended by Hilditch and Rigg (9, 10). The solvent was removed from the finished product by stripping with a current of hydrogen under the vacuum created by a Megavac pump. Even when using fractions of the solvents which had been carefully redistilled some difficulty was experienced in freeing the product of solvent without decomposition of the glycerides; in fact it is believed that some slight decomposition occurred in all cases, as in the presence of the catalyst the monoglycerides appeared to be unstable even under very mild stripping conditions. For example, in one experiment conducted in phenol the monoglyceride content of the product was 59.3% after stripping at 80-100° C., but 58.9% after continued treatment at 115-120° C. In another experiment in which *m*-cresol was used as the solvent the monoglyceride content was 63.0% after stripping at 80-100° C., but 61.8% after 45 minutes additional stripping at 125° C. to remove all solvent odor.

In experiments in which the product was steam deodorized, deodorization was carried out at a pressure of about 1 mm. of mercury in the apparatus described by Bailey and Feuge (3). Removal of the catalyst prior to deodorization was effected by treatment with strong phosphoric acid, according to the method of Eckey and Clark (5).

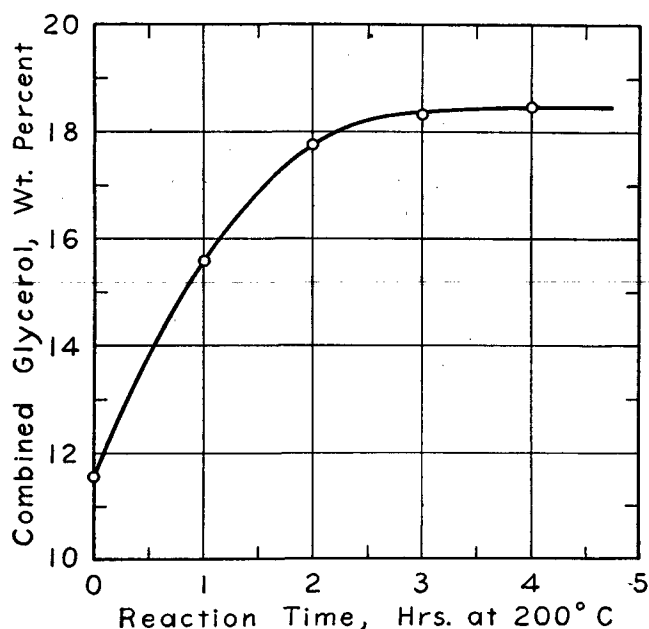


FIG. 1. Course of reaction of fat with 16.63% of its own weight of glycerol. Combined glycerol content of the fatty material vs. reaction time.

Reaction Time vs. Combined Glycerol in the Product

The course of reaction in a typical preparation of mono- and diglycerides is illustrated in Figure 1. In this experiment the fat was reacted at 200° C. with 16.63% of its own weight of glycerol and 0.1% sodium hydroxide as a catalyst. The results are expressed in terms of combined glycerol in the product. It is evident that under these conditions substantial equilibrium is attained in the reaction mixture after about 3.5 hours and shortly after the mixture becomes homogeneous.

Miscibility of Glycerol with the Reaction Product

It has been pointed out by Hilditch and Rigg (9, 10) that the comparative immiscibility of glycerides and glycerol imposes a limitation upon the extent to which reaction between fat and glycerol can be carried. Reaction takes place within the fatty phase, and

TABLE 1
Preparation of Mono- and Diglycerides by Reaction of Hydrogenated Cottonseed Oil With Glycerol:
Operational and Analytical Data.

Run No.	14	19	13	18	12	17	16	20	30*
Temp., °C.	200	200	200	200	200	230 ^b	200	230 ^b	200
Time, hrs.: min.	5:00	5:00	5:00	5:00	5:00	5:00	5:00	5:00	5:00
Glycerol, % on basis fat.	1.17	2.62	4.50	7.00	10.49	10.49	15.73	24.47	41.95
OH groups esterified, % ^c	89.2	80.2	70.2	60.2	50.6	51.0	40.5	30.7	22.9
Monoglyc. in fatty portion, %	1.27	4.86	10.75	18.12	28.20	26.99	38.50	49.10	61.9
Comb. glycerol in fatty portion, %	11.52	12.57	13.96	15.36	16.91	16.81	18.44	20.08	21.74
Total glycerol in whole material, % ^d	11.64	12.78	14.33	16.33	18.85	18.71	22.47	27.66
Composition of fatty portion, % by wt.:									
Monoglycerides.....	1.3	4.9	10.8	18.1	28.2	27.0	38.5	49.1	61.9
Diglycerides.....	18.4	29.2	39.9	45.5	45.3	47.3	43.7	43.5	36.1
Triglycerides.....	80.3	65.9	49.3	36.4	26.5	25.7	17.8	7.4	2.0
Composition of whole reaction mix., mole %:									
Free glycerol.....	1.2	1.9	3.0	7.0	12.4	12.3	22.0	34.3	46.0
Monoglycerides.....	2.8	9.9	19.5	28.6	38.1	36.7	42.4	41.9	40.1
Diglycerides.....	23.4	34.2	41.1	41.3	35.0	36.8	27.6	21.2	13.4
Triglycerides.....	72.6	54.0	36.4	23.1	14.5	14.2	8.0	2.6	0.5

* Reacted in cresol to make reaction mixture homogeneous; slight decomposition probably occurred during removal of cresol (see text). Reaction mixture could not be analyzed for total glycerol content; percent OH groups esterified and composition of whole reaction mixture were calculated on assumption that the free glycerol content corresponded to the principle of random distribution.

^b Probably some polymerization occurred at this temperature (see text), making reported percentages of mono- and triglycerides slightly low, and of diglycerides slightly high.

^c Calculated from analysis of final product; a small amount of glycerol always disappeared during the reaction.

^d Corrected for soap formed by NaOH used as catalyst; calculated on basis of soap-free fat.

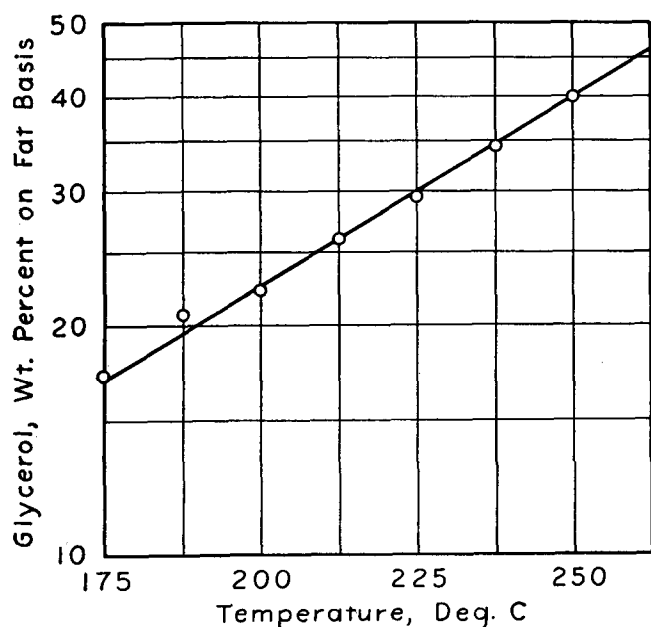


FIG. 2. Maximum amount of glycerol reactable and miscible with fat at different temperatures.

any excess glycerol forming a second phase of course does not participate in the reaction.

A series of experiments was carried out to determine the maximum amount of glycerol which is miscible in a reaction carried to equilibrium at different temperatures. Results, in terms of percent anhydrous glycerol on the basis of the fat, are shown graphically in Fig. 2. Within the range covered (175-250°C.) there appears to be a linear relationship between the temperature and the logarithm of the amount of glycerol miscible. It is to be noted that here the percentages of glycerol refer to the glycerol *added* to the fat, and are exclusive of the glycerol originally combined with the fat in the form of triglycerides.

In order to bring into reaction with the fat larger proportions of glycerol than those indicated at the different temperatures, it is necessary to employ a high-boiling solvent in which fat and glycerol are mutually soluble, as proposed by Hilditch and Rigg (9, 10).

Composition of the Reaction Products

Complete operational and analytical data on a series of reactions carried out with different proportions of reactants are given in Table 1. In all of these, conditions were chosen which would produce a condition of equilibrium within the time allowed for reaction, and which would yield a homogeneous reaction product, free from undissolved glycerol. Certain runs carried out at a higher temperature (250° C.) which yielded an abnormal, probably partially polymerized product, are excluded from the tabulation. These runs and their products will be discussed in a later paragraph.

As explained above, it was considered desirable to compare the actual composition of the various products with their theoretical composition calculated upon the basis of random distribution of fatty acid radicals to the esterifiable OH groups of the glycerol present. This calculation is easily carried out upon the assumption that all OH groups are esterifiable with equal readiness, in which case the molar percentages of free glycerol, monoglycerides, diglycerides, and triglycerides will conform to the random pattern of two elements (in this case, free OH groups and esterified OH groups) taken in combinations of three, as indicated in detail in Table 2.

TABLE 2
Random Distribution of Two Elements, A and B, in Different Proportions, in Combinations of Three

Percent of each element		Percent of each combination			
A	B	AAA	AAB	ABB	BBB
100	0	100.0	0	0	
95	5	85.7375	13.5375	0.7125	0.0125
90	10	72.9	24.3	2.7	0.1
85	15	61.4125	32.5125	5.7375	0.3375
80	20	51.2	38.4	9.6	0.8
75	25	42.1875	42.1875	14.0625	1.5625
70	30	34.3	44.1	18.9	2.7
65	35	27.4625	44.3625	23.8875	4.2875
60	40	21.6	43.2	28.8	6.4
55	45	16.6375	40.8375	33.4125	9.1125
50	50	12.5	37.5	37.5	12.5
45	55	9.1125	35.4125	40.8375	16.6375
40	60	6.4	28.8	43.2	21.6
35	65	4.2875	23.8875	44.3625	27.4625
30	70	2.7	18.9	44.1	34.3
25	75	1.5625	14.0625	42.1875	42.1875
20	80	0.8	9.6	38.4	51.2
15	85	0.3375	5.7375	32.5125	61.4125
10	90	0.1	2.7	24.3	72.9
5	95	0.0125	0.7125	13.5375	85.7375
0	100	0	0	0	100.00

TABLE 3
Theoretical Composition of Products Prepared by the Reaction of Fat With Glycerol. Calculated on the Basis of Random Distribution in a Homogeneous Reaction Mixture. Average Molecular Weight of the Fat, 876.2.

Percent of total OH groups esterified	Parts glycerol reacted with 100 parts fat	Composition of fatty product*						Glycerol content, %
		Percent by moles			Percent by weight			
		Mono-	Di-	Tri-	Mono-	Di-	Tri-	
100	0	0	0	100.0	0	0	100.0	10.51
95	0.55	0.7	13.5	85.8	0.3	9.9	89.8	11.00
90	1.17	2.7	24.3	73.0	1.2	18.7	80.1	11.53
85	1.86	5.8	32.6	61.6	2.7	26.4	70.9	12.10
80	2.63	9.7	38.7	51.6	4.7	32.9	62.4	12.71
75	3.50	14.3	42.9	42.8	7.3	38.2	54.5	13.35
70	4.50	19.4	45.3	35.3	10.5	42.5	47.0	14.03
65	5.66	25.0	46.3	28.7	14.1	45.6	40.3	14.74
60	7.01	30.8	46.1	23.1	18.3	47.7	34.0	15.48
55	8.60	36.8	44.9	18.3	22.9	48.8	28.3	16.25
50	10.51	42.9	42.8	14.3	28.0	48.8	23.2	17.06
45	12.85	49.0	40.1	10.9	33.6	47.8	18.6	17.87
40	15.77	55.1	36.7	8.2	39.6	45.9	14.5	18.71
35	19.52	61.2	32.9	5.9	46.0	43.0	11.0	19.57
30	24.52	67.1	28.8	4.1	52.7	39.3	8.0	20.45
25	31.53	73.0	24.3	2.7	59.8	34.7	5.5	21.35
20	42.04	78.7	19.7	1.6	67.3	29.2	3.5	22.27
15	59.56	84.2	14.9	0.9	75.1	23.0	1.9	23.22
10	94.59	89.6	10.0	0.4	83.0	16.1	0.9	24.16
5	199.69	94.9	5.0	0.1	91.4	8.4	0.2	25.09
0	α	100.0	0	0	100.0	0	0	26.05

* Composition of reaction product freed of uncombined glycerol.

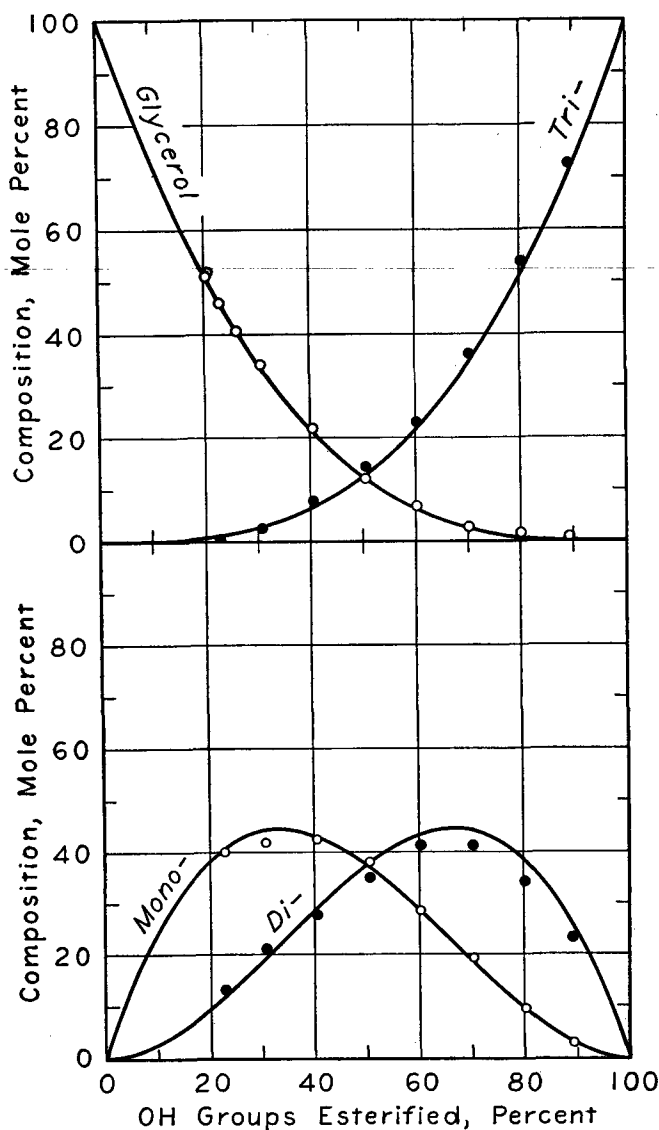


FIG. 3. Glyceride-glycerol distribution curves for homogeneous solutions of glycerol and glycerides at equilibrium. The curves represent theoretical values while the circles and dots represent values found experimentally.

In Figure 3 a comparison of the actual compositions with theoretical compositions is made graphically. It will be seen that the correspondence between the two is remarkably close, especially with respect to percentages of monoglycerides and free glycerol. It is possibly significant that the latter two components are the ones which are determined by direct methods of analysis.

The percentages of di- and triglycerides, which are calculated by indirect means, show some divergence

from the theoretical curves. It seems possible that this divergence may be a result of the limitations of the methods of estimation, rather than an indication of variance from a condition of true random distribution.

Since it appears that the composition of the reaction products may be calculated with a considerable degree of accuracy, Table 3 has been compiled as an aid to such calculation.

While based upon the use of a fat with the average molecular weight of hydrogenated cottonseed oil, it is applicable also with little error to other common oils and fats containing C_{16} and C_{18} fatty acids. It may be explained that in this table and in Figure 3 the quantity "percent OH groups esterified" is numerically equal to: (moles fatty acids/moles glycerol) (100/3). According to this terminology, in monoglycerides 33 $\frac{1}{3}$ % of the OH groups are esterified; in diglycerides 66 $\frac{2}{3}$ % are esterified, etc.

Composition of Products Reacted at High Temperatures

In order to attain complete miscibility in reaction mixtures containing high proportions of glycerol (corresponding to 20-30% hydroxyl groups esterified), it was necessary to operate at a temperature of about 250° C. Products obtained at this temperature were abnormal in composition as is evident from the data listed in Table 4. Whereas the principle of random distribution would predict a monoglyceride content in the fatty portion of about 66% (with 20-21% OH groups esterified), analysis actually indicated but 57-59%. In some cases calculation of the percent triglycerides yielded negative values, *i.e.*, after the proper amount of total combined glycerol was apportioned to the monoglycerides, there remained more glycerol than could be accounted for on the assumption that the remainder of the product consisted entirely of diglycerides.

Such a condition indicates the presence of some compound or compounds which contain a high percentage of glycerol, but which do not show by analysis as monoglycerides. These could be either β -monoglycerides (which do not react with periodic acid) or some polymerization product, as for example, a di-acid diglycerol of the following structure:

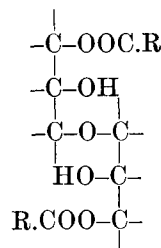


TABLE 4
Products Prepared by Reaction of Fat and Glycerol at 250° C.: Operational and Analytical Data.

Run No.	Reaction time, hrs.:min.	Glycerol, % on fat basis	% OH esterified		Total glyc. in reaction product, % ^b	Total glyc. in fatty portion, %	Mono-glycerides in fatty portion, %	Calculated composition of fatty portion, % by weight			Hydroxyl value, fatty portion
			On basis glyc. present originally	On basis glyc. in final product				Mono-	Di-	Tri-	
21.....	4:00	31.46	25	26.1	31.05	21.08	53.20	53.2	48.2	-1.4	212.7
22.....	4:00	41.95	20	20.4	36.49	21.95	57.53	57.5	46.6	-4.1	224.8
25.....	1:00	41.95	20	20.7	36.45	21.41	57.80	57.8	42.5	-0.3
31.....	0:20	41.95	20	59.30
29.....	5:00*	41.95	20	58.90

* Reacted at 250° C. for 1 hr., phenol added to make the material homogeneous, at a lower temperature, and reaction continued for 5 hours additional at 180° C.

^b Corrected for soap formed by NaOH used as catalyst; calculated on basis of soap free product.

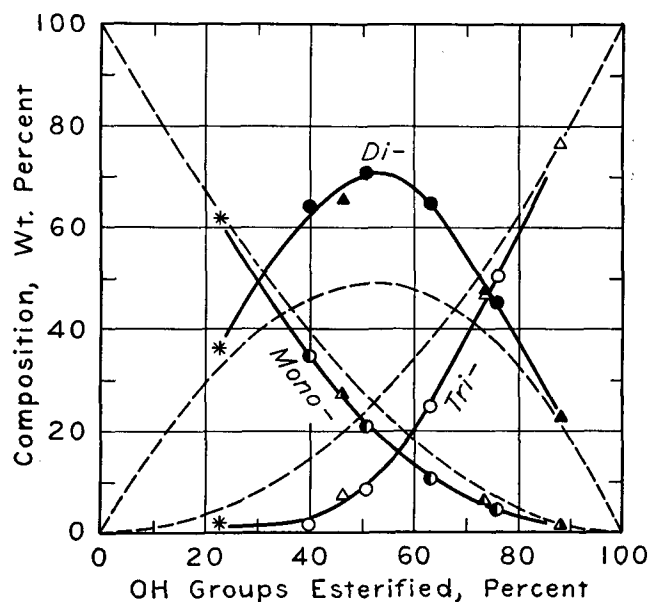


Fig. 4. Composition of glyceride mixtures partially decomposed by steam deodorization (plotted points and solid curves) in comparison with compositions obtainable by reaction with limited amounts of glycerol (broken curves, corresponding to random distribution). Circles represent products deodorized at 160° C. without removal of the catalyst; triangles represent products deodorized at 200° C. with catalyst removed. (Positions of the points along the abscissa correspond to those of glycerol-glyceride solutions at equilibrium which contain the same amount of combined glycerol.)

A number of items of evidence point to the latter possibility as being the more probable. In the first place, β -monoglycerides are known to be very unstable in an alkaline environment at elevated temperatures, readily rearranging to α -monoglycerides. Hence their appearance in any appreciable concentration would appear unlikely. On the other hand, exposure to a high temperature in the presence of alkalis is known to favor the polymerization of glycerol. In the second place, the effect leading to low analyses for monoglycerides appears to be to some extent a function of the reaction time, and also to be irreversible (see Table 4). An experiment in which the material was reacted first at 250° C. and thereafter at 180° C. in phenol (Run 29) demonstrates that the observed effect is not simply the result of allowing equilibrium to occur at a higher temperature. Finally, the assumption that polymerization occurs is more consistent with the hydroxyl values found for the reaction products. The theoretical hydroxyl value of α - or β -monoglycerides of the fats is 317.4, and of the diglycerides is 91.2. That of the diglycerol ester illustrated above is 162.9.

Product 22, for example, had a hydroxyl value of 224.8. If random distribution is assumed, this product must have contained 3.6% triglycerides, 29.8% diglycerides, 57.5% α -monoglycerides, and 9.1% of some unknown product comparable to monoglycerides with respect to OH groups esterified, but not showing as monoglycerides by analysis. If the latter material is assumed to be the polymerization product whose structure is shown above, the calculated hydroxyl value of the reaction product is 224.5. On the other hand, the assumption of 9.1% β -monoglycerides present leads to a calculated hydroxyl value of 238.6.

It is to be noted that if there is any deviation from random distribution at high temperatures, it occurs

only in the fatty portion of the reaction mixture; the percentage of free glycerol is in all cases very close to that demanded by theory (Figure 3). However, the method of analysis for glycerol would not distinguish a minor degree of polymerization in the free glycerol fraction.

It is believed that polymerization occurred to a slight extent at 230° C. (cf. Table 1), but that it was negligible at 200° C.

Composition of Steam Deodorized Products

It has long been recognized that mono- and diglycerides readily decompose with the loss of combined glycerol under conditions of commercial steam deodorization. Decomposition is greatly accelerated in the presence of catalysts effective in mono- and diglyceride formation (2). A series of experiments was carried out to determine whether reaction of the fat with a high proportion of glycerol and subsequent deodorization would produce glyceride mixtures different from those obtainable by direct interesterification with lesser proportions of glycerol.

The products prepared for deodorization were reacted with sufficient glycerol originally present to cause 20% of the OH groups to become esterified. In one case the reaction was carried out in *m*-cresol at 200° C.; in the other it was carried out without the assistance of a solvent at 250° C. Deodorization was performed at different temperatures, with and without removal of the catalyst. The results are shown graphically in Figures 4 and 5.

As explained above, it is probable that some polymerization occurred in the reaction at 250° C., data for which are presented in Figure 5. The values for di- and triglycerides in this figure are therefore to be regarded as apparent rather than true values, and are presented merely for comparison. In instances in this series where the total combined glycerol content was great enough to produce negative calculated val-

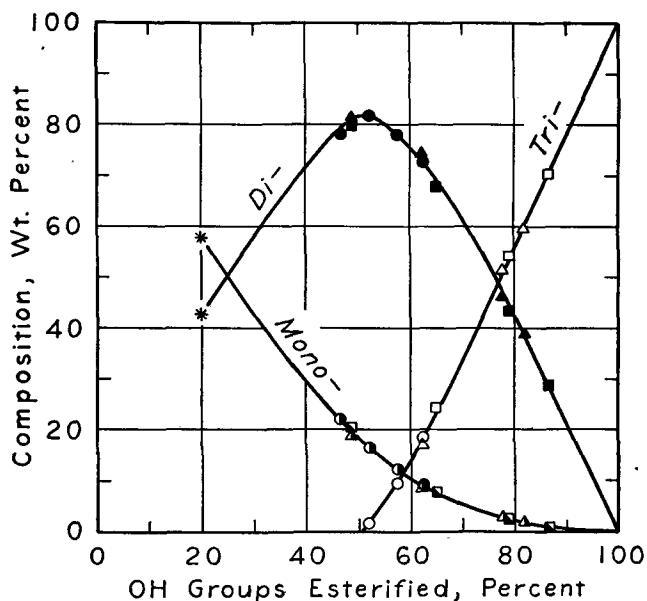


Fig. 5. Apparent composition of glyceride mixtures partially decomposed by steam deodorization. Circles represent products deodorized at 170° C. with catalyst removed; triangles represent products deodorized at 160° C. without removal of catalyst; squares represent products deodorized at 200° C. with catalyst removed. (Positions of the points along the abscissa correspond to those of glycerol-glyceride solutions at equilibrium which contain the same amount of combined glycerol.)

ues for triglycerides, the diglyceride content was taken as the difference between the monoglyceride content and 100 percent.

It may be seen that the composition of this deodorized product departs considerably from the random distribution pattern, in the direction of relatively high proportions of diglycerides, and that it is independent of deodorization temperature or the presence or absence of the catalyst.

The monoglyceride contents of some of the deodorized products, as a function of the deodorization time, are represented in Figure 6. The curves in this figure are probably not to be regarded as strictly reproducible, as the vacua and rates of steaming, while approximately constant throughout the different series of experiments, were not rigorously controlled. However, they serve to give some indication of the relative rates of monoglyceride decomposition under different conditions.

Summary

1. An investigation has been made of the composition of mixtures of mono-, di-, and triglycerides formed by the reaction of hydrogenated cottonseed oil with glycerol in the presence of an alkaline catalyst.

2. At temperatures below about 200° C., at equilibrium, and within the range of glycerol concentration in which the reaction product becomes homogeneous, the proportions of free glycerol, mono-, di-, and triglycerides conform closely to a pattern of random distribution with respect to glycerol OH groups esterified. Tables are presented for the calculation of compositions on the basis of random distribution.

3. Products produced at temperatures above about 200° C. contain minor proportions of some compound or compounds which are high in glycerol content, but are not α -monoglycerides. There is evidence that these are probably polymerization products, as for example, di-acid diglycerols.

4. An investigation has been made of the composition of reaction products whose combined glycerol content has been reduced by high-temperature steam distillation under a vacuum (deodorization). The composition of such products does not conform to the random distribution pattern, but shows marked deviations in the direction of increased percentages of diglycerides and decreased percentages of mono- and triglycerides. The composition of deodorized products is independent of the temperature of deodorization or of the presence or absence of the alkaline catalyst.

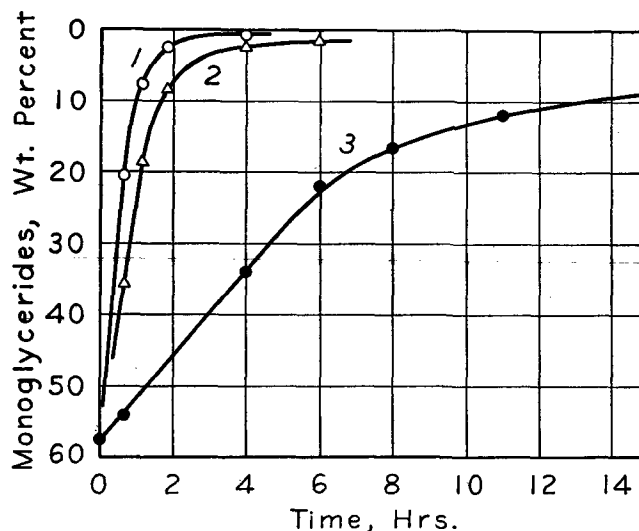


Fig. 6. Monoglyceride contents of some deodorized products as a function of deodorization time. Curve 1 represents a deodorization at 200° C. after removal of the catalyst, curve 2 is a deodorization at 160° C. with the catalyst present, and curve 3 represents a deodorization at 170° C. after removal of the catalyst.

5. Determinations have been made of the maximum amounts of glycerol miscible in reaction mixtures carried to equilibrium at different temperatures.

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