industry. Two of the six, those made with the butyl and hydrogenated butyl esters of maleinated jojoba acids, met the still more stringent low-temperature requirements of the aircraft industry (−55°C.).

In general, hydrogenation of a derivative adversely affected its compatibility in either the vinyl copolymer or the Buna-N formulations.

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Relative Esterifiability of the Primary and Secondary Hydroxyl Groups of Glycerol[1]

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MONOGLYCERIDES are made commercially either by the esterification of fatty acids with glycerol or by the alcoholysis of a fat with glycerol. The product is a mixture of mono-, di-, and triglycerides with unreacted glycerol. The last is frequently removed at the end of the reaction period.

Feuge and Bailey (5) recognized that since monoglycerides are customarily prepared at high temperatures in the presence of alkaline catalysts, conditions exist which are favorable to ester interchange equilibrium. They showed that the proportions of glycerol, mono-, di-, and triglycerides can be calculated statistically if one makes the following two assumptions: a) that there is a random distribution of acyl groups on the hydroxyls of glycerol and b) that there is equal probability that the primary and secondary hydroxyl groups will be esterified. According to Feuge and Bailey, the predicted and experimentally estimated compositions were in reasonably good agreement. Although the method of calculation presented by them has contributed greatly to elucidating the composition of commercial monoglycerides, there appears to be an inconsistency in their comparison of experimental and calculated compositions. In a recent review of the literature on monoglycerides Demarcq (4) noted the following: "Feuge and Bailey appear to rely on two contradictory postulates: that of equal chance of esterification of hydroxyls on the one hand and that of the nonformation of *beta* monoglyceride on the other hand." Demarcq attempted unsuccessfully to devise a method of estimating relative hydroxyl reactivity. The work reported here was directed at re-examining the assumptions required to predict the distribution of acyl groups.

The first assumption necessary to predict the equilibrium composition of mixed partial esters of any polyol is that the chance that any hydroxyl will be esterified is determined by the relative molar proportions of acyl groups to hydroxyl groups. It is further implied that the presence of one acyl group on a polyol is without effect on the esterifiability of the remaining hydroxyl groups. In order to test this assumption, the equilibrium composition of the reaction product of oleic acid and ethylene glycol was determined. Ethylene glycol (Carbide and Carbon) was reacted in approximately equimolar proportions with commercial oleic acid (Emersol 233LL, Emery Industries) at 175°C. under nitrogen, using 0.1% NaOH as catalyst. The contents of the flask were sampled after approximately 1¾, 5¼, and 12¼ hrs and analyzed for acid number and saponification number by essentially the A.O.C.S. methods; for hydroxyl number by a modification of the method of West, Hoagland, and Curtis (11); and for free ethylene glycol by periodate consumption. Results of the analyses are given below:

Time—hours	1¾	5¼	12¼
Acid number	42.1	5.3	2.4
Saponification number	177.5	178.0	178.5
Hydroxyl number	181.0	155.0	142.5
Weight % free glycol	5.9	3.8	3.6

The ester number and hydroxyl number of the ester portion can be calculated on a free glycol- and fatty acid-free basis by using 276 as the molecular weight of the acid as determined from its acid number. As has been shown elsewhere (1), the mole ratio of monoester to diester, M, can be computed from the relation

$$M = \frac{2}{(E/H) - 1}$$

where E and H are the ester number and hydroxyl number, respectively, of the ester portion. The weight ratio of monoester to diester is equal to 320M/578, where 320 and 578 are the average molecular weights of ethylene glycol mono- and diesters of commercial oleic acid, respectively. From the weight percentage of free glycol, monoester, and diester in the acid-free product, the mole fractions can be computed very simply with the results given below:

[1] Presented at the 50th annual meeting, American Oil Chemists' Society, New Orleans, La., April 20–22, 1959.

Time—hours	1¾ hrs.		5¼ hrs.		12¼ hrs.	
	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.
Ethylene glycol	0.338	0.328	0.210	0.224	0.204	0.200
Ethylene glycol monoester	0.470	0.489	0.526	0.499	0.486	0.494
Ethylene glycol diester	0.192	0.182	0.264	0.277	0.310	0.306
R, mole ratio acid/glycol	0.854		1.053		1.106	

The experimental results are compared above with the compositions calculated on the assumption of equal reactivity of all hydroxyls. These theoretical compositions are calculated from R, the moles of combined fatty acid per mole of glycol, as follows.

The chance that an hydroxyl will be esterified is R/2, and the chance that an hydroxyl will be free is 1–R2. Hence the mole fractions of free glycol, monoester, and diester in the general case are:

$$\text{Free glycol} = (1 - R/2)^2$$
$$\text{Monoester} = 2[R/2\,(1 - R/2)]$$
$$\text{Diester} = (R/2)^2$$

R is calculated from ester and hydroxyl numbers of the fatty acid-free product. The agreement is within the precision of the analyses and justifies the assumption of random esterification of all available hydroxyl groups. The first sample at 1¾ hrs. was incompletely esterified but, on a free acid-free basis, showed as good agreement of calculated and determined molar compositions as later samples. This demonstrates that, in the case of ethylene glycol, ester interchange equilibrium proceeds as rapidly as esterification. The observation that random esterification of primary hydroxyls occurs during esterification is in agreement with the conclusion reached in previous studies on the formation of polyoxyethylene (8) stearate by the reaction of ethylene oxide with commercial stearic acid (1).

Since the above data have demonstrated equal and independent reactivity of the primary hydroxyls of ethylene glycol, we believe it is reasonable to expect this to be true of the primary hydroxyls of glycerol. We do not intend to imply that the reactivity of a primary hydroxyl group on glycerol is the same as that of a primary hydroxyl on ethylene glycol.

We can now proceed to examine the second assumption of Feuge and Bailey of equal reactivity of primary and secondary hydroxyls of glycerol.

Theoretical

As was demonstrated above by results on ethylene glycol oleate, the probability that a primary OH will be esterified is equal to the mole ratio of the esterified primary OH's to total primary OH's or $a/(a+1)$, where a is the mole ratio of esterified to free primary hydroxyl groups. Similarly the probability that a secondary OH will be esterified is equal to $b/(b+1)$, where b is the mol ratio of esterified to free secondary hydroxyl groups.

As a general expression, the number of moles of acid esterified with a mole of polyol is equal to the number of primary hydroxyl groups in the polyol times the fraction of primary groups esterified plus the number of secondary hydroxyl groups in the polyol times the fraction of secondary hydroxyls esterified plus a similar term for tertiary hydroxyl groups if they are present. In the case of glycerol the expression for moles fatty acid esterified per mole of glycerol reduces to $2a/(a+1) + b/(b+1)$.

In a mixture of glycerol, mono-, di-, and triglycerides, under suitable ester interchange conditions, the following equilibria will be expected to be established:

1. 2-mono $\rightleftarrows$ 1-mono

$$K_1 = \frac{[1\text{ mono}]}{[2\text{ mono}]}$$

also 2-mono $\rightleftarrows$ 3-mono

$$K_1' = \frac{[3\text{-mono}]}{[2\text{-mono}]}$$

$$\text{Adding, } K_1 + K_1' = \frac{[1\text{-mono}] + [3\text{-mono}]}{[2\text{-mono}]}$$

Since $K_1 = K_1'$ and $[1\text{-mono}] + [3\text{-mono}]$ = observed α-monoester content

$$K_1 = \frac{[\alpha\text{-mono}]}{2[\beta\text{-mono}]}$$

The other ester interchange reactions and equilibrium expressions are summarized as follows:

2. 1,2-di $\rightleftarrows$ 1,3-di

$$K_2 = \frac{2[\alpha,\alpha\text{-di}]}{[\alpha,\beta\text{-di}]}$$

3. glycerol + 1,2-di $\rightleftarrows$ 1-mono + 3-mono

$$K_3 = \frac{[\alpha\text{-mono}]^2}{2[\text{glycerol}]\,[\alpha,\beta\text{-di}]}$$

4. 1-mono + 2-mono $\rightleftarrows$ glycerol + 1,3-di

$$K_4 = \frac{2[\text{glycerol}]\,[\alpha,\alpha\text{-di}]}{[\alpha\text{-mono}]\,[\beta\text{-mono}]}$$

5. 1,2-di + 2,3-di $\rightleftarrows$ 1-mono + tri

$$K_5 = \frac{2[\alpha\text{-mono}]\,[\text{tri}]}{[\alpha,\beta\text{-di}]^2}$$

6. glycerol + tri $\rightleftarrows$ 1-mono + 1,3-di

$$K_6 = \frac{[\alpha\text{-mono}]\,[\alpha,\alpha\text{-di}]}{2[\text{glycerol}]\,[\text{tri}]}$$

The above reactions are the only ones involving the migration of an acyl group from a primary to a secondary hydroxyl or *vice versa*.

A general expression for migration of acyl groups between primary and secondary hydroxyls is derived below, where R_pOH and R_sOH denote molecules containing a primary and secondary hydroxyl group, respectively:

$$R_p\text{–OH} + R'COOH \rightleftarrows R_p\text{–OOCR}' + H_2O$$
and $$R_s\text{–OH} + R'COOH \rightleftarrows R_s\text{–OOCR}' + H_2O$$

The above chemical equations of esterification of primary and secondary hydroxyl-containing compounds can be subtracted one from another with the following equation resulting:

$$R_p\text{–OH} + R_s\text{–OOCR}' \rightleftarrows R_s\text{–OH} + R_p\text{–OOCR}'$$

for which the equilibrium constant, K, can be expressed as follows:

$$K = \frac{[R_s\text{–OH}]\,[R_p\text{–OOCR}']}{[R_s\text{–OOCR}']\,[R_p\text{–OH}]}$$

The term $[R_p\text{–OOCR}']/[R_p\text{–OH}]$ is equal to the quantity "a" as defined earlier, and $[R_s\text{–OH}]/[R_s\text{–OOCR}']$ is equal to $1/b$. Consequently the equilibrium constant for migration of acyl groups between primary and secondary hydroxyl positions is simply equal to the following:

$$K = \frac{a}{b}$$

If one makes the assumption, as we have here, that any primary hydroxyl in glycerol has the same chance of being esterified as any other primary hydroxyl, regardless of whether other hydroxyls in the molecule are free or esterified, and similarly for secondary hydroxyls, it is obvious that

$$K_1 = K_2 = K_3 = K_4 = K_5 = K_6 = K$$

The molar composition can now be related to the probabilities that the primary and secondary hydroxyl groups will be esterified, as demonstrated below:

$$\text{Probability of esterified primary OH} = \frac{a}{a+1}$$

$$\text{Probability of free primary OH} = \frac{1}{a+1}$$

Likewise for the secondary hydroxyl,

$$\text{Probability of esterified secondary OH} = \frac{b}{b+1}$$

$$\text{Probability of free secondary OH} = \frac{1}{b+1}$$

The molar composition in terms of a and b is as follows:

$$\text{Glycerol} = \frac{1}{a+1} \cdot \frac{1}{a+1} \cdot \frac{1}{b+1} = \frac{1}{(a+1)^2(b+1)}$$

$$\alpha\text{-Monoglyceride} = 2 \cdot \frac{a}{a+1} \cdot \frac{1}{a+1} \cdot \frac{1}{b+1} = \frac{2a}{(a+1)^2(b+1)}$$

$$\beta\text{-Monoglyceride} = \frac{1}{a+1} \cdot \frac{1}{a+1} \cdot \frac{b}{b+1} = \frac{b}{(a+1)^2(b+1)}$$

$$\alpha,\alpha\text{-Diglyceride} = \frac{a}{a+1} \cdot \frac{a}{a+1} \cdot \frac{1}{b+1} = \frac{a^2}{(a+1)^2(b+1)}$$

$$\alpha,\beta\text{-Diglyceride} = 2 \cdot \frac{a}{a+1} \cdot \frac{1}{a+1} \cdot \frac{b}{b+1} = \frac{2ab}{(a+1)^2(b+1)}$$

$$\text{Triglyceride} = \frac{a}{a+1} \cdot \frac{a}{a+1} \cdot \frac{b}{b+1} = \frac{a^2b}{(a+1)^2(b+1)}$$

There are a number of ways in which the above equations may be combined to yield a value for "K" from the determined values of glycerol, *alpha* mono-, total mono-, di-, and triglycerides. The two most useful methods of calculation are derived below:

Method 1

$$\frac{\alpha\text{-mono}}{\beta\text{-mono}} = \frac{2a}{b}$$

$$\text{Since} \quad K = \frac{a}{b}$$

$$\text{Therefore} \quad K = \frac{\alpha\text{-mono}}{2 \times \beta\text{-mono}}$$

This is a very simple way of calculating K and of getting the ratio of "a" to "b." The only experimental data needed are *alpha*-mono content and total mono content.

Method 2

$$\frac{Di}{Tri} = \frac{a^2 + 2ab}{a^2b} = \frac{a+2b}{ab} = \frac{1}{b} + \frac{2}{a}$$

$$\text{Rearranged} \quad b = \frac{a\,Tri}{a\,Di - 2\,Tri}$$

$$\text{Also} \quad \frac{Di}{Mono} = \frac{a^2 + 2ab}{2a + b}$$

Substituting for "b" in terms of "a" and rearranging yields the quadratic $a^2\,Mono - 2a\,Di + 3\,Tri = 0$

$$\text{Whence} \quad a = \frac{Di \pm \sqrt{Di^2 - 3\,Mono \times Tri}}{Mono}$$

$$\text{Since} \quad \frac{Di}{Tri} = \frac{1}{b} + \frac{2}{a}$$

$$K = \frac{a}{b} = \frac{a\,Di}{Tri} - 2$$

This method of calculating K depends upon the total mono-, di-, and triglyceride contents and is independent of the free glycerol and *alpha*-monoester contents of the sample.

Under conditions of ester interchange equilibrium which exist during esterification of fatty acids with glycerol or glycerolysis of fats, one may expect the equilibrium constant, K, calculated by Method 1 to be the same as that calculated by Method 2. However, under certain conditions of temperature, catalyst, etc., migration of the acyl group may occur without establishment of equilibrium. Under these circumstances the values of K calculated by Methods 1 and 2, although they will not represent true equilibrium, will show the extent of acyl group migration. K calculated by Method 1 utilizes the *alpha*- and *beta*-monoester contents and therefore measures the extent of equilibration of acyl groups by intramolecular exchange. K calculated by Method 2 gives a measure of equilibration of acyl groups by intermolecular exchange. As will be shown by the experimental results, intramolecular exchange of acyl groups occurs more readily than intermolecular exchange.

Experimental

Partial glycerides were prepared by the alcoholysis of glycerol with triglyceride at 200°C. in a nitrogen atmosphere in the presence of 0.1 % sodium hydroxide as catalyst. Reaction times of 2 to 4 hrs. were used to insure ester interchange equilibrium. Several ratios of glycerol to triglyceride were employed, using both a hard fat (hydrogenated tallow) and a liquid triglyceride (glycerol trioleate). The ratios chosen were such as to insure homogeneity at reaction temperatures. At the end of the reaction period 0.25- to 1.0-g. samples were removed into tared beakers for analysis. The catalyst in the reaction mixture was then neutralized with 85% phosphoric acid, and additional small samples were taken. The procedure of taking small samples permitted rapid cooling from reaction temperature to room temperature and thus minimized any rearrangement prior to analysis.

The samples were analyzed for free glycerol and *alpha*-monoester content by the method of Pohle and Mehlenbacher (7). Total mono-, di-, and triglyceride contents were estimated by a modification of the col-

TABLE I

Preparation and Analysis of Glycerides

Run No.[a]	Grams of glycerol per 100 g. of fat	Catalyst neutralized	Uncorrected weight % composition						Corrected mole fractions				
			Glycerol (P & M)	Glycerol (column)	*alpha* Mono- (P & M)	Total mono-	Di-	Tri-	Glycerol	*alpha* Mono-	Total mono-	Di-	Tri-
1	11.8	No	2.25	2.04	26.2	29.0	49.8	19.2	0.101	0.360	0.402	0.385	0.111
		Yes	1.69	1.74	24.2	28,2	50.6	19.6	.087	.339	.399	.399	.116
2	6.5	No	0.57	0.61	12.7	14.6	48.6	36.2	.033	.216	.250	.458	.260
		Yes	0.18	0.34	11.6	14.0	49.6	37.0	.016	.199	.243	.473	.268
3	12.5	No	2.71	2.58	27.9	31.5	48.6	16.5	.123	.372	.425	.360	.093
		Yes	2.20	2.29	26.5	31.9	49.2	16.9	.108	.354	.430	.366	.095
4	6.6	No	0.75	0.73	15.0	16.5	49.5	32.0	.036	.250	.279	.460	.225
		Yes	0.54	0.57	13.9	15.9	50.9	32.4	.026	.233	.269	.476	.229
5	11.4	No	2.33	2.12	25.6	29.5	49.2	18.7	.103	.354	.411	.378	.109
		Yes	2.04	1.95	24.9	28.9	50.1	18.8	.095	.346	.406	.389	.110
6	15.5	Yes	3.95	3.78	32.0	38.1	44.6	11.8	.168	.391	.470	.302	.061
7	14.5	No	4.20	4.72	33.5	36.9	45.5	13.1	.190	.399	.437	.309	.065
		Yes	3.88	4.01	33.0	37.3	45.7	12.8	.177	.396	.446	.313	.064
8	23.1	No	8.70	.....	40.9	46.2	36.6	7.5	.321	.397	.446	.202	.031
		Yes	7.49	.....	39.3	46.5	37.0	7.7	.287	.397	.467	.214	.031

[a] Runs 1 to 6 were made from glycerol and hydrogenated tallow reacted 2 to 4 hrs. at 200°C., and Runs 7 and 8 from glycerol and glycerol trioleate reacted 2 to 2½ hrs. at 200°C.

umn chromatographic method of Quinlan and Weiser (8). The improved chromatographic method of Smullin and Olsanski (9), which was employed, also gives a value for free glycerol. All analyses were run in duplicate.

There was evidence of slight intermolecular rearrangement of hard mono- and diglyceride samples on the silica gel column, and therefore mixtures made up from known amounts of pure mono-, di-, and triglycerides were analyzed. Pure distearate was obtained from mixed esters by chromatographic separation and purification. *Alpha* monostearate was synthesized *via* the acetal route, and tristearin was used as is. The following correction factors were established:

$$\text{Corr. \% di} = \text{obs. mono}/0.99$$
$$\text{Corr. \% mono} = \text{obs. di} - 1.6$$
$$\text{Corr. \% tri} = \text{obs. tri}/0.96$$

In the case of oleate esters, the correction factors were found to be within the precision of analytical methods, and corrections were not considered necessary.

Table I presents data on the preparation and analysis of a number of partial glycerides.

Table II gives the equilibrium constants calculated by Methods 1 and 2 from the data of Table I. The K values for Methods 1 and 2 for samples taken before and after neutralizing the catalyst are averaged separately for oleate and stearate esters in the same table.

Discussion

Examination of Table II reveals that equilibrium constants at 200°C. are all substantially greater than 1, thereby demonstrating the preferential esterifiability of the primary hydroxyl. For stearates, the average K calculated by Method 2 is the same before and after neutralization of the catalyst. The average K calculated by Method 1 is substantially the same as the above for the samples taken after neutralizing the catalyst. However, for samples taken with catalyst still present, the average K by Method 1 is definitely higher. These results indicate that intermolecular rearrangement in hard monoglycerides is arrested by cooling even in the presence of catalyst. Intramolecular rearrangement, *i.e.*, the wandering of an acyl group from the *beta* to the *alpha* position within the molecule occurs on rapid cooling if a basic catalyst is present. The equilibrium constant at the reaction temperature of 200°C. appears to be about 2.3.

For liquid monoglycerides the average K by Method 2 is also about 2–2.5 independent of whether the catalyst is neutralized. The higher values for K calculated by Method 1 indicate that intramolecular rearrangement occurs in liquid monoglycerides regardless of whether the catalyst is neutralized. In the presence of catalyst intramolecular rearrangement occurs more rapidly. It is evident that K at room temperature must be considerably higher than at 200°C., *i.e.*, that there is a shift of acyl groups from secondary to primary hydroxyls on cooling.

The physical form of the partial glyceride is seen to have an effect on the rate of acyl group migration at room temperature. In order to estimate the equilibrium constant at room temperature and to establish whether the constant depends on the physical form of the glyceride, five preparations made from several months to two years earlier and stored at room temperature were analyzed with the results shown in Table III.

The apparent equilibrium constants are plotted in Figure 1 as a function of time, and the average K's for zero time are those given in Table II for neutralized samples. K by Method 2 for Sample E at 3 months was not plotted since the value is out of line with the 12 months' value, presumably because of error in the triglyceride analysis. The apparent K's calculated by Method 2 indicate that intermolecular

TABLE II

Calculated Equilibrium Constants of Glycerides

Run No.	Catalyst present		Catalyst neutralized	
	Method 1	Method 2	Method 1	Method 2
1	4.2	2.4	3.1	2.6
2	3.2	2.1	2.3	2.7
3	3.6	2.3	2.3	2.2
4	4.5	2.4	3.2	3.2
5	3.1	1.9	2.8	2.5
6	....	....	2.5	2.0
7	5.3	2.5	4.0	2.6
8	4.0	1.6	2.8	1.9
Average K for stearates (Runs 1 to 6)	3.7	2.2	2.7	2.5
Average K for oleates (Runs 7 and 8)	4.6	2.1	3.4	2.3

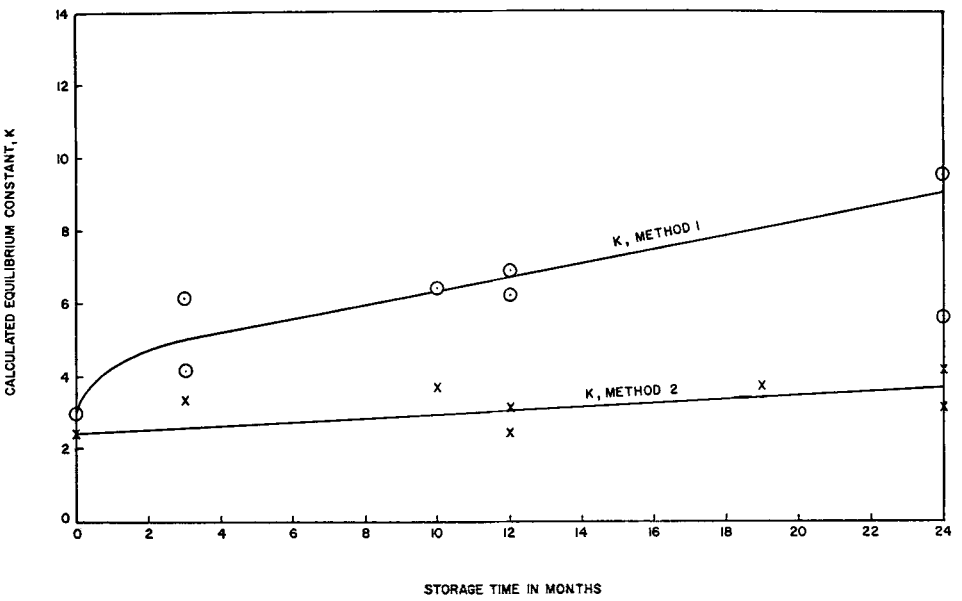

FIG. 1. Variation of calculated (apparent) equilibrium constant, K, with storage.

rearrangement may occur to a slight extent over the period of two years. The apparent K's from Method 1 show that the shift of the acyl group from the *beta* to *alpha* hydroxyl position on storage is very pronounced.

Crystalline structure of a partial glyceride may reduce the rate of intramolecular rearrangement. Evidence for this is the observation that a sample of pure *alpha* glycerol monostearate prepared more than seven years ago by the hydrolysis of 1,2-isopropylidene-3 stearate still analyzes 98% total monoester, 98% *alpha* monoester. Any treatment of this sample, resulting in destroying its crystallinity, reduces its *alpha*-mono *content*. For example, recrystallization from warm methanol gave a high yield of product analyzing 98.4% total mono but only 95.3% *alpha* mono. When the pure *alpha* monostearate was held molten at 100°C. over a weekend, it underwent some rearrangement to glycerol, di- and triesters, but most notably the monoglyceride analysis showed 87.7% total mono and 78.5% *alpha* mono. K calculated from these values by Method 1 is 4.3.

The migration of acyl groups during aging and the effect of fat composition thereon are mentioned in the literature. Brokaw, Perry, and Lyman (2) observed that freshly distilled monoglyceride from freshly prepared mono-diglyceride mixtures made from hydrogenated lard analyzes as low as 86% mono by periodic acid consumption. Upon standing 24 to 48 hrs. this increases to as much as 94% with an average change of 4 to 6%. This change was not observed on freshly distilled mono from aged mono-diglycerides. The above observations lead to an apparent K calculated by Method 1 of about 3 for fresh mono and about 6 for mono aged either before or after distillation. These authors further observed that monoglycerides from unsaturated fats were higher in *alpha*-mono content originally and did not change on aging, thus showing the fast shift of acyl groups in liquid products.

The method for determining total monoglycerides described by Martin (6) some years ago depends upon equilibration of acyl groups on *alpha* and *beta* hydroxyls because of the catalytic effect of perchloric acid at room temperature. The average factor proposed by Martin for converting from percentage of *alpha* monoester to total monoester is 1.15, corresponding with an equilibrium constant, K, by our Method 1 of 3.3. This value is lower than the K values obtained in this study on aged glycerides at room temperature and indicates that perchloric acid incompletely promotes *alpha-beta* equilibration, or that some intermolecular rearrangement occurs, or

TABLE III

Calculated Equilibrium Constants of Aged Glycerides

Sample	Type of glyceride[a]	Storage time in months	Percentage composition					K	
			Glycerol	*alpha* Mono-	Total mono-	Di-	Tri-	Method 1	Method 2
A	Plastic mono- from lard	*ca.* 24	0.60	43.9	46.2	42.6	8.9	9.5	3.1
B	Plastic mono- from lard	3	0.50	42.7	47.9	42.7	8.4	4.1	3.3
B	Plastic mono- from lard	12	0.51	44.1	47.3	42.1	8.5	6.9	3.1
C	Plastic mono- from lard	24	0.48	42.2	46.0	43.0	8.1	5.6	4.1
D	Hard mono- from hydrogenated tallow	10	0.95	52.9	57.0	34.5	4.4	6.4	3.7
D	Hard mono- from hydrogenated tallow	19	1.04	56.1	58.6	34.2	4.5	11.2	3.7
E	Plastic mono- from lard	3	0.61	55.5	60.0	33.1	3.3	6.2	5.1
E	Plastic mono- from lard	12	0.71	56.2	60.7	32.6	4.3	6.2	2.4

[a] These samples were all prepared by the alcoholysis of glycerol with fat, using caustic catalyst, and were stripped of glycerol at about 200°C. after neutralization of the catalyst.

that conditions may not be strictly comparable with those used in this study.

A recent paper by Crossley, Freeman, Hudson, and Pierce (3) presents data on acyl migration in monoglycerides and in diglycerides. In their work on monoglycerides they report pure 1-mono-oleate and 1-monostearate to form equilibrium mixtures containing 90% 1-monoglyceride in 3 hrs. at 100°C. This corresponds to a K by our Method 1 of 4.5 and agrees well with our results on heating pure *alpha* monostearate at this temperature. By selective crystallization these authors were able to separate quantitatively the 1,2- and the 1,3-diglycerides of several fatty acids. Given below are their determined quantities of 1,2- and 1,3-diglycerides in mixtures equilibrated at 165°C. in the presence of trace amounts of base catalyst.

Glycerine	% 1,3-Diglyceride	% 1,2-Diglyceride	Calculated equilibrium constant, K
Distearin	58	42	2.8
Dipalmitin	56	44	2.5
Dimyristin	55	45	2.4
Dilaurin	55	45	2.4
Diolein	53	47	2.3

The equilibrium constants were calculated as follows. As shown in the Theoretical Section, the amount of 1,2-diglyceride, in the general case, is equal to

$$\frac{2ab}{(a+1)^2(b+1)}$$

and the amount of 1,3-diglyceride is equal to

$$\frac{a^2}{(a+1)^2(b+1)}$$

The ratio of 1,3- to 1,2-diglycerides is then $a^2/2ab$ or $a/2b$. Since $K = a/b$

$$K = \frac{2(1,3\text{-diglyceride})}{(1,2\text{-diglyceride})}$$

Equilibrium constants at 165°C. calculated from the data of Crossley *et al.* and the constants determined in this work at 200°C. agree quite satisfactorily.

Since this paper was first presented, an article has appeared by Van Lohuizen and Verkade (10) which substantiates certain of our observations. In particular, the work cited above is further evidence that equilibrium can be established between *alpha* and *beta* monoglycerides. Under the acid-catalyzed conditions of equilibration at 25°C. in alcoholic solution, the ratio of *alpha* to *beta* monoesters was found to be 88/12. K calculated by our Method 1 from these data is 3.7. Since K appears to be lower under these conditions than under the conditions we employed, it is possible that some other factor may be involved here. These authors also reported more rapid migration of the acyl group within a molecule than between molecules. They found that the nature of the acyl group affects the migration rate but has very little influence on the position of equilibrium between *alpha* and *beta* monoglycerides. In citing the data of Crossley *et al.*, they concluded that the position of equilibrium in diglycerides and in monoglycerides is widely different. As we have shown earlier, the proportions of isomeric monoglycerides and diglycerides are exactly those to be expected if intramolecular migration of the acyl groups has proceeded to equilibrium, taking into account the relative esterifiabilities of primary and secondary hydroxyls.

It is not possible at this time to assign a precise value to K at room temperature. From the data on aged samples and the extrapolation of values observed at 100°, 165°, and 200°C., it appears that K at 25° has a value between 6 and 10. The value of K at room temperature may depend upon the physical form of the material.

The difference in free energy between the primary and secondary hydroxyl positions may be calculated from the expression,

$$\triangle F = -RT \ln K$$

The difference in free energy at room temperature is about 1.2 kcal/mole and somewhat less at higher temperatures.

From K one can calculate the equilibrium composition of homogeneous partial glycerides as follows. The number of moles of fatty acid reacted with a mole of glycerol is equal to $2a/(a+1) + b/(b+1)$. The value of K at a given temperature enables one to substitute for "a" in terms of "b" in the above expression. One can therefore solve the quadratic equation for "b" for any desired ratio of fatty acid to glycerol. Once "b" has been determined, "a" is easily found, and the mole fractions of free glycerol, *alpha* mono, *beta* mono-, di-, and triglycerides can now be computed.

This method of calculating the composition of partial glycerides is applied below. In Figure 2 are plotted experimentally determined, *alpha* monoglyceride contents for various ratios of glycerol to fat on a free glycerol-free basis. The experimental data are from Feuge and Bailey (5), Demarcq (4), and from unpublished work of this laboratory. The line passing

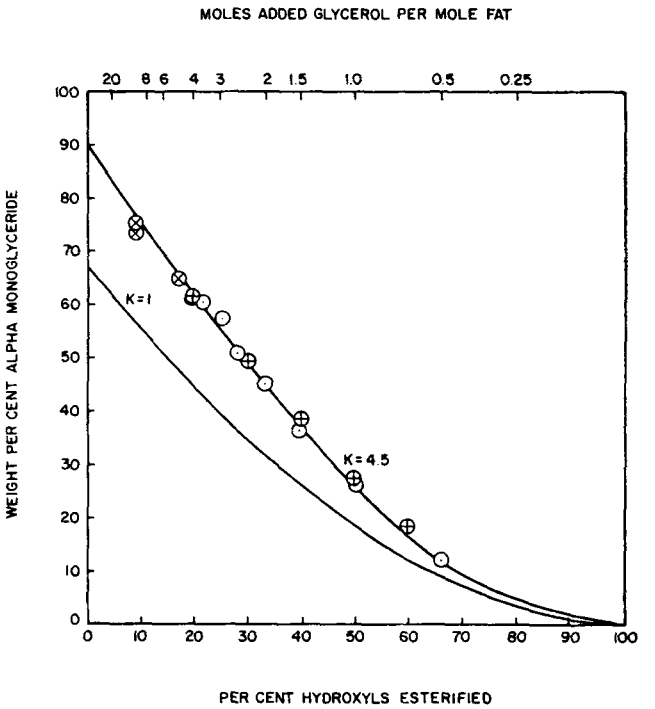

FIG. 2. Comparison of predicted and experimentally determined, *alpha*-monoester content of glycerides of varying degrees of esterification.

Sources of experimental data—
Feuge and Bailey—⊕
Demarcq—⊗
Unpublished Atlas data—○

through the experimental points was calculated according to procedures developed for K = 4.5. The calculated line for K = 1 (equal reactivity of primary and secondary OH's) is also shown. Obviously the experimental data fit the curve favoring esterification of the primary hydroxyls. Although the preparations were made at 200°C. or higher temperatures where K is about 2, the fact that the points fit well on a curve for K = 4.5 shows that a substantial degree of intramolecular rearrangement has occurred on cooling, prior to analysis of the samples.

Summary

A method has been devised for determining the relative esterifiability of the primary and secondary hydroxyl groups of glycerol. Contrary to the theory previously advanced by Feuge and Bailey, the primary and secondary hydroxyls are not equally esterifiable. The equilibrium constant favoring esterification of primary hydroxyl over secondary is *ca.* 2.3 at reaction temperature (200°C.) and between 6 and 10 at room temperature. Since the equilibrium constant is substantially different at room temperature from that at reaction temperature, monoglycerides as customarily prepared are not at equilibrium at room temperature and undergo intramolecular migration of acyl groups from *beta* to *alpha* hydroxyl positions. The rate of migration depends on the physical form of the ester and is accelerated by basic catalysts. In the vicinity of room temperature intermolecular rearrangement occurs only over very prolonged periods. The method of calculating relative esterifiability of primary and secondary hydroxyls should be applicable to other polyols.

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A General Method for the Chromatographic Analysis of Mono-, Di-, and Triglycerides and the Mono- and Diesters of Ethylene Glycol and Polyethylene Glycol

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IN THE COMMERCIAL manufacture of partial esters of polyhydric alcohol mixtures, the monoesters, diesters, and the triesters are usually obtained along with the acid and alcohol reactants. A direct, general method for the quantitative analysis of such complex mixtures has been lacking. Recently several specialized methods have been developed. Ravin, Meyer, and Higuchi (1) developed a chromatographic method of analysis of mixtures of glyceryl esters and mineral oil, and Quinlan and Weiser (2) also chromatographed a glyceryl system. Malkemus and Swan (3) developed a procedure for the analysis of polyethylene glycol ester mixtures, based on extraction.

This paper is concerned with the application of the chromatographic method of Ravin *et al.* (1) to esters of ethylene glycol, polyethylene glycol, and glycerol. Their method was based on the observation of Kaufman and Wolf (4) that silica gel will adsorb the most polar component of a mixture of glycerides to the greatest extent. Ravin *et al.* employed a mobile phase consisting of a series of solvents of increasing polarity to separate the components of mixtures of mono-, di-, and tristearin and mineral oil. It was hoped that this principle could be applied to any polyhydric alcohol and its esters.

Two solvent systems were developed. The first was a slight modification of the eluent system of Ravin *et al.* It separated the components of two types of mixtures, glyceryl esters and ethylene glycol esters. A second system was developed for the separation of polyethylene glycol ester mixtures.

The exact weight compositions of the ester mixtures chromatographed were determined by adding together the weights of the residues found in all fractions under each peak. The positive identification of the peak material was made by interpretation of infrared spectra and saponification values.

To determine whether this method of analysis was as general as it was originally hoped to be, the effects of such factors as unsaturation in the acid moiety of the glyceryl esters or a change in the molecular weight by 100 or 200 of the polyethylene glycol were investigated.

Since glyceryl ester mixtures which are to be ana-