Distribution of Monoesters Resulting from the Esterification of a Mixture of Glycols and Triols[1]

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Abstract

The distribution of monoesters resulting from the esterification of mixtures of C_3 to C_6 glycols and triols with lauric acid is reported. Glycols with two primary, two secondary, and one primary and one secondary, both vicinal and isolated, as well as triols with both vicinal and isolated hydroxyls, were investigated for their relative esterifiability. Nonvicinal glycols with only primary hydroxyls were found to have equal reactivity. Glycols and triols that have one secondary hydroxyl show a lower relative esterifiability than compounds with only primary hydroxyls. The reactivity is dependent on the position of the secondary hydroxyl in the molecule. Esterifiabilities relative to 1,4 butanediol ranged from 0.228 for the secondary hydroxyl of 1,2,6 hexanetriol up to 1.591 for the isolated primary hydroxyl of 1,2,4 butanetriol.

Introduction

THE DISTRIBUTION OF PARTIAL ESTERS of glycerol and 1,2 propanediol has been the subject of a number of investigations (1–6). Bailey (2) reported evidence that the fatty acid radicals became rearranged at random when a small excess of glycerol was reacted with a triglyceride fat in the presence of a suitable catalyst. In the classic work of Feuge and Bailey (6) they proposed that the composition of products from interesterifying a triglyceride fat and glycerol could be predicted by assuming complete random distribution of the acids on the glycerol hydroxyls. However the 2-monoglycerides were not considered because of the analytical problem. More recently Martin (7), Biswas (3), Brandner (4), Wood (9), and others have reported the presence of 2-monoglycerides in equilibrium mixtures of monoglycerides. The reported equilibrium ratios of 1 to 2-monoglycerides has not been 2:1, as would be expected from a simple random distribution, but has ranged from 80% 1-monoglyceride:20% 2-monoglyceride up to 92% 1-monoglyceride:8% 2-monoglyceride.

The equilibrium constant for esterification of the 1 and 2 hydroxyls of 1,2 propanediol were reported to be 3 to 1 at 175C by Brandner (5). He also found that the equilibrium ratio of 1 to 2 monoesters of glycerol was dependent on temperature. However Allen (1) reported that the equilibrium ratio of 1 to 2 propanediol monoesters was 2 to 1 and that this ratio was not dependent upon temperature.

Somewhat indirect methods of analysis have been used to measure the esters and to determine the relative esterifiability of primary and secondary hydroxyls. However Wood (9) recently found that isomeric monoglycerides could be measured quantitatively by gas-liquid chromatography of their trimethylsilyl derivatives. He also showed that the preparation of the trimethylsilyl derivative of monoglycerides could be accomplished without isomerization; therefore isomeric ratios of 1- and 2-monoglycerides could be measured directly. Also the present authors have found that the isomeric monoesters of glycols can be determined by the same technique. This made possible the determination of each monoester in a complex mixture.

Although the relative esterifiability for primary and secondary hydroxyls of glycerol and 1,2 propanediol have been determined separately, little has been done to determine the intermolecular relative esterifiability of the hydroxyls in a mixture of triols and glycols. This study was undertaken to determine the intermolecular and intramolecular relative esterifiability of triols and glycols which contained both primary and secondary hydroxyls.

Experimental Section

Esterifications resulted from the reaction of one mole of lauric acid with glycols and triols that furnish four moles of reactive hydroxyl in the presence of 0.1% NaOH catalyst in a N_2 atmosphere. P-toluenesulfonic acid catalyst was not used after it was found to catalyze the cyclization of some glycols used in the study. Reactions were allowed to proceed 24 hr in a 150C temperature-controlled oil bath. Reactions were not carried to completion; however reaction periods of 5, 10, and 72 hr showed no appreciable differences in relative esterifiabilities although the total amount of monoesters formed was different. All reaction systems became homogenous during the course of the reactions.

Trimethylsilyl derivatives were prepared according to the method of Wood (9), who did not observe detector-response differences for monoglycerides which were esterified with different fatty acids. In a preliminary study the present authors confirmed the work of Wood (9) and extended it to conclude that thermal conductivity, detector-response differences between the trimethylsilyl derivatives of monoglycerides and glycol monoesters were negligible.

Gas chromatographic separations of the trimethylsilyl derivatives were accomplished by utilizing a 30-ft × $\frac{3}{16}$-in. column, packed with 10% SE-52 and 5% QF-1 on 80/100 mesh Chromasorb W. The column temperature was held isothermal at 280C with 40 ml/min of He carrier gas. A thermal conductivity detector was used. Chromatographic peaks were measured by the triangulation method.

Calculations

Theoretical values were obtained by calculating according to the theory of random distribution. To exemplify this procedure, it may be assumed that one mole of lauric acid is reacted with 0.667 mole of glycerol and one mole of 1,2 propanediol. This means that a mole fraction of 0.250 of the total hydroxyls will be esterified and that a 0.750-mole fraction will be free hydroxyl. The mole ratio of glycerol to 1,2 propanediol, which is 0.4 to 0.6, must also be considered in the calculation. Bailey (2) considered reactions with glycerol only; therefore the mole fraction was one and need not be considered. One can now calculate T (theoretical mole %), based only on the total monoester present (Table I).

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TABLE I

	Species MF	Mole % (T)
Mole % 1 monolaurin = (MF esterified) (MF free OH) (MF free OH) (MF glycerol)		
= (.250) (.750) (.750) (.4)	= .0562	14.27
Mole % 2 monolaurin = (.750) (.250) (.750) (.4)	= .0562	14.27
Mole % 3 monolaurin = (.750) (.750) (.250) (.4)	= .0562	14.27
Mole % 1 hydroxy methyl ethyl laurate = (.750) (.250) (.6)	= .1125	28.58
Mole % 2 hydroxy propyl laurate = (.250) (.750) (.6)	= .1125	28.58

TABLE II

Compound	Ester	A[a]	T[b]	A/T
1,2 Propanediol	1 Hydroxy methyl ethyl laurate	8.96	7.83	1.144
1,2 Propanediol	2 Hydroxy propyl laurate	4.55	7.83	0.581
Glycerol	1 Monolaurin	5.42	4.39	1.235
Glycerol	2 Monolaurin	1.47	4.39	0.335
1,4 Butanediol	4 Hydroxy butyl laurate	11.93	8.45	1.412[c]

[a] Mole % based on total monoester and calculated from gas chromatogram.

[b] Mole % based on total monoester and calculated according to the theory of random distribution.

[c] $B_{(A/T)}$ value for this trial.

Esterifiabilities relative to one of the primary hydroxyls of 1,4 butanediol were calculated according to the following equation.

$$\frac{A}{T \times B_{(A/T)}} = RE$$

In this equation A represents the experimentally determined amounts of a particular monoester, expressed in mole % of the total monoester. The T value is obtained as a theoretical value, calculated according to the theory of random distribution and expressed in mole % of the total monoester (2). The $B_{(A/T)}$ is the A/T for the base compound or common denominator. In these experiments the A/T for one of the hydroxyls of 1,4 butanediol was used as the common denominator. This compound was used as the common denominator because of its large A/T value; however any hydroxyl of another compound would be equally effective. The RE represents the esterifiability relative to the base compound (Typical data, Table II).

Typical calculation:

$$\frac{A}{T \times B_{(A/T)}} = \frac{8.96}{7.83 \times 1.412} = 0.810 = RE$$

Discussion

The first phase of the study was concerned with a binary glycol:triol mixture. Figure 1 shows the results of the reaction of one mole of 1,2 propanediol (peaks 1 and 2) and four moles of glycerol (peaks 3 and 4) with lauric acid. In this experiment the primary objective was to determine the equilibrium ratios of 1 and 2 esters of 1,2 propanediol and glycerol at a 150C reaction temperature. If the primary and secondary hydroxyls were esterified at random, the ratio would be 1:1 for the glycol and 2:1 for the glycerol. However the actual ratio is 88:12 for the 1 to 2-monoglycerides and 65:35 for the 1 to 2-glycol monoesters. These data support the ratios reported by Van Lohuizen and Verkade (8), Wood (9), Allen (1), Brandner and Birkmeier (4) for glycerides but differ somewhat from those reported by Brandner and Birkmeier for propylene glycol esters (5).

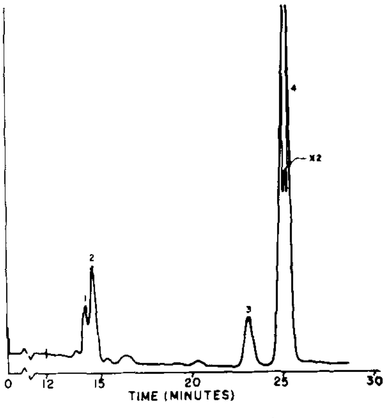

FIG. 1. Separation of TMS derivatives of 1,2 propanediol monoesters and monoglycerides by gas chromatography.

Figure 2 shows the results of the partial esterification of an equal-molar mixture of four glycols and three polyols with lauric acid. As can be seen, the 2-monoglyceride peak is not resolved from peak 6 (4 hydroxy 1 methyl pentyl laurate). However, since the amount of 2-monoglyceride may be calculated by using the equilibrium ratio and the area of peak 7 (1-monoglyceride), the 4 hydroxy 1 methyl pentyl laurate can be determined. Other isomeric species were sufficiently resolved so that accurate measurements could be made.

Esterifiability values relative to 1,4 butanediol for the hydroxyls of some glycols and triols are reported

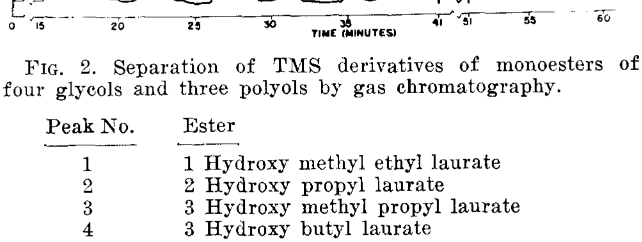

FIG. 2. Separation of TMS derivatives of monoesters of four glycols and three polyols by gas chromatography.

Peak No.	Ester
1	1 Hydroxy methyl ethyl laurate
2	2 Hydroxy propyl laurate
3	3 Hydroxy methyl propyl laurate
4	3 Hydroxy butyl laurate
5	4 Hydroxy butyl laurate
6	4 Hydroxy 1 methyl pentyl laurate
7	1 Monolaurin
8	1 Hydroxy methyl 3 hydroxy propyl laurate
9	2,4 Dihydroxy butyl laurate
10	3,4 Dihydroxy butyl laurate
11	1 Hydroxy methyl 5 hydroxy pentyl laurate
12	2,6 Dihydroxy hexyl laurate
13	5,6 Dihydroxy hexyl laurate

TABLE III
Relative Esterifiability Values of Primary and Secondary Hydroxyls of Glycols and Triols

Compound	Position of hydroxyl	Relative esterifiability
1,2 Propanediol	1 2	0.812 0.408
1,3 Propanediol	1 3	1.000 1.000
1,3 Butanediol	1 3	1.075 0.504
1,4 Butanediol	1 4	1.000 1.000
2,5 Hexanediol	2 5	0.305 0.305
1,6 Hexanediol	1 6	0.992 0.992
Glycerol	1 2	0.996 0.271
1,2,4 Butanetriol	1 2 4	0.770 0.244 1.591
1,2,6 Hexanetriol	1 2 6	0.642 0.228 1.516

in Table III. All values are relative to one of the primary hydroxyls of 1,4 butanediol, which has an arbitrary relative esterifiability of 1.000.

It is apparent from the data in Table I that there are distinct differences in the esterifiabilities of primary and secondary hydroxyls of the glycols and triols under study. The primary hydroxyls of 1,3 propanediol and 1,6 hexanediol have the same RE as 1,3 butanediol. This fact indicates that these primary hydroxyls will react with equal ease unless there are other vicinal groups present in the molecule to affect its RE. The RE of the primary hydroxyl of 1,2 propanediol is reduced to 0.812 when a secondary hydroxyl is on the adjacent carbon atom. If the secondary hydroxyl is once removed from the primary (1,3 butanediol), its effect on the RE of the primary hydroxyl seems to disappear. The RE of the secondary hydroxyl also increases when it is once removed from the primary. Apparently when two hydroxyls are adjacent, the RE is decreased. If this vicinal theory is accepted, then the low (0.305) RE of 2,5 hexanediol and the high RE of the isolated primary hydroxyl of 1,2,4 butanetriol and 1,2,6 hexanetriol is probably attributable to the steric properties of the molecule. Isomerization may also play an important role in bringing about these differences in RE.

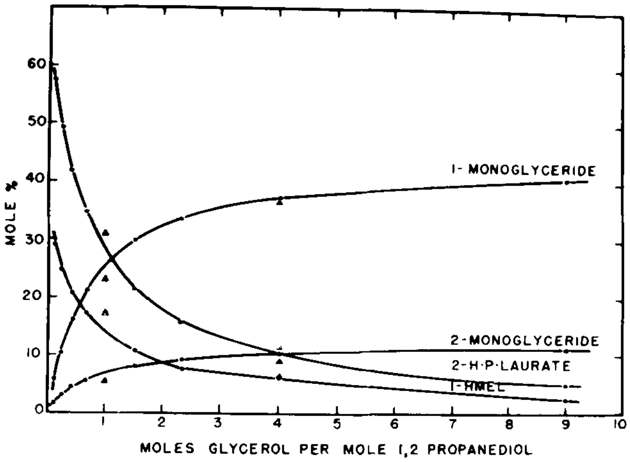

FIG. 3. Theoretical distribution of monoesters of 1,2 and 1,3 propanediols. △ = experimentally determined values.

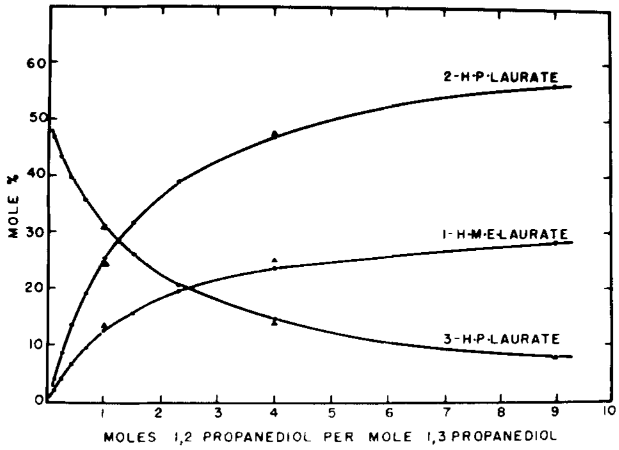

FIG. 4. Theoretical distribution of monoesters of glycerol and 1,2 propanediol. △ = experimentally determined values.

After the esterifiability has been determined, a prediction equation can be formulated that will indicate quantitatively the monoester products of a specific reaction mixture which is based on the total monoester.

$MF \times RE = P$
MF = mole fraction, calculated according to the theory of random distribution (2).
RE = esterifiability.
P = predicted mole fraction.

This equation can also be used to plot prediction curves for the distribution of monoesters. Figures 3 and 4 depict examples of such curves, calculated by utilizing a digital computer. As shown, the experimental data fit these curves quite well. The curve in Figure 3, depicting the 3 hydroxy propyl laurate, represents only one of the hydroxyls of 1,3 propanediol; however the 1 hydroxy propyl laurate would be an identical curve.

The RE values may be used to calculate Brandner's (4,5) equilibrium constant K intramolecularly or intermolecularly for any combination of hydroxyls. The intramolecular K for glycerol is 0.996/0.271 or 3.63. The intramolecular K for 1,2 propanediol would be 0.812/0.408 or 1.99.

This study does not encompass the relative esterifiability of hydroxyls after one ester has been formed in the molecule. Therefore further work must be done to determine RE and K values for the formation of multiple esters.

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