[CONTRIBUTION NO. 609 FROM THE DEPARTMENT OF CHEMISTRY AND PHYSICS, UNIVERSITY OF PITTSBURGH]

X-Ray Investigation of Glycerides. V. Diffraction Analyses of Synthetic Diacid Diglycerides[1]

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In a previous publication[2] in this series of X-ray investigations of synthetic glycerides it was pointed out that it was not possible to correlate the long-spacing diffraction data of an apparently homologous series of triacid triglycerides with a theoretical concept of molecular structure. Neither was a classification of the triglycerides according to the scheme proposed by Malkin[3] for diacid triglycerides possible, primarily for the reason that the triacid triglycerides, based upon the relationship of molecular weights, long spacings, and melting points of the β and β' forms, fell into four distinct groups.

For the purpose of determining whether a triacid triglyceride in its crystalline state could be related to a definite molecular pattern or structure, it was proposed to synthesize a type of triacid triglyceride in which the fatty acid in the 1-position of the glycerol molecule would be of a chain length of two and four carbon atoms, respectively, greater than the fatty acids in the 2- and 3-positions, respectively. Three triacid triglycerides of this type have been prepared in a high degree of purity. The physical data on these compounds will be reported in a separate communication.

The purpose of the present paper is to report the experimental and physical data on the symmetrical diacid diglycerides used as intermediates for the preparation of the homologous triacid triglycerides.

Experimental

Preparation of Intermediates.—The fatty acid chlorides of carbon chain length C_{10} to C_{18}, inclusive, were prepared from highly purified saturated fatty acids, respectively, by the method of McMaster and Ahmann.[4]

The 1-monoglycerides, 1-monostearin, m. p. 81.5°, 1-monopalmitin, m. p. 77.0°, and 1-monomyristin, m. p. 70.5°, were prepared by the method of Malkin and Shurbagy.[3]

Tritylation of the 1-monoglycerides with triphenylchloromethane in quinoline solution to prepare 1-stearyl-3-tritylglycerol m. p. 66.0°, 1-palmityl-3-tritylglycerol, m. p. 61.5°, 1-myristyl-3-tritylglycerol, m. p. 56.0°, was carried out essentially by the method of Verkade and van Der Lee.[5]

Preparation of 1-Myristyl-3-caprylglycerol.—1-Myristyl-3-tritylglycerol (10 g.) was dissolved in a mixture of quinoline (8 ml.) and dry chloroform (25 ml.). To this solution there was added capryl chloride (3.8 g., 1 mole = 3.3 g.). The mixture was then warmed on a steam-bath, under reflux, for four hours. The mixture after cooling to room temperature was dissolved in ethyl ether (250 ml.) and the ethyl ether solution washed successively with cold 0.1 *N* sulfuric acid, 5% potassium carbonate solution, and finally water. After drying the ethyl ether solution over anhydrous sodium sulfate, the ethyl ether was removed from the filtered liquid by distillation under reduced pressure. The pale yellow liquid residue, after washing repeatedly with absolute ethanol, was redissolved in dry petroleum ether (75 ml.). The solution was cooled in an ice-bath to approximately 5° and dry hydrogen chloride passed through the solution for about twenty minutes. A flocculent precipitate of diglyceride began to separate almost immediately. The mixture was allowed to stand at room temperature for one hour, during which time the diglyceride redissolved to a large extent, leaving a residue of triphenylcarbinol. The petroleum ether solution was filtered, diluted with an equal volume of ethyl ether, and the solution washed successively with 5% potassium carbonate solution and water, and dried over anhydrous sodium sulfate. The solvent was removed from the filtered liquid and the residue dissolved in a 1:1 mixture of ethyl ether and 95% ethanol. Slow crystallization several times from this mixture of solvents and finally from ethyl ether yielded a product melting at 47.5–48.0°; mol. wt.[6] 454 (calcd. 457).

Anal.[7] Calcd. for $C_{27}H_{52}O_5$: C, 71.01; H, 11.47. Found: C, 71.02, 69.96; H, 11.42, 11.36.

1-Palmityl-3-laurylglycerol, m. p. 59.0–59.5°, mol. wt., 514 (calcd. 513), and 1-stearyl-3-myristylglycerol, m. p. 66.5–67.0°, mol. wt., 564 (calcd. 569), were prepared by essentially the same procedure. Preparation of the latter diacid diglyceride had previously been reported by Verkade, *et al.*[5] (m. p. 66.0–66.5°). Carbon and hydrogen values were determined for one compound only as proof against errors of synthesis.

Chromatographic Adsorption.—Although chromatographic techniques by the Tswett's adsorption method[8] have been used by several investigators[9-13] for the separation of fatty acids, and glyceride mixtures, it has been shown by both Cassidy[12] and Kaufmann[14] that the chromatographic method "constitutes a powerful tool for proving the homogeneity of a sample of fatty acid." To the knowledge of the authors this method has not heretofore been applied to the determination of the homogeneity of synthetic glycerides.

Accordingly, each diacid diglyceride reported in this communication was subjected to chromatographic techniques essentially by the methods of Cassidy.[12] Silica gel[15] (10 g.) in a column 12 mm. in diameter was used as the adsorbent for approximately 0.5 g. of diglyceride. Petroleum ether, carefully purified, was used as the developing solvent, and mixtures of acetone and petroleum ether as the eluting solvents. Based upon the criterion of con-

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[1] The generous financial assistance of the Buhl Foundation in support of this investigation is gratefully acknowledged.

[2] Filer, Sidhu, Chen and Daubert, THIS JOURNAL, **67**, 2085 (1945).

[3] A series of papers by Malkin, *et al.*, *J. Chem. Soc.*, 666 (1934); 1628 (1936); 1409 (1937); 103, 577, 1141 (1939).

[4] McMaster and Ahmann, THIS JOURNAL, **50**, 147 (1928).

[5] Verkade and van Der Lee, *Rec. trav. chim.*, **55**, 267 (1936).

[6] All molecular weights were determined by the method of Hanson and Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939).

[7] The microanalysis was performed in our Organic Microanalytical Laboratory by Mr. George Stragand.

[8] L. Zechmeister and L. Cholnoky, "Principles and Practice of Chromatography," translated from the 2nd edition by A. L. Bacharach and F. A. Robinson, Chapman and Hall, Ltd., London, 1931.

[9] Condo, *J. Pharm. Soc. Japan*, **57**, 218 (1937).

[10] Manunta, *Helv. Chim. Acta*, **22**, 1156 (1939).

[11] Kaufmann, *Fette u. Seifen*, **46**, 268 (1939).

[12] Cassidy, THIS JOURNAL, **62**, 2735, 3073, 3076 (1940).

[13] Graff and Skau, *Ind. Eng. Chem., Anal. Ed.*, **15**, 340 (1943).

[14] Kaufmann, *Angew. Chem.*, **53**, 98 (1940).

[15] Davison Silica Gel, 11-08-08-01, 200 mesh.

stancy of melting point of the diglyceride obtained from each percolate fraction, the diglycerides were found to be entirely homogeneous.

Polymorphism of the Diacid Diglycerides.—The thermometric techniques which were used to determine the transition temperatures of the different crystalline forms of the diacid diglycerides have been described in previous publications.[16,17]

X-Ray Diffraction Analysis.—As described previously,[2,18] the X-ray diffraction patterns of the glyceride specimens were made by the usual powder method. A powdered specimen of the solvent free material was packed into a thin-walled nylon tube of an internal diameter of 0.8 mm. The nylon tube was then mounted in a cylindrical camera of 17.19 cm. effective diameter and rotated during the exposure. The same nylon tube with the same specimen was mounted in a pin-hole type camera using a 5-inch by 7-inch flat Cassette. The patterns were made with specimen-to-film distances of 10 and 24 cm., respectively.

The radiation employed was filtered CuK_α of effective wave length 1.5386 Å. and was supplied by a diffraction tube with beryllium windows.

TABLE I

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF DIACID DIGLYCERIDES[a]

V = very, S = strong, M = medium, W = weak.

1-Myristyl-3-caprin β phase $d \times 10^{-8}$ cm.	I/I_0	1-Palmityl-3-laurin β phase $d \times 10^{-8}$ cm.	I/I_0	1-Stearyl-3-myristin β phase $d \times 10^{-8}$ cm.	I/I_0
18.9	M	21.2	M	15.9	S
14.6	VW	14.3	S	11.8	W
12.8	M	12.6	VW	9.44	W
9.51	W	10.7	W$^+$	7.91	VW
7.54	W	8.55	W$^+$	6.80	W
6.57	VW	7.17	VW	5.57	VW
6.01	VW	6.23	W	4.60	VS
5.42	VW	5.74	VW	4.13	VW
4.87	VW	5.30	W	3.76	VS
4.55	VS	5.00	VW	3.53	VW
4.23	VW	4.63	VS	3.31	VW
3.84	VS	3.80	VS	3.00	VW
3.73	VS	3.76	VS	2.55	M
2.65	W	2.67	VW	2.31	W
2.50	W	2.62	VW	2.18	W$^+$
2.42	W$^+$	2.49	M	2.06	M
2.31	VW	2.41	M	1.99	VW
2.24	VW	2.36	VW	1.88	W$^+$
2.17	W$^+$	2.31	W	1.66	W
2.06	M	2.17	W$^+$		
1.90	W	2.06	M		
1.86	W	1.90	W		
1.81	VW	1.86	W		
1.65	W	1.66	W		

[a] The interplanar spacings are those below 22 Å.

The side-spacing data given in Table I are composite data obtained from the 17.19-cm. cylindrical film and the flat film taken with specimen-to-film distance of 10 cm. The long-spacing values were calculated from the diffraction patterns obtained with the pin-hole type of camera at specimen-to-film distances of 10 and 24 cm. The diffraction pattern obtained with a 24-cm. specimen-to-film distance permitted observation of the first and higher orders of reflection. The long-spacing values reported represent the arithmetical mean of the long spacings calculated from the individual reflections.

In order to ascertain that the diffraction data on the glycerides contained diffraction lines obtained from the specimens only, the diffraction patterns for the nylon tubes used as specimen holders were taken with the same radiation, cameras, and specimen-to-film distance. The lines thus obtained were carefully noted for structure, intensity, and position on the pattern. In estimating the intensities of the diffraction lines originating from the specimen the effects of any superimposition of the nylon tube lines were taken into consideration.

Discussion

It may be noted from the data in Table I that the strong side-spacing lines for 1-myristyl-3-caprin and 1-palmityl-3-laurin correspond to those reported by Malkin[3] for the β-form of monacid diglycerides (type *a* pattern, 4.6 strong, 3.9 strong, 3.73 strong) obtained from a pressed layer. The side-spacing data for 1-stearyl-3-myristin do not show a strong line at 3.9 Å. The diffraction pattern for this diglyceride seems to correspond more nearly to Malkin's[3] type *b* pattern (4.6 strong, 3.9 weak, 3.73 strong, 3.6 weak) which he obtained from a melted layer, although our crystallization conditions were as nearly identical for each diglyceride as it was possible to obtain them. We had observed in previous work[19] on the synthesis of triacid triglycerides that it was quite possible to obtain the β' form from solvent by rapid crystallization techniques. It is reasonable to assume, however, that the side-spacing data in Table I are typical and characteristic for the β form type of synthetic glyceride as obtained by solvent crystallization, particularly when the data are considered in the light of long-spacing evidence.

The long-spacing values for 1-stearyl-3-myristin, 1-palmityl-3-laurin, and 1-myristyl-3-caprin are 47.6, 42.7 and 38.0 Å., respectively (Table II). In a plot of the long-spacing values against double the number of carbon atoms in the fatty acid of greater chain length, the long spacings fall on a straight line and correspond to a "double molecule" of a structure similar to that postulated by Malkin.[3] The intercept of zero carbon atoms gives approximately 8 Å. for space occupied by the glyceryl residues and their nearest distance of approach in the crystalline state, which fact also tends to support the double molecule struc-

TABLE II

LONG SPACINGS AND TRANSITION TEMPERATURES OF THE DIACID DIGLYCERIDES

	Long spacing $d \times 10^{-8}$ cm. β-form	Transition temperature Form I	Form II	Form III
1-Myristyl-3-caprin	38.0	48.0	44.0	39.0
1-Palmityl-3-laurin	42.7	59.5	56.0	51.0
1-Stearyl-3-myristin	47.6	67.0	63.0	56.0

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[16] Daubert and Clarke, THIS JOURNAL, **66**, 690 (1944).

[17] Daubert and Clarke, *Oil & Soap*, **22**, 113 (1945).

[18] Filer, Sidhu, Daubert and Longenecker, THIS JOURNAL, **66**, 1333 (1944); **68**, 167 (1946).

[19] Chen and Daubert, *ibid.*, **67**, 1256 (1945).

ture.[6] Furthermore, a straight line relationship is obtained in a plot of long-spacing values and molecular weights. Thus, the relationships of long-spacing values, molecular weights, and melting points of the diacid diglycerides, solvent crystallized in the β-form, indicate that they represent a truly homologous series.

Transition temperatures for the different polymorphic forms for each diglyceride obtained from warming and cooling curves and capillary tube determinations are given in Table II. Since X-ray diffraction patterns were not obtained on forms other than those obtained on crystallization from solvent, the system of nomenclature used is the same as that previously reported.

Acknowledgment.—The assistance of Miss Gretta L. Scott in obtaining some of the X-ray diffraction data is gratefully acknowledged.

Summary

X-Ray diffraction and thermal data are reported for a series of three symmetrical diacid diglycerides, two of which, namely, 1-palmityl-3-laurin and 1-myristyl-3-caprin, are new compounds.

The side-spacing diffraction data for 1-myristyl-3-caprin and 1-palmityl-3-laurin correspond to Malkin's type *a* pattern for the *beta* form of monoacid diglycerides, while the data for 1-stearyl-3-myristin seemed to correspond more nearly to Malkin's type *b* pattern.

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The Reversible Esterification of Carboxylic Acids with Isobutene and Trimethylethylene. Quantitative Studies and Synthetic Applications

BY ROLF ALTSCHUL

The literature contains only scattered publications dealing with esterifications of carboxylic acids with olefins, such as the catalyzed additions of fatty acids to butene-2 and pentene-2,[1] to trimethylethylene,[2,3] or to isobutylene.[1,4]

The thermal and the acid-catalyzed decompositions of tertiary esters represent the reverse reaction, and these constitute in contrast a generally recognized phenomenon[5] and have been fully characterized in the presence of hydroxylic reagents, leading to hydrolysis with water,[6] formation of ethers with anhydrous alcohols,[7] or acetolysis with acetic acid.[8]

In the past the opposing reactions have been studied separately under irreversible conditions by either expelling the volatile alkenes at elevated temperature, by exposing them to solvolysis, or by conducting esterifications with an excess of carboxylic acid sufficient to mask the attainment of an equilibrium state.

If such additions or decompositions are carried out reversibly in an inert solvent, an equilibrium results, analogous to that between alcohols and acids. In the following, we will present in turn the study of the equilibrium system and of the rates and mechanism, followed by a brief appraisal of its value as a general preparative tool.

Equilibrium.—Equation 1 represents the relevant equilibrium

$$\text{Acid} + \text{Olefin} \underset{k_1}{\overset{k_2}{\rightleftarrows}} \text{Ester} \qquad (1)$$

$$K = (\text{Ester})/(\text{Acid}) \times (\text{Olefin}) = k_2/k_1 \qquad (2)$$

Quantitative measurements were carried out on the esterifications of benzoic acid, p-nitrobenzoic acid and acetic acid with isobutylene and, for the first acid, with trimethylethylene leading to t-butyl benzoate (I), t-butyl p-nitrobenzoate (II), t-butyl acetate (III), and t-amyl benzoate (IV),

TABLE I

EQUILIBRIUM BETWEEN ISOBUTENE, BENZOIC ACID AND t-BUTYL BENZOATE IN DIOXANE SOLUTIONS CONTAINING SULFURIC ACID AT 25 ± 0.1° AND 35 ± 0.1°

Initial concn., moles/liter					
(Ester)	(Bz acid)	(i-Bu)	(H_2O)	(H_2SO_4)[a]	K
			At 25°		
0.928	0.629	0	0.062	0.545	1.39
.928	.0	0	.119	1.040	1.52
.928	.280	0	.119	1.040	1.43
.928	.0	0	.238	1.141	1.39
.928	.0	0	.149	1.302	1.59
.0	.247	0.855	.0	0.483	1.59
					Av. 1.47 ± 0.08
			At 35°		
0.928	0	0	0	1.075	1.18
.696	0	0	0	0.664	1.04
1.392	0	0	0	.664	0.98
1.113	0	0	0	1.128	1.10
0.928	0	0	0	0.441	0.94
.0	0.620	0.540	0	.664	.93
					Av. 1.03 ± .08

[a] Concentration of sulfuric acid given as equivalents/liter.

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(1) Zavgorodnii, *C. A.*, **33**, 5805 (1939).

(2) Kondakow, *J. Russ. Phys. Chem. Soc.*, **25**, 442 (1893).

(3) Timofejev and Andreasov, *Chem. Zentr.*, **96**, II, 1652 (1925).

(4) Scovill, Burk and Lankelma, THIS JOURNAL, **66**, 1039 (1944).

(5) (a) Bilger and Hibbert, *ibid.*, **58**, 823 (1936); (b) Tronov and Sibgatulin, *Ber.*, **62B**, 2850 (1929); (c) Barkenbus, Roswell and Mitts, THIS JOURNAL, **62**, 1251 (1940); (d) Zaki, *J. Chem. Soc.*, 983 (1928).

(6) Day and Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941). This paper presents an extensive summary of data on ester hydrolyses.

(7) Cohen and Schneider, THIS JOURNAL, **63**, 3382 (1941).

(8) Cohen, *ibid.*, **66**, 1395 (1944).