[CONTRIBUTION NO. 573 FROM THE DEPARTMENT OF CHEMISTRY AND PHYSICS, UNIVERSITY OF PITTSBURGH]

X-Ray Investigation of Glycerides. II. Diffraction Analyses of Synthetic Triacid Triglycerides[1]

BY L. J. FILER, JR., S. S. SIDHU, CHIADAO CHEN AND B. F. DAUBERT

Introduction

In the first paper of this series[2] of X-ray investigations on highly purified synthetic glycerides, the value of X-ray diffraction data in characterizing the glycerides of natural fats and oils was discussed.

The X-ray diffraction studies of Malkin and coworkers have clearly established the polymorphic nature of glycerides.[3] Lutton[4] recently has presented experimental data and discussed in detail the factors to be considered in relating X-ray diffraction patterns to the phenomena of multiple melting.

In a recent publication on the synthesis of triacid triglycerides,[5] it was pointed out that some of the triglycerides could be crystallized from solvent in such a fashion as to give rise to two crystalline products having distinctly different melting points. That these two different melting forms represented different crystalline modifications of the same glyceride was proved by preliminary X-ray diffraction studies.

The purpose of this publication is to present the complete X-ray diffraction data upon which the polymorphic nature of the solvent-crystallized glycerides was established. In addition to these identification data, the determined long-spacing values for the triacid triglycerides are correlated with their molecular weights and melting points.

TABLE I

INTERPLANAR SPACINGS AND RELATIVE INTENSITIES OF TRIACID TRIGLYCERIDES; 1-STEARYL-2-ACYL-3-R GLYCEROL

R = Palmityl								R = Lauryl									
Myristyl β phase		Myristyl β' phase		Lauryl β phase		Capryl β phase		Palmityl β phase		Palmityl β' phase		Myristyl β phase		Myristyl β' phase		Capryl β phase	
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
20.8	M	13.7	S	20.0	M	20.2	M	20.8	S	14.0	S	19.3	S	13.2	S	18.2	M
15.7	M	11.9	VW	15.3	S	14.8	S	15.7	VW	10.9	W	14.9	M	11.7	VW	13.6	M
12.5	M	10.4	VW	12.4	W+	12.6	VW	12.6	M	8.25	W	12.0	M	10.3	M	10.7	VW
10.9	VW	8.25	W	10.4	VW	9.92	VW	10.4	VW	6.30	VW	10.0	W	8.15	M	9.07	W
9.20	W	6.74	W	8.77	W+	8.54	W+	8.86	W	5.96	VW	7.61	M	5.73	W+	7.77	W+
7.65	VW	5.88	$\overline{\mathrm{W}}$	7.73	W	7.82	W	7.75	VW	5.61	W	6.62	W	5.43	W	6.33	W
6.55	VW	5.30	M	6.94	VW	6.71	W	6.22	W	5.09	W	6.06	W	5.35	W	5.73	VW
5.95	VW	4.87	W	6.30	W	6.19	VW	5.20	M	4.29	VS	5.77	W	5.04	W	5.28	M
5.51	VW	4.60	W	5.91	W	5.66	VW	4.87	W	4.11	S	5.42	M	4.95	W	4.83	W
5.24	M	4.34	VS	5.19	M	5.41	M	4.62	VS	3.82	S	5.02	M	4.77	W	4.60	VS
4.99	W	4.11	VS	4.83	M	4.78	M	4.34	M	3.57	W	4.82	S	4.45	M	4.29	W
4.81	W	3.80	VS	4.61	VS	4.61	VS	4.08	VW	3.15	W	4.61	VS	4.26	VS	4.11	VW
4.62	VS	3.50	W	4.33	M	4.36	W	3.82	VS	2.81	VW	4.45	VW	4.05	W	3.82	VS
4.34	W+	3.27	W	4.08	W	4.21	M	3.71	W	2.53	W	4.32	S	3.81	VS	3.74	W
3.83	VS	3.02	$\overline{\mathrm{W}}$	3.84	VS	3.96	W	3.60	W	2.27	M	4.15	W	3.51	W	3.62	VW
3.68	VW	2.83	W	3.65	VW	3.82	VS	3.29	W	2.09	W	3.98	W	3.34	W	3.56	W
3.54	VW	2.53	M	3.43	VW	3.54	W+	3.03	W+	1.91	W	3.82	VS	3.15	W	3.26	W
3.40	W	2.41	W	3.36	VW	3.33	W	2.77	W	1.80	W	3.66	M	3.02	W	3.04	VW
3.28	VW	2.29	W+	3.27	VW	3.17	W	2.54	VW			3.52	W	2.82	W	2.75	VW
3.03	W	2.23	W	3.03	M	3.00	W	2.47	M			3.31	M	2.53	W	2.53	M
2.75	VW	2.18	W	2.75	W	2.76	W	2.35	W			3.17	VW	2.38	VW	2.46	M
2.47	$\overline{\mathrm{W}}$	2.02	VW	2.63	VVW	2.65	VW	2.23	W			3.03	M	2.26	M	2.35	W
2.31	VW			2.48	$\overline{\mathrm{M}}$	2.49	$\overline{\mathrm{M}}$	2.09	M			2.75	W	2.10	W	2.25	W
2.24	W			2.34	W	2.34	W	1.90	W+			2.65	VW	1.97	VVW	2.18	W
2.10	$\overline{\mathrm{W}}$			2.24	W	2.25	W	1.85	VW			2.51	W	1.89	W	2.09	M
1.91	$\overline{\mathrm{W}}$			2.18	VW	2.19	VW	1.69	VW			2.46	M	1.78	W	2.02	VW
1.84	$\overline{\mathrm{W}}$			2.09	M	2.09	M	1.65	W			2.35	W			1.95	W
1.69	VW			1.90	M	1.94	VW					2.24	M			1.90	W
1.65	W					1.90	M					2.18	VW			1.84	W
						1.83	W					2.09	M				
						1.64	W					2.01	VW				
												1.94	VW				
												1.90	W+				
												1.84	W				
												1.77	VW				
												1.69	W				
												1.65	W+				
												1.60	W				

Experimental Procedure

Preparation of Glycerides.—The experimental details for the preparation of the triacid triglycerides have been published recently by Chen and Daubert.[5] These authors presented methods for obtaining two crystal modifications

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[1] Grants by the Buhl Foundation and Swift and Company in support of this investigation are gratefully acknowledged.

[2] L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, THIS JOURNAL, **66**, 1333 (1944).

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

[4] E. S. Lutton, THIS JOURNAL, **67**, 524 (1945).

[5] C. Chen and B. F. Daubert, *ibid.*, **67**, 1256 (1945).

TABLE I (*Concluded*)

R = Myristyl						R = Capryl											
Palmityl β phase		Lauryl β phase		Capryl β phase		Palmityl β phase		Palmityl β' phase		Myristyl β phase		Myristyl β' phase		Lauryl β phase		Lauryl β' phase	
d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0	d	I/I_0
13.5	S	19.9	S	28.4	S	19.3	VS	28.8	VS	13.8	W	27.0	S	17.6	S	17.5	M
5.30	M	14.8	S	18.6	M	15.0	VW	20.0	S	11.6	W$^+$	17.8	M	14.0	VW	14.1	W
5.01	W	11.9	M	14.2	S	12.8	M	14.7	VS	9.95	W	13.5	S	11.8	M	13.4	VW
4.61	VS	8.54	W	11.4	VW	11.1	VW	11.8	VW	9.42	W$^+$	10.8	M	10.3	VW	10.6	W
4.48	W	8.38	W	11.0	W	9.73	VW	9.84	W	8.80	W	9.09	W	9.15	M	9.05	W$^+$
4.34	W	7.57	M	7.64	M	8.68	W$^+$	8.44	M	7.56	S	7.71	M	7.46	W	8.89	W
4.04	W	6.56	VW	6.59	W	7.68	VW	7.36	VW	7.08	VW	6.89	W	7.22	W	8.24	VVW
3.89	VS	6.02	W	6.36	VW	7.21	VW	6.27	W	6.81	VW	6.74	VW	6.71	W	7.56	W
3.75	VS	5.78	W	5.74	W	6.40	W	5.95	W	6.23	VW	6.39	W	6.10	W	7.01	W
3.64	W	5.37	M	5.35	M	5.53	M	5.19	M	5.89	VW	6.27	VW	5.50	W	6.71	W
3.46	W	5.02	W	5.18	S	5.35	M	4.77	S$^-$	5.59	S	5.59	M	5.32	W	6.59	W
3.29	VW	4.80	M	4.82	M	4.82	M	4.49	W	5.30	VW	5.16	W	4.94	W	5.93	W
3.15	W	4.61	VS	4.62	S	4.51	W	4.22	VS	4.91	VW	5.01	W	4.62	W	5.50	M
3.03	W$^+$	4.44	VW	4.40	W	4.33	S	4.04	W	4.69	VW	4.89	VW	4.40	W	4.82	W
2.85	VW	4.25	S	4.30	M	4.14	VS	3.86	S	4.61	W	4.58	S	4.19	VS	4.46	S
2.69	VW	3.83	VS	4.05	W	3.98	VW	3.76	S	4.45	S	4.45	VS	3.92	W$^+$	4.29	S
2.57	M	3.75	VW	3.82	VS	3.85	VS	3.53	W$^+$	4.34	W	4.32	W	3.81	S	4.16	VS
2.40	M	3.60	W	3.58	W	3.53	W	3.28	W$^+$	4.20	VS	4.19	S	3.70	W	3.99	M
2.28	M	3.54	W	3.41	VW	3.32	W	3.05	W$^+$	4.04	W	4.05	S	3.52	W	3.83	S
2.21	M	3.32	W	3.24	VW	3.14	W	2.94	W	3.83	VS	3.84	VS	3.32	W	3.71	VW
2.08	M	3.15	VW	3.16	VW	3.04	W	2.77	VW	3.56	S	3.73	S	3.19	W	3.60	M
2.01	VW	3.02	M	3.02	W	2.82	W	2.69	VW	3.28	VW	3.53	VW	3.02	W$^+$	3.28	VW
1.95	M	2.86	VW	2.92	W	2.53	W	2.50	M	3.11	M	3.42	W$^+$	2.96	VW	3.08	VW
1.91	M	2.76	W	2.76	W	2.26	W$^+$	2.28	W	3.01	M	3.29	W	2.87	VW	3.02	W
1.88	W	2.64	VW	2.66	VW	2.10	W	2.21	W	2.88	VW	3.10	W$^+$	2.81	VW	2.82	VW
1.79	W	2.50	M	2.54	M	1.91	W	2.15	W	2.72	VW	2.97	W	2.73	VW	2.61	W
		2.44	W$^+$	2.44	M	1.78	$\overline{\text{W}}$	2.10	W	2.60	M	2.76	W	2.60	VW	2.53	VW
		2.33	VW	2.32	VW			2.04	VW	2.45	W$^+$	2.66	M	2.51	M	2.45	W
		2.23	W	2.23	VW			1.95	W$^+$	2.39	VW	2.52	VW	2.36	$\overline{\text{VW}}$	2.39	VW
		2.18	VW	2.17	VW			1.89	W$^+$	2.26	$\overline{\text{M}}$	2.44	VW	2.25	W$^+$	2.33	VW
		2.09	M	2.09	M					2.15	W	2.36	M	2.18	W	2.24	M$^-$
				2.02	VW					2.07	VW	2.28	VW	2.09	W	2.15	VW
				1.95	VW					2.04	VW	2.21	M	2.05	VW	2.07	W
										1.98	VW	2.14	VW	1.95	VW	1.89	W
										1.89	W	2.07	VW	1.89	W	1.74	W
										1.86	W	2.01	VW	1.71	W		
										1.74	W	1.96	VW				

of the same glyceride by solvent crystallization. In general, rapid crystallization from solvent yielded the low melting form, the higher melting form being produced by slow crystal growth at constant temperature. These two modifications could be produced independently of the solvent used for crystallization purposes.

X-Ray Diffraction Analyses.—The X-ray diffraction patterns of the glycerides were made by the usual powder method. A finely-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 patterns were repeated with the same specimen and with a pin-hole type of camera using a flat cassette and specimen-to-film distances of both 10.15 and 24.35 cm., respectively.

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

The short-spacing diffraction data given in Table I are composite data obtained from the 17.19-cm. cylindrical film and the flat film taken with the specimen-to-film distance of 10.15 cm. The interplanar spacings of the diffraction lines that appeared on both films were the same, but the intensities in many cases were different. This was due to the fact that in one case the specimens were rotated, while in the other they were stationary.

The long-spacing values reported in Table II were calculated from the diffraction patterns obtained with the pin-hole camera at specimen-to-film distances of 10.15 and 24.35 cm. In some instances as high as ten orders were registered. The diffraction pattern obtained with a 24.35-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 individual reflections.

Discussion

Both short and long-spacing X-ray diffraction data have been obtained for a series of highly purified triacid triglycerides. These data have been determined upon glycerides crystallized from solvent. Since it was possible to obtain two distinct crystalline modifications of certain of these triglycerides, diffraction data are reported for these two specific forms.

From a consideration of the short-spacing data, it is possible to identify specific polymorphic forms of these triglycerides and thus to establish the form most readily obtained from solvent. Rapid crystal growth has been shown to lead to the formation of the β' phase, while slow crystal growth gave rise to the β phase. These experimental findings indicated that in all instances of rapid crystal growth of these triacid triglycerides, the crystalline form most readily obtained from solvent was not the more stable and higher melting β phase, but rather the lower melting β' phase. This effect stands in contrast to the generally accepted observation that glycerides, fatty acids, and many other polymorphic organic compounds crystallize from solvent in their most stable or highest melting form.

In the many attempts made to obtain two crystalline modifications from solvent of those triglycerides for which diffraction data on one form

TABLE II

LONG-SPACING VALUES AND MELTING POINTS FOR TRIACID TRIGLYCERIDES

Glyceride, 1-stearyl-2-acyl-3-R-glycerol	Acyl radical	Polymorphic form	Long-spacing, 10^{-8} cm.	Capillary m. p., °C.	Calcd. mol. wt.
R = palmityl	Palmityl[a]	β	43.9	62.5	835
		β′	42.5	59.5	
	Myristyl	β	63.4	59.5	807
		β′	41.5	56.1	
	Lauryl	β	61.2	57.5	779
	Capryl	β	60.0	55.0	751
R = myristyl	Palmityl	β	40.5	58.5	807
	Myristyl[a]	β	61.4	56.0	779
		β′	41.7	52.0	
	Lauryl	β	59.8	55.0	751
	Capryl	β	57.3	52.5	723
R = lauryl	Palmityl	β	62.4	52.0	779
		β′	43.3	47.0	
	Myristyl	β	59.6	49.5	751
		β′	40.1	45.5	
	Lauryl[a]	β	57.0	45.0	723
		β′	38.7	41.5	
	Capryl	β	54.9	41.8	695
R = capryl	Palmityl	β	38.5	50.0	751
		β′	59.0	46.5	
	Myristyl	β	56.1	45.0	723
		β′	54.3	42.0	
	Lauryl	β	35.6	44.0	695
		β′	53.0	40.0	
	Capryl[a]	β	52.6	41.0	677
		β′	51.0	38.0	

[a] Data from Malkin's investigations.

only appear in Table I, some variation in melting point (1 to 2°) was obtained for samples having the same X-ray diffraction pattern. This effect is due to a variation in the crystal perfection or crystallite size of the glyceride specimen.

The question of nomenclature as applied to polymorphism in glycerides has been discussed recently by Lutton.[4] The nomenclature of Malkin,[3] as corrected by Lutton,[4] and applied to the glycerides reported in this study, shows that the polymorphic forms previously reported[5] from thermal curve data as Forms I and II are β and β′ forms, respectively.

It should be observed, however, in Table I that the triacid triglycerides of the type 1-stearyl-2-acyl-3-capryl glycerol do not show the side-spacings characteristic for the β and β′ phases. The over-all X-ray diffraction data clearly establish the existence of the two forms in this series of solvent-crystallized glycerides. Since this is the first instance of anomalies in side-spacing data for the different polymorphic forms of mixed triglycerides,[6] judgment as to the positive association of specific and characteristic side-spacings for distinguishing the β and β′ phases of triacid triglycerides must be reserved until additional information can be obtained on this type of synthetic compound. On the basis of our present X-ray and thermal data, the higher melting form has been termed tentatively the β phase.

In most X-ray diffraction studies of long-chain compounds, long-spacing values are correlated with some postulated molecular configuration. Thus, concepts have been formed regarding the arrangement of molecules in such substances as paraffin hydrocarbons, fatty acids, monoglycerides, simple triglycerides, etc. These data are usually presented graphically, the long-spacing values being plotted as a function of the number of carbon atoms in a particular hypothetical structure or as a function of their molecular weights.[7] Correlation of long-spacing values with the molecular weights of soaps has been made by Ferguson and Nordsieck.[8]

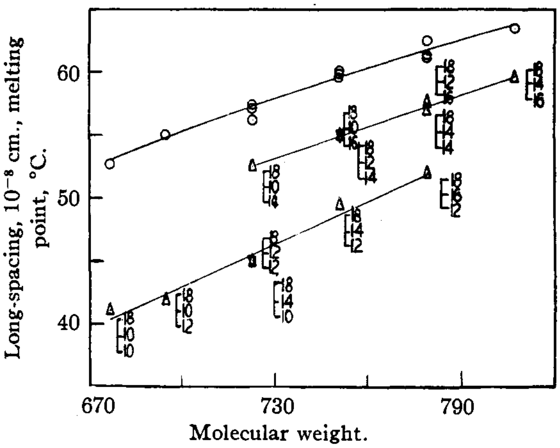

Fig. 1.—Melting points and long-spacing values for the β phase of triacid triglycerides as a function of their molecular weights: ○, long spacings; △, melting points.

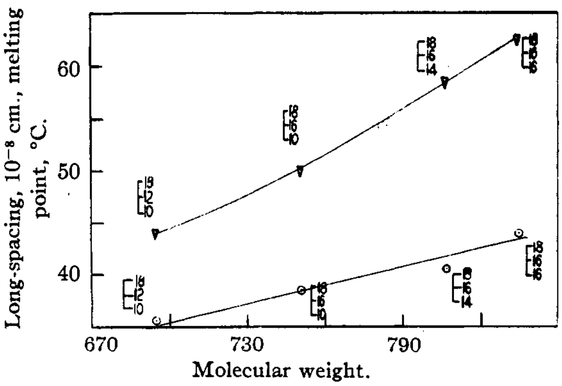

Fig. 2.—Melting points and long spacing values for the β phase of triacid triglycerides as a function of their molecular weights: ○, long spacings; ▽, melting points.

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(6) Malkin (ref. 3) observed a similar anomaly with side-spacing data for the β phase of the simple triglycerides, trielaidin and tribrassidin.

(7) R. D. Vold and M. J. Vold, *States of Aggregation of Some Paraffin Chain Compounds*, "Colloid Chemistry," Vol. 5, Reinhold Publishing Corporation, New York, N. Y., 1944.

(8) R. H. Ferguson and H. Nordsieck, *Ind. Eng. Chem.*, **36**, 748 (1944).

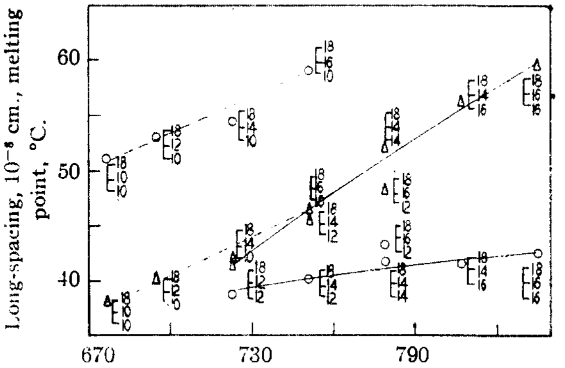


Fig. 3.—Melting points and long spacing values for the β' phase of triacid triglycerides as a function of their molecular weights: O, long spacings; △, melting points.

Since it is not known whether these triacid triglycerides represent an homologous series of compounds whose long-spacing values can be related to some theoretical concept of molecular structure, and also since they cannot be classified in any such schematic arrangement as proposed by Malkin,[3] and as discussed by Ferguson and Lutton,[9] the long-spacing values therefore have been plotted as a function of their molecular weights. The data used in the preparation of these graphs are given in Table II.

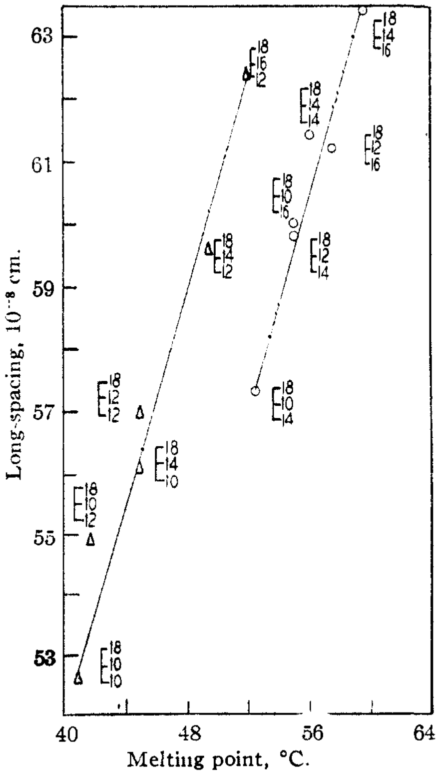
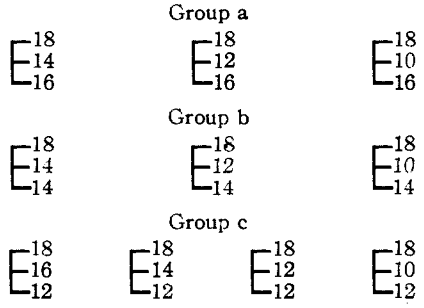


Fig. 4.—Melting points for the β phase of triacid triglycerides as a function of their long spacing values.

In Fig. 1 the long-spacing values for some of the glycerides in the β phase are found to group themselves along a common line. The melting points for these same compounds fall into two distinct classes. On the basis of the relationships observed in Fig. 1, the glycerides seem to fall into the following groups, where E is the symbol used for the glyceryl radical and the numbers represent the number of carbon atoms in the attached fatty acid:



In Fig. 2 the data are plotted for those glycerides whose long-spacing values for the β phase are of the order of 40 Å. An explanation for the pronounced difference in the long-spacing values between this group and those represented in Fig. 1 is not now apparent.

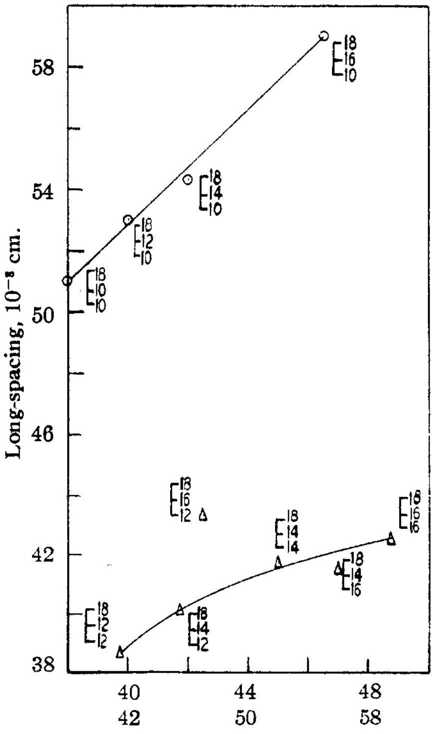


Fig. 5.—Melting points for the β' phase of triacid triglycerides as a function of their long spacing values. The triangles have been placed with reference to the melting point scale 38 to 62° and the circles have been placed with reference to the melting point scale 38 to 50°.

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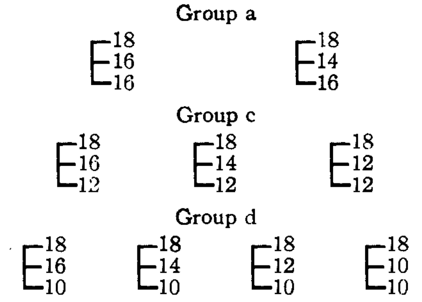
(9) R. S. Ferguson and E. S. Lutton, *Chem. Rev.*, **29**, 355 (1941).

In Fig. 3 are plotted the long-spacing and melting-point data for those glycerides which were crystallized from solvent in the β' phase. The glycerides may be grouped as follows on the basis of the relationships observed in Fig. 3.



Figures 4 and 5 correlate the determined long-spacing values with capillary melting points. A definite relationship seems to exist among the members of the individual groups of glycerides which have been designated as Groups a, b and c of Fig. 1 and a, c and d of Fig. 3, respectively.

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

An X-ray diffraction unit, given by the Picker X-Ray Corporation, was used to obtain some of the diffraction patterns.

Summary

The polymorphism of solvent-crystallized synthetic triacid triglycerides has been established by X-ray diffraction data.

Crystallization of the triacid triglycerides from solvent in either the β or β' phase seems to be dependent upon the rate of crystal growth.

Correlations between molecular weights and melting points and molecular weights and long-spacing values have been indicated.

PITTSBURGH, PENN. RECEIVED AUGUST 6, 1945

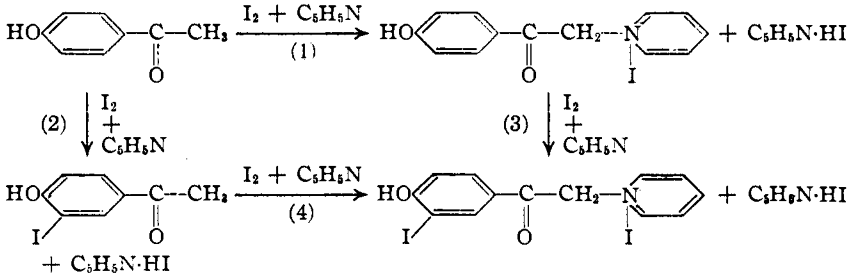
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Reactions of Acetophenols with Iodine and Pyridine and the Preparation of Hydroxybenzoic Acids

BY L. CARROLL KING, MARGARET MCWHIRTER AND DANIEL M. BARTON

In former papers from this Laboratory[1a,b] the reaction of iodine and pyridine with ketones, to give substituted β-ketoalkylpyridinium iodides was reported. This reaction has now been extended to a number of hydroxyacetophenones. *o*-Hydroxyacetophenones and resacetophenone gave the corresponding 1-(hydroxybenzoylmethyl) pyridinium iodides, *p*-hydroxyacetophenones and *m*-hydroxyacetophenone gave a mixture of the corresponding 1-(hydroxybenzoylmethyl)-pyridinium iodide and a 1-(hydroxymonoiodobenzoylmethyl)-pyridinium iodide. In each of the reactions studied approximately half of the iodine used appeared as pyridine hydroiodide. Each of the substituted β-ketoalkylpyridinium iodides produced by the above reactions gave characteristic hydroxy acids when cleaved by means of aqueous alkali.

Since about half of the iodine which enters into the reaction appears as pyridine hydroiodide (Table I), the reaction products can be best explained if it is assumed that one mole of the pyridine hydroiodide is obtained for each mole of iodine that enters the ring, and one mole of it for each mole of iodine which becomes a part of a substituted β-ketoalkylpyridinium iodide group. If *p*-hydroxyacetophenone is used as an example the reactions may be written as



The 1-(hydroxybenzoylmethyl)-pyridinium iodides could result only from reaction 1 but the 1-(hydroxymonoiodobenzoylmethyl)-pyridinium iodides could arise either from reaction 3 or from a combination of (2) and (4). No attempt was made to find in the reaction mixtures hydroxyiodoacetophenones such as might have been produced by reaction (2).

A list of the various pyridinium iodides obtained together with their yields and a list of the hydroxybenzoic acids obtained by alkaline cleavage of the iodides is shown in Table I.

The structures listed for eleven of the pyridinium salts prepared were supported by cleavage of the iodides or perchlorates with aqueous alkali to known substituted benzoic acids according to the general plan described in previous papers.[1a,b] In

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(1) (a) L. C. King, THIS JOURNAL, **66**, 894 (1944); (b) *ibid.*, **66**, 1612 (1944).