[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, AND THE PROCTER AND GAMBLE COMPANY]

X-Ray Diffraction Analyses of Synthetic Unsaturated Monacid Diglycerides[1]

BY B. F. DAUBERT AND E. S. LUTTON

The synthesis of unsymmetrical triglycerides containing unsaturated fatty acid chains in the 1- and the 1,2-positions of the glycerol molecule have been reported in the literature during the past several years. Physical constants, including polymorphic and X-ray diffraction data, on many of these compounds have been obtained. However, little information is available on symmetrical triglycerides containing unsaturated fatty acids in the 1,3-position of the glycerol molecule.

In order to provide satisfactory intermediates for the preparation of the latter type of symmetrical triglycerides, it was necessary to synthesize several unsaturated symmetrical monacid diglycerides.

Although the preparation of 1,3-diolein and 1,3-dilinolein has been reported by a number of investigators,[2-8] in most instances the materials and methods that were used were not wholly satisfactory. Consequently, the purity of the diglycerides prepared using these earlier methods was somewhat questionable.

The present communication is concerned therefore with the preparation, in a high degree of purity, of 1,3-diolein, 1,3-dilinolein and 1,3-dilinolenin by now accepted methods of synthesis. The preparation of 1,3-dilinolenin has not previously been reported in the literature. All three of the symmetrical diglycerides have been subjected to polymorphic and X-ray diffraction studies.

Experimental

Preparation of Intermediates.—The 1-monotrityl glycerol, m. p. 109.5–110.0°, was prepared according to the method of Verkade, *et al.*[9]

The oleyl, linoleyl and linolenyl chlorides were prepared from the respective highly purified fatty acids by methods described by Wood, *et al.*[10]

Preparation of 1,3-Diolein.—1-Monotrityl glycerol (27.5 g.) was dissolved, with slight warming, in a mixture of dry quinoline (30 ml.) and dry chloroform (125 ml.). To this mixture there was added slowly oleyl chloride (50 g., theoretical, 49.5 g.). The mixture, after standing at room temperature for one hour, was refluxed on a steam-bath for four hours. The mixture was cooled to room temperature and then dissolved in ethyl ether (500 ml.) and the solution washed successively with cold water, cold 0.5 N sulfuric acid, 5% potassium carbonate solution, water, and finally dried over anhydrous sodium sulfate. The solution, after treatment with a decolorizing carbon, was filtered and the ethyl ether removed on a steam-bath *in vacuo*. The residual colorless, somewhat viscid liquid was washed repeatedly with cold 95% ethanol, and then warmed *in vacuo* to remove traces of the solvent. The liquid trityl derivative was dissolved in petroleum ether (75 ml.) and the solution cooled in an ice-bath to 5°. Dry hydrogen chloride was then bubbled through the cooled solution for thirty minutes. During this time a copious separation of triphenylcarbinol occurred. The supernatant liquid was decanted and allowed to stand at room temperature for one hour. The petroleum ether solution was then washed successively with water, 5% potassium carbonate solution, water, and finally dried over anhydrous sodium sulfate. The petroleum ether was removed from the filtered liquid *in vacuo*, on a steam-bath. The colorless liquid remaining was dissolved in 95% ethanol and the solution cooled to −20° for twelve hours. The flaky crystalline deposit was suction-filtered at −20° and recrystallized several times from 95% ethanol, and finally from ethyl ether. After removal of traces of solvent *in vacuo*, the 1,3-diolein had the following constants: iodine value, 81.5 (calcd. 81.8); mol. wt., 617 ± 2 (calcd. 621); n^{30}_{D} 1.46416; m. p., 21.5°.

The analytical constants of 1,3-dilinolein and 1,3-dilinolenin prepared in a similar manner are given in Table I.

Hydrogenation of the Diglycerides.—Further proof of the identity of the unsaturated symmetrical diglycerides was provided by hydrogenation to 1,3-distearin, m. p. 79.0°. The hydrogenations were carried out essentially by the method of Daubert, *et al.*[11] Mixed melting point determinations with a 1,3-distearin prepared by an alternate and direct method showed no significant depression.

Chromatographic Purification.—Each unsaturated diglyceride was chromatographed in petroleum ether solution through a silica gel column by the procedure described by Sidhu and Daubert[12] for diacid diglycerides. In this manner residual traces of triphenylcarbinol were effectively removed.

X-Ray Diffraction.—The diffraction data were obtained with CuK$_{\alpha}$ radiation from a standard G. E. XRD unit with 0.025 inch pinhole system. The K$_{\beta}$ radiation was eliminated by a nickel strip over the center of the flat film which was located at either 5.0 or 10.0 cm. from the sample. Samples were sealed in 1-mm. thin-walled Pyrex capillaries. The capillaries were housed in a small brass block through which cold alcohol was circulated. Temperature was tested by means of a single-junction thermocouple in a well close to the sample. Samples were prepared by melting, chilling until clouded at −70°, and then holding one hour within 10° of their melting points. They were treated outside the cold block and transferred to the block without melting. During exposure condensed moisture or ice crystals were removed by swabbing lightly with glycerol–alcohol solution at fifteen-minute intervals. Some fogging of the pattern due to diffuse radiation from the liquid was unavoidable. Accordingly, fewer lines could be recorded for lower melting samples. Detailed diffraction data appear in Table II.

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

[2] Artom and Reale, *Boll. soc. ital. biol. sper.*, **10**, 880 (1935).

[3] M. Berthelot, *Compt. rend.*, **37**, 398 (1853); *Ann. chim. phys.*, **41**, 216 (1854); *Chim. organique fondée sur la synthèse II*, **65**, 209 224, Paris (1860).

[4] Guth, *Z. Biol.*, **44**, 78 (1903).

[5] Kawai and Nobori, *J. Soc. Chem. Ind. Japan*, Suppl. Binding, **43**, 59B, 110B, 170B, 220B, 428B (1940).

[6] Long, Kittelberger, Scott and Egge, *Ind. Eng. Chem.*, **21**, 950 (1929).

[7] Grün and Schönfeld, *Z. angew. Chem.*, **29**, 37, 46 (1916); *J. Soc. Chem. Ind.*, **35**, 366 (1916).

[8] Izar, *Biochem. Z.*, **60**, 320 (1914).

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

[10] Wood, Jackson, Baldwin and Longenecker, THIS JOURNAL, **66**, 287 (1944).

[11] Daubert, Fricke and Longenecker, *ibid.*, **65**, 2142 (1943).

[12] Sidhu and Daubert, *ibid.*, **68**, 2603 (1946).

TABLE I

ANALYTICAL CONSTANTS FOR UNSATURATED SYMMETRICAL DIGLYCERIDES

Diglyceride	M. p.,[a] °C.	$n^{30.0}_{\text{D}}$	Mol. wt.[b] Calcd.	Mol. wt.[b] Found	Iodine value[c] Calcd.	Iodine value[c] Found	M. p. of hydrogenated product, °C.
1,3-Diolein[d]	21.5	1.46416	621	617 ± 2	81.8	81.5	78.5–79.0
1,3-Dilinolein	− 2.6	1.47610	617	614 ± 3	164.6	164.4	78.5–79.0
1,3-Dilinolenin	−12.3	1.48781	613	609 ± 2	248.5	247.5	78.5–79.0

[a] Melting points were determined by the capillary tube method. Samples in glass tubes cooled to −30° for several days before melting point determination. [b] Molecular weights determined by the method of Hanson and Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939). [c] Wijs reagent, one hour reaction time. [d] *Anal.* Calcd. for $C_{39}H_{72}O_5$: C, 75.43; H, 11.69. Found: C, 75.26, 75.32; C, 11.61, 11.52.

TABLE II

X-RAY DIFFRACTION DATA FOR 1,3-UNSATURATED C_{18} DIGLYCERIDES

Long Spacings

Diolein *d/n*	Diolein *I*	Diolein *n*	Dilinolein *d/n*	Dilinolein *I*	Dilinolein *n*	Dilinolenin *d/n*	Dilinolenin *I*	Dilinolenin *n*
39.3	S+	1	45.0	VS	1	40.1	S	1
19.5	VW	2	22.6	W	2	(19.5)	VW	2
13.1	M	3	15.15	M	3	13.5	M−	3
7.93	VW+	5						
Average *d* = 39.3			Average *d* = 45.2			Average *d* = 40.3		

Short Spacings

Diolein *d/n*	Diolein *I*	Dilinolein *d/n*	Dilinolein *I*	Dilinolenin *d/n*	Dilinolenin *I*
4.73	S+	5.74	VW	4.70	S−
4.46	W	4.69	S	4.40	S
4.25	M	4.20	M	4.13	W
3.82	S−	4.13	VVW	3.87	W
3.59	M+	3.84	VW	3.62	W−
3.40	W	3.72	M−	3.43	W
3.21	W−	3.59	VVW	3.27	VW
3.02	VW	2.59	VW		
2.88	VVW	2.37	VVW		
2.72	VW				
2.55	VVW				
2.46	VVW				
2.30	VVW				
2.31	VVW				
2.25	VVW				
2.18	VVW				
2.10	VVW				
2.01	VVW				
1.94	VVW				

Discussion

In applying X-ray diffraction to these low-melting 1,3-unsaturated diglycerides one is faced with the usual possibility of polymorphism and with a special problem of low-temperature technique.

The solids X-rayed were all crystallized from the melt; no attempt was made to study solvent-crystallized samples. These compounds supercool tremendously, but, once crystallized, show only one melting point, and they are believed to exhibit only one polymorphic form. There are minor changes in appearance (degree of translucence) on warming, but these are not regarded as indicating polymorphic change. Such visual changes were not associated with any diffraction pattern change that could be observed. Nevertheless, final patterns were taken about 10° below the respective melting points, *i. e.*, in a range above which no visual changes except melting occurred. Therefore, if a given pattern, as reported, does not represent the only form for a given compound, as it is thought to do, it almost certainly represents the highest melting form.

In achieving satisfactory low-temperature procedure, it is essential, of course, to maintain temperatures below the sample melting point and to control the "frost" in the X-ray path. It was possible to meet both requirements to a sufficient degree as described in the Experimental section.

For most homologous series of glycerides corresponding forms, *e. g.*, beta, show very similar short spacings and an interpretable variation in long spacings, *i. e.*, constant increment in long spacing with given increment in molecular weight. From the abbreviated record of short and long spacings in Table III, it can be seen that the four C_{18} 1,3-diglycerides there compared (which are, of course, not homologous) do not show a series of comparable highest melting forms.

TABLE III

COMPARISON OF C_{18} DIGLYCERIDES

Glyceride	Two strongest Short spacings in Å.	Long spacings in Å.
1,3-Distearin[a]	4.6 S, 3.9 S, also 3.7 S	49.5
1,3-Diolein	4.73 S+, 3.82 S−	39.3
1,3-Dilinolein	4.69 S, 4.20 M	45.2
1,3-Dilinolenin	4.70 S−, 4.40 S	40.3

[a] Malkin, *et al.*, *J. Chem. Soc.*, 1409 (1937).

The X-ray data are highly distinctive for the four different compounds in the table. There is no uniformity in the next to the strongest short spacings, nor is there any simple interpretable variation in the long spacings. It seems idle to speculate concerning structural relationships except to suggest that kinking at the supposedly "*cis*" double bonds probably precludes any close correspondence in crystal architecture. This is in contrast to the relationship of tristearin and triolein which show somewhat similar α, β' and β forms.[13]

Summary

The preparation of the monacid diglycerides, 1,3-diolein, 1,3-dilinolein and 1,3-dilinolenin in a high degree of purity is reported.

There appears to be but a single polymorphic

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(13) Ferguson and Lutton, THIS JOURNAL, **69**, 1445 (1947).

form for each of these 1,3-unsaturated diglycerides. X-Ray diffraction data for the three compounds are highly distinctive as indicated by long spacings—diolein, 39.3; dilinolein, 45.2; dilinolenin, 40.3 (1,3-distearin in the β-form, 49.5). The forms are therefore not so closely comparable as are the stable (and unstable) forms of many groups of glycerides.

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RECEIVED MARCH 1, 1947

[CONTRIBUTION NO. 626 FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, UNIVERSITY OF PITTSBURGH]

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

BY S. S. SIDHU AND B. F. DAUBERT

Ferguson and Lutton[2] in their review on the polymorphic phases of fats excellently discussed and summarized the significance of the X-ray diffraction work on glycerides of Malkin and his co-workers.[3] Although it is not our intention to review again previous X-ray investigations, it is perhaps desirable to present briefly some of the background of the X-ray diffraction of glycerides in order to provide an explanation of the basis for the present research.

From X-ray diffraction studies of the different polymorphic forms of the simple triglycerides, Malkin proved by the magnitude of the long spacings of the different polymorphic forms the structural units of the crystalline simple triglycerides to be of a double chain length. In later work on symmetrical mixed diacid triglycerides where the chain length of the two fatty acids differed by two carbon atoms, the long spacings corresponded to two chain lengths in line with the structure for the simple triglycerides. However, when the fatty acids in the molecule differed by more than two carbon atoms, the long spacings, with few exceptions, corresponded to a structural unit of four chain lengths according to Malkin. The same relationships appeared to be true in the case of the unsymmetrical mixed diacid triglycerides. As pointed out by Ferguson and Lutton,[2] "The significance of this behavior is obviously related in some manner to the disparity in length between fatty acid chains."

Filer, *et al.*,[4] were not able to postulate a molecular arrangement in the crystalline state of a series of triacid triglycerides based upon X-ray diffraction, because it was not known whether they represented a series of compounds whose long spacings could be related to some theoretical concept of molecular structure; neither was it possible to fit them into the schematic arrangement of Malkin for diacid triglycerides. As a matter of fact, it was found by Filer, *et al.*, that the triacid triglycerides fell into four distinct groups on the bases of their molecular weight, melting point and long-spacing relationships. Recently Lutton,[5] on a re-examination of the abnormally large long-spacing values reported by Malkin for some of the symmetrical and unsymmetrical saturated diacid triglycerides and by Filer, *et al.*,[4] for some of the saturated triacid triglycerides, found that these abnormal values could be interpreted as due to triple chain structures.

In the present investigation, in order to determine whether a molecular configuration in the crystalline state could be postulated for a homologous series of triacid triglycerides, three glycerides were synthesized in which the fatty acids in the 1-position of the glycerol molecule were of a chain length two and four carbon atoms greater, respectively, than the fatty acids in the 2- and 3-positions, the difference in corresponding chains between homologs being two carbon atoms. X-Ray diffraction patterns were then made of the solvent-crystallized forms.

Experimental

Preparation of Intermediates.—The fatty acids and fatty acid chlorides were prepared by previously described methods.[6]

The diacid diglycerides, 1-myristyl-3-caprin, m. p. 48.0°, 1-palmityl-3-laurin, m. p. 59.5°, and 1-stearyl-3-myristin, m. p. 67.0°, were prepared after the method of Verkade, *et al.*,[7] as described by Sidhu and Daubert.[8]

Preparation of Triacid Triglycerides.—All three of the triacid triglycerides reported in this communication were prepared essentially by the same procedure. The method is given in detail for 1-palmityl-2-myristyl-3-laurin: 1-palmityl-3-laurin (5 g.) was dissolved in a mixture of quinoline (7 ml.) and chloroform (20 ml.). To this mixture there was added slowly myristyl chloride (2.8 g., 1 mole = 2.4 g.). The mixture after refluxing on a steam-bath for four hours, was cooled, and taken up in ethyl ether (300 ml.). The solution was washed successively with water, cold 0.5 N sulfuric acid, 5% potassium carbonate solution, water, and then dried over anhydrous sodium sulfate. The ethyl ether was removed *in vacuo* from the filtered liquid, and the solid residue remaining was dissolved in warm 95% ethanol. After cooling to 5° for several hours the crystal mass was suction-filtered and recrystallized several times

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

(2) Ferguson and Lutton, *Chem. Rev.*, **28**, 355 (1941).

(3) Malkin, *et al.*, *J. Chem. Soc.*, 666 (1934); 1628 (1936); 1409 (1937); 103, 577, 1141 (1939).

(4) Filer, Sidhu, Chen and Daubert, THIS JOURNAL, **67**, 2085 (1945).

(5) E. S. Lutton, paper presented at a meeting of the American Society for X-Ray and Electron Diffraction, Mellon Institute, Pittsburgh, Pa., December 5-7, 1946.

(6) Daubert, Fricke and Longenecker, THIS JOURNAL, **65**, 1718 (1943).

(7) Verkade and van der Lee, *Rec. trav. chim.*, **55**, 267 (1936).

(8) Sidhu and Daubert, THIS JOURNAL, **68**, 2603 (1946).