X-ray Diffraction Analysis of Synthetic Unsaturated Diacid Diglycerides[1,2]

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THE polymorphism of the saturated monacid 1,3-diglycerides of the series dicaprin through distearin was described by Malkin, Shurbagy, and Meara (1). The even members of this series were recently re-examined by Baur *et al.* (2). The x-ray diffraction analyses of the monacid unsaturated 1,3-diglycerides of oleic (3,4), linoleic (3), linolenic (3), elaidic (4,5), brassidic (4), and erucic (4) acids have also been reported.

The only diacid 1,3-diglycerides whose x-ray data have been reported thus far are 1-stearyl-3-myristin, 1-palmityl-3-laurin, and 1-myristyl-3-caprin (6). It therefore seemed desirable to study the polymorphism of the saturated-unsaturated diglycerides. The purpose of this paper is to report the physical data including results of x-ray diffraction for three unsaturated diacid diglycerides obtainable from stearic, oleic, and elaidic acids.

Experimental

Preparation of Intermediates. The oleyl, elaidyl, and stearyl chlorides were prepared from the respective highly purified fatty acids by methods described by Wood *et al.* (7). The 1-monostearin, m.p. 81.5°, was prepared by the method of Malkin and Shurbagy (8), and the 1-monoelaidin was prepared by the method of Fischer (9) as modified by Daubert (10). Reaction of 1-monostearin with triphenylchloromethane in quinoline solution to prepare 1-trityl-3-stearin, m.p. 66°, was carried out essentially by the method of Verkade and van Der Lee (11).

Preparation of 1-Stearyl-3-elaidin. 1-Trityl-3-stearin (9.0 g.) was dissolved in a mixture of quinoline (6 ml.) and dry chloroform (25 ml.). To this solution elaidyl chloride (5 g.) was slowly added. The mixture was allowed to stand with occasional shaking for two days at room temperature. After dissolving the mixture in ethyl ether (250 ml.), the mixture was washed successively with cold 0.5 *N* sulfuric acid, 5% potassium carbonate solution, and water, and then dried over anhydrous sodium sulfate. The ethyl ether was removed from the filtered solution on a steam bath *in vacuo*, and the residue washed repeatedly with ethanol. In order to remove the trityl grouping accompanied by a shift of the elaidyl group from the *2* to the *3* position, the oily residue dissolved in dry petroleum ether was cooled to 5°C. and dry hydrogen chloride was bubbled through the solution for 20 minutes. When the mixture had stood at room temperature for one hour, the supernatant liquid was decanted, diluted with ethyl ether (220 ml.), and the solution washed successively with water, 5% potassium bicarbonate, and finally water. The solvent was removed from the filtered liquid, which was dried over anhydrous sodium sulfate, and the residue dissolved in a 2:1 mixture of ethyl ether and 95% ethanol. Slow crystallization several times from this mixture of solvents yielded a product melting at 65.5-65.9° C.; mol. wt. (12), 618 (calcd. 623); iodine value, 40.5 (calcd. 40.7).

Anal.[3] calcd. for $C_{58}H_{88}O_5$; C. 75.19; H, 11.97. Found: C, 75.01, 74.87; H, 11.81, 11.63.

1-Stearyl-3-olein, m.p. 52°, mol. wt. 614 (calcd. 623), iodine value 40.1 (calcd. 40.7) was prepared by essentially the same procedure.

Preparation of 1-Oleyl-3-elaidin. The direct esterification of the monoglyceride with the acid chloride to produce the diglyceride was carried out by a modification of the procedure of Malkin *et al.* (1). To a solution of 1-monoelaidin (5.5 g.) in quinoline (5 ml.) and chloroform (30 ml.) was slowly added oleyl chloride (4.2 g.). The mixture was refluxed on a steam bath for three hours under anhydrous conditions. After cooling to room temperature it was dissolved in ethyl ether (300 ml.) and the solution washed with cold 0.5 *N* sulfuric acid, 5% bicarbonate solution, and distilled water. The ethyl ether was removed by suction after drying the solution over anhydrous sodium sulfate and the syrupy residue taken up in petroleum ether (30 ml.). This solution was slowly cooled to 5° and then the small amount of unreacted monoelaidin which precipitated was filtered off. When the petroleum ether had been removed, the residue was dissolved in methyl alcohol and cooled to 5°. The product was recrystallized several times from a 2:1 mixture of ethyl ether and methanol: melting point 28.8°C.; iodine value 81.5 (calcd. 81.8); mol. wt. 632 (calcd. 621).

All three diglycerides when hydrogenated (13) in ethyl acetate with a palladium black catalyst yielded 1,3-distearin (m.p. 79.0°).

X-ray Diffraction Analyses. The x-ray diffraction patterns of the diglycerides were made by the usual powder method previously described (5,6). The low-melting glyceride, 1-oleyl-3-elaidin, was maintained in the solid state by placing the nylon tube containing the sample in a brass block mounted on the pin-hole camera and circulating cold water (15°C.) through the block. In order to avoid fogging of the pattern, careful regulation of the water temperature was necessary so that no moisture condensed on the block or specimen.

The unstable polymorphic forms were obtained by carefully melting the specimens packed in nylon tubes, immediately immersing the tubes in a small acetone-dry ice bath, and then holding for three minutes at —70°. The specimens were transferred to the x-ray unit without melting. After exposure the specimens were removed and melting points determined on the specimens directly. Detailed x-ray data are shown in Table I.

Discussion

Baur *et al.* (2) found two polymorphic forms for each of the even, saturated diglycerides, dilaurin through distearin. Both of these forms were classi-

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[3] The microchemical analyses were performed by George Stragand.

TABLE I

X-ray Spacings, in Å, for the Diglycerides

(hkl)	1-Stearyl-3-olein		1-Stearyl-3-elaidin		1-Oleyl-3-elaidin
	$Beta_1$	$Beta_2$	$Beta_1$	$Beta_2$	$Beta_1$
	Long Spacings				
001	48.4 VS	39.0 VS	52.5 VS	50.3 VS	48.5 VS
002	23.9 VS	19.4 M	26.1 S	25.1 S	24.3 M
003	16.1 VS	13.0 M	**17.6 S**	16.6 VS	16.1 S
004		9.70 VW		12.6 VW	
005	9.69 M	7.80 W+	10.5 M	9.87 W	9.68 W
006	8.06 M	6.52 VW	8.84 M	8.31 W	8.04 W
007	6.83 W		8.25 W		
008	6.02 M		6.59 W	6.24 W	6.04 W
av. d	48.2	39.0	52.6	50.0	48.4
M.P.	52.0	.....	65.9	62.0	28.8
	Short Spacings				
	5.12 VW	5.18 W	5.03 W	5.08 W	4.65 S
	4.74 S	4.88 VW	4.58 VS	4.61 VS	4.58 W
	4.62 VS	4.67 VS	4.20 W	4.20 W	4.24 W
	4.46 M	4.51 M	3.86 VS	3.90 VS	4.07 M
	4.11 M	4.38 W	3.76 VS	3.75 VS	3.81 S
	3.78 VS	4.19 M	3.27 VW	3.42 VW	3.70 S
	3.73 M	4.01 M	3.04 VW	3.14 VW	3.40 M
	3.63 M	3.88 S—	2.50 M	2.52 M	3.26 W+
	2.95 VW	3.78 M	2.40 M	2.40 W	3.14 W
	2.70 VW	3.67 M	2.29 W	2.25 W	2.97 W
	2.46 M	3.51 M+	2.20 VW	2.16 W	2.83 W
	2.35 VW	3.30 VW	2.16 W	2.10 W	2.70 M
	2.26 VW	2.97 VW	2.08 M	2.03 W	2.56 W
	2.17 M	2.84 W	1.92 W	1.98 W	2.42 M
	2.08 VW	2.60 VW	1.86 W	1.91 VW	2.32 W
	2.00 VW	2.36 VW	1.80 VW	1.86 VW	2.26 W
	1.88 W	2.19 VW	1.69 VW	1.76 VW	2.18 M
	1.77 VW	2.06 VW	1.63 VW	1.57 W	2.09 M
	1.75 VW	1.94 VW	1.57 VW		2.02 W
		1.76 VW	1.489 VW		1.98 W
			1.365 VW		1.88 VW
			1.322 VW		1.80 VW

fied as beta-like on the basis of strong 4.6 Å short spacings. Following the suggestion of Malkin *et al.* (1), they called the two forms beta-a and beta-b. Beta-a has characteristic strong short spacings of 4.6 and 3.7 Å and a medium 3.9 spacing, whereas beta-b has characteristic strong short spacings 4.6 and 3.75 Å. In contrast to the data of Malkin *et al.* (1), Baur *et al.* (2) have shown that the beta-a short spacings are uniformly associated with the lesser long spacing for each diglyceride. Daubert and Sidhu (5) for 1,3-dielaidin associated the beta-a form with the greater long spacing.

In the case of dipalmitin and distearin Malkin (1) observed only the lesser long spacings, and these were associated with the beta-a type short spacings. This discontinuity was not confirmed by Baur *et al.* (2), who obtained both the beta-a and beta-b patterns for these two diglycerides. However no x-ray evidence has been reported for an alpha form for any diglyceride.

Daubert (6) presented x-ray data for 1-stearyl-3-myristin which corresponded more closely to the beta-b form because of the absence of a 3.9 line whereas the other diacid diglycerides examined had the beta form.

In the case of the monacid diglycerides of oleic, linoleic, and linolenic acids, the x-ray data indicated a single polymorphic form for each glyceride which bore no relationship to any of the known glyceride structures (3). The unusual feature was that these three glycerides had a strong short spacing in the 4.7 Å region plus one additional strong line which was different in each case.

The unsaturated diglycerides, dielaidin (4,5), and dibrassidin (4), paralleled the saturated diglycerides in the existence of beta-a and beta-b forms, while dierucin (4) (a *cis* acid containing compound) is similar to diolein (3,4).

The stable form of 1-stearyl-3-olein has a long spacing similar to that for distearin but does not possess the same characteristic short spacings. Although the 3.9 line of a typical beta-a pattern is missing, there is an additional strong line at 4.74 similar to that shown for the *cis* unsaturated diglycerides.

The unstable form however gives all the characteristic lines for a beta-a type, also an exceedingly shorter long spacing than the stable form. The long spacing and its higher orders of reflection are the same as those for 1,3-diolein (3,4). The pattern for this form was not readily obtained by the techniques employed as only one attempt out of four was successful in producing this unstable form, and no melting point was observed for it. To distinguish the two polymorphic forms, the stable form is designated as $beta_1$ and the unstable form as $beta_2$. The subscripts *1* and *2* hold no further significance.

The long spacings for both crystalline forms of 1-stearyl-3-elaidin are identical to those for the two forms of dielaidin (4,5). But whereas both compounds possess the same stable structure, dielaidin has an unstable form of beta-b type, and 1-stearyl-3-elaidin yields a beta short-spacing type unstable form.

The pattern for 1-oleyl-3-elaidin is a beta type. There may be additional polymorphic forms, but the limitations of the equipment prevented their realization.

The conclusions are that no alpha forms exist for any of the diglycerides examined and that two of the diglycerides are unusual in that they can exist in two polymorphic forms which are of the same short-spacing type, namely, beta. An interesting fact concerning the stable forms of the three diglycerides is the absence of a fourth order reflection in the long spacings.

Summary

Chemical and physical data are reported for the three diacid 1,3-diglycerides obtainable from stearic, oleic, and elaidic acids. Two of these are new, namely 1-stearyl-3-elaidin and 1-oleyl-3-elaidin.

X-ray data have revealed one form for 1-oleyl-3-elaidin and two forms for the other two diglycerides, with considerable individuality in the diffraction patterns of the compounds.

REFERENCES

1. Malkin, Shurbagy, and Meara, J. Chem. Soc., 1409 (1937).
2. Baur, Jackson, Kolp, and Lutton, J. Am. Chem. Soc., *71*, 3363 (1949).
3. Daubert and Lutton, J. Am. Chem. Soc., *69*, 1449 (1947).
4. Carter and Malkin, J. Chem. Soc., 554 (1947).
5. Daubert and Sidhu, J. Am. Chem. Soc., *70*, 1884 (1948).
6. Sidhu and Daubert, J. Am. Chem. Soc., *68*, 2603 (1946).
7. Wood, Jackson, Baldwin, and Longenecker, J. Am. Chem. Soc., *66*, 287 (1944).
8. Malkin and Shurbagy, J. Chem. Soc., 1682 (1936).
9. Fischer, Ber., *53*, 1621 (1920).
10. Daubert, J. Am. Chem. Soc., *66*, 290 (1944).
11. Verkade and van Der Lee, Rec. trav. chim., *55*, 267 (1936).
12. Hanson and Bowman, Ind. Eng. Chem., Anal. Ed., *11*, 440 (1939).
13. Daubert, Fricke, and Longenecker, J. Am. Chem. Soc., *65*, 2142 (1943).

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