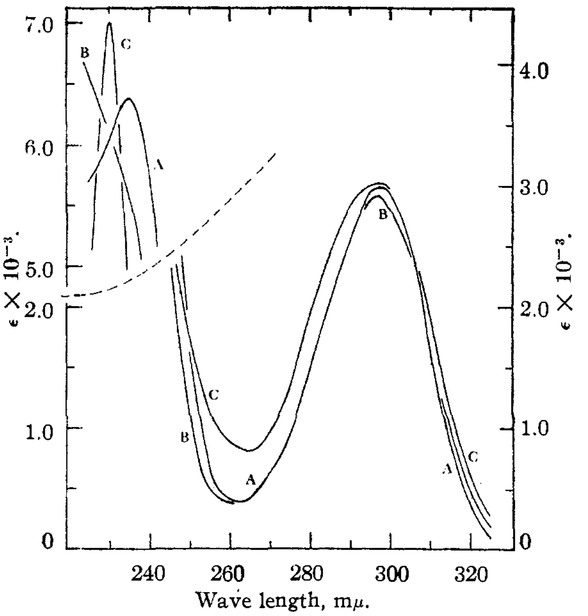

Fig. 1.—Absorption spectra in 0.1 *M* hydrochloric acid: A, 2-amino-3-hydroxybenzoic acid; B, 2-amino-3-methoxybenzoic acid; C, 2-(N-methyl-N-formyl)-amino-3-methoxybenzoic acid.

Anal. Calcd. for $C_7H_7NO_3$: C, 54.90; H, 4.61; N, 9.15. Found: C, 55.00; H, 4.83; N, 9.13.

2-Amino-3-hydroxybenzoic Acid Hydrochloride.—This compound crystallized from a hot solution of 2-amino-3-hydroxybenzoic acid in concentrated aqueous hydrochloric acid, m. p. 227° (cor.). *Anal.* Calcd. for $C_7H_8NO_3Cl$: N, 7.39; Cl, 18.70. Found: N, 7.68; Cl, 18.59.

2-Amino-3-hydroxybenzoic Acid. Method II.—2-(N-Methyl-N-formyl)-amino-3-methoxybenzoic acid was prepared according to the procedure of Kaufmann and Rothlen.[9] A mixture of 200 mg. of this compound, 50 mg. of red phosphorus and 4 ml. of hydriodic acid (sp. gr. 1.7) was heated in a sealed tube at 135° for twelve hours. The product was isolated and purified by the procedure described under Method I, yield 57 mg., m. p. 254–255° (cor.), hydrochloride m. p. 227° (cor.).

The products from both methods I and II possessed identical absorption spectra and biological activity on a nicotinic acid requiring mutant of *Neurospora*.[2]

Discussion

Hydroxyanthranilic acid (2-amino-3-hydroxybenzoic acid) has been synthesized by two independent methods each providing in itself nearly conclusive evidence for the structure of the product. It is evident from a consideration of the properties of these products and from the facts given by Keller that the latter investigator did not prepare hydroxyanthranilic acid as reported. No evidence has been found for a synthesis of the compound prior to the present work.

It is to be noted from Fig. 1 that the absorption spectra of some methyl and formyl substituted 2-amino-3-hydroxybenzoic acids are quite similar to that of the parent compound. This is true also for damascenine and damasceninic acid. In the case of the unsubstituted acid considerable variations in spectrum have been observed at wave lengths below 260 mμ. This is evidently due to traces of impurities derived from oxidation of the compound in mildly acid or alkaline solutions. A pure white product can be obtained only from acidic solutions since oxidation is rapid even at neutrality.

Summary

1. Two independent methods have been described for the synthesis of 2-amino-3-hydroxybenzoic acid.

2. Data have been presented to show that the product previously obtained by Keller and reported to be 2-amino-3-hydroxybenzoic acid was actually 2-amino-3-methoxybenzoic acid.

Pasadena 4, California Received December 9, 1947

[Contribution No. 638 from the Departments of Chemistry and Physics, University of Pittsburgh]

X-Ray Investigation of Glycerides. VII. Diffraction Analyses of Synthetic 1,3-Dielaidin[1]

By B. F. Daubert and S. S. Sidhu

In a recent publication by Carter and Malkin,[2] X-ray diffraction data were reported for a series of unsaturated symmetrical 1,3-diglycerides, including 1,3-diolein, 1,3-dierucin, and their *trans* isomers, 1,3-dielaidin and 1,3-dibrassidin.

In our study of the physical properties of synthetic glycerides, an X-ray diffraction study of 1,3-dielaidin had been completed but not reported prior to the publication by Carter and Malkin,[2] although X-ray diffraction data for 1,3-diolein, 1,3-dilinolein, and 1,3-dilinolenin were recently reported by Daubert and Lutton.[3]

The purpose, therefore, of the present communication is to report the X-ray data on 1,3-dielaidin prepared both by direct synthesis and elaidinization of 1,3-diolein.

Experimental

Preparation of 1,3-Dielaidin.—1-Monotrityl glycerol (10 g.) (m. p. 109.5–110.0°) was dissolved, with slight warming, in a mixture of quinoline (15 ml.) and dry chloroform (40 ml.). To this mixture elaidyl chloride (18.0 g.) was added slowly. The mixture, after standing

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

(2) Carter and Malkin, *J. Chem. Soc.*, 554 (1947).

(3) Daubert and Lutton, This Journal, **69**, 1449 (1947).

at room temperature for one hour, was refluxed on a steam-bath for a similar period of time. The mixture, after cooling, was dissolved in ether and the ether solution washed successively with cold 0.5 *N* sulfuric acid, 5% potassium carbonate solution, distilled water, and finally dried over anhydrous sodium sulfate. The ether was removed *in vacuo* and the sirupy liquid remaining was dissolved in a 1:1 mixture of ether and ethyl alcohol. The solution was cooled to −20° for twenty-four hours. The crystalline mass was suction-filtered, recrystallized several times from ethyl ether, and dried over phosphorus pentoxide. The 1-trityl-2,3-dielaidin melted at 36.5–37.0°; mol. wt. 857 (calcd. 863); iodine value 58.5 (calcd. 58.8); yield, 20.2 g., 75.6%.

Anal. Calcd. for $C_{58}H_{86}O_5$: C, 80.69; H, 10.04. Found: C, 80.37, 80.46; H, 10.02, 10.08.

The 1-trityl-2,3-dielaidin (10 g.) was hydrolyzed to 1,3-dielaidin after the method of Verkade, *et al.*[4] The 1,3-dielaidin on slow crystallization from petroleum ether had the following constants: m. p. 54.0–54.5°; mol. wt. 619 (calcd. 621); iodine value 81.6 (calcd. 81.8), yield, 5.3 g., 73.6%. Slow crystallization was accomplished by slowly cooling to room temperature (approximately 25°) a petroleum ether solution of the 1,3-dielaidin saturated at 30–35°. Rapid crystallization, on the other hand, was accomplished by quickly chilling a subsaturated solution of the compound to −20°. Carter and Malkin[2] reported a melting point of 55° for the β form of this diglyceride when prepared by the direct reaction of elaidyl chloride with 1-monoelaidin.

The 1,3-dielaidin was also prepared by the elaidinization of 1,3-diolein[3] (m. p. 21.5°) as follows: 1,3-diolein (2 g.) was floated on 100 ml. of 30% nitric acid at room temperature. Small additions (*ca.* 250 mg.) of sodium nitrite were made, with stirring, until solidification occurred. A total of 1.0 g. of sodium nitrite was required over a period of thirty minutes. The 1,3-dielaidin was suction-filtered and washed with water until free of mineral acid. Slow crystallization from petroleum ether yielded 0.5 g. of a product melting at 55°. Mixed melting point with 1,3-dielaidin obtained by hydrolysis of the trityl derivative showed no depression.

The dielaidins prepared by the two different methods were hydrogenated to 1,3-distearin (m. p. 79.0°) by the method of Daubert, *et al.*[5]

X-Ray Diffraction Analysis.—The X-ray diffraction patterns of the different polymorphic forms were obtained by the same procedure as described by Sidhu and Daubert[6] for symmetrical diacid diglycerides.

In view of the comments of Malkin[2] in a recent publication criticising the X-ray procedure used in the first paper of this series, it is perhaps appropriate to emphasize again that *filtered* radiation has been used exclusively in the diffraction analyses of all of the glycerides thus far reported from this laboratory.

With reference to the mounting of specimens in nylon tubes, the standard procedure in X-ray diffraction work was followed. The diffraction pattern of the tube was taken with and without the specimens, exposing the tube to the same X-ray beam for the same length of time. This procedure has been followed in obtaining all of the data we have published so far on glycerides. The diffraction patterns of the nylon capillary tubes were taken and the lines thus obtained were carefully noted for structure, intensity, and position of the pattern. The effect on the intensities of the diffraction lines originating from the specimen due to superimposition of the nylon tube lines was ascertained by obtaining diffraction patterns of a few of the specimens without the use of nylon capillary tubes. Knowing the number of diffraction lines originating from the nylon tube, their position on the pattern, their intensities, and their effect on the intensities of the lines originating from the specimen, *d* values of the specimen were determined and intensities of the lines estimated. The diffraction data on all glycerides reported by us contain lines obtained from the specimens only.

Discussion

In confirmation of the observations of Carter and Malkin,[2] it was noted that slow crystallization of 1,3-dielaidin from solvent invariably yielded the *beta* form.

The *beta prime* form in the present investigation was obtained by rapid crystallization from solvent. Previous observations in our laboratory on the crystallization of diacid diglycerides[6] demonstrated that under similar crystallization conditions *beta* (*beta-a*) was obtained for some compounds, *beta prime* (*beta-b*) for others. Malkin obtained the *beta prime* form for 1,3-dielaidin from melted layers and rods. It will be seen from the data in Table I that the side spacings for the form obtained by rapid crystallization of dielaidin from solvent are in good agreement with those reported by Malkin for the *beta prime* form. No X-ray evidence could be found for an *alpha* form.

TABLE I

COMPARISON OF X-RAY DIFFRACTION DATA FOR 1,3-DIELAIDIN

	Malkin[2]			This study	
M. p. °C.	β	β′	α	β	β′
Long spacing,	55	53	49	54.5–55.0	52.5
Å.	52.6	49.8		52.4	50.0
Side spacing, Å.	4.6 (S)	4.61 (S)		4.63 (S)	4.62 (S)
	3.9 (S)	3.95 (W)		3.88 (S)	3.91 (W)
	3.7 (S)	3.75 (S)		3.73 (S)	3.74 (S)
		3.6 (W)			3.66 (W)

S = strong. W = weak.

In contrast to the data obtained for 1,3-dielaidin, Daubert and Lutton[3] found no X-ray or melting evidence for other than one form of 1,3-diolein. The complexity of the side-spacing data for that diglyceride was not conducive to characterization of the form as *beta prime* or *beta*. Although Carter and Malkin[2] reported a melting point (18°) based on cooling curve data for a supposed *alpha* form of diolein, they were not able to confirm the existence of the form by X-ray evidence.

In agreement with Malkin, it seems that the side-spacing data for the *beta* and *beta prime* forms correspond to those of the saturated diglycerides originally called *beta-a* and *beta-b*, respectively, by Malkin, *et al.*[7]

Summary

The preparation of 1,3-dielaidin by (1) direct synthesis from 1-trityl-2,3-dielaidin, a new compound, and (2) elaidinization of 1,3-diolein is reported.

The X-ray and melting point data confirm the observations of Malkin relative to the existence of two crystalline forms called by him *beta* and *beta prime*.

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RECEIVED NOVEMBER 10, 1947

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

(5) Daubert, Fricke, and Longenecker, THIS JOURNAL, **65**, 2142 (1943).

(6) Sidhu and Daubert, *ibid.*, **68**, 2603 (1946).

(7) Malkin, Shurbagy and Meara, *J. Chem. Soc.*, 1409 (1937).