the undissolved material were made by boiling it, for half an hour each time, with solutions of 20 g. of sodium hydroxide in 500 ml. of water. The combined filtered extracts were acidified with hydrochloric acid, and the crude product was collected, washed thoroughly with water and dried (79 g.).

Crystallization of the brownish solid from 300 ml. of petroleum naphtha (boiling range 100–150°) with the addition of some "Filtrol" gave 43 g. of nearly colorless crystals, m.p. 183–184°. An additional 3.1 g. (m.p. 181–183°) was isolated by concentration of the mother liquor. Recrystallization of both crops from 200 ml. of naphtha yielded the pure compound (37 g.), m.p. 183–184°.

Anal. Calcd. for $C_8H_7OBrCl_2$: C, 35.6; H, 2.6; Br, 29.6; Cl, 26.3. Found: C, 35.8; H, 2.4; Br, 30.4; Cl, 25.8.

2,6-Dichloro-3,5-xylenol.—4-Bromo-2,6-dichloro-3,5-xylenol (34 g.) and 600 ml. of 20% potassium hydroxide solution were heated to 90° with stirring. Zinc dust (80 g.) was added slowly to the solution during two hours; stirring and heating 90° was then continued for three hours. The unreacted zinc was filtered off and washed with hot water. The cold filtrate was acidified with hydrochloric acid with ice cooling. The crude product was collected, washed with water and dried in air. It was then refluxed with 100 ml. of alcohol and a small amount of decolorizing carbon and the solution was filtered and diluted with water. The precipitate was washed with water and dried (26 g., containing some inorganic impurities).

On distillation, 18.3 g., b.p. 105–110° (1 mm.), of a colorless solid was obtained. Crystallization from 50 ml. of naphtha yielded 14.4 g. of the pure 2,6-dichloro-3,5-xylenol, m.p. 87–88°, mixed m.p. with 2,4-dichloro-3,5-xylenol 60–65°.

Anal. Calcd. for $C_8H_8OCl_2$: C, 50.2; H, 4.2; Cl, 37.1. Found: C, 50.2; H, 4.2; Cl, 36.9.

For identification, the benzoates of the two dichloroxylenols were prepared: 2,4-dichloro-3,5-xylenyl benzoate, m.p. 114–115°; 2,6-dichloro-3,5-xylenyl benzoate, m.p. 143–145°.

Anal. Calcd. for $C_{15}H_{12}O_2Cl_2$: C, 61.0; H, 4.1. Found for the 2,4-isomer: C, 61.0; H, 4.3; for the 2,6-isomer: C, 61.2; H, 4.2.

Acknowledgment.—We are indebted to Dr. A. R. Cade and his staff for the bacteriological data.

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The Isolation of *n*-Octanyl Alcohol from a Marine Tube Worm

BY D. R. IDLER AND U. F. M. FAGERLUND

RECEIVED AUGUST 3, 1953

During recent years several interesting aliphatic acids have been isolated from parasitic worms. However, the mechanism of formation and biochemical function of these acids is not yet determined.[1–3]

Preliminary examination of the tube worm *Eudistylia vancouveri* suggested the presence of an aliphatic alcohol.[4,5]

The alcohol has now been identified as *n*-octanyl alcohol. It possibly arises as a metabolic product of fatty acid degradation or serves as a fatty acid precursor. Preliminary chromatographic evidence indicates that one of the more abundant aliphatic acids present in the tube worm has a chain length similar to *n*-octanoic acid.

This appears to be the first reported isolation of free *n*-octanyl alcohol from an animal organism.

Experimental[6]

Isolation of *n*-Octanyl Alcohol.—The worms were collected at Brockton Point, Vancouver, B. C. They were immediately extruded from their protective casings, by means of a glass rod, into a jar containing a known volume of sea water. Twelve kg. of these fresh worms were put through a meat grinder and the mash was immediately steam distilled. Distillation was continued until one-third of the original volume had distilled over. The distillate was then extracted three times with equal portions of diethyl ether and the ether extract was washed with dilute sodium hydroxide, hydrochloric acid and finally with water.

The ether extract was dried with sodium sulfate and the ether removed on a water-bath. The dry neutral extract represented 0.09% of the wet weight of worms.

A 6.85-g. sample of the neutral material was fractionated through a Todd still fitted with a narrow-bore column. The first fraction (0.59 g.) distilled over at 78° and the second (4.06 g.) at 192°. A further 1.21 g. distilled over *in vacuo* and left a residue of 0.14 g.

The fraction boiling at 192° was identified with synthetic *n*-octanyl alcohol. Both boiled at 192°, d^{20}_4 0.825. Both gave identical infrared spectra.

Anal. Calcd. for $C_8H_{18}O$: C, 73.77; H, 13.93. Found: C, 73.50; H, 14.01.

Derivatives.—Both synthetic *n*-octanyl alcohol and the tube worm alcohol gave the same phenylurethan, m.p. 74°, mixed m.p. 74°, 3,5-dinitrobenzoyl ester, m.p. 61°, mixed m.p. 61°, and α-naphthylurethan, m.p. 66°, mixed m.p. 66°.

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(1) E. Bueding and H. W. Yale, *J. Biol. Chem.*, **193**, 411 (1951).

(2) E. Bueding, *ibid.*, **202**, 505 (1953).

(3) V. Moyle and E. Baldwin, *Biochem. J.*, **51**, 504 (1952).

(4) B. E. Maxwell, *J. Fish. Res. Bd. Can.*, **9**, 164 (1952).

(5) U. Fagerlund and L. A. Swain, *Fish. Res. Bd. Can. Prog. Rep. Pac.*, **92**, 16 (1952).

(6) Boiling points uncorrected. Melting points corrected.

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The Molecular Configuration of the Aliphatic Dibasic Acid, $C_4H_4O_6\cdot 2H_2O$

BY M. P. GUPTA

RECEIVED JUNE 18, 1953

The object of the present investigation was to determine, using X-ray crystallographic methods, whether molecules of the aliphatic dibasic acid $C_4H_4O_6\cdot 2H_2O$ had the *cis*- or the *trans*-configuration. Chemical evidence in favor of each of these configurations had been presented (see the preceding paper by Dr. E. F. Hartree[1]). Crystals were kindly provided in a form suitable for X-ray examination, by Dr. Hartree, and the results may be summarized as follows.

Crystal Morphology.—The crystals were thin, diamond-shaped colorless plates, showing a good cleavage parallel to the bisectrix of the acute angle and straight extinction parallel to this direction to within 1°. This is in agreement with the data first given by Fenton,[2] who is quoting the results of a crystallographic examination by Mr. Solly. The latter believed that the crystals possessed orthorhombic symmetry.

Unit Cell Determination.—Laue photographs taken with the short diagonal (subsequently taken as the [100] axis) vertical, and with the incident X-ray beam normal and parallel, respectively, to the platy face, showed the existence of strong pseudo-orthorhombic symmetry. The *positions* of the Laue spots corresponded with a strictly rectangular unit cell, but their *intensity* corre-

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(1) E. F. Hartree, THIS JOURNAL, **75**, 6244 (1953).

(2) H. J. H. Fenton, *J. Chem. Soc.*, **65**, 899 (1894).

sponded to monoclinic symmetry only, the platy face (which had been called the (001) by Solly) being the unique (010) plane. Oscillation and Weissenberg photographs confirmed that the symmetry was monoclinic only, though pseudo-orthorhombic, and these, with rotation photographs, showed that the pseudo-orthorhombic cell was *B*-face-centered. The dimensions of the true monoclinic cell chosen were a = 6.40, b = 13.03, c = 5.34 Å., β = 126.5°. Those of the pseudo-orthorhombic unit cell may be expressed in terms of the above by means of the matrix 100/010/102. Solly's original orthorhombic unit cell vectors are related to the monoclinic vectors by the matrix 100/102/010. All further data are referred to the above monoclinic unit cell; M = 184.1, V = 358.0 Å.^{3}, d (obsd.) = 1.715. Two molecules in the unit cell would give d (calcd.) = 1.708.

Space-group Determination.—Reflections were observed for $0k0$ only with k even and for $h0l$ only with l even. There were no other systematic extinctions. The class is therefore 2/m and the space group is unequivocally determined as $P2_1/c$.

Molecular Symmetry and Configuration.—The two molecules in the unit cell must occupy the spacial positions 0,0,0, 0,$^1/_2$,$^1/_2$, and must be centro-symmetrical. No other twofold symmetry is possible in this space group. It follows therefore that the molecule must have the *trans*-configuration; it must be dihydroxyfumaric acid. The four molecules of water of crystallization occupy general positions. A complete structure analysis is in progress.

Experimental

The preparation of the crystals was as described by Dr. Hartree. They were reasonably stable, although powder lines appeared on X-ray photographs after exposures of several hours. Six diamond-shaped plates were used, measuring about 0.36 mm. (long axis) × 0.23 mm. (short axis) × 0.05 mm.

Copper Kα radiation was used in taking the oscillation and Weissenberg photographs. In the case of the Laue photographs the radiation was unfiltered and contained white radiation down to λ = 0.4 Å.

For the space-group determination $0k0$ reflections up to k = 16 were observed and $h0l$ reflections as far as 804. Altogether 29 out of a possible 71 $h0l$ reflections were found and 63 out of a possible 85 $0kl$.

The author is indebted to Professor K. Lonsdale for guidance in this research and to Dr. E. F. Hartree for the crystals provided by him.

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Thermal and Dielectric Study of Octamethylcyclotetrasiloxane

BY JOHN D. HOFFMAN

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The dielectric constant and the cooling and warming curves of a purified sample of octamethylcyclotetrasiloxane (hereafter called *cyclic tetramer*) have been investigated in the region 40° to −60°. The temperature measurements were made with an N.B.S. calibrated platinum resistance thermometer, and the dielectric data were obtained at 1, 5 and 10 kc. with a parallel resistance capacity bridge using a coaxial cell with 14.95 $\mu\mu$f. capacitance. The cell was carefully calibrated with standard liquids. Since no dispersion was ever observed, the dielectric data presented here represented the static dielectric constant, ϵ_0. The dielectric constant data for the liquid, and solid phase just below the freezing point are correct to within at least 0.5%. As is commonly the case for dielectric data obtained with such cells, the observations well below the freezing point and particularly below the transition, are less accurate (probably about 5% low below the transition) owing to the presence of an air-film capacitance. This capacitance is a result of the shrinkage of the solid material between the condenser plates. The data near and below the transition are nonetheless useful in that they show clearly where the transition takes place (see below).

On cooling, cyclic tetramer froze into an α-modification at 17.54°. On further cooling, a new polymorphic form (β) appeared at about −35°. The α-form undoubtedly had supercooled considerably before it finally nucleated. On rewarming after brief storage at −60°, the first-order α–β transition appeared at −16.30°. This transition was accompanied by a latent heat and a sharp break in the dielectric constant curve (Fig. 1). The sample remelted at 17.54°. Analysis of the cooling curve indicated the sample was close to 99.7$_1$ mole per cent. pure.[1]

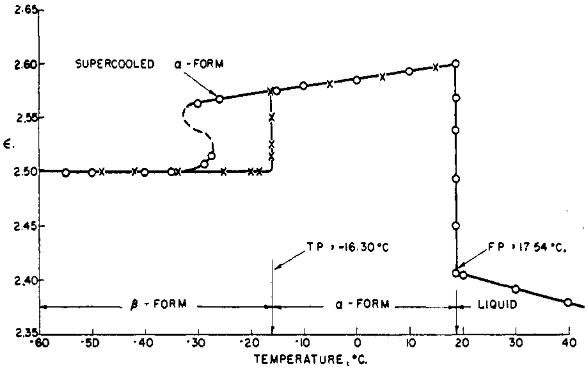

Fig. 1.—Dielectric constant of tetramer as a function of temperature: —O— data obtained with lowering temperature; —×—, rising temperature.

The α–β transition in cyclic tetramer may be the result of the onset of hindered intermolecular rotation which begins at −16.30°. The low heat of fusion[2] of cyclic tetramer is consistent with the suggestion that there is considerable molecular freedom in the α-form. It is interesting to note that molecules of similar shape (*e.g.*, cyclohexane, chlorocyclohexane and cyclohexanone) also exhibit first-order solid state transitions, low heats of fusion, and dielectric properties which have been interpreted in terms of molecular rotation.[3] The rotation in the α-forms of the polar compounds mentioned above should not be considered "free," since the observed dielectric relaxation times are

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(1) Drs. R. C. Osthoff and W. T. Grubb of this Laboratory have recently prepared cyclic tetramer, m.p. 17.58°, estimated to be 99.8$_2$ mole per cent. pure (to be published).

(2) R. C. Osthoff, W. T. Grubb and C. A. Burkhard, THIS JOURNAL, **75**, 2227 (1953).

(3) R. W. Crowe and C. P. Smyth, *ibid.*, **73**, 5406 (1951).