ylic acid, identified by its melting point (280–281°) and failure to depress the melting point of an authentic sample.[3]

β-(4-Methoxy-1-dibenzofuran)-acrylic Acid.—A mixture of 13.0 g. (0.058 mole) of 4-methoxy-1-dibenzofurancarboxaldehyde, 13.0 g. (0.125 mole) of malonic acid and 15 ml. of dry pyridine was heated on the steam-bath for 2.5 hours. Several minutes after heating was begun, the mixture became a homogeneous liquid, and shortly thereafter evolution of carbon dioxide commenced. The solution solidified to a yellow cake to which water was added. The insoluble material was filtered off and then dissolved in 200 ml. of a hot 5% solution of sodium carbonate. After filtration, the clear, colorless basic solution was acidified with hydrochloric acid. A pale yellow precipitate formed. Recrystallization from glacial acetic acid gave 9.5 g. (61%) of light yellow needles melting at 281–282°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.50; neut. equiv., 268. Found: C, 71.41, 71.57; H, 4.67, 4.61; neut. equiv., 266.

β-(4-Methoxy-1-dibenzofuran)-propionic Acid.—Solution of 1.5 g. (0.0056 mole) of β-(4-methoxy-1-dibenzofuran)-acrylic acid in 75 ml. of water was accomplished by the addition of 0.2 g. of sodium hydroxide; to this was added 2 g. of palladium–calcium carbonate catalyst.[6] The mixture was hydrogenated at 20 p.s.i. for 2 hours. The catalyst was filtered off and the product precipitated from the filtrate by addition of hydrochloric acid. The crude material weighed 1.5 g., m.p. 165–175°. Recrystallization from 95% ethanol gave 1.3 g. (86%) of thick needles, m.p. 176–178°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.11; H, 5.22; neut. equiv., 270. Found: C, 71.29, 71.18; H, 5.20, 5.18; neut. equiv., 265, 269.

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2,6-Dichloro-3,5-xylenol

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2,4-Dichloro-3,5-xylenol, m.p. 95–96°, was prepared by Lesser and Gad[1] by chlorination of 3,5-xylenol with sulfuryl chloride. Jones[2] obtained the same dichloroxylenol by treating 4-chloro-3,5-xylenol with N-chloroacetamide, but reported m.p. 83° for his substance after crystallization from ligroin. This difference in m.p. was apparently why Huntress[3] listed Jones' compound as the 2,4-dichloro-3,5-xylenol and that of Lesser and Gad as the 2,6-dichloro isomer.

In view of its antibacterial and antifungal properties, 2,4-dichloro-3,5-xylenol was the subject of a recent study by Gemmell.[4] He duplicated the syntheses of Lesser, Gad and Jones and found that the procedures of these workers led to the same isomer, namely, the 2,4-dichloro compound. It would seem that Jones had a mixture of 2,4-dichloro-3,5-xylenol and of some unchanged 4-chloro-3,5-xylenol.

Gemmell further mentioned that the literature contains no reference to the synthesis of the 2,6-dichloro isomer and that he was not able to prepare it. Direct chlorination of 3,5-xylenol or of 2-chloro-3,5-xylenol yields mixtures containing mostly the 2,4-dichloro derivative, but we have obtained the desired 2,6-dichloro-3,5-xylenol by an indirect method. 4-Bromo-3,5-xylenol was chlorinated to yield 4-bromo-2,6-dichloro-3,5-xylenol which was debrominated by zinc and alkali, following a procedure previously described[5] for the preparation of certain bis-phenols, to the 2,6-dichloro compound.

2,6-Dichloro-3,5-xylenol is a colorless, crystalline substance, melting at 87–88°. Its benzoate melts at 143–145°, that of the 2,4-dichloro isomer at 114–115°. Both isomers have a similar, not too pleasant odor.

It is interesting to note that 2,6-dichloro-3,5-xylenol is much less active bactericidally than the 2,4-isomer, as seen from the data of Table I. The tests were made employing the U. S. Food and Drug Administration method[6]; a plate-count modification[7] also was employed in order to get a more quantitative picture.

TABLE I

BACTERICIDAL ACTIVITY OF DICHLORO-3,5-XYLENOLS

A. Against *S. typhosa*

Substance	Dilution[a]	Contact time of 10 min. at 20° Growth in tubes	Contact time of 10 min. at 20° Number of colonies on plates
2,4-Dichloro cpd.	1–1000	−[b]	0
	1–5000	−	0
2,6-Dichloro cpd.	1–1000	+	6,000[c]
	1–5000	+	10,000

B. Against *M. pyogenes* var. aureus

		Contact time of			
		10 min. at 20°		5 min. at 37°	
Substance	Dilution	Tubes	Plates	Tubes	Plates
2,4-Dichloro cpd.	1–1000	∓	50	−	0
	1–2500	+	180	∓	70
2,6-Dichloro cpd.	1–1000	+	7000	+	800
	1–2500	+	9000	+	2000

[a] 0.1 g. dissolved in 1 ml. of 0.5 *N* alcoholic potassium hydroxide plus 1 ml. of alcohol and diluted with distilled water. [b] −, no growth; +, growth. [c] Counts above 5,000 are estimated.

While it has been previously observed[8] that *p*-chloro-alkylphenols show somewhat greater germicidal potency than their isomers with chlorine in the ortho and alkyl in the para position, the large difference in the antibacterial activity of the two dichloroxylenols is surprising.

Experimental

4-Bromo-2,6-dichloro-3,5-xylenol.—Chlorine (150 g.) was bubbled into a moderately stirred solution of 4-bromo-3,5-xylenol[9] (78 g.) in 1,500 ml. of carbon tetrachloride at 70–75° during 10 hours. The large excess of chlorine was used since an experiment employing the theoretical amount of chlorine (56 g.) resulted in 4-bromo-2-chloro-3,5-xylenol as main product.

The orange solution was poured into water and the organic layer was separated and washed twice with water. After drying and filtering, the solvent was removed by distillation, and the yellow residue (120 g.) was extracted by refluxing it for one hour with a solution of 100 g. of sodium hydroxide in 600 ml. of water. Three more extractions of

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(1) R. Lesser and G. Gad, *Ber.*, **56**, 975 (1923).

(2) B. Jones, *J. Chem. Soc.*, 275 (1941).

(3) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 258 and 283.

(4) J. Gemmell, *Mfg. Chemist*, **23**, 63 (1952); *Soap, Perfumery & Cosmetics*, **25**, 1160 (1952).

(5) G. Tassinari, *Gazz. chim. ital.*, **17**, 90 (1887); W. S. Gump and J. C. Vitucci, THIS JOURNAL, **67**, 238 (1945).

(6) G. L. A. Ruehle and C. M. Brewer, U. S. Dept. of Agriculture, Circular No. 198, December 1931.

(7) A. R. Cade and H. O. Halvorson, *Soap*, **10**, [8], 17; [9], 25 (1934).

(8) E. Klarmann, V. A. Shternov and L. W. Gates, THIS JOURNAL, **55**, 2576 (1933).

(9) K. v. Auwers and E. Borsche, *Ber.*, **48**, 1715 (1915).

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.

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

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

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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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(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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