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3,3'-DIBROMO-4,4',5,5'-TETRAHYDROXYBIBENZYL, A NEW BROMOPHENOL FROM THE RED ALGA, POLYSIPHONIA URCEOLATA[1,2)]

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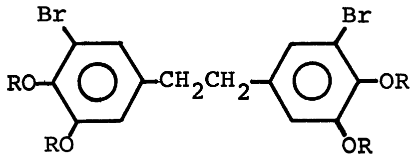
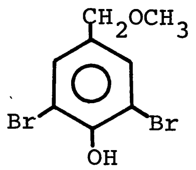
The new bromophenol, 3,3'-dibromo-4,4',5,5'-tetrahydroxybibenzyl has been isolated from the red alga, Polysiphonia urceolata, and identified. Besides this phenol, three bromophenols have been obtained and shown to be 3,5-dibromo-4-hydroxybenzyl methyl ether, 3-bromo-4,5-dihydroxybenzyl methyl ether and 3-bromo-4,5-dihydroxybenzaldehyde, which were previously reported in the literature.

Many bromophenols have been previously isolated from the red marine algae, Rhodomelaceae.[3-11)] In the course of the investigation of the constituents of the red marine algae, the present authors obtained a new bromophenol, 3,3'-dibromo-4,4',5,5'-tetrahydroxybibenzyl (I) together with bromophenols, 3,5-dibromo-4-hydroxybenzyl methyl ether (II)[8,12)], 3-bromo-4,5-dihydroxybenzyl methyl ether (III)[9,12)] and 3-bromo-4,5-dihydroxybenzaldehyde (IV)[3)] from Polysiphonia urceolata.

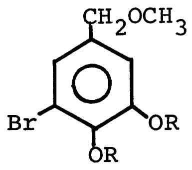
In this paper the isolation and structural elucidation of the above four compounds are described. The alga was collected in May at Matsumae Bay near Hakodate, Hokkaido and air dried. The dried alga (2.5 kg) was soaked for ten days at room temperature in methanol. The methanol extract was evaporated to a syrup, which was treated with ether. The acidic fraction obtained from the ether extract was chromatographed on silica gel. It was eluted with benzene and then benzene – ether (19 : 1). Recrystallization of the substance obtained from the benzene – ether fraction from benzene – methanol gave a crystalline material, 2 g, as a main constituent, and 0.4 g of a crystalline substance from the mother liquor, as a minor constituent. The former gave compound IV, m.p. 230°, upon further recrystallization from the same solvents. This compound was shown to be 3-bromo-4,5-dihydroxybenzaldehyde. The latter afforded compound I, 120 mg, m.p. 205 – 206°, upon further recrystallization from the same solvents. Anal. Calcd. for $C_{14}H_{12}O_4Br_2$: C, 41.62; H, 2.99. Found : C, 41.38; H, 2.92. IR ν_{max}(KBr) 3550, 3470, 3250(OH), 1630, 1610, 1595, 1520(benzene ring) cm^{-1}. UV λ_{max}(EtOH) 287 nm. NMR (CD_3SOCD_3) τ 7.42(4H, s, $-CH_2CH_2-$), 3.46(2H, d, J=2 Hz, aromatic H), 3.27(2H, d, J=2 Hz, aromatic H), 1.28(2H, s, OH), 0.51(2H, s, OH). Mass spectrum m/e (M^+) 406, 404, 402. Treatment of I with diazomethane afforded its tetramethyl ether (V). The oxidation of compound V with potassium permanganate in acetone yielded an oxidation product. This compound was shown to be identical with 3-bromo-4,5-dimethoxybenzoic acid (VI) by comparison of the IR spectrum. All of these results confirmed the structure of compound I. The



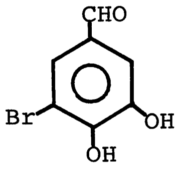
(I) R=H
(V) R=CH$_3$



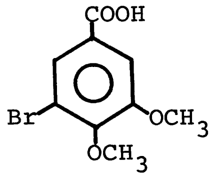
(II)



(III) R=H
(VII) R=CH$_3$



(IV)



(VI)

early fractions of the benzene eluate gave a crystalline material, 650 mg, which afforded compound II, m.p. 70 – 71°, upon recrystallization from n-hexane. The late fractions of the benzene eluate afforded compound III, 460 mg, m.p. 98 – 99°, upon recrystallization from benzene – methanol. The structures of II and III were deduced from elemental analysis as well as IR, UV, NMR and Mass spectral data1), and confirmed by syntheses of II and the dimethyl derivative (VII) of III, respectively.

REFERENCES

1) This study was presented at the annual meetings of the Japanese Society of Scientific Fisheries held in Tokyo, March 1973, March 1974 and March 1976, and in Nagasaki, October 1975.
2) Studies on constituents of this alga had also been carried out and was presented at the 34th annual meeting of the Chemical Society of Japan held in Hiratsuka, March 1976 by M. Nakayama, K. Kumai, S. Eguchi, A. Matsuo, S. Hayashi and H. Akimori.
3) T. Saito and Y. Ando, J. Chem. Soc. Japan (Nippon Kagaku Zasshi), 76, 478 (1955).
4) J. H. Hodgikin, J. S. Craigie, and A. G. McInnes, Can. J. Chem., 44, 74 (1966).
5) J. S. Craigie and D. E. Gruenig, Science, 1058, (1967).
6) N. Katsui, Y. Suzuki, S. Kitamura, and T. Irie, Tetrahedron, 23, 1185 (1967).
7) J. Chantraine, G. Combaut, and J. Teste, Phytochemistry, 12, 1793 (1973).
8) M. Pedersén, P. Seanger, and L. Fries, ibid., 13, 2273 (1974).
9) K. W. Glombitza and H. Stoffelen, Planta media, 22, 391 (1972). H. Stoffelen, K. W. Glombitza, U. Murawski, U. Bielaczek, and H. Egge, ibid., 22, 396 (1972). K. W. Glombitza, H. Stoffelen, U. Murawski, U. Bielaczek, and H. Egge, ibid., 25, 104 (1975).
10) M. Pedersén and L. Fries, Z. Pflanzenphysiol., 74, 272 (1975).
11) B. Weinstein, T. D. Rold, C. E. Harrel Jr., M. W. Burns III, and J. B. Waaland, Phytochemistry, 14, 2667 (1975).
12) Compounds II and III can be artifacts which are derived by methylation of the corresponding alcohols during the extraction procedure.9,11)

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