

DISODIUM 2,3,6-TRIBROMO-5-HYDROXYBENZYL 1',4-DISULFATE,
A NEW BROMOPHENOL FROM THE RED ALGA, SYMPHYOCLADIA LATIUSCULA¹⁾

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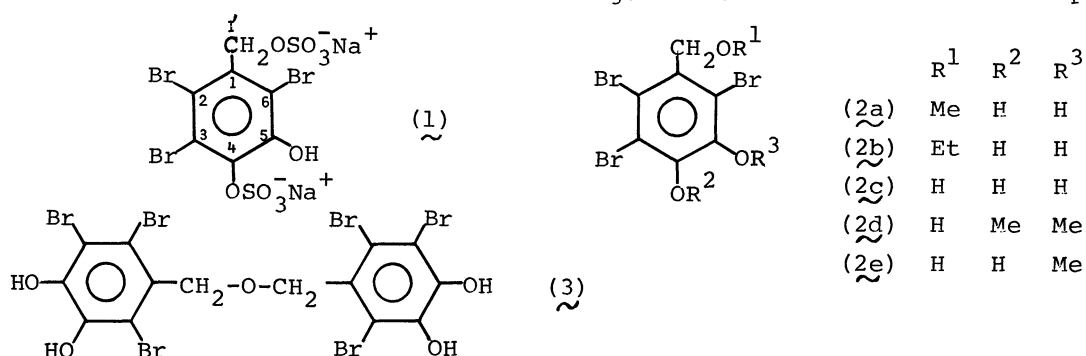
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A new sulfated bromophenol, disodium 2,3,6-tribromo-5-hydroxybenzyl 1',4-disulfate has been isolated from the red alga, Symphyclocladia latiuscula. Its structure was established from the spectral properties and the chemical transformations.

A study on the constituents of the red marine alga, Symphyclocladia latiuscula (Japanese name; isomurasaki), has been reported, but has not been so extensive.²⁾ We have obtained 2,3,6-tribromo-4,5-dihydroxybenzyl methyl ether (2a) from the methanol extract and the corresponding ethyl ether (2b) from the ethanol extract of this alga.³⁾ Treatment of the frozen alga with boiling 80% acetone has given bis(2,3,6-tribromo-4,5-dihydroxybenzyl) ether (3).⁴⁾ However, 2a, 2b and 3 seem to be artifacts derived from a bromophenol precursor during the extraction procedure, because a structurally related alcohol, 2,3,6-tribromo-4,5-dihydroxybenzyl alcohol (2c), has been identified in Polysiphonia lanosa and Rhodomela subfusca on the basis of the mass spectrum of the TMS derivative.⁵⁾ In the course of the investigation of the bromophenol precursor of this alga, disodium 2,3,6-tribromo-5-hydroxybenzyl 1',4-disulfate (1) has been yielded. This compound is considered to be the precursor of 2a, 2b and 3. The present authors wish to report the isolation and structural elucidation of this compound.

The alga was collected in May at Hakodate Bay, Hokkaido and immediately soaked in 80% acetone at room temperature. The extract was evaporated to dryness, and the residue was treated with dry acetone. The acetone-insoluble material was suspended in water and filtrated. The filtrate was thoroughly extracted with ether. The aqueous solution was concentrated and refrigerated. A crude solid was deposited



and filtrated. The crude solid was purified by preparative paper partition chromatography (Rf 0.95, solvent 80% acetone) to yield unstable fine colorless needles of 1. Found: C, 14.35; H, 0.48; Br, 41.25; S, 11.42%. Calcd for $C_7H_3O_9Br_3S_2Na_2$: C, 14.47; H, 0.52; Br, 41.27; S, 11.04%. The presence of sodium was confirmed by atomic absorption spectrophotometry. The IR showed the presence of OH group at 3400 cm^{-1} , phenyl ring at $1545, 1410\text{ cm}^{-1}$, phenolic C-O at 1040 cm^{-1} , and the anion of a sulfate ester at 1240 cm^{-1} . The UV in H_2O exhibited maximum at 302 nm. The 1H -NMR (CD_3SOCD_3) showed methylene proton signal at δ 5.20 (2H, s), phenolic proton signal at δ 10.16 (1H, br s) and did not demonstrate the presence of aromatic ring proton. The ^{13}C -NMR spectrum (CD_3SOCD_3) of 1 showed the presence of a methylene (δ 69.4, t, C-1'). Six aromatic carbon signals were observed in the downfield region at δ 114.8 (s), 117.8 (s), 121.4 (s), 133.4 (s), 139.5 (s) and 147.8 (s) corresponding to the carbons C-6, C-2, C-3, C-1, C-5 and C-4, respectively. Hydrolysis of 1 yielded 2c⁵⁾; m.p. 128–130°C; 1H -NMR (CD_3COCD_3) δ 3.87 (1H, br s), 4.88 (2H, s) and 8.53 (2H, br s); UV λ_{max} (EtOH) 297 nm; IR (KBr) ν 3450, 1580, 1445, 1390, 1280, 1160, 1030, 980 and 900 cm^{-1} . 2c was treated with diazomethane in ether to afford a dimethyl ether (2d), which was identified by comparison with a synthetic sample.⁶⁾ Heating of 1 in 80% acetone for a brief period quantitatively afforded 3 and sodium sulfate. Refluxing of 2c in methanol yielded 2a. 3 and 2a were identical with previously obtained samples, respectively.^{3,4)} Treatment of 1 with diazomethane in 50% ethanol followed by the hydrolysis in 0.01 N HCl provided 2,3,6-tribromo-4-hydroxy-5-methoxybenzyl alcohol (2e); m.p. 152–153°C; UV λ_{max} (EtOH) 294 nm; 1H -NMR ($CDCl_3 + CD_3COCD_3$) δ 3.86 (3H, s), 3.8–4.3 (1H, br s), 5.06 (2H, s) and 9.03 (1H, br s); IR (KBr) ν 3400, 2940, 1550, 1515, 1445, 1390, 1280, 1055, 1010 and 945 cm^{-1} . The structure of 2e was confirmed by comparison with a synthetic sample. A summary of the synthesis is as follows. Bromination of 2,6-dibromovanillin⁷⁾ gave 2,5,6-tribromovanillin, which was reduced with sodium borohydride to give 2e.

On the basis of these results, disodium 2,3,6-tribromo-5-hydroxybenzyl 1',4-disulfate for 1 was proposed. A similar precursor, dipotassium 2,3-dibromo-5-hydroxybenzyl 1',4-disulfate,⁸⁾ has been obtained from the other red algae.

References and Notes

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- 6) 2e in ether was treated with diazomethane, yielding 2d. M.p. 122–123°C. 1H -NMR ($CDCl_3$) δ 2.17 (1H, br s), 3.92 (6H, s), 5.12 (2H, s).
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