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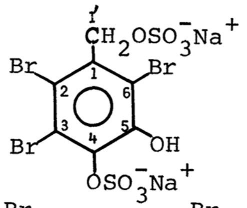
DISODIUM 2,3,6-TRIBROMO-5-HYDROXYBENZYL 1',4-DISULFATE, A NEW BROMOPHENOL FROM THE RED ALGA, *SYMPHYOCLADIA LATIUSCULA*[1]

Kazuya KURATA* and Takashi AMIYA**
* Department of Industrial Chemistry, Hakodate Technical College,
227 Tokura-cho, Hakodate 042
** Hokkaido Institute of Pharmaceutical Sciences, 7-1 Katsuraoka,
Otaru 047-02

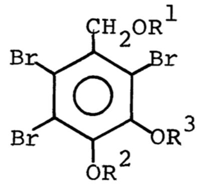
A new sulfated bromophenol, disodium 2,3,6-tribromo-5-hydroxybenzyl 1',4-disulfate has been isolated from the red alga, *Symphyocladia latiuscula*. Its structure was established from the spectral properties and the chemical transformations.

A study on the constituents of the red marine alga, *Symphyocladia 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.

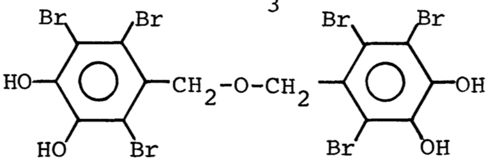
The alga was collected in May at Hakodate Bay, Hokkaido and immediately soaked in 80% acetone at room temperature. The extract was evaporated to dryness, and the residue was treated with dry acetone. The acetone-insoluble material was suspended in water and filtrated. The filtrate was thoroughly extracted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



(**1**)



	R^1	R^2	R^3
(**2a**)	Me	H	H
(**2b**)	Et	H	H
(**2c**)	H	H	H
(**2d**)	H	Me	Me
(**2e**)	H	H	Me



(**3**)

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 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 2c[5]; 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-dibromovanillin[7] 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, has been obtained from the other red algae.[8]

References and Notes

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5) K. W. Glombitza, H. Stoffelen, U. Murawski, U. Bielaczek, and H. Egge, Planta Med., 25, 105 (1974).
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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