

A New Poly Brominated Dibenzylphenol from *Rhodomela confervoides*

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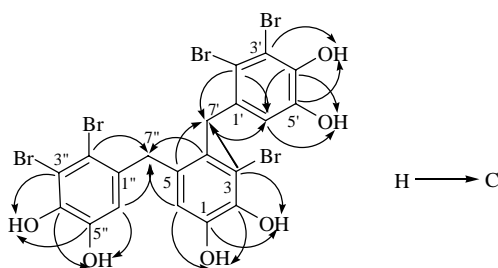
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Abstract: A new poly brominated dibenzylphenol named as rhodomevoidin was isolated from *Rhodomela confervoides*. Its structure was elucidated as 3-bromo-4, 5-bis (2, 3-dibromo-4, 5-dihydroxybenzyl)pyrocatechol by spectroscopic methods including IR, HRFABMS, 1D and 2D NMR techniques.

Keywords: red algae, Rhodomelaceae, *Rhodomela confervoides*, bromophenol, rhodomevoidin, 3-bromo-4, 5- bis (2,3-dibromo-4,5-dihydroxybenzyl)pyrocatechol

Rhodomela confervoides is a red alga belonging to Rhodomelaceae family. A number of bromophenols have been previously isolated from the red marine algae of this family¹⁻⁸. Some chlorinated bromophenols and 2,3,2',3'-tetrabromo-4,5,4',5'-tetrahydroxydiphenylmethane were identified from *R. confervoides* by stepwise extraction followed by GC-MS⁵. In our investigation of chemical constituents of this red alga collected at the coast of Qingdao, a new poly brominated dibenzylphenol 3-bromo-4, 5-bis(2,3-dibromo-4,5-dihydroxybenzyl)pyrocatechol **1** was obtained. In this paper we describe the isolation and structural elucidation of this compound.

Figure 1 The key HMBC correlations of **1**



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The air-dried red alga *R. confervoides* was grounded and extracted with 95% EtOH, the concentrated extract was suspended in water, and then partitioned with EtOAc. The EtOAc extract was subjected to column chromatography over silica gel eluting with a gradient increasing MeOH (0-100%) in CHCl₃. The fraction eluted by 30% MeOH in CHCl₃ was purified by size-exclusion chromatography over Bio-Beads SX-3 with CHCl₃-EtOAc (1:1) as eluent to yield compound **1**, white needles (Me₂CO), m.p. 237-238°C. Its IR spectrum (KBr) showed a strong broadened absorption band for hydroxyl groups at 3410 cm⁻¹ and characteristic absorption bands for aromatic rings at 1606, 1577 and 1489 cm⁻¹. The positive FABMS spectrum with glycol as matrix exhibited a group of peaks for the molecular ion at *m/z* 743, 745, 747, 749, 751 and 754, which suggested the presence of five bromine atoms in the molecule of **1**. The molecular formula was determined as C₂₀H₁₃Br₅O₆ by HRFABMS at *m/z* 743.6645 (calcd. for C₂₀H₁₃⁷⁹Br₅O₆ 743.6629). The ¹H NMR spectrum of **1** in acetone-d₆ showed three singlets attributed to aromatic protons at δ 6.56 (1H, s, 6''-H), 6.49 (1H, s, 6-H) and 6.20 (1H, s, 6'-H) and two singlets assigned to methylene protons at δ 4.04 (2H, s, 7'-H) and 3.78 (2H, s, 7''-H), as well as six exchangeable broadened singlet for phenolic hydroxyl protons at δ 8.83 (1H, br s, 5''-OH), 8.73 (1H, br s, 5'-OH), 8.72 (1H, br s, 1-OH), 8.35 (1H, br s, 4''-OH), 8.19 (1H, br s, 4-OH) and 8.03 (1H, br s, 4'-OH). The ¹³C NMR and DEPT spectra of **1** displayed 20 carbon signals attributed to three *penta*-substituted benzene rings and a pair of methylenes. The protonated carbons were assigned by the HMQC experiment of **1** and the oxygenated quaternary carbons were recognized by their chemical shifts (δ > 140 ppm) (see **Table 1**). All of the above spectral data evidenced that **1** was a poly brominated dibenzylphenol⁹. In the HMBC spectrum (see **Figure 1**), cross peaks from aromatic and phenolic protons to their correlated long range carbons unambiguously established the substituted patterns of the three aromatic rings. Long range correlations from 7'-H to C-3, C-5, C-2' and C-6' and from 7''-H to C-4, C-6, C-2'' and C-6'' unequivocally revealed that two 2,3-dibromo-4,5-dihydroxybenzyl groups substituted at C-4 and C-5 of the 3-bromopyrocatechol unit. Accordingly, the structure of **1** was determined as 3-bromo-4, 5-bis(2,3-dibromo-4,5-dihydroxybenzyl)pyrocatechol.

Table 1 ¹H and ¹³C NMR data of compound **1** ^a

No.	δ _H	δ _C	No.	δ _H	δ _C	No.	δ _H	δ _C
1		144.5 s	1'		131.1 s	1''		132.2 s
2		142.0 s	2'		115.8 s	2''		116.3 s
3		114.4 s	3'		113.2 s	3''		113.3 s
4		128.6 s	4'		143.0 s	4''		143.3 s
5		131.1 s	5'		145.0 s	5''		144.9 s
6	6.49 s	115.7 d	6'	6.20 s	114.2 d	6''	6.56 s	116.2 d
			7'	4.04 s	39.5 t	7''	3.78 s	40.4 t

^a NMR data were measured in acetone-d₆ at 300 MHz for proton and at 75 MHz for carbon. The assignments were based on DEPT, ¹H-¹H COSY, HMQC and HMBC experiments.

Acknowledgments

The authors are grateful to professor Ablez zeper for mass spectra measurements, and financial support from the NSF (Grant No.99-929-01-26), and national "863" program (Grant No. 2001AA620403).

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Received 29 August, 2002