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A New Bromophenol from the Brown Alga *Leathesia nana*

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Abstract: A novel bromophenol was isolated from ethanolic extract of the brown alga *Leathesia nana* S.et G. The structure was elucidated as (*E*)-3-(2,3-dibromo-4,5-dihydroxyphenyl)-2-methyl-propenal by spectroscopic methods including IR, HREIMS, 1D and 2D NMR techniques.

Keywords: Brown alga, Leathesiaceae, *Leathesia nana*, bromophenol.

Leathesia nana S.et G is a brown alga belonging to Leathesiaceae family and widely distributed in the gulf of the Yellow Sea, China. A number of bromophenols have been previously isolated from marine red algae[1~9], but few from brown algae. In our investigation of chemical constituents of seaweeds along the Qingdao coast of China, several bromophenols have been reported from the red alga *Rhodomela confervoides* (Huds.) Silva[10]. We describe here the isolation and structural elucidation of a new bromophenol (*E*)-3-(2,3-dibromo-4,5-dihydroxyphenyl)-2-methylpropenal **1** from the brown alga *L. nana*.

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

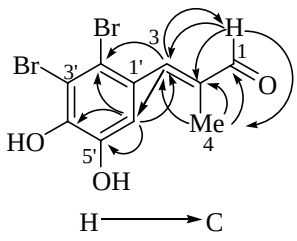
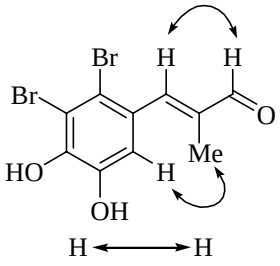


Figure 2 The key NOE correlations of **1**



The air-dried brown alga *L. nana* was powdered and extracted with 95% EtOH. After the solvent was removed under reduced pressure, the residue was suspended in water, and then partitioned with EtOAc. The EtOAc extract was subjected to column

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chromatography over silica gel eluting with a gradient increasing acetone (0-100%) in petroleum ether. The fraction eluted by 30% acetone in petroleum ether was rechromatographed over Sephadex LH-20, and then purified by reverse phase HPLC with 80% MeOH and 0.1% AcOH in H_2O as eluent to yield compound **1**.

Compound **1** was obtained as a red power, m.p. 138-140°C. The IR spectrum showed a strong broadened absorption band for hydroxyl groups (3402 cm^{-1}), characteristic absorption bands for carbonyl (1647 cm^{-1}) and aromatic rings (1591, 1509 and 1486 cm^{-1}). In the negative ion FAB mass spectrum, a quasi-molecular ion peak cluster at *m/z* 337.0/335.0/333.0 (1:2:1) indicated the presence of two bromine atoms in the molecule of **1**. The molecular formula of **1** was determined as $C_{10}H_8Br_2O_3$ in combination with the NMR data (see **Table 1**). The ^{1}H NMR spectrum showed a diagnostic singlet for aldehyde proton at δ9.66 (s, 1H, H-1) and a methyl proton doublet at δ1.88 (d, 3H, *J*=1.5 Hz, H-4) coupling with an olefinic proton at δ7.47 (d, 1H, *J*=1.5 Hz, H-3) in addition to a singlet assignable to an aromatic proton at δ7.30 (s, 1H, H-6′). The ^{13}C-NMR spectrum and DEPT experiments of **1** showed 10 carbon signals including one methyl, three sp^2 methines (one aldehyde), six sp^2 quaternary carbons (two oxygenated, δ >145) (see **Table 1**). These data suggested that **1** is a phenyl propenal substituted by two bromines, two hydroxyls and one methyl. The location of the substituents was established by HMBC experiment in combination with the chemical shift values of the carbons and protons. In the HMBC spectrum of **1** (see **Figure 1**), long range correlations from H-6′ to C-2′, C-4′, C-5′ and C-3 revealed the 2′,3′-dibromo-4′,5′-dihydroxy substitution pattern of the phenyl moiety. Long range correlations from H-1 to C-2, C-3 and C-4 and from H-4 to C-1, C-2 and C-3 indicated that the methyl group was substituted at C-2 of the propenal moiety. The connection between the phenyl and propenal moieties was confirmed by the HMBC correlations from H-3 to C-2′ and C-6′, and from H-6′ to C-3. The geometric configuration of the propenal moiety was determined to be *E* by the NOE difference experiment of **1** (see **Figure 2**). The irradiation of H-1 gave the NOE enhancement of H-3, in turn the irradiation of H-3 resulted in the enhancement of H-1. In addition, the NOE enhancement of H-4 was observed by the irradiation of H-6′. Therefore, the structure of **1** was determined as (*E*)-3-(2,3-dibromo-4,5-dihydroxy-phenyl)-2-methylpropenal.

Table 1 ^{1}H and ^{13}C NMR data of compound **1**[a] (δ ppm, *J* Hz)

No.	δ_H	δ_C	No.	δ_H	δ_C
1	9.66(s, 1H)	195.5 d	2′		117.5 s
2		139.6 s	3′		114.4 s
3	7.47(d, 1H, 1.5)	149.3 d	4′		146.4 s
4	1.88(d, 3H, 1.5)	10.8 q	5′		145.3 s
1′		128.5 s	6′	7.30(s, 1H)	116.6 d

[a] NMR data were measured in acetone-d_6 at 500 MHz for proton and at 125 MHz for carbon. The assignments were based on DEPT and HMBC experiments.

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