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NEW POLYBROMINATED DIPHENYL ETHER FROM THE MARINE SPONGE *Dysidea herbacea*

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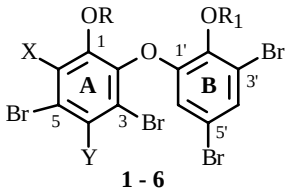
Tropical marine sponges of the family Dysideidae contain a series of antimicrobial polybrominated diphenyl ethers with varying degrees of hydroxylation, methoxylation, and bromination [1]. Recently this class of metabolites has attracted attention because of their ability to inhibit 15-lipoxygenase in mammals [2] and the assembly of microtubular proteins [3] and to regulate interleukin-8 production [4].

We investigated the marine sponge *Dysidea herbacea* collected in the Large Barrier Reef during the ninth cruise of R/V Academic Oparin. Sponge (3 g) was lyophilized and extracted with $CHCl_3$. The extract was repeatedly chromatographed over silica gel to produce **1** (0.9 mg), **2** (10 mg), **3** (4.5 mg), **4** (0.6 mg), **5** (0.5 mg), and **6** (0.5 mg). Compounds **2**-**6** were identified by comparing their spectral properties with those in the literature [5, 6]. Diphenyl ether **1**, mp 181-183°C ($CHCl_3$) was a new representative of this class.



1 - 6

1: R = R_1 = X = Y = H

2: R = R_1 = H, X = Y = Br

3: R = R_1 = Y = H, X = Br

4: R = R_1 =Me, X = Y = Br

5: R = Me, R_1 = Y = H, X = Br

6: R = X = Y = H, R_1 = Me

The mass spectrum of **1** showed a molecular ion as a cluster of peaks at *m*/*z* 522, 520, 518, 516, and 514 and a molecular weight of 517.7898, which corresponded with the empirical formula $C_{12}H_6Br_4O_3$. The PMR spectrum had two pairs of protons with a *meta*-coupling constant. Each pair of protons was determined by selective decoupling. The ^{13}C NMR spectrum showed signals for 12 C atoms. C atoms bound to protons were determined by HSQC. The presence of two pairs of *meta*-coupled protons suggested that the molecule had two asymmetric 1,2,3,5-tetrasubstituted aromatic rings.

Comparison of the ^{13}C NMR spectrum of **1** with those of **6**, **2**, and **3** showed that the chemical shifts of C-1 to C-6 of **1** corresponded with those of C atoms in ring A of **6** [7]; those of C-1′ to C-6′, of C atoms of ring B in **2** and **3** [5] (Table 1). C atoms in **1** were assigned using HMBC. Methylation of **1** by MeI gave a dimethyl ether, the spectral properties of which agreed with the literature data for 2-(3′,5′-dibromo-2′-methoxyphenoxy)-3,5-dibromoanisole [5]. Thus, **1** had the structure 2-(3′,5′-dibromo-2′-hydroxyphenoxy)-3,5-dibromophenol.

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TABLE 1. ^{13}C NMR (125 MHz), PMR (500 MHz), and HMBC Spectra of **1** (acetone-d_6)

C atom	δ_C	δ_H (J/Hz)	HMBC
1	152.6		
2	139.3		
3	118.6		
4	126.8	7.38 d (J = 2.1)	2, 3, 5, 6
5	119.6		
6	120.7	7.24 d (J = 2.1)	1, 2, 4, 5
1′	146.7		
2′	144.5		
3′	111.2		
4′	129.1	7.37 d (J = 2.1)	2′, 3′, 5′, 6′
5′	110.7		
6′	116.3	6.64 d (J = 2.1)	1′, 2′, 4′, 5′

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