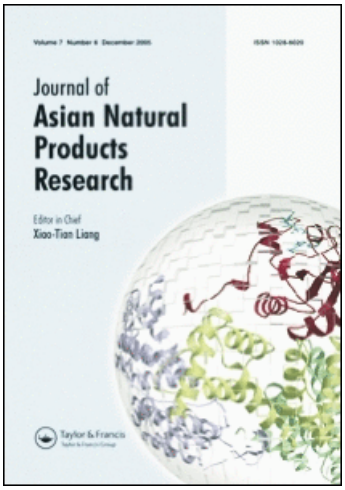

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Six compounds from marine fungus Y26-02

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Two new compounds, together with four known compounds, have been isolated from the ethyl acetate extract of the fermentation broth of the marine fungus Y26-02. Their structures were elucidated, respectively, as 5-(ethynyloxy)-3-hydroxy-3,6-dihydro-2H-pyran-2-one (**1**), 4-(butoxymethyl)benzene-1,2-diol (**2**), 4-(methoxymethyl)benzene-1,2-diol (**3**), 2-acetoxymethylphenol (**4**), *N*-(2-phenylethyl)acetamide (**5**), and 4-hydroxyphenethyl acetate (**6**) on the basis of their spectroscopic and physico-chemical properties.

Keywords: *Clerodendrum inerme*; phenol compounds; 4-(butoxymethyl)benzene-1,2-diol; 5-(ethynyloxy)-3-hydroxy-3,6-dihydro-2H-pyran-2-one

1. Introduction

Nowadays, marine natural products attract more and more attention of biologists and chemists all over the world. The second metabolites of marine microorganisms comprise the compounds that repel predators by their toxicity, and those which are attractive to make reproduction more probable [1]. Among the diverse marine microorganisms, marine fungi have been proven to be a promising source of structurally diverse secondary metabolites possessing a broad range of biological activities [2].

The strain Y26-02 is a marine fungus isolated from *Clerodendrum inerme*, a tree from the inter-tidal zone of the South China Sea. In our recent research, six compounds have been isolated from the ethyl acetate extract of the fermentation broth, among which compounds **1** and **2** were new; compound **3** was a new natural product (Figure 1).

2. Results and discussion

Compound **1** was obtained as a white amorphous powder with $[\alpha]_D^{20}$ −4.1 ($c = 2.5$, MeOH). The molecular formula was determined to be $C_7H_6O_4$ by HR-FAB-MS at *m/z* 155.0329 $[M+H]^+$. The IR spectrum showed absorption bands due to hydroxyl moiety (3553 cm^{-1}), ethynyl group (3119 cm^{-1}), carbonyl group (1766 cm^{-1}), and double bond (1642 cm^{-1}). The signal at δ 7.36 (1H, d, $J = 6.0$ Hz) in the ^{1}H NMR spectrum belonged to a hydrogen bond-associated hydroxyl proton, which was also supported by the HMQC spectrum in which there was no cross-peak at δ_H 7.36. The presence of the moiety **1a** was deduced from the ^{1}H NMR signals at δ 7.36 (1H, d, $J = 6.0$ Hz), 6.25

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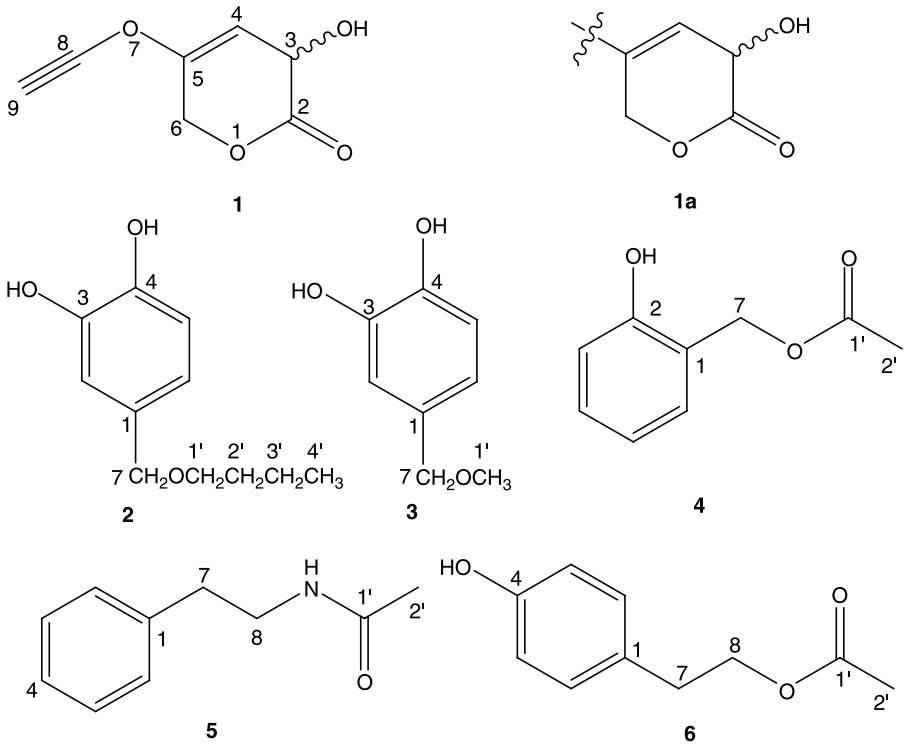

Figure 1. The structures of compounds **1**–**6**.

(1H, d, $J = 1.8$ Hz), 5.94 (1H, dd, $J = 1.8$, 6.0 Hz), 3.71 (1H, d, $J = 12.0$ Hz), 3.78 (1H, d, $J = 12.0$ Hz), and the ^{13}C NMR signals at δ 169.8, 166.9, 118.5, 89.5, 60.9, together with the HMQC cross-peaks: δ_H 6.25/δ_C 118.5, δ_H 5.94/δ_C 89.5, δ_H 3.78, 3.71/δ_C 60.9. The deduction was also supported by the HMBC correlations of 3-OH/C-2 (δ_C 166.9) and C-3 (δ_C 89.5), H-3/C-2, C-4 (δ_C 118.5), C-5 (δ_C 169.8) and C-6 (δ_C 60.9), H-4/C-2, C-3 (δ_C 89.5) and C-5 (δ_C 169.8), and H-6 (2H, δ_H 3.78, 3.71)/C-3 (δ_C 89.5). The ^{1}H NMR signal at δ 2.86 (1H, s) and the ^{13}C NMR signals at δ 40.8 and 86.4 suggested that compound **1** might have an ethynyloxyl substituent, which could be located at C-5 of the moiety **1a** on the basis of the HMBC cross-peaks: H-9/C-5 (δ_C 169.8), C-6 (δ_C 60.9) and C-8 (δ_C 86.4), H-4/C-8 (Figure 2). Thus, compound **1** was elucidated as 5-(ethynyloxy)-3-hydroxy-3,6-dihydro-2H-pyran-2-one.

Compound **2** was obtained as a colorless oil. The molecular formula was determined to be $C_{11}H_{16}O_3$ by HR-FAB-MS at *m/z* 219.0987 $[M + Na]^+$. The IR spectrum of **2** showed absorption bands at 1615, 1510, and

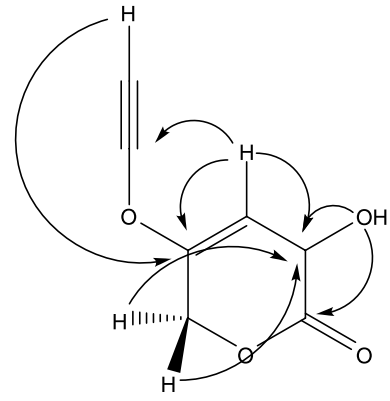

Figure 2. The key HMBC correlations of compound **1**.

1445 cm^{-1}, indicating the presence of an aromatic ring, which was also supported by the UV absorption at λ_{max} 281 and 230 nm. The ^{1}H NMR spectrum of compound **2** showed aromatic proton signals at δ 6.66 (1H, d, $J = 3.0$ Hz), 6.58 (1H, d, $J = 8.4$ Hz), and 6.46 (1H, dd, $J = 3.0$, 8.4 Hz) and two phenolic hydroxyl proton signals at δ 8.62 and 8.66. The ^{13}C NMR spectrum of **2** showed six aromatic carbon signals at δ 149.8, 147.0, 125.7, 115.5, 114.9, and 114.3. Hence, compound **2** might contain a 1,3,4-trisubstituted benzene moiety with two vicinal phenolic groups. Moreover, the ^{1}H NMR signals at δ 4.33 (2H, s), 3.42 (2H, t, $J = 6.6$ Hz), 1.52 (2H, m), 1.33 (2H, m), and 0.88 (3H, t, $J = 7.2$ Hz), together with the corresponding carbon signals at δ 69.5, 66.9, 31.5, 19.0, and 13.9, proved that compound **2** contained a butoxymethyl group. Then, on the basis of the above information, compound **2** was elucidated as 4-(butoxymethyl)benzene-1,2-diol.

The structures of the other four known compounds, 4-(methoxymethyl)benzene-1,2-diol (**3**), 2-acetoxymethylphenol (**4**), *N*-(2-phenylethyl)acetamide (**5**), and 4-hydroxyphenethyl acetate (**6**), were established by comparing their spectral data with the reported data or with those of the authentic sample [3–5].

3. Experimental

3.1 General experimental procedures

Optical rotations were measured on a Perkin-Elmer 241 polarimeter. UV spectra were measured on a Shimadzu UV-1601. IR spectra were taken on a Bruker IFS-55 infrared spectrophotometer. The NMR data were recorded on a Bruker AV-600 (600 MHz for ^{1}H and 150 MHz for ^{13}C) in DMSO-d_6 with TMS as an internal standard. The HR-FAB-MS data were obtained on a Micross Mass Autospec-UltimaE TOF mass spectrophotometer. Chromatography was performed on silica gel (200–300 mesh; Qingdao Haiyang Chemical Factory, Qingdao, China), Sephadex LH-20 (Pharmacia, Uppsala, Sweden), and reversed-phase HPLC (Shimadzu LC-8A vp, Kyoto, Japan).

3.2 Fungal material

The strain Y26-02 was isolated from *C. inerme* collected in the inter-tidal zone of the South China Sea in December 2006. A voucher specimen (No. HTTA-Z06001) was identified by Prof. Li Tian and has been deposited in the Marine Microbial Medicinal Resource Library of the First Institute of Oceanography SOA funded by the Chinese Ministry of Science and Technology.

3.3 Extraction and isolation

The supernatant of the fermentation broth of the strain Y26-02 (50 l) was concentrated to 5 l *in vacuo* and extracted with ethyl acetate and *n*-butanol, successively. The EtOAc-soluble fraction (20.7 g) was subjected to silica gel column, eluted with $CHCl_3$–CH_3OH (100:1–0:1), yielding 12 fractions. Fraction 2 (2.5 g) was then subjected to silica gel column again, eluted with petroleum ether–EtOAc (100:1–0:1), yielding 14 fractions. Then, of these 14 fractions, fraction 12 (23 mg) afforded compound **1** (15 mg) using the method of recrystallization, while fraction 2 (255 mg) was subjected to Sephadex LH-20 eluted

Table 1. ^{1}H NMR (DMSO-d_6, 600 MHz) and ^{13}C NMR (DMSO-d_6, 150 MHz) spectral data of compound **1**.

Position	δ_C	δ_H, J
1	–	–
2	166.9	–
3	89.5	5.94 (dd, 1.8, 6.0)
4	118.5	6.25 (d, 1.8)
5	169.8	–
6	60.9	3.71 (d, 12.0), 3.78 (d, 12.0)
7	–	–
8	86.4	–
9	40.8	2.86 (s)
—OH	–	7.36 (d, 6.0)

Table 2. ^{1}H NMR (DMSO-d_6, 600 MHz) and ^{13}C NMR (DMSO-d_6, 150 MHz) spectral data of compounds **2** and **3**.

2			**3**		
Position	δ_C	δ_H, J	Position	δ_C	δ_H, J
1	125.7	–	1	125.2	–
2	114.9	6.66 (d, 3.0)	2	115.1	6.63 (d, 3.0)
3	147.0	–	3	147.2	–
4	149.8	–	4	149.8	–
5	114.3	6.58 (d, 8.4)	5	114.2	6.59 (d, 8.4)
6	115.5	6.46 (dd, 3.0, 8.4)	6	115.6	6.47 (dd, 3.0, 8.4)
7	69.5	4.33 (2H, s)	7	68.8	4.30 (2H, s)
1′	66.9	3.42 (t, 6.6, 2H)	1′	57.7	3.30 (s, 3H)
2′	31.5	1.52 (m, 2H)	2′	–	–
3′	19.0	1.33 (m, 2H)	3′	–	–
4′	13.9	0.88 (t, 7.2, 3H)	4′	–	–
—OH	–	8.66 (s); 8.62 (s)	—OH	–	8.65 (s); 8.60 (s)

with $CHCl_3$–CH_3OH (1:1), preparative-TLC developed with petroleum ether–acetone (2:1), and preparative-HPLC eluted with CH_3OH–H_2O (48%) successively to obtain compounds **2** (3 mg), **4** (5 mg), and **6** (5 mg). Fraction 3 (300 mg) was subjected to Sephadex LH-20 eluted with CH_3OH and preparative-TLC successively to obtain compound **3** (4 mg). Fraction 10 (105 mg) was subjected to silica gel column (400–500 mesh) eluted with $CHCl_3$–CH_3OH (10:1) and preparative-HPLC eluted with CH_3OH–H_2O (60%) successively to afford compound **5** (4 mg).

*3.3.1 5-(Ethynyloxy)-3-hydroxy-3,6-dihydro-2H-pyran-2-one (**1**)*

A white amorphous powder; $[\alpha]_D^{20}$ −4.1 (c = 2.5, MeOH); UV (MeOH) λ_{max}: 225 nm; IR (KBr) ν_{max} (cm^{-1}): 3553, 3119, 1766, 1642; ^{1}H and ^{13}C NMR spectral data, see Table 1; HR-FAB-MS *m/z*: 155.0329 $[M+H]^+$ (calcd for $C_7H_7O_4$, 155.0339).

*3.3.2 4-(Butoxymethyl)benzene-1, 2-diol (**2**)*

A colorless oil; UV (MeOH) λ_{max}: 281, 230 nm; IR (KBr) ν_{max} (cm^{-1}): 3560, 1615, 1510, 1445; ^{1}H and ^{13}C NMR spectral data, see Table 2; HR-FAB-MS *m/z*: 219.0987 $[M+Na]^+$ (calcd for $C_{11}H_{16}NaO_3$, 219.0992).

*3.3.3 4-(Methoxymethyl)benzene-1,2-diol (**3**)*

A colorless oil; ^{1}H and ^{13}C NMR spectral data, see Table 2.

Acknowledgements

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References

[1] D.S. Bhakuni and D.S. Rawat, *Bioactive Marine Natural Products* 21 (2005).
[2] B.S. Moore, J.A. Trischman, and D. Seng, *J. Org. Chem.* **64**, 1145 (1999).
[3] P. Allevi, P. Ciuffreda, and A. Longo, *Tetrahedron: Asymmetry* **9**, 2915 (1998).
[4] B.C. Maiti, O.C. Musgrave, and D. Skoyles, *Tetrahedron* **61**, 1765 (2005).
[5] L. Jeanine, E. Jose, F. Robert, and V. Emile Jean, *Org. Magn. Reson.* **14**, 20 (1980).