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Journal of Asian Natural Products Research

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713454007>

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Online publication date: 08 November 2010

To cite this Article Cai, Yang-Peng , Xie, Chun-Bo , Wang, Bao-Chao , Li, Ping-Lin and Li, Ba-Fang(2010) 'Two new resorcinols from *Sargassum thunbergii*', Journal of Asian Natural Products Research, 12: 11, 1001 – 1004

To link to this Article: DOI: 10.1080/10286020.2010.522179

URL: <http://dx.doi.org/10.1080/10286020.2010.522179>

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Two new resorcinols from *Sargassum thunbergii*

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(Received 11 March 2010; final version received 6 September 2010)

Two new resorcinols, 1-(5-acetyl-2,4-dihydroxyphenyl)-3-methylbutan-1-one (**1**) and 1-(5-acetyl-2-hydroxy-4-methoxyphenyl)-3-methylbutan-1-one (**2**), have been isolated from the brown algae *Sargassum thunbergii* (Mert.) O'Kuntze. Their structures were elucidated on the basis of spectroscopic methods.

Keywords: *Sargassum thunbergii*; resorcinol; spectroscopic methods

1. Introduction

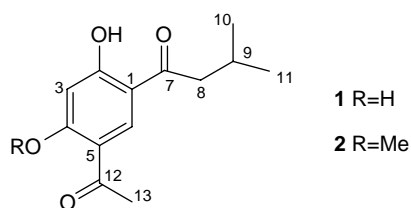
The genus *Sargassum* has more than 260 species all over the world, and about 100 of them are distributed in China. Many of these brown algae were used as medicine and functional foods [1,2], because of their contents of a great diversity of active chemical components such as the polysaccharides fucoidan [3,4], fucan sulfate [5,6], and also those compounds with small molecular weights like phenols and their substitution products [7–9]. During the investigation of the chemical components of *Sargassum thunbergii*, which is one of the main species of *Sargassum* distributed in the Shandong coastal area [10], two new resorcinols **1** and **2** (see Figure 1) were obtained from the MeOH extract of the algae sample. In this paper, we report the isolation and structural elucidation of these compounds.

2. Results and discussion

The air-dried and pulverized *S. thunbergii* was extracted with MeOH to give a residue which was chromatographed on silica gel, Sephadex LH-20, and ODS columns to afford two new phenolic compounds **1** and **2**.

Compound **1** was obtained as colorless acicular crystals. The molecular formula $C_{13}H_{16}O_4$ of **1** was deduced from the HR-ESI-MS spectrum at m/z 237.1127 $[M + H]^+$. Absorptions for the phenolic hydroxyl (3470 cm^{-1}), carbonyl group (1645 cm^{-1}), and benzene ring (870 and 865 cm^{-1}) were observed in the IR spectrum. The UV spectrum showed an absorption maximum at 275 nm, which can be assigned to the benzoyl group. In the NMR experiment, the low field of the ^1H NMR spectrum (see Table 1) of **1** showed the presence of two hydroxyl groups at δ_{H} 12.90 (1H, s), 13.16 (1H, s) and two aromatic protons at δ_{H} 6.43 (1H, s) and 8.23 (1H, s). In the high field of the ^1H NMR spectrum of **1**, the signals at δ_{H} 1.04 (6H, d, $J = 6.4\text{ Hz}$), 2.81 (2H, d, $J = 6.4\text{ Hz}$), especially the signal of a proton splitted as a nonet at δ_{H} 2.30 (1H, m) indicated the presence of an isobutyl group, which was further confirmed by the $^1\text{H}-^1\text{H}$ COSY experiment (see Figure 2). The relatively low field of the methylene protons at δ_{H} 2.81 (2H, d, $J = 6.4\text{ Hz}$) mentioned above showed that it was on the carbon α to a carbonyl group, and the signal at δ_{H} 2.64 (3H, s) exhibited the presence of another Me connected to a

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Figure 1. Structures of compounds **1** and **2**.

carbonyl group. The ^{13}C NMR (DEPT) spectrum (see Table 1) showed 13 carbon signals, including two carbonyl carbons [δ_{C} 204.8 (s), 202.6 (s)], six sp^2 carbons of an oxygenated benzene ring [δ_{C} 169.4 (s), 168.9 (s), 135.9 (d), 113.7 (s), 113.7 (s), and 105.3 (d)], one methylene [δ_{C} 46.7 (t)], one methine [δ_{C} 26.3 (d)], and three methyl groups [δ_{C} 25.9 (q), 23.0 (q), and 23.0 (q)]. In the HMBC experiment (see Figure 2), the key correlations of H-8 with C-7, Me-13 with C-5 and C-12, and H-6 with C-7 and C-12 revealed the location of two carbonyl groups. In the NOE difference experiment, irradiation of H-6 produced NOE enhancement of H-8 and Me-13 as 3.35 and 1.84%, respectively, and irradiation of the proton at δ_{H} 13.16 (1H, s) of the hydroxyl group located at C-4 produced NOE

enhancement of Me-13 as 1.60%, which further confirmed the assignment of the hydroxyl groups. Together with the singlet pattern of protons in the benzene ring, ESI-MS spectral data (see Figure 2) and comparing NMR spectral data with the analogues [11], compound **1** was determined as a 1-(5-acetyl-2,4-dihydroxyphenyl)-3-methylbutan-1-one.

Compound **2**, colorless acicular crystals, showed its molecular formula $\text{C}_{14}\text{H}_{18}\text{O}_4$ from the HR-ESI-MS spectrum at m/z 251.1291 $[\text{M} + \text{H}]^+$. The IR spectrum also showed the absorptions for the hydroxyl (3480 cm^{-1}), carbonyl group (1650 cm^{-1}), and benzene ring (870 and 860 cm^{-1}). The UV spectrum exhibited an absorption maximum at 265 nm. The NMR spectral data of compound **2** (see Table 1) were very similar to those of compound **1** except that the hydroxyl group at δ_{H} 13.16 (1H, s) in compound **1** was substituted by a methoxyl group at δ_{H} 3.95 (3H, s) and δ_{C} 56.1 (q) in compound **2**. Irradiation of the OMe group of compound **2** in the NOE difference experiment produced NOE enhancement of Me-13 as 3.35%, which indicated that

Table 1. ^1H and ^{13}C NMR spectral data of compounds **1** and **2** (in CDCl_3).

| | Proton | | Carbon | |
|-----|------------------------|------------------------|----------|----------|
| | 1 | 2 | 1 | 2 |
| 1 | | | 113.7 s | 113.9 s |
| 2 | | | 168.9 s | 170.4 s |
| 3 | 6.43 s | 6.45 s | 105.3 d | 102.1 d |
| 4 | | | 169.4 s | 167.7 s |
| 5 | | | 113.7 s | 117.7 s |
| 6 | 8.23 s | 8.26 s | 135.9 d | 135.4 d |
| 7 | | | 204.8 s | 199.7 s |
| 8 | 2.81 d ($J = 6.4$ Hz) | 2.82 d ($J = 6.8$ Hz) | 46.7 t | 52.8 t |
| 9 | 2.30 m | 2.31 m | 26.3 d | 26.5 d |
| 10 | 1.04 d ($J = 6.4$ Hz) | 0.96 d ($J = 6.8$ Hz) | 23.0 q | 22.9 q |
| 11 | 1.04 d ($J = 6.4$ Hz) | 0.96 d ($J = 6.8$ Hz) | 23.0 q | 22.9 q |
| 12 | | | 202.6 s | 197.0 s |
| 13 | 2.64 s | 2.62 s | 25.9 q | 25.9 q |
| OMe | | 3.95 s | | 56.1 q |
| OH | 12.90 s | 12.93 s | | |
| OH | 13.16 s | | | |

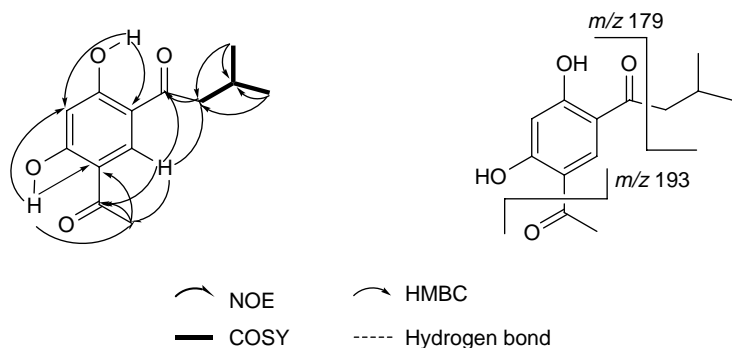


Figure 2. Key correlations of HMBC ($H \rightarrow C$), NOE, 1H - 1H COSY, and key MS fragmentations of compound **1**.

the hydroxyl group at C-4 in **1** was substituted by a methoxyl group in **2**. Thus, the structure of compound **2** was determined as 1-(5-acetyl-2-hydroxy-4-methoxyphenyl)-3-methylbutan-1-one.

3. Experimental

3.1 General experimental procedures

Melting points were determined on a Yanaco MP-500D micro-melting point apparatus and are uncorrected. The UV spectra were obtained on a Beckman DU[®] 640 spectrophotometer. IR spectra were recorded on a Nicolet Nexus 470 spectrophotometer in KBr disks. 1H and ^{13}C NMR were measured with a JEOL Eclipse-600 spectrometer. Chemical shifts are reported in parts per million (δ), using TMS as an internal standard, with coupling constants (J) in Hertz. The ESI-MS and HR-ESI-MS spectra were taken on a Q-TOF Ultima Global GAA076 LC mass spectrometer. Commercial silica gel (100–200 and 200–300 mesh; Qingdao Haiyang Chemical Group Co., Qingdao, China) was used for column chromatography. LiChroprep RP-18 (25–40 μm) and Sephadex LH-20 (E. Merck Factory, Darmstadt, Germany) were used for column chromatography. Spots were detected on TLC under UV or by heating after spraying with sulfuric acid/ethanol (5:95, v/v).

3.2 Algal material

S. thunbergii was supplied by the Guanghua algae company in Weihai city, Shandong Province of China, in August 2008. It was identified by Dr You Kui, School of Life Sciences, Ocean University of China. A voucher specimen (No. 20080823) has been deposited in the College of Food Sciences and Engineering, Ocean University of China.

3.3 Extraction and isolation

The air-dried and pulverized *S. thunbergii* (2 kg) was extracted with MeOH three times (2 days each time) at room temperature. The extract was concentrated under reduced pressure, and the residue (100 g) was suspended in hot H₂O (50°C, 500 ml). The suspension was extracted successively three times with equal volumes of petroleum ether (60–90°C), AcOEt, and *n*-BuOH, respectively. The phenolic compounds were detected in the AcOEt phase on TLC under UV and by heating after spraying with ferric chloride solution. The AcOEt residue was subjected to a silica gel column chromatography (200–300 mesh) and eluted with a step gradient of petroleum ether/acetone (20:1, 10:1, 5:1, 3:1, and 1:1). Five fractions were collected according to TLC analysis. Fraction 3 (petroleum ether/acetone 5:1, 1 g) was purified by repeatedly

chromatographed over Sephadex-LH₂₀ (MeOH/H₂O 1:1), silica gel column (petroleum ether/AcOEt 3:1), and finally by RP-18 silica gel column (acetone/H₂O 4:1) to afford **1** (1.5 mg) and **2** (0.8 mg).

3.3.1 Compound 1

3.3.1.1 *1-(5-Acetyl-2,4-dihydroxyphenyl)-3-methylbutan-1-one (1)*. Colorless acicular crystals; mp 202–204°C; UV (CHCl₃) λ_{\max} 275 nm; IR (film) ν_{\max} 3470, 2922, 1645, 1459, 1264, 1242, 870, 865 cm⁻¹; ¹H and ¹³C NMR spectral data: see Table 1; ESI-MS: m/z 236 (20, M⁺), 193 (30, [M - C₂H₃O]⁺), 179 (100, [M - C₄H₉]⁺), 161 (30), 133 (5), 105 (8), 77 (6). HR-ESI-MS: m/z 237.1127 [M + H]⁺ (calcd for C₁₃H₁₇O₄, 237.1127).

3.3.2 Compound 2

3.3.2.1 *1-(5-Acetyl-2-hydroxy-4-methoxyphenyl)-3-methylbutan-1-one (2)*. Colorless acicular crystals; mp 198–200°C; UV (CHCl₃) λ_{\max} 265 nm; IR (film) ν_{\max} 3480, 2855, 1650, 1634, 1455, 1236, 870, 860 cm⁻¹; ¹H and ¹³C NMR spectral data: see Table 1; ESI-MS: m/z 250 (3, M⁺), 207 (5, [M - C₂H₃O]⁺), 193 (100, [M - C₄H₉]⁺), 165 (30), 137 (5), 105 (8), 95

(6); HR-ESI-MS: m/z 251.1291 [M + H]⁺ (calcd for C₁₄H₁₉O₄, 251.1283).

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