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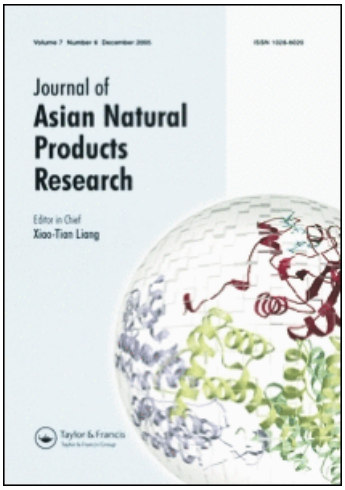

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Chemical constituents of the brown alga *Dictyopteris divaricata*

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A novel sesquiterpene-substituted benzoic acid, named dictyvaric acid (**1**), together with nine known compounds (**2**–**10**), have been isolated from the brown alga *Dictyopteris divaricata* Okam. The structure of **1** was elucidated as 3-[(decahydro-2-hydroxy-2,5,5,8a-tetramethyl-1-naphthalenyl)-methyl]-4-hydroxybenzoic acid by spectroscopic methods, including IR, FABMS, HR-FABMS, 1D and 2D NMR techniques. All compounds were obtained from this species for the first time.

Keywords: Brown alga; *Dictyopteris divaricata* Okam; Sesquiterpene-substituted benzoic acid; Dictyvaric acid; 3-[(Decahydro-2-hydroxy-2,5,5,8a-tetramethyl-1-naphthalenyl)-methyl]-4-hydroxy-benzoic acid

1. Introduction

Dictyopteris divaricata Okam. is a brown alga belonging to the Dictyotaceae family, and is widely distributed along the coast of the Yellow Sea, China. Although various sesquiterpene-substituted phenols [1–4], sesquiterpenes [5–10] and C_{11} hydrocarbons [11–18] have been isolated from species of *Dictyopteris*, few compounds have been reported from the title species [7–9]. In our investigation of the chemical diversity of Chinese seaweeds, a new sesquiterpene-substituted phenol, named dictyvaric acid (**1**) and the nine known compounds 3-farnesyl-*p*-hydroxybenzioc acid (**2**) [19], chromazonarol (**3**) [2,20], fucosterol (**4**) [21], (−)-torreyol (**5**) [22], 4β,5α-dihydroxycubenol (**6**) [10], dehydrovomifoliol (**7**) [23], 3β-hydroxy-5α,6α-epoxy-7-megastigmen-9-one (**8**) [24], loliolide (**9**) [25] and isololiolide (**10**) [26], have been isolated from the ethanolic extract of *D. divaricata* Okam. The structures of the known compounds were determined on the basis of comparing their spectral data with those of reported in the literature. This paper reports the structure elucidation of the new compound (**1**).

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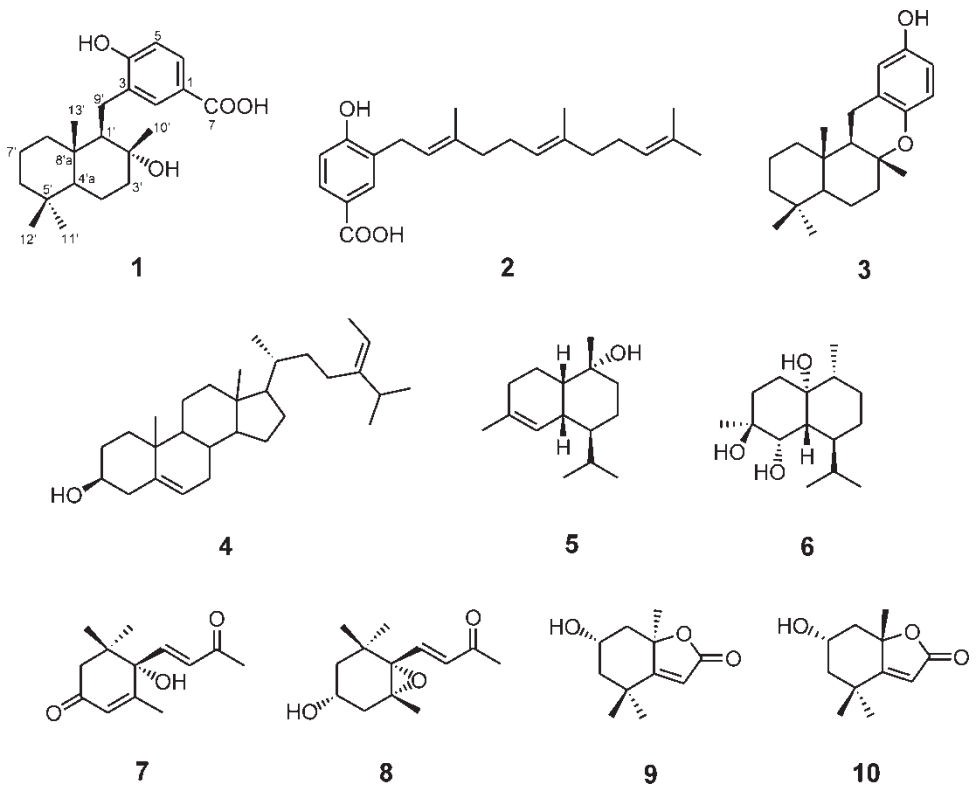

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2. Results and discussion

The EtOAc-soluble fraction of the ethanolic extract of the brown alga *Dictyopteris divaricata* Okam. was chromatographed successively over silica gel, Sephadex LH-20 and by reversed-phase HPLC to afford compounds (**1**–**10**). The structures of the known compounds (**2**–**10**) were identified by comparison of their spectral data with those reported in literature.

Compound **1** (white needles) was assigned a molecular formula of $C_{22}H_{32}O_4$ by negative-ion HR-FABMS at *m*/*z* 359.2248 ($[M - H]^-$). Its IR spectrum (KBr) exhibits a strong, broad absorption band for hydroxyl groups (3429 cm^{-1}), and bands for conjugated carbonyl (1678 cm^{-1}) and an aromatic ring (1614, 1587 and 1502 cm^{-1}). The ^1H NMR spectrum of **1** shows an ABX system at δ 7.63 (1H, dd, $J = 10.5, 2.0$ Hz), 6.68 (1H, d, $J = 10.5$ Hz) and 7.78 (1H, d, $J = 2.0$ Hz), which is attributed to a 1,3,4-trisubstituted benzene moiety, and signals assignable to four methyl groups attached to quaternary carbons at δ 0.77 (3H, s), 0.80 (3H, s), 0.94 (3H, s) and 1.21 (3H, s). The ^{13}C NMR and DEPT spectra of **1** showed 22 carbon signals, including one carboxyl, three quaternary carbons (one oxygenated), two methines and six methylenes besides the signals attributed to four methyl groups and the 1,3,4-trisubstituted benzene moiety (see table 1). These data suggest that compound **1** has a sesquiterpene-substituted phenol structure [2]. A comparison of the ^1H and ^{13}C NMR data of **1** with those of sesquiterpene-substituted phenol yahazunol [2] demonstrated that the 1,4-dihydroxy-phenyl moiety in yahazunol was replaced by the 3-substituted 4-hydyxybenzoic

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		123.1s	5′		34.1s
2	7.78 (d, 1H, 2.0)	134.5d	6′α	1.01 (td, 1H, 13.0, 3.5)	
3		131.1s	6′β	1.26 (m, 1H)	43.0t
4		161.0s	7′α	1.55 (m, 1H)	
5	6.68 (d, 1H, 10.5)	116.7d	7′β	1.27 (m, 1H)	19.3t
6	7.63 (dd, 1H, 10.5, 2.0)	130.2d	8′α	0.57 (td, 1H, 13.0, 3.5)	
7		171.7s	8′β	1.69 (br.d, 1H, 13.0)	41.7t
1′	1.53 (dd, 1H, 11.5, 1.5)	62.9d	8′a		41.0s
2′		75.3s	9′α	2.56 (dd, 1H, 15.0, 11.5)	
3′α	1.48 (td, 1H, 13.0, 3.5)	44.7t	9′β	2.80 (dd, 1H, 15.0, 1.5)	27.3t
3′β	1.84 (dt, 1H, 13.0, 3.5)		10′	1.21 (s, 3H)	24.2q
4′α	1.63 (ddt, 1H, 13.0, 2.0, 3.5)	21.4t	11′	0.80 (s, 3H)	33.9q
4′β	1.30 (ddt, 1H, 13.0, 2.0, 3.5)		12′	0.77 (s, 3H)	21.9q
4′a	0.89 (dd, 1H, 13.0, 2.0)	57.5d	13′	0.94 (s, 3H)	15.9q

a NMR data measured in CD_3OD at 500 MHz for proton and at 125 MHz for carbon; assignments based on DEPT, $^{1}H-^{1}H$ COSY, HMQC and HMBC experiments.

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acid moiety in **1**. The structure of **1** was further confirmed by 2D NMR experiments. The proton signals in the ^{1}H NMR spectrum and carbon signals in ^{13}C NMR spectrum were unambiguously assigned by $^{1}H-^{1}H$ COSY and HMQC experiments (see table 1). In the HMBC spectrum (see figure 1), correlations from H-9′ to C-1′, C-2′ and C-8a′, H-10′ to C-1′, C-2′ and C-3′, both H-11′ and H-12′ to C-4a′, C-5′ and C-6′, H-13′ to C-1′, C-8′ and C-8a′ confirm the sesquiterpene moiety, while correlations from both H-2 and H-6 to C-4 and C-7, and from H-5 to C-1 and C-3 confirm the 3-substituted-4-hydroxybenzoic acid moiety. In addition, the connectivity between the two moieties was established by the correlations from H-9′ to C-2, C-3 and C-4, and from H-2 to C-9′. The NOESY spectrum of **1** exhibits NOE correlations among H-10′, H-12′ and H-13′, and between H-1′ and H-4a′, indicating that **1** and yahazunol possess identical relative stereochemistry (figure 2). Therefore, the structure of **1** was determined as 3-[(decahydro-2-hydroxy-2,5,5,8a-tetramethyl-1-naphthalenyl)-methyl]-4-hydroxybenzoic acid, named dictyvaric acid.

3. Experimental section

3.1 General experimental procedures

Melting points were determined on an XT-4 micro melting point apparatus and are uncorrected. Optical rotations were measured with Perkin–Elmer 241 polarimeter.

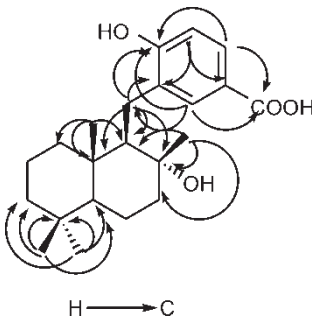

Figure 1. Key HMBC correlations of **1**.

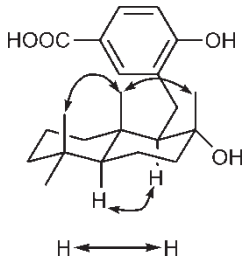

Figure 2. Key NOESY correlations of **1**.

IR spectra were recorded as KBr disks on a Nicolet Impact 400 FT–IR spectrophotometer. NMR spectra were obtained at 500 and 125 MHz for ^{1}H and ^{13}C, respectively, on an Inova 500 MHz spectrometer in CD_3OD with solvent peaks as references. The negative-ion FABMS and HR-FABMS were obtained on a Micromass Autospec-Ultima ETOF spectrometer. Column chromatography was performed with silica gel (200–300 mesh) and Sephadex LH-20. HPLC was performed using an Alltima C18 preparative column (10 μ, 22 × 250 mm). TLC was carried out with glass precoated silica gel GF254 plates. Spots were visualized under UV light or by spraying with 5% sulfuric acid in EtOH followed by heating.

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3.2 Plant material

The brown alga *Dictyopteris divaricata* Okam. was collected at the coast of Qingdao, Shandong, China, in April 2002 and was identified by Dr Kui-Shuang Shao (Institute of Oceanology, Chinese Academy of Sciences).

3.2.1 Extraction and isolation. The brown alga *Dictyopteris divaricata* Okam. (4.40 kg) was extracted with 95% EtOH at room temperature for 3 × 72 h, and the solvent was removed under reduced pressure at $< 40^{\circ}C$ to give a dark residue (320.2 g). The residue was suspended in water and then partitioned with EtOAc. The EtOAc-soluble fraction (120.3 g) was chromatographed over silica gel, eluting with an increasing gradient of Me_2CO (0–100%) in light petroleum. The first fraction, eluted by 20% Me_2CO in light petroleum, was chromatographed over Sephadex LH-20 using light petroleum–$CHCl_3$–MeOH (5:5:1) to afford eight subfractions. The seventh subfraction was further separated by reversed-phase preparative HPLC using MeOH as mobile phase to yield compounds **1** (10 mg) and **2** (30 mg). The fifth subfraction was further separated by reversed-phase preparative HPLC using MeOH–H_2O (80:20) as mobile phase to yield compounds **9** (11 mg) and **10** (9 mg).

The second fraction, eluted by 3% Me_2CO in light petroleum, was chromatographed over Sephadex LH-20 using light petroleum–$CHCl_3$–MeOH (5:5:1) to afford four subfractions. The second subfraction was further separated by reversed-phase preparative HPLC, using MeOH–H_2O (80:20), as mobile phase to yield compound **3** (8 mg), and the third subfraction was recrystallized in acetone to yield compound **4** (15 mg).

The fraction eluted by 2% Me_2CO in light petroleum was recrystallized in acetone to yield compounds **5** (4 mg) and **6** (18 mg). The fraction eluted by 10% Me_2CO in light petroleum was chromatographed over Sephadex LH-20 using light petroleum–$CHCl_3$–MeOH (5:5:1) to afford four subfractions, the fourth of which was further separated by reversed-phase

preparative HPLC, using MeOH–H_2O (80:20) as mobile phase, to yield compounds **7** (8 mg) and **8** (13 mg).

3.3 Dictyvaric acid (1)

White needles (MeOH), mp 256–258°C; $[\alpha]_D^{20} + 29°$ (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} (cm^{-1}); 3429, 2939, 2679, 1678, 1614, 1587, 1450, 1388, 1298, 1244, 1122, 937, 758, 640. ^{1}H NMR (CD_3OD, 500 MHz) and ^{13}C NMR (CD_3OD, 125 MHz) see table 1; negative-ion FABMS *m/z* 359 $[M - H]^-$; negative-ion HR-FABMS *m/z* 359.2248 (calcd for $C_{22}H_{31}O_4$, 359.2222).

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