New Briaranes from the South China Sea Gorgonian *Junceella juncea*

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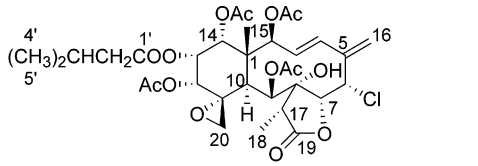
Three new briarane diterpenes, juncins O−Q (**1**−**3**), along with five known briaranes, praelolide, junceellin A, gemmacolide A, gemmacolide B, and junceellolide D, were isolated from the EtOH/CH_2Cl_2 extracts of the South China Sea gorgonian coral *Junceella juncea*. The structures of **1**−**3** were established by extensive spectroscopic analysis, including 1D and 2D NMR data.

Gorgonians belonging to the genus *Junceella* are known to produce highly oxidized diterpenoids of the briarane class (3,8-cyclized cembranoids). About 45 briaranes, three steroids, six *N*-acylsphingosines, and an amine derivative (triacetonamine) have been isolated from the four species of *Junceella*, namely, *J. squamata*, *J. fraglis*, *J. gemmacea*, and *J. juncea*.[1] Among these 55 secondary metabolites, 21 briaranes, including juncins A−H,[2,3] (+)-gemmacolides A and B,[3] juncenolides A−D,[4,5] and junceellolide C,[5] juncins I−M,[6] juncin N,[7] and three steroids[3] were obtained from *J. juncea*. Most briaranes obtained from *Junceella* possess a chloro substituent at C-6 (27 compounds), an 11,20-epoxide group (32 compounds), or a $\Delta^{(11),20}$ double bond (9 compounds). In our current chemical investigation on the South China Sea gorgonian coral *J. juncea*, we have succeeded in obtaining three new briarane diterpenes, juncins O−Q (**1**−**3**), along with five known briaranes. This paper deals with the isolation and structural elucidation of compounds **1**−**3**.



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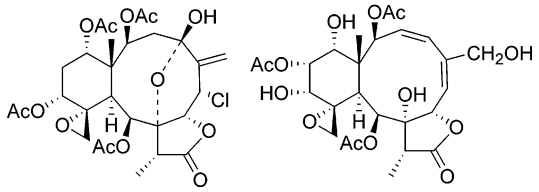

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3

The residue from the EtOH/CH_2Cl_2 extracts of *J. juncea* was partitioned in H_2O and extracted with EtOAc and n-BuOH, respectively. The EtOAc and n-BuOH solubles were chromatographed over silica, and selected fractions were rechromatographed on Sephadex LH-20 and Si gel chromatography to yield eight compounds. All the compounds possessed a briarane-type skeleton, and the known compounds were identified as praelolide,[8] junceellin A,[8] gemmacolide A,[9] gemmacolide B,[9] and junceellolide D[10] by comparison of their spectral data with literature values, respectively. The structures of **1**−**3** are described below.

Juncin O (**1**) had the molecular formula of $C_{33}H_{43}ClO_{14}$ as deduced from NMR spectra and ESIMS, which showed a pair of peaks at *m/z* 699/701 (3:1) $[M + H]^+$, suggesting one chlorine atom in **1**. It showed a UV absorption at λ 220 nm and IR absorptions at ν 3542, 1780, 1750, 1732, and 1720 cm^{-1}, which indicated the presence of a conjugated diene system, a hydroxyl, a γ-lactone, and esters. The ^1H and ^{13}C (DEPT) NMR spectra showed signals for four acetate esters and an isovalerate ester [δ_C 171.7 (s), 42.7 (t), 25.0 (d), 22.3 (2q)], a tertiary methyl (δ_H 1.28, s), a secondary methyl (δ_H 1.23, d, J = 7.5 Hz), a γ-lactone (δ_C 174.4), an exocyclic 11(20)-epoxide [δ_H 2.65 (δ, J = 3 Hz), 2.90 (d, J = 2 Hz), δ_C 49.3 (t), 56.4 (s)],[8,9] a double bond [δ_H 6.90 (d, J = 16 Hz), 5.96 (dd, J = 10, 16 Hz)], an exocyclic methylene [δ_H 5.34, 5.26 (each br s), δ_C 115.2 (t)], an oxygenated quaternary carbon, and six oxygenated methines (Tables 1 and 2). These data showed that **1** was a briarane-type diterpene, similar to the structures of gemmacolide B,[9] juncins A−F,[2] and junceellolide C.[5] Comparison of the ^1H and ^{13}C NMR spectral data of **1** with those of gemmacolide B revealed that the only difference between them was that **1** showed an additional double bond [δ_H 6.90 (d, J = 16 Hz), 5.96 (dd, J = 10, 16 Hz), δ_C 133.4 (d), 129.7 (d)] instead of two higher field methylenes. The double bond was placed between C-3 and C-4, which was supported by the presence of a UV absorption at λ 220 nm and HMBC correlations (Table 3). The large coupling constant (16.0 Hz) between H-2 and H-3 suggested the uncommon *E* configuration. Four acetate moieties were assigned to C-2, C-9, C-12, and C-14 because their carbonyl carbons were correlated with the corresponding methine protons in the HMBC spectrum, and the isovalerate group was attached to C-13 because of the existence of HMBC correlations between H-13/2′/3′ and C-1′ (δ_C 171.7) (Table 3). In the NOESY spectrum of **1**, NOE correlations between Me-15 and H-13/14/20/9-OAc, H-20 and H-12, and H-6 and H-9-OAc suggested that H-20, H-13, H-12, H-14, and Me-15 were all in the β-orientation (Figure 1). NOE correlations of H-2 with H-10, H-9 with H-10/OH-8, and Me-18 with H-9/10 indicated that H-2, H-9, H-10, OH-8, and Me-18 were all in the α-orientation, with a corresponding correlation of H-17 with H-7 suggesting the β-orientation of H-17 and H-7 (Figure 1). On the basis of NOESY correlations (Figure 1) and the measured coupling constants (Table 2), the relative stereochemistry of juncin O (**1**) was

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Table 1. ^{13}C NMR Spectral Data for Compounds **1**−**3** and Gemmacolide B[a]

carbon	**1**	**2**	**3**	gemmacolide B
1	48.3 qC	45.6 qC	48.3 qC	47.2 qC
2	75.5 CH	72.6 CH	75.8 CH	72.6 CH
3	133.4 CH	40.5 CH_2	132.5 CH	28.2 CH_2
4	129.7 CH	97.4 qC	128.3 CH	33.4 CH_2
5	142.0 qC	138.0 qC	147.0 qC	146.5 qC
6	64.9 CH	55.3 CH	121.6 CH	53.6 CH
7	72.5 CH	78.6 CH	81.8 CH	71.4 CH
8	82.8 qC	81.6 qC	82.0 qC	81.3 qC
9	80.5 CH	71.6 CH	65.7 CH	81.2 CH
10	33.6 CH	36.0 CH	31.3 CH	35.3 CH
11	56.4 qC	56.5 qC	60.4 qC	56.8 qC
12	73.8 CH	73.6 CH	76.6 CH	73.5 CH
13	66.3 CH	28.8 CH_2	70.0 CH	66.5 CH
14	73.2 CH	73.3 CH	77.3 CH	73.0 CH
15	14.7 CH_3	14.8 CH_3	13.8 CH_3	14.2 CH_3
16	115.2 CH_2	117.9 CH_2	63.0 CH_2	121.1 CH_2
17	50.2 CH	50.0 CH	45.6 CH	51.4 CH
18	6.9 CH_3	6.9 CH_3	7.4 CH_3	6.8 CH_3
19	174.4 qC	174.0 qC	176.9 qC	174.3 qC
20	49.3 CH_2	50.0 CH_2	47.5 CH_2	50.4 CH_2
OAc	169.2 qC	169.1 qC	168.2 qC	169.1 qC
	169.8 qC	169.4 qC	170.3 qC	169.3 qC
	170.0 qC	169.5 qC	171.0 qC	170.0 qC
	170.2 qC	173.3 qC		171.3 qC
	21.2 CH_3	20.8 CH_3	20.8 CH_3	20.5 CH_3
	21.3 CH_3	20.9 CH_3	21.1 CH_3	20.8 CH_3
	22.3 CH_3	21.1 CH_3	21.4 CH_3	21.2 CH_3
	22.4 CH_3	21.5 CH_3		21.6 CH_3
1′	171.7 qC			171.7 qC
2′	42.7 CH_2			42.6 CH_2
3′	25.0 CH			24.9 CH
4′, 5′	22.3 2CH_3			22.3 2 CH_3

[a] All compounds were determined at 125 MHz with TMS as internal standard; **1**, **2**, and gemmacolide B were determined in $CDCl_3$, while **3** was measured in pyridine-d_5; chemical shifts are in ppm.

determined to be 1*R**, 2*S**, 3*E*, 6*S**, 7*R**, 8*R**, 9*S**, 10*S**, 11*R**, 12*R**, 13*R**, 14*R**, and 17*R**.

Juncin P (**2**) exhibited a molecular ion peak at *m/z* 615/617 (3:1) $[M + H]^+$ in its ESIMS. Together with ^1H and ^{13}C NMR spectral data, a molecular formula of $C_{28}H_{35}ClO_{13}$ was established and confirmed by HRESIMS. The infrared

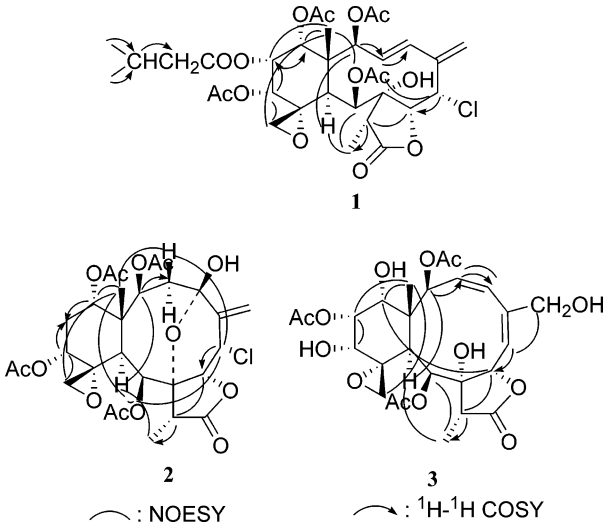

Figure 1. Key NOESY and $^1H-^1H$ COSY correlations for compounds **1**−**3**.

spectrum of **2** showed strong carbonyl absorption at 1790 cm^{-1}, indicating a γ-lactone. Another strong infrared absorption was observed at 3542 cm^{-1}. This observation, in combination with a D_2O exchangeable proton singlet at δ_H 6.58 in the ^1H NMR spectrum, showed **2** to possess a hydroxyl functionality. The hydroxyl group was concluded to be part of a hemiketal constellation on the basis of a characteristic carbon signal at δ_C 97.4 (a quaternary hemiketal carbon) in the ^{13}C NMR spectrum. Comparison of overall ^1H and ^{13}C NMR spectral data revealed similarities between **2** and **1**. However, there were several significant differences in the spectral data. The ^1H and ^{13}C (DEPT) NMR spectra of **2** showed an additional hemiketal carbon (δ_C 97.4) and two additional higher field methylenes [δ_C 40.5, 28.8, δ_H 3.41 (dd, J = 7.7, 16.3 Hz), 1.60 (d, J = 16.3 Hz), 2.00 (dt, J = 16.3, 2.5 Hz), 2.31 (dt, J = 16.3, 2.5 Hz)], but lacked signals for a double bond, an isovalerate ester, and an oxygenated methine (Tables 1 and 2). In the HMBC spectrum of **2**, correlations of δ_C 97.4 with H-2 (δ_H 5.44, d, J = 7.5 Hz), −OH (δ_H 6.58), and H-16 (δ_H 5.65,

Table 2. ^1H NMR Spectral Data of Compounds **1**−**3**[a]

H	**1**	**2**	**3**
2	5.59 (d, 10)	5.44 (d, 7.5)	6.55 (d, 10.7)
3	5.96 (dd, 10, 16)	3.41 (dd, 7.7, 16.3), 1.60 (d, 16.3)	6.54 (t, 10.7, 10.2)
4	6.90 (d, 16)		6.33 (d, 10.2)
6	5.29 (d, 2.5)	4.90 (d, 2.4)	6.53 (d, 8.3)
7	4.16 (d, 2.5)	4.33 (d, 2.7)	5.64 (d, 8.3)
9	5.13 (br s)	5.67 (br s)	5.52 (br s)
10	3.77 (br s)	3.29 (br s)	4.33 (br s)
12	4.88 (d, 3.0)	4.53 (br s)	4.05 (br s)
13	5.20 (t, 3.5)	2.00, 2.31 (each dt, 16.3, 2.5)	5.23 (br s)
14	5.29 (d, 4.0)	5.03 (br s)	4.30 (br s)
15	1.28 (s)	1.27 (s)	1.24 (s)
16	5.34, 5.26 (each br s)	5.65, 5.93 (each br s)	4.63, 5.44 (each d, 16.3)
17	2.85 (q, 7.0)	2.76 (q, 7.0)	3.05 (q, 7.0)
18	1.23 (d, 7.5)	1.38 (d, 7.0)	1.63 (d, 7.0)
20	2.65 (d, 3), 2.90 (d, 2)	2.49 (d, 3.2), 2.80 (d, 2.8)	2.81, 3.50 (each br s)
2-OAc	2.01 (s)	2.07 (s)	1.85 (s)
9-OAc	2.15 (s)	2.25 (s)	2.26 (s)
12-OAc	2.10 (s)	2.05 (s)	
13-OAc			1.97 (s)
14-OAc	2.09 (s)	2.05 (s)	
2′	2.09 (2H, m)		
3′	1.99 (1H, m)		
4′ and 5′	0.93 (6H, d, 6.5)		
OH	3.10 (s)	6.58 (s)	

[a] All compounds were determined at 500 MHz; **1** and **2** were determined in $CDCl_3$, while **3** was measured in pyridine-d_5; chemical shift values δ are in ppm, and coupling constant values J in Hz.

Table 3. HMBC Correlation Data of Compounds **1**−**3**

H	1	2	3
2	C-1, 3, 4, 10, 14, 15, Me*C*OO	C-1, 3, 4, 10, 14, 15, Me*C*OO	C-1, 3, 4, 10, 14, 15, Me*C*OO
3	C-1, 2, 5	C-1, 2, 5	C-1, 2, 5
4	C-2, 6		C-2, 6
6	C-4, 5, 7, 16	C-5, 16	C-4, 5, 16
7	C-5, 6, 9	C-5, 6, 8	C-5, 6, 8, 9
9	C-1, 7, 8, 10, 11, 17, Me*C*OO	C-1, 7, 8, 10, 11, 17, Me*C*OO	C-1, 7, 8, 10, 11, 17, Me*C*OO
10	C-1, 2, 8, 9, 11, 12, 14, 15, 20	C-1, 2, 8, 9, 11, 12, 15, 20	C-1, 2, 8, 9, 11, 12, 14, 15, 20
12	C-11, 13, 14, Me*C*OO	C-10, 11, 13, 14, Me*C*OO	C-11, 13, 14
13	C-1, 12, 1′	C-1, 11, 12, 14	Me*C*OO
14	C-1, 12, 13, Me*C*OO	C-1, 2, 10, 12, 13, Me*C*OO	C-1
15	C-1, 2, 10, 14	C-1, 10, 14	C-1, 2, 10, 14
16	C-4, 5, 6	C-4, 5, 6	C-4, 5, 6
17	C-8, 9, 18, 19	C-8, 9, 18, 19	C-8, 9, 18, 19
18	C-8, 17, 19	C-8, 17, 19	C-8, 17, 19
20	C-11, 12	C-11, 12	C-11, 12
2′	C-1′, 3′, 4′, 5′		
3′	C-1′, 2′, 4′, 5′		
4′	C-2′, 3′, 5′		
5′	C-2′, 3′, 4′		
OH	C-8	C-2, 3, 4, 5, 6	

5.93, each br s) allowed the assignment of C-4 (δ_C 97.4), and a weak *W* correlation of C-4 with H-17 (δ_H 2.76, q, 7.0) indicated an ether linkage between C-4 and C-8. This was rare that the briarane class of marine diterpenoids possessed a hemiketal group at C-4 which was connected to C-8 by an ether linkage. The previous examples were junceellolide A,[10] pteroidine,[11] and 4-hydroxymiloline C.[12] The assignment of C-3 (δ_C 40.5, t) was inferred from the HSQC spectrum and ^{1}H−^{1}H COSY spectrum with the cross-peaks between H-2 and δ_H 3.41 (dd, J = 7.7, 16.3 Hz). Meanwhile, HMBC correlations of δ_H 2.00, 2.31 (each dt, J = 16.3, 2.5 Hz) with C-11, C-1, and C-14 allowed the assignment of H-13 [δ_H 2.00, 2.31 (each dt, J = 16.3, 2.5 Hz)] and corresponding C-13 (δ_C 28.8, t). Four acetate moieties were assigned to C-2, C-9, C-12, and C-14 because of their HMBC correlations in the HMBC spectrum of **2** (Table 3). In the NOESY spectrum of **2**, NOE cross-peaks of Me-15 with H-3β/14/20/9-OAc, H-20 with H-12, and H-3β with H-6/4-OH suggested the β-configuration of H-6, H-20, OH-4, H-12, H-14, and Me-15, while NOE correlations of H-2 with H-10, H-9 with H-10, and Me-18 with H-10 indicated the α-configuration of H-2, H-9, H-10, and Me-18, with corresponding correlation of H-17 with H-7 suggesting the β-orientation of H-17 and H-7 (Figure 1). On the basis of the above evidence, the relative stereochemistry of juncin P (**2**) was determined as 1*R**, 2*S**, 4*S**, 6*S**, 7*R**, 8*R**, 9*S**, 10*S**, 11*R**, 12*R**, 14*S**, and 17*R**.

Juncin Q (**3**) was assigned the molecular formula of $C_{26}H_{34}O_{13}$ on the basis of its ESIMS and ^{13}C (DEPT) NMR spectra. Its IR and UV spectra indicated the presence of hydroxyls (3480 cm^{-1}), a γ-lactone (1779 cm^{-1}), esters (1743 cm^{-1}), and a conjugated diene system (274 nm). Comparison of overall ^{1}H and ^{13}C NMR spectral data revealed similarities between **3** and **1**. The most obvious difference between them was the lack of a chlorine atom and an exocyclic methylene group in **3**. These groups were replaced by a trisubstituted olefin [δ_H 6.53 (d, J = 8.3 Hz), δ_C 121.6 (d), 147.0 (s)] and an oxymethylene group [δ_H 4.63, 5.44 (each d, J = 16.3 Hz), δ_C 63.0 (t)]. The same type of replacement had previously been observed in compounds gemmacolide F and juncenolides B−D.[5,9] The ^{1}H and ^{13}C (DEPT) NMR spectra of **3** showed signals for three acetates instead of five esters in **1** (Tables 1 and 2). The three acetoxyl groups were assigned to C-2, C-9, and C-13 because their carbonyl carbons were correlated with the corresponding methine protons in the HMBC spectrum of **3** (Table 3), and the loss of one acetate group and one isovalerate group in **3** could be explained by the replacements of acetate groups at C-12 and C-14 by hydroxyl groups. These were proved by the HMBC spectrum (Table 3). The relative stereochemistry of **3** was determined from a NOESY spectrum. NOE correlations between Me-15 and H-13/14/20 and between H-13 and H-12 in **3** suggested that H-20, H-13, H-12, H-14, and Me-15 were all in the β-orientation. Correlations of H-2 with H-10, H-9 with H-10, and Me-18 with H-9/10 indicated that H-2, H-9, H-10, and Me-18 were all in the α-orientation; correspondingly, correlation of H-17 with H-7 suggested the β-orientation of H-17 and H-7. Meanwhile, correlations of H-3 with H-4 and H-6 with H-16 suggested the 3*Z* and 5*E* orientation (Figure 1). Thus, the relative stereochemistry of juncin Q (**3**) was proposed as 1*R**, 2*S**, 3*Z*, 5*E*, 7*S**, 8*R**, 9*S**, 10*S**, 11*R**, 12*R**, 13*R**, 14*R**, and 17*R**.

Experimental Section

General Experimental Procedures. Optical rotations were measured with a Horiba SEAP-300 spectropolarimeter. UV spectra were measured with a Shimadzu double-beam 210A spectrophotometer in MeOH solution. IR (KBr) spectra were obtained on a Bio-Rad FTS-135 infrared spectrophotometer. ^{1}H, ^{13}C NMR and 2D NMR spectra were recorded on a Bruker DRX-500 MHz NMR spectrometer with TMS as internal standard. MS spectral data were obtained on an LCQ^{DECA} XP HPLC/MS^n spectrometer for ESIMS. Si gel (200−300 mesh) for column chromatography and GF_{254} for TLC were obtained from the Qindao Marine Chemical Factory, Qindao, People's Republic of China.

Animal Material. The South China Sea gorgonian coral *Junceella juncea* (Ellisellidae) (12 kg, wet weight) was collected in Sanya, Hainan Province, China, in October 2003 and identified by Prof. Zou R. L., the South China Sea Institute of Oceanology, Academia Sinica. A voucher specimen (No. 0310) was deposited in the South China Sea Institute of Oceanology, Academia Sinica, Guangzhou, China.

Extraction and Isolation. The frozen specimen was extracted with EtOH/CH_2Cl_2 (2:1) three times at room temperature, and the solvent was evaporated in vacuo. The residue was partitioned in H_2O and extracted with EtOAc and n-BuOH three times, respectively. The EtOAc and n-BuOH extracts were concentrated in vacuo to afford 85 and 56 g of residue, respectively. The EtOAc portion was subjected to column chromatography (CC) on silica, using petroleum ether/EtOAc (from 10:1 to 0:10) as eluent. By combining the fractions with TLC (GF_{254}) monitoring, 12 fractions were obtained. Fraction 4 was subjected to CC on silica gel, eluted with $CHCl_3$/Me_2CO (10:1), to afford junceellin A (36 mg). Fraction 5 was subjected

to CC on silica gel, eluted with $CHCl_3/Me_2CO$ (from 10:1 to 9:1), to give three subfractions (A−C). Fractions A and B were chromatographed over Sephadex LH-20 eluting with $CHCl_3$/MeOH (1:1), respectively, then subjected to CC on silica gel, eluted with $CHCl_3$/MeOH (10:1), to yield junceellolide D (25 mg), gemmacolide B (29 mg), praelolide (38 mg), and juncin O (**1**) (18 mg), respectively. Fraction 6 was chromatographed over Sephadex LH-20 eluting with $CHCl_3$/MeOH (1:1), then subjected to CC on silica gel, eluted with $CHCl_3$/MeOH (11:1), to give gemmacolide A (21 mg) and juncin P (**2**) (16 mg). The n-BuOH portion was passed through a column of highly porous absorption resin (Diaion HP-20), eluting with H_2O and methanol. The methanol fraction (35 g) was subjected to column chromatography (CC) on silica gel, eluted with $CHCl_3$/MeOH gradients (from 1:0 to MeOH), to give juncin Q (**3**) (26 mg).

Juncin O (1): white powder; $[\alpha]_D$ +36° (*c* 1.0, $CHCl_3$); UV (MeOH) λ_{max} 220 nm; IR (KBr) ν_{max} 3542, 1780, 1750, 1732, 1720, 1450, 1389, 1065 cm^{-1}; ^1H NMR spectral data, see Table 2; ^{13}C NMR spectral data, see Table 1; ESIMS(+) *m/z* 699 $[M + H]^+$; HRESIMS *m/z* 699.2412 $[M + H]^+$ (calcd for $C_{33}H_{44}ClO_{14}$, 699.2419).

Juncin P (2): white powder; $[\alpha]_D$ −6.8° (*c* 0.24, $CHCl_3$); IR (KBr) ν_{max} 3542, 1790, 1750, 1738, 1720, 1450, 1389, 1031 cm^{-1}; ^1H NMR spectral data, see Table 2; ^{13}C NMR spectral data, see Table 1; ESIMS(+) *m/z* 615 $[M + H]^+$; HRESIMS *m/z* 615.1839 $[M + H]^+$ (calcd for $C_{28}H_{36}ClO_{13}$, 615.1844).

Juncin Q (3): white powder; $[\alpha]_D$ −14° (*c* 0.4, pyridine); UV (MeOH) λ_{max} 274 nm; IR (KBr) ν_{max} 3564, 3480, 1779, 1743, 1646, 1458, 1335, 1067, 984 cm^{-1}; ^1H NMR spectral data, see Table 2; ^{13}C NMR spectral data, see Table 1; ESIMS(+) *m/z* 555 $[M + H]^+$; HRESIMS *m/z* 555.2070 $[M + H]^+$ (calcd for $C_{26}H_{35}O_{13}$, 555.2077).

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References and Notes

(1) Sung, P. J.; Guo, H. H.; Fan, T. Y.; et al. *Biochem. Syst. Ecol.* **2004**, *32* (2), 185−196.
(2) Isaacs, S.; Carmely, S.; Kashman, Y. *J. Nat. Prod*. **1990**, *53*, 596−602.
(3) Anjaneyulu, A. S. R.; Rao, N. S. K. *J. Chem. Soc.*, *Perkin Trans. 1* **1997**, 959−962.
(4) Shen, Y. C.; Lin, Y. C.; Chiang, M. Y. *J. Nat. Prod.* **2002**, *65*, 54−56.
(5) Shen, Y. C.; Lin, Y. C.; Ko, C. L.; Wang, L. T. *J. Nat. Prod.* **2003**, *66*, 302−305.
(6) Anjaneyulu, A. S. R.; Rao, V. L.; Sastry, V. G.; Venugopal, M. J. R. V.; Schmitz, F. J. *J. Nat. Prod.* **2003**, *66*, 507−510.
(7) Sung, P. J.; Fan, T. Y.; Fang, L. S.; Sheu, J. H.; Wu, S. W.; Wang, G. H.; Lin, M. R. *Heterocycles* **2003**, *61*, 587−592.
(8) Lin, Y.; Long, K. *Zhongshan Daxue Xuebao, Ziran Kexueban* **1983**, *2*, 46−51.
(9) He, H. Y.; Faulkner, D. J. *Tetrahedron* **1991**, *47*, 3271−3280.
(10) Shin, J.; Park, M.; Fenical, W. *Tetrahedron* **1989**, *45*, 1633−1638.
(11) Clastres, A.; Ahond, A.; Poupat, C.; Potier, P.; Kan, S. K. *J. Nat. Prod.* **1984**, *47*, 155−161.
(12) Kwak, J. H.; Schmitz, F. J.; Williams, G. C. *J. Nat. Prod*. **2001**, *64*, 754−760.

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