

## Study on the Chemical Constituents of the South China Sea Gorgonian *Junceella juncea*

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**A new steroidal glycoside—4'-*O*-acetyl-3-*O*-[ $\beta$ -D-arabino-pyranosyl-oxy]-cholest-5-ene-3 $\beta$ ,19-diol (1), and a new glycerol derivative—1,2-*O*-[2'-hydroxyoctadecyl]-glycerol (2), along with 16 known compounds were isolated from the EtOH/CH<sub>2</sub>Cl<sub>2</sub> extracts of the South China Sea gorgonian coral *Junceella juncea*. The structures of 1 and 2 were established by extensive spectroscopic analysis, including 1D and 2D NMR data.**

**Key words** *Junceella juncea*; gorgonian; chemical constituent; steroidal glycoside; glycerol derivative

According to literatures, 39 briarane-type diterpenoids, three steroids, six *N*-acylsphingosines and an amine derivative (triacetonamine) had been isolated from the four species of *Junceella*, namely, *J. squamata*, *J. fragilis*, *J. gemmacea* and *J. juncea*.<sup>1)</sup> Among these 49 secondary metabolites, 15 briaranes, including juncins A—H,<sup>2,3)</sup> (+)-gemmacolides A—B,<sup>3)</sup> juncenolides A—D,<sup>4,5)</sup> juncellolide C,<sup>5)</sup> and three steroids, namely, 24 $\alpha$ -methylcholest-7,22-dien-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol,<sup>3)</sup> 24 $\alpha$ -methylcholest-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ ,25-tetrol<sup>3)</sup> and 24 $\alpha$ -methylcholest-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol-25-monoacetate<sup>3)</sup> were obtained from *J. juncea*. During the course of our investigation on the chemical constituents of the South China Sea gorgonian coral *J. juncea*, a new steroidal glycoside—4'-*O*-acetyl-3-*O*-[ $\beta$ -D-arabino-pyranosyl-oxy]-cholest-5-ene-3 $\beta$ ,19-diol (1), and a new glycerol derivative—1,2-*O*-[2'-hydroxyoctadecyl]-glycerol (2), along with 16 known compounds were obtained. The 16 known compounds were identified as four sterols, namely, 24 $\alpha$ -methylcholest-7,22-dien-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol (3),<sup>3)</sup> 24 $\alpha$ -methylcholest-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol-25-monoacetate (4),<sup>3)</sup> 24 $\alpha$ -methylcholest-3 $\beta$ ,5 $\alpha$ ,6 $\beta$ -triol (5),<sup>3)</sup> 24 $\alpha$ -methylcholest-5,23-dien-3 $\beta$ -ol (6),<sup>6)</sup> five briarane diterpenes, namely, praelolide (7),<sup>7)</sup> juncellin A (8),<sup>7)</sup> gemmacolide A (9),<sup>8)</sup> gemmacolide B (10),<sup>8)</sup> juncellolide D (11),<sup>9)</sup> six amine derivatives, namely, 1-*O*- $\beta$ -D-glucopyranosyl-(2*S*,3*S*,4*R*,8*Z*)-2-*N*-(2'-hydroxypalmitoyl) octadecaspingina-8-ene (12),<sup>10)</sup> (2*S*,3*R*)-2-*N*-palmitoyloctadecaspingina (13),<sup>6)</sup> (2*S*,3*R*,4*E*)-2-*N*-palmitoyl-octadecaspingina-4-ene (14),<sup>6)</sup> thymine (15),<sup>6)</sup> uracil (16),<sup>6)</sup> adenosine (17),<sup>11)</sup> and batyl alcohol (18)<sup>6)</sup> by NMR spectral analysis in comparison with authentic sample, respectively. It was the first time that steroidal glycoside was isolated from *Junceella*. Compound 2 was a batyl alcohol derivative which was firstly obtained from gorgonian coral and was used as a medicine for increasing human leucocyte in clinic. Glycerides were widely distributed in nature, but literatures about glycerol ether were few. This type of glycerol ether derivatives such as batyl alcohol (glyceryl 1-octadecyl ether), batyl- $\alpha$ -palmitate,<sup>12)</sup> batyl- $\alpha$ -stearate<sup>13)</sup> had been isolated from gorgonian coral and soft coral. It was interesting that glycerol derivative isolated from coral were mostly batyl alcohol derivatives. This paper deals with the isolation and structural elucidation of compounds 1 and 2.

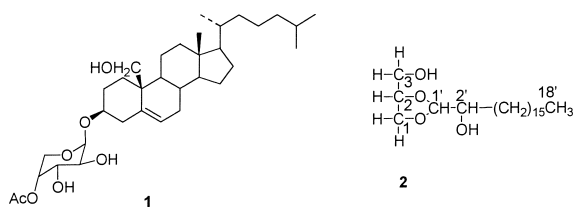
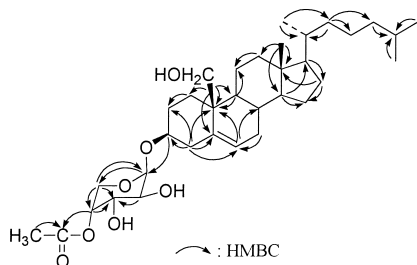
### Results and Discussion

Compound 1 was obtained as white powder, showing the molecular formula of C<sub>34</sub>H<sub>58</sub>O<sub>7</sub> as determined by negative ion ESI-MS and NMR spectra. Its IR spectrum showed absorption bands for a glycosidic structure (3350, 1066 cm<sup>-1</sup>). With the assistance of 2D NMR studies, including <sup>1</sup>H-<sup>1</sup>H COSY, HMQC and HMBC experiments, all of the assignments of <sup>13</sup>C- and <sup>1</sup>H-NMR data of 1 were determined. The <sup>1</sup>H-NMR spectrum exhibited signals for one tertiary methyl at  $\delta_{\text{H}}$  0.82 (3H, s), three secondary methyls at  $\delta_{\text{H}}$  1.0 (3H, d,  $J=6.5$  Hz), 1.09 (6H, d,  $J=6.4$  Hz), and an acetate methyl at  $\delta_{\text{H}}$  2.17 (3H, s). The <sup>13</sup>C (DEPT)-NMR spectra showed 34 carbon signals, including 27 basic skeleton carbons, a pentose unit [ $\delta_{\text{C}}$  99.1 (d), 70.7 (d), 68.8 (d), 73.2 (d), 61.6 (t)] and an acetyl [ $\delta_{\text{C}}$  170.7 (s), 21.0 (q)]. Two carbon signals at  $\delta_{\text{C}}$  62.9 (t) and 77.8 (d) indicated that one methyl and one methylene were oxygenated in the basic skeleton of 1. These data suggested that 1 was a cholest-type monoglycoside.

Comparison with the <sup>13</sup>C- and <sup>1</sup>H-NMR spectral data of cholest-5-ene-3 $\beta$ ,7 $\beta$ ,19-triol<sup>14)</sup> and other analogous cholestane derivatives,<sup>14-16)</sup> the NMR spectra of 1 permitted us to assign the signals of Me-18 ( $\delta_{\text{H}}$  0.82, s), Me-21 ( $\delta_{\text{H}}$  1.0, d,  $J=6.5$  Hz), Me-26/Me-27 ( $\delta_{\text{H}}$  1.09, d,  $J=6.4$  Hz), H-19 ( $\delta_{\text{H}}$  4.11 and 3.86, each 1H, d,  $J=11.3$  Hz), H-3 ( $\delta_{\text{H}}$  3.52, 1H, m) and H-6 ( $\delta_{\text{H}}$  5.64, 1H, br s), indicating the oxygenation of C-3 ( $\delta_{\text{C}}$  77.5, d), C-19 ( $\delta_{\text{C}}$  62.8, t) and a double bond between C-5/C-6 [ $\delta_{\text{C}}$  137.7 (s, C-5), 125.3 (d, C-6)]. These were supported by the HMBC spectrum (Fig. 2). NOE interactions between H-3 with H-4 $\alpha$  [ $\delta_{\text{H}}$  2.74, br d,  $J=10.2$  Hz], and H-19 with H-4 $\beta$  [ $\delta_{\text{H}}$  2.58, t,  $J=11.9$  Hz] in the NOESY spectrum, indicated a 3 $\beta$ -hydroxy substituent. According to all the above data, the aglycone moiety of 1 was inferred to be cholest-5-ene-3 $\beta$ ,19-diol.

Furthermore, comparison with those NMR data of sugar moiety in 3-*O*-[ $\beta$ -D-arabino-pyranosyl-oxy]-24(*S*)-campesta-5-ene-3 $\beta$ ol,<sup>6)</sup> 3-*O*-[ $\beta$ -D-arabino-pyranosyl-oxy]-24-methylcholest-5-ene-3 $\beta$ ,25-diol<sup>17)</sup> and 3'-*O*-acetyl-4-*O*-[ $\beta$ -D-arabino-pyranosyl-oxy]-pregn-20-ene-3 $\beta$ ,4 $\alpha$ -triol,<sup>18)</sup> the NMR data of a pentose unit [ $\delta_{\text{C}}$  99.1 (d, C-1'), 70.7 (d, C-2'), 68.8 (d, C-3'), 73.2 (d, C-4'), 61.6 (t, C-5'),  $\delta_{\text{H}}$  5.56 (1H, d,  $J=3.2$  Hz, H-1'), 4.53 (1H, dd,  $J=3.2, 9.8$  Hz, H-2'), 4.62 (1H, dd,  $J=3.1, 9.7$  Hz, H-3'), 5.74 (1H, br s, H-4'), 4.24, 4.00 (each 1H, d,  $J=12.4$  Hz, H-5')] in 1 indicated the exist-

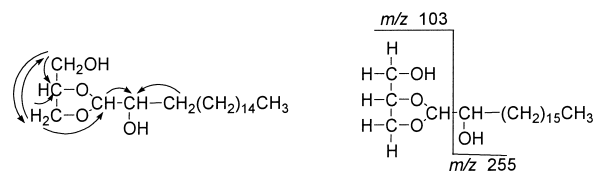
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Fig. 1. Structures of Compounds **1** and **2**Fig. 2. Key HMBC Correlations of Compound **1**

tence of a  $\beta$ -D-arabinopyranosyl unite. This was supported by acid hydrolysis of **1** with 2 mol/l HCl affording D-arabinose as the carbohydrate component. The  $J$  value of the anomeric proton ( $J=3.2$  Hz) indicated the  $\beta$ -orientation at the anomeric center of D-arabinose. The down-field chemical shift of H-4' and the HMBC correlation of H-4' with  $\delta_C$  171.0 (s) in the HMBC spectrum suggested an acetyl attached to the hydroxyl of C-4'. In addition, HMBC correlations of H-3, H-2' and H-5' with C-1' indicated that the  $\beta$ -D-arabinopyranosyl unit was placed at the aglycone C-3. Based on the above evidence, the structure of **1** was elucidated to be 4'-O-acetyl-3-O-[ $\beta$ -D-arabino-pyranosyl-oxy]-cholest-5-ene-3 $\beta$ ,19-diol (Fig. 1).

Compound **2** was obtained as white powder. It showed in its negative-ion ESI-MS spectrum a quasimolecular ion peak at  $m/z$  357  $[M-1]^-$  in accordance with the formula of  $C_{21}H_{42}O_4$  as determined by HR-ESI-MS, and confirmed from the  $^{13}C$  and DEPT NMR spectra. Its IR showed absorption at  $\nu$  3420 and  $3350\text{ cm}^{-1}$ , which indicated the presence of hydroxyls. In the  $^{13}C$  (DEPT)- and  $^1H$ -NMR spectra of **2**, a long hydrocarbon chain was observed with the characteristic signals at  $\delta_C$  14.0 (q), 31.9 (t), 25.4 (t), 22.6 (t), 31.8 (t) and 29.1–29.7 (t), correspondingly  $\delta_H$  0.88 (3H, t,  $J=6.5$  Hz), 1.55, 1.51 (each 1H, m), 1.53, 1.47 (each 1H, m) and 1.35–1.25 (26H, m), together with a characteristic acetal carbon [ $\delta_C$  105.6 (d),  $\delta_H$  4.90 (1H, d,  $J=3.5$  Hz)]. The NMR spectra of **2** also showed the presence of an unsymmetrically substituted glycerol moiety with signals at  $\delta_C$  76.2 (d, C-2), 66.7 (t, C-1) and 62.6 (t, C-3), and correspondingly  $\delta_H$  4.14 (1H, dd,  $J=6.7, 8.0$  Hz, H-1a), 3.75 (1H, dd,  $J=6.8, 8.0$  Hz, H-1b), 4.29 (1H, m, H-2), 3.74 (1H, dd,  $J=3.8, 11.9$  Hz, H-3a), 3.65 (1H, dd,  $J=5.5, 11.9$  Hz, H-3b). This was supported by the HMBC correlations of H-1, H-3 with C-2, H-1 with C-3, and H-3 with C-1 in the HMBC spectrum of **2** (Fig. 3).

The HMBC spectrum also showing the correlations of H-1, H-2 with C-1' ( $\delta_C$  105.6, d) indicated the acetal carbon C-1' attached to C-1 and C-2 of the glycerol moiety by ether bond, which was supported by the basal fragment at  $m/z$  103  $[M-255]^+$  in the EI-MS spectrum (Fig. 3). Furthermore,

Fig. 3. Key HMBC Correlations and Main EI-MS Mass Fragments of Compound **2**

HMBC correlations of H-3' ( $\delta_H$  1.55 and 1.51, each 1H, m), H-1' ( $\delta_H$  4.90, 1H, d,  $J=3.5$  Hz) with C-2' ( $\delta_C$  71.9, d), and H-2' ( $\delta_H$  3.58, 1H, dt,  $J=3.5, 8.6$  Hz) with C-1', C-3' ( $\delta_C$  31.9, t), and  $^1H$ - $^1H$  COSY correlations of H-3' with H-2', H-2' with H-1' in the  $^1H$ - $^1H$  COSY spectrum, suggested the acetal carbon C-1' and the long hydrocarbon chain attached to the same oxymethine C-2', respectively. According to the integral of  $\delta_H$  1.35–1.25 (26H, m) in the  $^1H$ -NMR spectrum and the quasimolecular ion peak at  $m/z$  357  $[M-1]^-$  in the negative-ion ESI-MS spectrum, the long hydrocarbon chain was inferred to be hexadecyl unit. Based on these data, the structure of **2** was elucidated as 1,2-O-[2'-hydroxyoctadecyl]-glycerol (Fig. 1).

## Experimental

**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.  $^1H$ -,  $^{13}C$ -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 a LCQ<sup>DECA</sup> XP HPLC/MS<sup>n</sup> spectrometer for ESI-MS. Si gel (200–300 mesh) for column chromatography and GF<sub>254</sub> for TLC were obtained from the Qindao Marine Chemical Factory, Qindao, People's Republic of China.

**Animal Material** The South China Sea gorgonian coral *J. juncea* (12 kg, wet weight) was collected in Sanya, Hainan province, People's Republic of China in October 2003 and was immediately frozen. 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 g and 56 g of residue, respectively. The EtOAc portion was subjected to column chromatography (CC) on a silica gel, using petroleum ether/EtOAc (from 10:1 to 0:1) as eluent. By combining the fractions with TLC (GF<sub>254</sub>) monitoring, 12 fractions were obtained. Fraction 4 was subjected to CC on silica gel, eluted with  $CHCl_3/Me_2CO$  (from 10:1 to 8:2) to afford **8** (36 mg), **18** (20 mg) and **6** (25 mg). Fraction 5 was subjected to CC on silica gel, eluted with  $CHCl_3/Me_2CO$  (from 10:1 to 9:1) to give four 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  $CHCl_3/MeOH$  to yield **11** (25 mg), **10** (29 mg), **7** (38 mg) and **2** (14 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 **14** (18 mg) and **9** (21 mg). Fraction 9 was subjected to CC on silica gel, eluted with  $CHCl_3/Me_2CO$  to afford **3** (56 mg), **4** (16 mg), **13** (16 mg) and **5** (19 mg). Fraction 11 was subjected to CC on silica gel, eluted with  $CHCl_3/MeOH$  (from 12:1 to 8:2) to give four subfractions (A–D). Fractions A and D were chromatographed over Sephadex LH-20 eluting with  $CHCl_3/MeOH$  (1:1), respectively, then subjected to CC on silica gel, eluted with  $CHCl_3/MeOH$  to yield **1** (41 mg), and **12** (46 mg), respectively. The *n*-BuOH portion was submitted through a column chromatography of high 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 **15** (20 mg), **16** (35 mg), **17** (54 mg).

**Acid Hydrolysis of Compound 1** A solution of compound **1** (2 mg) in

1 ml HCl–MeOH (2 mol/l) was refluxed at 100 °C for 2 h, and then neutralized with sat. Ba(OH)<sub>2</sub> aq. Removal of MeOH followed by participation between H<sub>2</sub>O and CHCl<sub>3</sub>. The mixture of methyl arabinoside in water layer was treated with 1 mol/l HCl at 190 °C for 1.5 h. D-Arabinose was revealed in water layer by TLC and PC analyses in comparison with authentic sample.

4'-O-Acetyl-3-O-[β-D-arabino-pyranosyl-oxy]-cholest-5-ene-3β,19-diol (**1**): White powder. <sup>1</sup>H-NMR (500 MHz, pyridine-*d*<sub>5</sub>) δ<sub>H</sub>: 2.28, 1.05 (each 1H, m, H-1), 2.11, 1.91 (each 1H, m, H-2), 3.85 (1H, m, H-3), 2.74 (1H, br d, *J*=10.2 Hz, H-4a), 2.58 (1H, t, *J*=11.9 Hz, H-4b), 5.64 (1H, br s, H-6), 1.98, 1.65 (each 1H, m, H-7), 2.17 (1H, m, H-8), 0.99 (1H, m, H-9), 1.99, 1.67 (each 1H, m, H-11), 2.08, 1.17 (each 1H, m, H-12), 1.19 (1H, m, H-14), 1.63, 1.15 (each 1H, m, H-15), 1.38 (2H, m, H-16), 0.92 (1H, m, H-17), 0.82 (3H, s, Me-18), 4.11, 3.86 (each 1H, d, *J*=11.3 Hz, H-19), 1.42 (1H, m, H-20), 1.0 (3H, d, *J*=6.5 Hz, Me-21), 1.05, 1.58 (each 1H, m, H-22), 1.43, 1.54 (each 1H, m, H-23), 1.13 (2H, m, H-24), 1.42 (2H, m, H-25), 1.09 (6H, d, *J*=6.4 Hz, Me-26 and Me-27), 2.05 (s, CH<sub>3</sub>CO–), 5.56 (1H, d, *J*=3.2 Hz, H-1'), 4.53 (1H, dd, *J*=3.2, 9.8 Hz, H-2'), 4.62 (1H, dd, *J*=3.1, 9.7 Hz, H-3'), 5.74 (1H, br s, H-4'), 4.24, 4.00 (each 1H, d, *J*=12.4 Hz, H-5'). <sup>13</sup>C-NMR (125 MHz, pyridine-*d*<sub>5</sub>) δ<sub>C</sub>: 33.8 (t, C-1), 30.5 (t, C-2), 77.8 (d, C-3), 39.5 (t, C-4), 137.7 (s, C-5), 125.3 (d, C-6), 32.0 (t, C-7), 33.3 (d, C-8), 51.2 (d, C-9), 42.1 (s, C-10), 22.3 (t, C-11), 40.5 (t, C-12), 42.8 (s, C-13), 56.3 (d, C-14), 24.5 (t, C-15), 28.5 (t, C-16), 57.6 (d, C-17), 12.3 (q, C-18), 62.9 (t, C-19), 36.0 (d, C-20), 19.0 (q, C-21), 32.0 (t, C-22), 24.5 (t, C-23), 40.5 (t, C-24), 28.5 (d, C-25), 21.2 (q, C-26), 21.3 (q, C-27), 21.0 (q, CH<sub>3</sub>CO–), 170.7 (s, CH<sub>3</sub>CO–), 99.1 (d, C-1'), 70.7 (d, C-2'), 68.8 (d, C-3'), 73.2 (d, C-4'), 61.6 (t, C-5'). IR (KBr) ν<sub>max</sub>: 3352, 2930, 1730, 1066, 996 cm<sup>-1</sup>. Negative-ion ESI-MS *m/z*: 577 [M–H]<sup>–</sup>. HR-ESI-MS *m/z*: 577.4100 [M–H]<sup>–</sup> (Calcd for C<sub>34</sub>H<sub>57</sub>O<sub>7</sub>: 577.4104). [α]<sub>D</sub><sup>20.0</sup> –110.0° (*c*=0.60, pyridine).

1,2-O-[2'-Hydroxyoctadecyl]-glycerol (**2**): White powder. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ<sub>H</sub>: 4.14 (1H, dd, *J*=6.7, 8.0 Hz, H-1a), 3.75 (1H, dd, *J*=6.8, 8.0 Hz, H-1b), 4.29 (1H, m, H-2), 3.74 (1H, dd, *J*=3.8, 11.9 Hz, H-3a), 3.65 (1H, dd, *J*=5.5, 11.9 Hz, H-3b), 4.90 (1H, d, *J*=3.5 Hz, H-1'), 3.58 (1H, m, H-2'), 1.55 and 1.51 (each 1H, m, H-3'), 1.53 and 1.47 (each 1H, m, H-4'), 1.35–1.25 (26H, m, H-5' to H-17'), 0.88 (3H, t, *J*=6.5 Hz, H-18'). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ<sub>C</sub>: 66.7 (t, C-1), 76.2 (d, C-2), 62.6 (t, C-3), 105.6 (d, C-1'), 71.9 (d, C-2'), 31.9 (t, C-3'), 25.4 (t, C-4'), 29.1–29.7 (t, C-4' to C-15'), 22.6 (t, C-16'), 31.8 (t, C-17'), 14.0 (q, C-18'). IR (KBr) ν<sub>max</sub>: 3420, 3350, 2920, 2850, 1465, 1329, 1130, 1050 cm<sup>-1</sup>. EI-MS *m/z*: 253 (2), 134 (2), 125 (2), 103 (100), 97 (2), 71(4), 57 (33), 43 (11). Negative-ion

ESI-MS *m/z*: 357 [M–1]<sup>–</sup>. HR-ESI-MS *m/z*: 357.2998 [M–H]<sup>–</sup> (Calcd for C<sub>21</sub>H<sub>41</sub>O<sub>4</sub>: 357.3004).

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