Chemistry of Natural Compounds, Vol. 48, No. 4, September, 2012 [Russian original No. 4, July–August, 2012]

CHEMICAL CONSTITUENTS OF THE BROWN ALGA *Sargassum henslowianum* COLLECTED FROM THE SOUTH CHINA SEA

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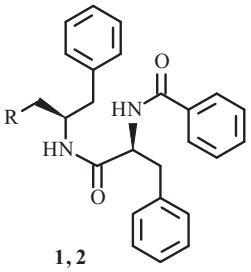
UDC 547.972+547.18

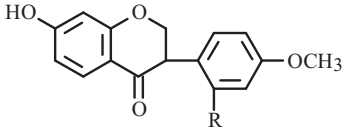
Sargassum henslowianum is a brown algae species of the family Sargassaceae and is widely distributed along the coast of China Sea. To the best of our knowledge, only sulfated polysaccharides were isolated from *S. henslowianum*, which was collected from Guangdong and Fujian Provinces, China [1]. To date, there have been no reports concerning the secondary metabolites of *S. henslowianum*. As part of our program to discover new bioactive secondary metabolites from marine materials collected from the South China Sea [2–4], the secondary metabolites of the ethanol extract of the brown alga *S. henslowianum* collected from Guangdong Province, China was studied for the first time, and eight natural compounds were isolated.

The brown alga *S. henslowianum* (4.5 kg) was air-dired and extracted with 95% EtOH at room temperature. The extract was concentrated under reduced pressure to yield a residue and partitioned between EtOAc and H_2O. After removal of the solvent under reduced pressure, the EtOAc extract (6.5 g) was subjected to vacuum liquid chromatography (VLC) on silica gel and eluted with petroleum ether containing increasing amounts of EtOAc to produce five fractions (Fr. A1–Fr. A5) on the basis of TLC analysis. Fraction A3 was first subjected to repeated silica gel chromatography and then purified by preparative HPLC to obtain compounds **1** (6.0 mg), **2** (25.0 mg), **3** (4.0 mg), **4** (3.0 mg), **5** (2.0 mg), **6** (3.0 mg), **7** (4.0 mg), and **8** (40.0 mg). Their structures were identified as aurantiamide acetate (**1**) [5], aurantiamide (**2**) [5], vestitone (**3**) [6], liquiritigenin (**4**) [7], 7-hydroxy-2′,4′-dimethoxyisoflavanone (**5**) [8], 5,6-dihydroxy-7-methoxyflavone (**6**) [9], 5,7-dihydroxy-8-methoxyflavone (**7**) [10], and saringosterol (**8**) [11] on the basis of their ^{1}H NMR and ESI-MS spectra and by comparison with literature data. All the isolated compounds were reported for the first time from the brown alga *S. henslowianum*.

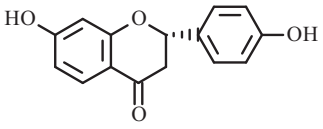
Aurantiamide Acetate (1). Colorless needle ($CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.80 (1H, d, J = 7.6, H-1), 4.79 (1H, m, H-2), 6.08 (1H, d, J = 8.2, H-4), 4.34 (1H, m, H-5), 2.74 (2H, m, H-6), 7.15 (3H, m, H-8, 10, 12), 7.09 (2H, m, H-9, 11), 3.07 (1H, dd, J =13.7, 8.2, H-13), 3.21 (1H, dd, J = 13.7, 6.0, H-13), 7.21–7.29 (5H, m, H-15–19), 3.82 (1H, dd, J = 11.0, 3.8, H-20), 3.91 (1H, dd, J = 11.0, 3.8, H-20), 2.02 (3H, s, H-2″), 7.71 (2H, m, H-3′, 7′), 7.43 (2H, m, H-4′, 6′), 7.52 (1H, br.s, J = 7.2, H-5′).



1, 2

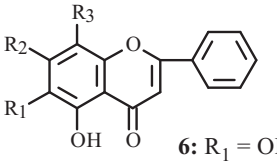


3, 5



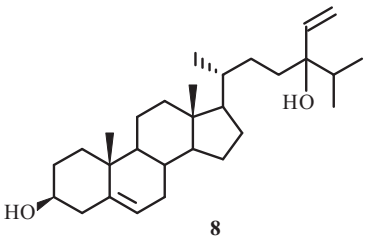
4

1: R = OAc; **2, 3:** R = OH; **5:** R = OCH_3



6, 7

6: R_1 = OH, R_2 = OCH_3, R_3 = H
7: R_1 = H, R_2 = OH, R_3 = OCH_3



8

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Aurantiamide (2). Colorless needle ($CHCl_3$).^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.10–7.32 (10H, m, H-2–6, 15–19), 2.67 (1H, dd, J = 14.2, 8.7, H-7), 2.95 (1H, dd, J = 13.2, 10.8, H-7), 4.86 (1H, m, H-8), 7.87 (1H, d, J = 8.8, H-9), 3.28 (1H, m, H-11), 3.33 (1H, m, H-11), 4.80 (1H, t, J = 5.4, H-12), 2.85 (1H, dd, J =13.2, 5.4, H-13), 3.02 (1H, dd, J = 13.2, 4.3, H-13), 8.47 (1H, d, J = 7.6, H-20), 7.78 (2H, d, J = 7.7, H-23, 27), 7.64 (2H, t, J = 6.6, H-24, 26), 7.51 (1H, t, J = 7.6, H-25).

Vestitone (3). Yellow amorphous powder ($CHCl_3$). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.65 (1H, d, J = 8.2, H-5), 6.39 (1H, dd, J = 8.2, 2.2, H-6), 6.30 (1H, d, J = 2.2, H-8), 6.39 (1H, d, J = 2.2, H-2′), 6.89 (1H, d, J = 8.2, H-5′), 6.51 (1H, dd, J = 8.2, 2.2, H-6′), 4.57 (1H, t, J = 10.9), 4.40 (1H, dd, J = 10.9, 5.5), 4.08 (1H, dd, J = 10.9, 5.5), 3.67 (3H, s, OCH_3). ESI-MS *m/z* 287 $[M + H]^+$.

Liquiritigenin (4). Yellow amorphous powder ($CHCl_3$). ^{1}H NMR (500 MHz, DMSO-d_6, δ, ppm, J/Hz): 5.41 (1H, dd, J = 13.2, 2.7, H-2), 3.09 (1H, dd, J = 16.4, 13.2, H-3), 2.60 (1H, dd, J = 16.4, 2.1, H-3), 7.62 (1H, d, J = 7.6, H-5), 6.47 (1H, dd, J = 8.7, 2.2, H-6), 6.29 (1H, d, J = 2.2, H-6), 7.31 (2H, d, J = 8.2, H-2′, H-6′), 6.78 (2H, d, J = 8.2, H-3′, H-5′). ESI-MS *m/z* 257 $[M + H]^+$.

7-Hydroxy-2′,4′-dimethoxyisoflavanone (5). Yellow amorphous powder ($CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.90 (1H, d, J = 8.2, H-5), 6.45 (1H, dd, J = 8.2, 2.2, H-6), 6.40 (1H, d, J = 2.2, H-8), 6.48 (1H, d, J = 2.2, H-2′), 6.99 (1H, d, J = 8.2, H-5′), 6.52 (1H, dd, J = 8.2, 2.2, H-6′), 4.57 (1H, t, J = 10.9, H-3), 4.47 (1H, dd, J = 11.5, 5.4, H-2), 4.25 (1H, dd, J = 11.5, 5.4, H-2), 3.79 (3H, s, OCH_3), 3.76 (3H, s, OCH_3). ESI-MS *m/z* 301 $[M + H]^+$.

5,6-Dihydroxy-7-methoxyflavone (6). Yellow amorphous powder ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.98 (1H, s, H-3), 6.60 (1H, s, H-8), 8.09 (2H, d, J = 7.8), 7.55–7.64 (3H, m, H-3′–5′), 3.77 (3H, s, OCH_3). ESI-MS *m/z* 285 $[M + H]^+$.

5,7-Dihydroxy-8-methoxyflavone (7). Yellow amorphous powder ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.05 (1H, s, H-3), 6.35 (1H, s, H-6), 8.09 (2H, d, J = 6.5, 1.2), 7.60–7.64 (3H, m, H-3′–5′), 3.88 (3H, s, OCH_3). ESI-MS *m/z*: 285 $[M + H]^+$, 307 $[M + Na]^+$.

Saringosterol (8). Colorless needle ($CHCl_3$).^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 5.79 (1H, dd, J = 17.5, 10.9, H-28), 5.34 (1H, br.d, H-6), 5.17 (1H, dd, J = 17.5, 1.6, H-29), 5.11 (1H, dd, J = 10.9, 1.6, H-29), 3.51 (1H, m, H-3), 1.00 (3H, s, H-19), 0.92 (3H, d, J = 7.3, H-21), 0.89 (3H, d, J = 6.1, H-27), 0.85 (3H, d, J = 6.8, H-26), 0.67 (3H, s, H-18).

ACKNOWLEDGMENT

This work was supported by the Fund of the Key Scientific and Technical Innovation Project, Zhanjiang (No. 2009C3106011).

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