Column Diamonsil C_{18} (200 mm × 4.6 mm, 5 μm). The mobile phase was methanol-water (80 : 20). Detection wavelength was 323 ± 1 nm. The flow rate was set at 1.0 ml/min. The retention time was of 8.1 min for osthol.

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Chemcial constituents from the marine sponge *Iotrochoto birotulata*

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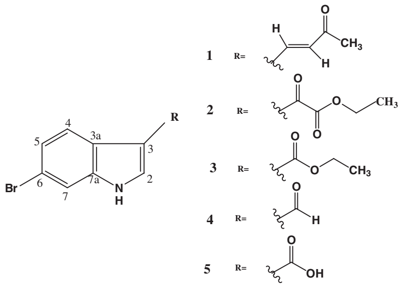
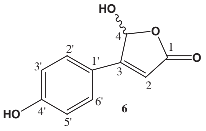
In continuation to investigate bioactive secondary metabolites from Chinese marine organisms, the sponge *Iotrochoto birotulata* [1–5] was collected from Southern China sea, a tropical area in southern Hainan island. The MeOH extract of *I. birotulata* was partitioned between H_2O and EtOAc, and the EtOAc extract was concentrated and subjected to column chromatography repeatedly to afford six compounds (**1**–**6**). The basic structural pattern of **1** to **5** was that of 6-bromoindole analogues, and **2** to **5** were identified as (6-bromo-indol-3-yl)-oxo-acetic acid ethyl ester (**2**) [6], bromoester (**3**) [7–8], 6-bromoindole-3-carboxylic acid (**4**) [9] and 6-bromoindole-3-carbaldehyde (**5**) [9], by comparison of the physical and chemical properties as well as the spectral data with those reported in the literature. Compound **2** was obtained previously as synthesized product [6], but the ^1H and ^{13}C NMR data have not been concluded before we elucidated them by extensive 2D NMR spectroscopy. Compound **6** was identical to hydroxybutenolide [10] due to an extensive 2D NMR spectral analysis. This is the first report to reveal the species *I. birotulata* containing brominated indole derivatives.




6

Compound **1** was isolated as a white powder. Its positive ESI-MS spectrum showed the molecular ion peak at *m/z* 264 and 266 with integration 1 : 1, suggesting the presence of a bromine element. The molecular formula $C_{12}H_{10}NOBr$ was established by the negative HRESIMS spectrometry data (*m/z* 261.9850, calcd. for 261.9872). The IR spectrum exhibited absorptions at 3160, 1707,

Table: Spectroscopic data of compounds 1, 2, 6

Compd.	Description	UV (MeOH) λ_{max} (nm)	IR (KBr) ν_{max}	^{1}H NMR δ (DMSO-d_6, ppm)	HRESIMS (neg.) *m/z*:
2	Pale yellow amorphous solid	270, 320	3424, 2925, 1732, 1627, 1505, 1407 cm^{-1}	12.46 (br), 8.47 (d, J = 3.0 Hz), 8.10 (d, J = 8.0 Hz), 7.43 (dd, J = 8.0, 1.5 Hz), 7.75 (d, J = 1.5 Hz), 1.33 (t, J = 7.0 Hz), 4.37 (q, J = 7.0 Hz) ^{13}C NMR δ (DMSO-d_6, ppm): 139.82 (d), 116.32 (s), 125.43 (s), 123.65 (d), 126.59 (d), 117.17 (s), 116.32 (d), 138.50 (s), 180.01 (s), 163.80 (s), 14.79 (q), 62.61 (t).	293.9752, 295.9721 (M$^+$−1, 1 : 1; calcd for 293.9844)
6	pale white powder, m.p. 205–207°C	310	3356, 3194, 2940, 1734, 1613, 1518, 1450, 1128	10.20 (s, OH), 7.89 (d, J = 8.5 Hz, OH), 7.65 (d, J = 8.5 Hz, H-2′, 6′), 6.86 (d, J = 8.5, H-3′,5′), 6.52 (d, J = 8.5 Hz, H-4), 6.50 (s, H-2) ^{13}C NMR δ (CDCl$_3$, ppm): 172.10 (s, CO), 164.25 (s, C-3), 161.24 (s, C-4′), 131.03 (d, C-2′,4′), 121.00 (s, C-1′), 116.55 (d, C-3′,5′), 111.86 (d, C-2), 98.65 (d, C-4)	ESI-MS (neg.) *m/z*: 191(M$^-$−1); HRFABMS *m/z*: 191.0359 (calcd. for 191.0344)
1	pale white powder, m.p. 145–148 °C	270, 290, 340	3160, 2919, 1707, 1637, 1614, 1523, 1243 cm^{-1}	^{1}H NMR δ (CDCl$_3$, ppm): 8.59 (br), 7.54 (s), 7.81 (d, J = 8.5 Hz), 7.38 (dd, J = 8.5, 2.0 Hz), 7.62 (d, J = 2.0 Hz), 6.80 (d, J = 16.5 Hz), 7.77 (d, J = 16.5 Hz), 2.41 (s) ^{13}C NMR δ (CDCl$_3$, ppm): 129.66 (d), 114.00 (s), 124.00 (s), 122.03 (d), 126.82 (d), 117.70 (s), 115.23 (d), 138.30 (s), 135.81 (d), 123.72 (d), 199.00 (s), 27.85 (q)	261.9850, 263.9848 (M$^+$−1, 1 : 1, calcd. for 261.9872). ESI-MS (positive) *m/z*: 264, 266 (M$^+$+1, 1 : 1); 222, 224 (1 : 1)

1637 and 1614 cm^{-1}, indicating the presence of an active proton (NH) and a conjugated carbonyl group as well as an aromatic group. The ^{1}H NMR spectrum showed an ABX coupled system at δ7.81 (d, $J = 8.5$ Hz, H-4), 7.38 (dd, $J = 8.5$, 2.0 Hz, H-5) and 7.62 (d, $J = 2.0$ Hz, H-7), as well as a singlet at δ7.54 (s, H-2) and a broadening signal at δ8.59 (br, NH), in association with ^{13}C NMR data, **1** was characteristic of 3,6-disubstituted indole unit corresponding to that of **3**, **4** and **5**. Additionally, there were two olefinic protons at δ6.80 (d, $J = 16.5$ Hz) and 7.77 (d, $J = 16.5$ Hz) with coupling constant $J = 16.5$ Hz for a trans geometry, and a singlet at δ2.41 (s 3 H) was due to a methyl group. The ^{13}C NMR spectral data of **1** displayed 12 carbon signals, of which eight δ 129.66 (d, C-2), 114.00 (s, C-3), 124.00 (s, C-3a), 122.03 (d, C-4), 126.82 (d, C-5), 117.70 (s, C-6), 115.23 (d, C-7), 138.30 (s, C-7a)] were assigned for indole unit, and four [δ 199.00 (s), 135.81 (d), 123.72 (s) and 27.85 (q)] were attributed to a side chain. The HMQC spectrum assigned the signals of protonated carbons as well as their associated protons. In HMBC spectrum, the olefinic proton at δ6.80 correlated to carbonyl carbon (δ 199.00, s), C-3 (δ 114.00) and methyl carbon (δ 27.85, q), and the other olefinic proton at δ 7.77 correlated with C-3a (δ 124.00) and carbonyl carbon respectively, indicating a but-1-en-3-one moiety annexed to position C-3 of indole ring. A bromine element was considered to be substituted to C-6 by comparison of the ^{1}H and ^{13}C NMR data of **1** with those of known 6-bromoindoles **3**, **4** and **5** [9, 11] as well as HMBC correlation. Consequently, the structure of **1** was established as 3-(but-1-*E*-en-3-one)-6-bromoindole.

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