Steroids from the Gorgonian *Isis hippuris*

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Six new polyoxygenated steroids, hippuristerones J−L (**1**−**3**), hippuristerols E−F (**4**, **5**), and a novel gorgosteroid, 1α,3β,5β,11α-tetrahydroxygorgostan-6-one (**6**), were isolated from the gorgonian *Isis hippuris*. The structures of these metabolites were elucidated by extensive spectroscopic analyses and comparison of the NMR data with those of related steroids.

Previous chemical investigations on the gorgonian *I. hippuris* have led to the isolation of a series of new natural products, including suberosane-type sesquiterpenes,[1,2] highly oxygenated spiroketal steroids that were named as hippurins or hippuristanols,[2−7,9,10] hippuristerones, and hippuristerols,[7−9] and polyoxygenated gorgosteroids.[11−13] Our continuing study on the chemical constituents of *I. hippuris*, collected by hand using scuba at Green Island, located off the southeast coast of Taiwan, in February 1999, has again afforded a series of polyoxygenated steroids, namely, hippuristerones J−L (**1**−**3**), hippuristerols E−F (**4**, **5**), and a gorgosteroid (**6**). We describe herein the isolation and structure elucidation of these new compounds.

Results and Discussion

Compound **1** was obtained as a white powder. The HRFABMS of **1** exhibited a $[M + H]^+$ peak at *m/z* 635.3802 and established a molecular formula of $C_{35}H_{54}O_{10}$, implying nine degrees of unsaturation. The ^{13}C NMR and DEPT spectra displayed 35 signals: eight methyls, ten methylenes, eight methines, and nine quaternary carbons including one ketone (δ_C 211.6, s). From the ^{13}C NMR spectral data, the carbon resonances at δ_C 171.8 (s), 171.0 (s), and 170.5 (s) along with three methyl groups at δ_C 21.1 (q), 21.0 (q), and 20.9 (q) disclosed the presence of three acetyl groups. The above data suggest that compound **1** possesses a pentacyclic structure. The presence of a C-3 ketone (δ_C 211.6, s), a C-17, C-20 tetrasubstituted epoxide (δ_C 79.3, s and 66.8, s), a secondary alcohol at C-16 (δ_H 4.12 t, $J = 7.2$ Hz; δ_C 70.6, d), and a tertiary hydroxy group at C-25 (δ_C 74.6), which were all confirmed by HMBC correlations (Figure 1), revealed that compound **1** should be a member

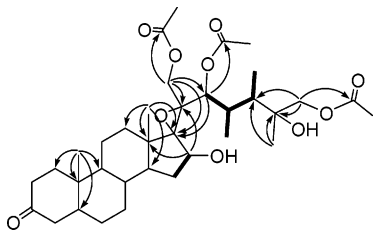
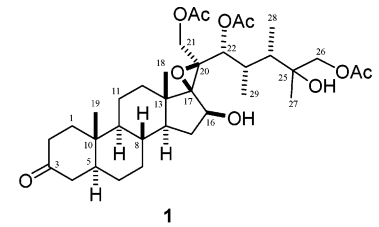
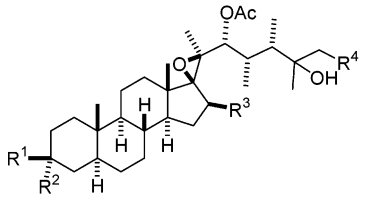


Figure 1. Selected HMBC and $^1H-^1H$ COSY correlations of **1**.

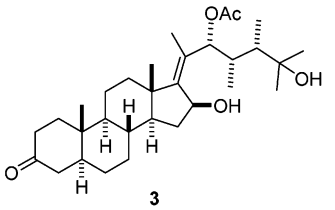
of the hippuristerones.[7,9] Acetyl groups attached at C-22, C-26, and C-21, respectively, were confirmed by the key HMBC correlations shown in Figure 1. On the basis of the above results and by comparison of NMR spectral data with those of hippuristerone I (**7**),[7] the structure of **1** was established and named hippuristerone J.



1



2: $R^1 = R^2 = O$, $R^3 = H$, $R^4 = OAc$
4: $R^1 = H$, $R^2 = OH$, $R^3 = R^4 = H$
5: $R^1 = H$, $R^2 = OH$, $R^3 = OH$, $R^4 = H$
7: $R^1 = R^2 = O$, $R^3 = R^4 = H$
8: $R^1 = R^2 = O$, $R^3 = OH$, $R^4 = H$



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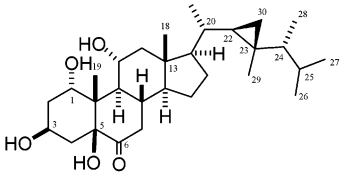

6

The metabolite **2** was isolated as a white powder, and its molecular formula was found to be $C_{33}H_{52}O_7$, as deduced from HRFABMS spectral data. By comparison of the NMR spectral data with those of hippuristerone I (**7**), an additional acetoxy group was found to be attached at C-26. Thus, the structure of **2** was deduced and named hippuristerone K.

Compound **3** was obtained as a white powder, which gave a $[M + H]^+$ peak at *m/z* 503.3734 in the HRFABMS. Thus, a molecular formula of $C_{31}H_{50}O_5$ was established. This metabolite was found to be unstable in $CDCl_3$. Thus, the

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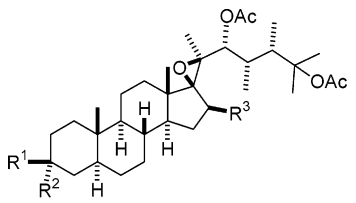
Table 1. ^{13}C NMR Spectral Data of Compounds **1**–**6**

C #	**1**[b]	**2**[a]	**3**[c]	**4**[b]	**5**[a]	**6**[a]
1	38.4 (CH_2)[d]	38.4 (CH_2)[d]	38.7 (CH_2)[d]	32.2 (CH_2)[d]	32.0 (CH_2)[d]	70.4 (CH)[d]
2	38.1 (CH_2)	38.1 (CH_2)	38.5 (CH_2)	29.1 (CH_2)	28.9 (CH_2)	37.4 (CH_2)
3	211.6 (C)	211.9 (C)	209.1 (C)	66.6 (CH)	66.5 (CH)	68.0 (CH)
4	44.6 (CH_2)	44.6 (CH_2)	45.0 (CH_2)	35.9 (CH_2)	35.7 (CH_2)	37.3 (CH_2)
5	46.5 (CH)	46.5 (CH)	46.6 (CH)	39.1 (CH)	38.9 (CH)	84.0 (C)
6	28.7 (CH_2)	28.7 (CH_2)	29.2 (CH_2)	28.4 (CH_2)	28.3 (CH_2)	210.5 (C)
7	31.5 (CH_2)	31.3 (CH_2)	31.7 (CH_2)	31.8 (CH_2)	31.7 (CH_2)	41.1 (CH_2)
8	34.7 (CH)	35.4 (CH)	35.2 (CH)	35.7 (CH)	34.7 (CH)	36.0 (CH)
9	53.6 (CH)	53.2 (CH)	53.9 (CH)	54.2 (CH)	54.1 (CH)	50.2 (CH)
10	35.7 (C)	35.6 (C)	35.9 (C)	36.1 (C)	36.1 (C)	50.6 (C)
11	21.4 (CH_2)	21.5 (CH_2)	21.9 (CH_2)	20.9 (CH_2)	20.6 (CH_2)	66.3 (CH)
12	36.3 (CH_2)	36.4 (CH_2)	38.9 (CH_2)	36.7 (CH_2)	36.8 (CH_2)	49.0 (CH_2)
13	41.4 (C)	43.8 (C)	46.0 (C)	43.8 (C)	43.1 (C)	43.3 (C)
14	49.3 (CH)	55.0 (CH)	53.1 (CH)	55.2 (CH)	49.5 (CH)	55.4 (CH)
15	33.2 (CH_2)	23.6 (CH_2)	35.2 (CH_2)	23.5 (CH_2)	33.2 (CH_2)	24.5 (CH_2)
16	70.6 (CH)	31.3 (CH_2)	71.8 (CH)	30.9 (CH_2)	70.1 (CH)	28.0 (CH_2)
17	79.3 (C)	79.0 (C)	155.6 (C)	79.3 (C)	79.2 (C)	57.8 (CH)
18	15.2 (CH_3)	15.3 (CH_3)	17.3 (CH_3)	15.4 (CH_3)	15.5 (CH_3)	12.7 (CH_3)
19	11.5 (CH_3)	11.4 (CH_3)	11.5 (CH_3)	11.3 (CH_3)	11.1 (CH_3)	14.6 (CH_3)
20	66.8 (C)	67.1 (C)	125.4 (C)	67.3 (C)	67.7 (C)	35.2 (CH)
21	63.4 (CH_2)	17.2 (CH_3)	12.9 (CH_3)	17.0 (CH_3)	16.4 (CH_3)	21.0 (CH_3)
22	75.9 (CH)	78.4 (CH)	81.2 (CH)	78.5 (CH)	77.7 (CH)	31.9 (CH)
23	31.6 (CH)	32.5 (CH)	34.2 (CH)	33.4 (CH)	33.0 (CH)	25.9 (C)
24	41.4 (CH)	38.4 (CH)	42.5 (CH)	41.6 (CH)	41.6 (CH)	50.7 (CH)
25	74.6 (C)	74.3 (C)	73.2 (C)	73.9 (C)	73.7 (C)	32.0 (CH)
26	68.3 (CH_2)	71.0 (CH_2)	27.8 (CH_3)	30.6 (CH_3)	30.8 (CH_3)	21.5 (CH_3)
27	25.6 (CH_3)	20.3 (CH_3)	29.8 (CH_3)	26.4 (CH_3)	26.0 (CH_3)	22.1 (CH_3)
28	10.8 (CH_3)	10.8 (CH_3)	10.9 (CH_3)	11.2 (CH_3)	11.4 (CH_3)	15.5 (CH_3)
29	12.6 (CH_3)	12.2 (CH_3)	12.7 (CH_3)	11.9 (CH_3)	12.0 (CH_3)	14.3 (CH_3)
30						21.3 (CH_2)
OAc	171.8 (C)	170.6 (C)	172.5 (C)	170.6 (C)	171.6 (C)	
	171.0 (C)	170.9 (C)				
	170.5 (C)					
OAc	21.1 (CH_3)	21.0 (CH_3)	21.0 (CH_3)	21.1 (CH_3)	21.0 (CH_3)	
	21.0 (CH_3)	21.1 (CH_3)				
	20.9 (CH_3)					

[a] Spectra recorded at 125 MHz in $CDCl_3$ at 25 °C. [b] Spectra recorded at 75 MHz in $CDCl_3$ at 25 °C. [c] Spectra recorded at 125 MHz in C_6D_6 at 25 °C. [d] Multiplicity deduced by DEPT. The values are in ppm downfield from TMS.

NMR spectra of **3** were measured in C_6D_6. By comparison of the ^{13}C NMR spectral data of **3** with those of a known steroid hippuristerone H (**8**),[7] it was found that the 17,20-epoxide (δ_{C-17} 79.2 s and δ_{C-20} 67.8 s) in hippuristerone H was converted to an olefinic group (δ_C 155.6 s and δ_C 125.4 s) in **3**, as also confirmed by HMBC cross-peaks (H_3-21/C-17, C-20, and C-22). Thus, the structure of **3** was established and named hippuristerone L.

Hippuristerol E (**4**) was obtained as a white powder. The formula of **4** was found to be $C_{31}H_{52}O_5$, as deduced from HRFABMS spectral data. By comparison of the NMR spectral data of **4** with those of the known steroid hippuristerol B (**9**),[9] it was found that two methyl signals appearing at δ_H 1.51 s (H_3-26) and 1.55 s (H_3-27) in hippuristerol B were converted to δ_H 1.21 s (H_3-26) and 1.27 s (H_3-27) in **4**, revealing that the acetoxy group attached at C-25 in hippuristerol B has been deacetylated in compound **4**.



9: R^1 = H, R^2 = OH, R^3 = H
10: R^1 = H, R^2 = OH, R^3 = OH

Compound **5** was obtained as a white powder. The HRFABMS of **5** established a molecular formula of $C_{31}H_{52}O_6$. By comparison of the NMR spectral data of **5** with those of a known steroid, hippuristerol A (**10**),[9] it was found that the ^1H and ^{13}C spectral data of both compounds were nearly the same, except that the proton signals of H_3-26 and H_3-27 and the carbon shift of C-25 of **5** were shifted upfield relative to those of **10**. Thus, **5** is the 25-*O*-deacetylated product of **10** and was named hippuristerol F.

Compound **6** was isolated as an amorphous powder. The HRFABMS of **6** established a molecular formula of $C_{30}H_{50}O_5$, implying six degrees of unsaturation. The IR spectrum of **6** showed the presence of hydroxy (ν_{max} 3356 cm^{-1}) and ketonic carbonyl (ν_{max} 1718 cm^{-1}) groups. ^{13}C NMR and DEPT spectra showed signals of seven methyl, seven methylene, 11 methine, and five quaternary carbons, including one ketone (δ 210.5, s) and four oxygenated sp^3 carbons (δ 84.0, C; 70.4, CH; 68.0, CH; 66.3, CH) (Table 1). The above spectroscopic data suggested a pentacyclic structure with four hydroxy groups and one ketone in **6**. The upfield region of the ^1H NMR spectrum afforded two signals at δ −0.11 (1H, dd, J = 4.5, 5.5 Hz) and 0.49 (1H, dd, J = 4.5, 9.5 Hz), which was found to be correlated to a methylene signal at δ_C 21.3 (t), and a multiplet at δ 0.17 (1H, m) correlated to a carbon signal at δ 31.9 (d) in the HMQC spectrum of **6**. The above observations together with the presence of a quaternary carbon signal at δ 25.9 further suggested the presence of a trisubstituted cyclopropane ring.[12] On the basis of these structure features and the presence of seven methyl signals, it was proposed that compound **6** was a tetrahydroxylated steroid bearing one ketone functional group and a cyclopropane-containing side chain.

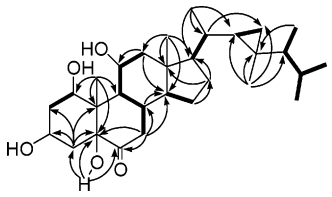


Figure 2. Selected HMBC and $^1H-^1H$ COSY correlations of **6**.

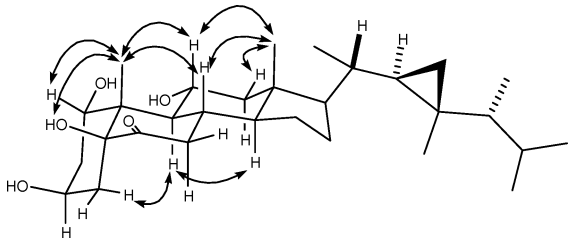


Figure 3. Selected NOESY correlations of **6**.

From the ^1H NMR, HMBC, and COSY spectra of **6** (Figure 2 and Table 1), seven methyl signals observed at δ 0.64 (3H, s); 0.86 (3H, d, J = 6.5 Hz); 0.90 (3H, s); 0.93 (3H, d, J = 7.0 Hz); 0.95 (3H, d, J = 6.5 Hz); 1.05 (3H, s) and 1.05 (3H, s) were assigned to H_3-18, H_3-26, H_3-29, H_3-28, H_3-27, H_3-19, and H_3-21, respectively. From the COSY spectrum of **6** (Figure 2), it was possible to establish the proton sequences from H-1 to H-2, H_2-7 to H-9, H-9 to H-11, H-11 to H_2-12, H-14 to H-15, H-17 to H-20, H-22 to H_2-30, H-24 to H_3-27, and H-24 to H-28. Three proton signals appearing at δ 4.34 (1H, dd, J = 13.0, 3.5 Hz), 4.20 (1H, brs), and 3.96 (1H, m) were assigned to H-1, H-3, and H-11, respectively, by the assistance of COSY and HMBC correlations (Figure 2). An additional proton signal at δ 4.63 (1H, s) was deduced to be the resonating peak of a tertiary hydroxy group attaching to C-5 (δ 84.0, s), as confirmed by the HMBC correlations of this proton to C-4 and C-5. The ketone functionality of C-6 was confirmed by its HMBC correlations with 5-OH (δ 4.63) and H_2-7 (2H, δ 2.47, dd, J = 14.0, 4.5 Hz and 2.32, t, J = 14.0). Therefore, the planar structure of **6** was established unambiguously.

An unusual feature was the ^1H NMR signal of H_3-21, which appeared as a singlet rather than the doublet that was expected by the spin−spin splitting from these protons with H-20. This feature has been previously described in compounds 9-hydroxygorgosterol and 9,11α,14- trihydroxygorgosterol,[14] both possessing a gorgosterol-like side chain, and could be attributed to the fact that H_3-21 and H-20 are coincidentally isochronous.

The relative stereochemistry and the detailed ^1H NMR spectral data assignment of **6** were determined mainly by the assistance of a NOESY experiment (Figure 3). In the NOESY spectrum of **6**, H-8 and H-11 were found to show NOE correlations with both H_3-18 and H_3-19, suggesting the β-orientation of H-8 and H-11. Moreover, H-1 also exhibited a NOE correlation with H_3-19. Thus, H-1 should also be placed on the β-face. The H-14 signal did not exhibit a NOE interaction with H_3-18, but instead showed a correlation with H-9, which in turn showed a NOE correlation with a proton attached to C-4 (δ_H 2.31, dd, J = 14.0, 3.5), suggesting the α-orientation of these protons. The 5-OH proton showed a weak NOE correlation to H_3-19, which indicated the β-orientation of the 5-OH group. Furthermore, although H-3 did not show any correlation in the NOESY spectrum of **6**, the β-orientations of 3-OH and 5-OH were confirmed by a comparison of the ^1H and ^{13}C NMR spectral data with those of gibberoketosterol,[15] a known metabolite possessing a similar carbon skeleton

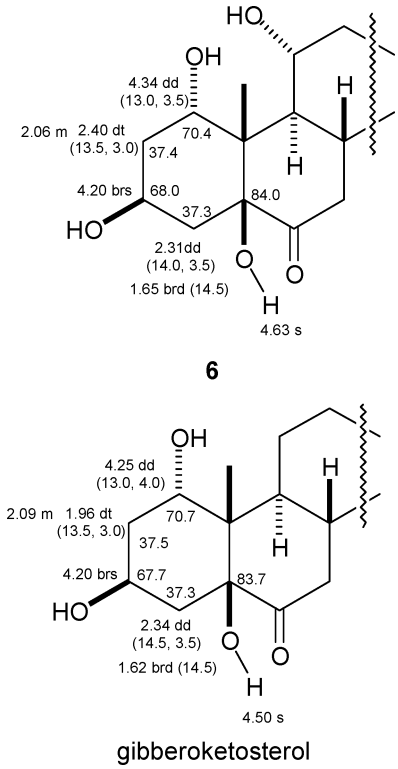


Figure 4. Comparison of ring A ^1H and ^{13}C NMR data of **6** and gibberoketosterol (J values are in Hz in parentheses).

(Figures 3 and 4). The stereochemistry of the side chain moiety could be determined by comparison of the ^1H and ^{13}C NMR spectral data with those of a gorgosteroid that was isolated previously and structurally elucidated by a single-crystal X-ray diffraction analysis from *I. hippuris*.[12] Thus, the structure of **6**, including the stereochemistry, was determined unambiguously and assigned as 1α,3β,5β,11α-tetrahydroxygorgostan-6-one.

Although many hippuristerones and hippuristerols have been isolated from *I. hippuris*, a highly substituted side chain like that of **1**, which contains four oxygenated substituents at C-21, C-22, C-25, and C-26 and two methyl substituents at C-23 and C-24, respectively, has never been found before. Furthermore, this is the first report of a gorgosteroid possessing a 5β-hydroxy-6-one functionality.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter. IR spectra were recorded on a Jasco FT-5300 infrared spectrophotometer. NMR spectra were recorded on a Bruker Avance DPX300 FT-NMR at 300 MHz for ^1H and 75 MHz for ^{13}C or on a Varian Unity INOVA 500 FT-NMR at 500 MHz for ^1H and 125 MHz for ^{13}C, respectively, in $CDCl_3$ using TMS as internal standard. Low-resolution and high-resolution FABMS were recorded on a JEOL JMS-700 spectrometer. Silica gel (Merck, 230−400 mesh) was used for column chromatography. Precoated silica gel plates (Merck, Kieselgel 60 F-254, 0.2 mm) were used for analytical TLC. High-performance liquid chromatography (HPLC) was performed on a Hitachi L-7100 apparatus equipped with a Bischoff refractive index detector or a Hitachi L-7400 UV detector and with the Merck Hibar Si-60 column (250 × 21 mm, 7 μm).

Animal Material. The gorgonian coral *I. hippuris* was collected by hand using scuba at Green Island, which is located off the southeast coast of Taiwan, in February 1999, at a depth of 25 m, and was stored in a freezer until extraction. A voucher specimen was deposited in the Department of Marine Re-

Table 2. ^{1}H NMR Spectral Data of Compounds **1**−**6** (values are in ppm downfield from TMS)

C #	**1**[b]	**2**[a]	**3**[c]	**4**[b]	**5**[a]	**6**[a]
1	2.05 m	2.00 m	1.48 m	1.50 m	1.45 m	4.34 dd (13.0, 3.5)
	1.33 m	1.32 m	0.83 m	1.29 m	1.30 m	
2	2.30 m	2.34 m	2.18 m	1.62 m	1.66 m	2.40 dt (13.5, 3.0)
						2.06 m
3				4.06 br s	4.06 br s	4.20 br s
4	2.28 m	2.27 m	1.97 m	1.56 m	1.52 m	2.31 dd (14.0, 3.5)
	2.11 m	2.08 m	1.88 m	1.40 m	1.38 m	1.65 br d (14.5)
5	1.58 m	1.52 m	1.05 m	1.55 m	1.53 m	
6	1.40 m	1.36 m	0.93 m	1.24 m	1.24 m	
7	1.82 m	1.78 m	1.44 m	1.78 m	1.76 m	2.47 dd (14.0, 4.5)
	0.92 m	0.94 m	0.53 m	0.95 m	0.94 m	2.32 t (14.0)
8	1.56 m	1.52 m	1.22 m	1.42 m	1.51 m	1.79 m
9	0.70 m	0.74 m	0.35 m	0.72 m	0.73 m	1.98 br t (10.0)
10						
11	1.63 m	1.60 m	1.28 m	1.64 m	1.61 m	3.96 m
	1.42 m	1.38 m		1.26 m	1.27 m	
12	1.42 m	1.38 m	2.21 m	1.35 m	1.34 m	1.34 m
	1.84 m	1.79 m	1.41 m	1.78 m	1.79 m	2.44 dd (14.0, 4.5)
13						
14	1.07 m	1.23 m	0.96 m	1.24 m	1.06 m	1.37 m
15	2.20 m	1.64 m	2.31 m	1.67 m	2.22 m	1.61 m
	1.46 m	1.34 m	1.63 m	1.31 m	1.38 m	
16	4.12 t (7.2)[c]	2.10 m	5.06 t (7.0)	2.08 m	4.05 t (7.5)	1.37 m
		1.87 m		1.88 m		2.12 m
17						1.36 m
18	1.00 s	0.92 s	1.18 s	0.91 s	0.93 s	0.64 s
19	1.02 s	1.01 s	0.56 s	0.78 s	0.78 s	1.05 s
20						1.05 m
21	5.02 d (12.6)	1.56 s	1.81 s	1.57 s	1.59 s	1.05 s
	4.38 d (12.6)					
22	4.74 d (10.5)	4.74 d (10.5)	5.56 d (10.5)	4.75 d (10.7)	4.61 d (11.0)	0.17 m
23	2.45 m	2.43 m	2.33 m	2.37 m	2.44 m	
24	1.70 m	1.77 m	1.61 m	1.64 m	1.55 m	0.25 m
25						1.57 m
26	4.07 d (11.2)	3.92 d (11.5)	0.95 s	1.27 s	1.25 s	0.86 d (6.5)
	4.03 d (11.2)	4.04 d (11.5)				
27	1.26 s	1.17 s	1.01 s	1.21 s	1.20 s	0.95 d (6.5)
28	0.95 d (7.4)	0.90 d (7.5)	0.75 d (7.0)	0.93 d (7.0)	0.89 d (7.5)	0.93 d (7.0)
29	0.85 d (6.6)	0.85 d (6.5)	0.91 d (6.5)	0.84 d (7.0)	0.85 d (7.0)	0.90 s
30						−0.11 dd (4.5, 5.5)
						0.49 dd (4.5, 9.5)
OH			5.37 s			4.63 s (5-OH)
OAc	2.11 s	2.10 s	1.59 s	2.09 s	2.12 s	
	2.11 s	2.13 s				
	2.11 s					

[a] Spectra recorded at 500 MHz in $CDCl_3$ at 25 °C. [b] Spectra recorded at 300 MHz in $CDCl_3$ at 25 °C. [c] Spectra recorded at500 MHz in C_6D_6 at 25 °C.

sources, National Sun Yat-Sen University (specimen no. GISC-102).

Extraction and Isolation. The gorgonian coral (4.3 kg fresh wt) was collected and freeze-dried. The freeze-dried organism was minced and extracted exhaustively with *n*-hexane and CH_2Cl_2. The combined organic extract was evaporated to give a dark green residue (37.0 g), which was chromatographed on a silica gel column using eluents of increasing polarity from *n*-hexane to EtOAc to get fractions 1−31. Fraction 24 was subjected to normal-phase HPLC column chromatography (acetone/hexane, 14%) to afford compounds **3** (4 mg) and **4** (2 mg). Compounds **2** (1 mg) and **5** (4 mg) were obtained from fraction 25 by repeated HPLC column chromatography (acetone/hexane, 16%). Fraction 26 was subjected to repeated normal-phase HPLC column chromatography (EtOAc/hexane, 20%) to afford compound **1** (2 mg). Repeated chromatography of fraction 30 over a RP-18 HPLC column (CH_3CN/MeOH/H_2O, 1:5:1) led to the isolation of compound **6** (1 mg).

Hippuristerone J (1): white powder; mp 124−125 °C; $[\alpha]_D$ −5° (*c* 0.32, $CHCl_3$); IR (KBr) ν_{max} 3448, 1729, and 1250 cm^{-1}; ^{13}C and ^{1}H NMR data, see Tables 1 and 2; FABMS *m/z* 635 ([M + H]$^+$, 2); HRFABMS *m/z* 635.3802 [M + H]$^+$ (calcd for $C_{35}H_{55}O_{10}$, 635.3797).

Hippuristerone K (2): white powder; mp 103−105 °C; $[\alpha]_D$ +8° (*c* 1.56, $CHCl_3$); IR (KBr) ν_{max} 3481, and 1738 cm^{-1}; ^{13}C and ^{1}H NMR data, see Tables 1 and 2; FABMS *m/z* 583 ([M + Na]$^+$, 1), HRFABMS *m/z* 583.3609 [M + Na]$^+$ (calcd for $C_{33}H_{52}O_7Na$, 583.3613).

Hippuristerone L (3): white powder; mp 204−205 °C; $[\alpha]_D$ +9° (*c* 1.28, $CHCl_3$); IR (KBr) ν_{max} 3447 and 1711 cm^{-1}; ^{13}C and ^{1}H NMR data, see Tables 1 and 2; FABMS *m/z* 503 ([M + H]$^+$, 10), HRFABMS *m/z* 503.3734 [M + H]$^+$ (calcd for $C_{31}H_{51}O_5$, 503.3738).

Hippuristerol E (4): white powder; mp 134−136 °C; $[\alpha]_D$ +8° (*c* 0.45, $CHCl_3$); IR (KBr) ν_{max} 3449, 1724, and 1252 cm^{-1}; ^{13}C and ^{1}H NMR data, see Tables 1 and 2; FABMS *m/z* 505 ([M + H]$^+$, 3); HRFABMS *m/z* 505.3893 [M + H]$^+$ (calcd for $C_{31}H_{53}O_5$, 505.3895).

Hippuristerol F (5): white powder; mp 98−100 °C; $[\alpha]_D$ −1° (*c* 2.44, $CHCl_3$); IR (KBr) ν_{max} 3337 and 1728 cm^{-1}; ^{13}C and ^{1}H NMR data, see Tables 1 and 2; FABMS *m/z* 543 ([M + Na]$^+$, 14), HRFABMS *m/z* 543.3663 [M + Na]$^+$ (calcd for $C_{31}H_{52}O_6Na$, 543.3664).

1α,3*β*,5*β*,11α-Tetrahydroxygorgostan-6-one (6): white powder; mp 218−220 °C; $[\alpha]_D$ −5° (*c* 0.44, $CHCl_3$); IR (KBr) ν_{max} 3356, 1718, and 1284 cm^{-1}; ^{13}C and ^{1}H NMR data, see Tables 1 and 2; FABMS *m/z* 491 ([M + H]$^+$, 0.5), HRFABMS *m/z* 491.3733 [M + H]$^+$ (calcd for $C_{30}H_{51}O_5$, 491.3738).

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