Sulfated Steroids: Ptilosteroids A−C and Ptilosaponosides A and B from the Solomon Islands Marine Sponge *Ptilocaulis spiculifer*

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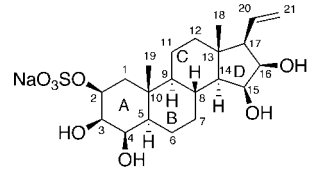
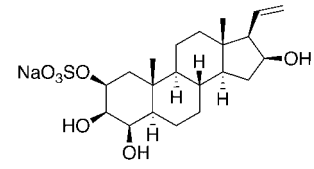
Three new pregnanes, ptilosteroid A (**1**), ptilosteroid B (**2**), and ptilosteroid C (**3**), and two new pregnane glycosides, ptilosaponoside A (**4**) and ptilosaponoside B (**5**), were isolated from the marine sponge *Ptilocaulis spiculifer* collected in the Solomon Islands. The structures were determined by spectroscopic methods. Biological tests of these compounds showed that they are not cytotoxic against KB cells.

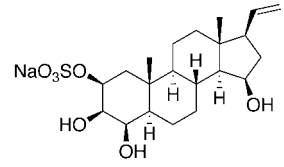
Modified steroids have long been recognized as terpene constituents of plants and animals. In recent years it has been found that steroids deriving from cholesterol are also quite generally present in marine invertebrates.[1] Pregnane derivatives have been isolated from gorgonian octocorals,[2,3] soft corals,[4] and a few sponges.[5−8] Marine sponges are a prolific source of interesting new pregnane steroids and their oxygenated derivatives, including steroids with rearranged main skeletons as well as rearranged side chains. In our ongoing research on the exhaustive isolation of new molecules from the Solomon Islands sponge *Ptilocaulis spiculifer*, it was found that this species contains other terpenes than previously isolated.[9,10] Purification of the methanolic extract by conventional methods afforded a series of five new modified steroids, named ptilosteroids A−C and ptilosaponosides A and B. Herein, we report the isolation and structural elucidation of these polyoxygenated steroids.

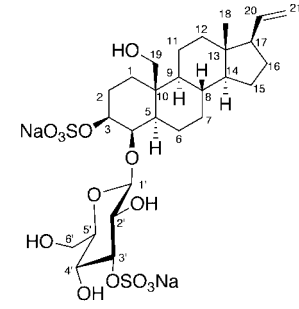
The MeOH extract of freeze-dried *P. spiculifer* (Lamark, 1813; Porifera, class Demospongiae, order Halichondrida, family Axinellidae) collected in July 2004 off the Solomon Islands accounted for 21% of the total dry weight of the sponge. This extract was partitioned between BuOH and H_2O. The organic fraction was successively purified by silica gel chromatography columns. Further reversed-phase HPLC of the minor fractions resulted in the isolation of ptilosteroids A−C (**1**−**3**) and ptilosaponosides A and B (**4**, **5**).

HRESIMS of compound **1** (8.3 mg, 0.024%) supported the molecular formula of $C_{21}H_{33}O_8S$ from the pseudomolecular ion *m*/*z* 445.1893 $[M - H]^-$ and indicated seven degrees of unsaturation. The IR spectrum suggested that **1** possessed a sulfate group at 1214 cm^{-1}. The MS/MS fragmentation showed a 96.9603 fragment corresponding to HSO_4^-. ^{13}C NMR and DEPT135 spectra of **1** exhibited the presence of two methyls, five methylene sp^3 C atoms, four methine sp^3 C atoms, one methine sp^2 C atom, two sp^3 quaternary carbons, and one methylene sp^2 C atom, indicating that **1** was a tetracyclic structure. The ^1H and ^{13}C NMR spectra including 2D analyses (Table 1) implied the presence of two tertiary methyls at δ_H 0.89 (H-18) and 1.29 (H-19), a terminal vinyl group (δ_H 5.01 and 5.07, H-21), and five oxygenated methines at δ_H 4.79, 3.61, 3.75, 4.20, and 4.16. The IR spectrum showed the presence of an OH function (3388 cm^{-1}). The foregoing spectral data and a literature survey provided evidence that **1** has a pregnane skeleton,[11] with several oxygenated methine groups. These methine groups were assigned to C-2, C-3, C-4, C-15, and C-16. The downfield chemical shift of δ_H 4.79 and the loss of 80 observed in the electrospray mass spectrum (negative mode) suggested a sulfate group at C-2,[12] which is in agreement with the IR spectrum (1214 cm^{-1}).[13] Regarding the relative configuration of **1**, the tetracyclic steroidal skeleton was considered to adopt an all-*trans* arrangement typical for pregnane steroids and supported by coupling constant values and NOESY analysis (Figure 1). The coupling constant between H-8 and H-9 (J = 10.7 Hz) implied a *trans* configuration for the B and C ring junction. The coupling constants of all protons from ring A indicated that all substituents were above the plane. The NOESY correlations observed from H-19 to H-8 and H-11β,









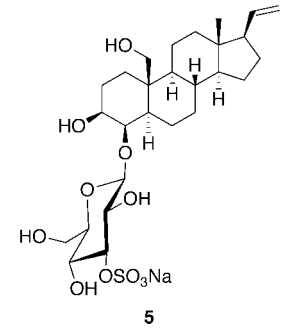


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Table 1. NMR Spectroscopic Data for Ptilosteroids A, B, and C in CD_3OD (600 MHz for ^1H data of **1**, 500 MHz for ^1H data of **2** and **3**, 125 MHz for ^{13}C data)

	ptilosteroid A (**1**)		ptilosteroid B (**2**)		ptilosteroid C (**3**)	
position	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	42.7, CH_2	2.48, dd (3.1, 14.8) 1.24, dd (3.3, 14.8)	42.5, CH_2	2.47, dd (3.2, 14.7) 1.24, m	42.7, CH_2	2.49, dd (3.4, 14.7) 1.26, m
2	79.4, CH	4.79, ddd (3.1, 3.3, 14.8)	79.5, CH	4.79, m	79.4, CH	4.80, m
3	73.0, CH	3.62, dd (2.8, 4.0)	72.7, CH	3.60, dd (3.1, 4.3)	72.9, CH	3.62, dd (3.8, 4.5)
4	76.4, CH	3.76, dd (2.6, 2.8)	76.2, CH	3.74, dd (3.1, 3.8)	76.4, CH	3.76, dd (3.1, 3.8)
5	50.7, CH	1.20, td (2.8, 12.7)	50.5, CH	1.17, bd (12.8)	50.8, CH	1.20, m
6	27.2, CH2	1.97, dddd (3.9, 12.5, 12.7, 13.0) 1.42, m	27.1, CH_2	1.91, m 1.39, m	27.1, CH_2	1.96, m 1.39, m
7	33.1, CH2	2.18, dd (3.1, 14.8) 1.09, dddd (4.2, 12.0, 12.5, 12.9)	33.8, CH_2	1.81, m 0.99, m	33.0, CH_2	2.15, m 1.06, m
8	32.3, CH	1.93, m	36.4, CH	1.58, m	32.6, CH	1.87, m
9	58.3, CH	0.71, ddd (4.0, 10.7, 12.3)	57.9, CH	0.67, dt (4.4, 11.6)	58.4, CH	0.71, m
10	36.6, qC		36.1, qC		36.6, qC	
11	21.1, CH2	1.48, m 1.35, dddd (3.8, 12.3, 12.8, 13.0)	21.2, CH2	1.51, m 1.39, m	21.5, CH_2	1.51, m 1.37, m
12	40.5, CH2	1.54, ddd (3.1, 3.8, 12.6) 0.93, ddd (4.2, 12.6, 13.0)	39.3, CH2	1.59, m 0.97, m	40.4, CH_2	1.64, m 1.01, m
13	44.7, qC		44.9, qC		44.4, qC	
14	60.1, CH	0.86, dd (5.3, 11.3)	55.0, CH	0.91, m	61.9, CH	0.85, m
15	71.6, CH	4.20, dd (5.3, 6.7)	37.9, CH2	2.24, ddd (5.8, 7.7, 12.7) 1.26, m	71.7, CH	4.26, ddd (2.0, 6.0, 8.1)
16	75.0, CH	4.16, dd (6.7, 7.4)	74.8, CH	4.25, dt (5.3, 7.7)	41.6, CH_2	2.28, ddd (8.1, 8.3, 14.2) 1.60, m
17	63.0, CH	1.86, dd (7.4, 9.7)	63.3, CH	1.85, m	57.1, CH	1.88, m
18	17.5, CH_3	0.89, s	14.9, CH_3	0.83, s	16.2, CH_3	0.86, s
19	16.8, CH_3	1.29, s	16.7, CH_3	1.26, s	16.8, CH_3	1.29, s
20	137.0, CH	6.03, ddd (9.7, 10.1, 17.4)	136.9, CH	5.98, ddd (10.0, 10.4, 17.3)	140.6, CH	5.81, ddd (7.9, 10.7, 17.3)
21	116.9, CH_2	5.07, dd (2.7, 10.1) 5.02, (2.7, 17.4)	117.2, CH_2	5.09, dd (2.6, 10.4) 5.02, (2.6, 17.3)	115.3, CH_2	4.97, dd (2.2, 10.7) 4.96, dd (2.2, 17.3)

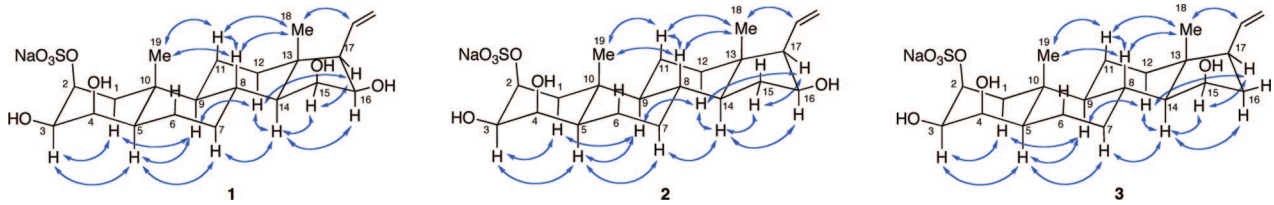

Figure 1. Selected NOE correlations for **1**, **2**, and **3**.

from H-18 to H-8, H-11β, and H-20, from H-5 to H-3, H-7α, and H-9, and from H-14 to H-7, H-9, and H-12α indicated the relative configurations for each ring junction to be *trans*. On the D ring, the NOESY correlations from H-20 to H-18 and from H-14 to H-15/H-16 allowed us to place the terminal vinyl group and the hydroxy substituents above the plane. This configuration was supported by the coupling constants between H-14 and H-15 ($J = 5.3$ Hz)[14] and between H-16 and H-17 ($J = 7.4$ Hz), which were characteristics of H-14α/H-15α and H-16α/H-17α arrangements. On the basis of these findings, the structure of this compound has been established as **1** and named ptilosteroid A.

The molecular formula $C_{21}H_{34}O_7S$ was assigned by HRESIMS to both compounds **2** and **3**, indicating that they were isomers. The IR spectra of both compounds showed the presence of OH (3391 cm^{-1}) and sulfate groups (1219 cm^{-1}). The ^1H and ^{13}C NMR data of **2** closely resembled those of **1**, except for the presence of a methylene group for **2** (δ_H 2.24/1.26; δ_C 37.9) and **3** (δ_H 2.28/1.60; δ_C 41.6) instead of an oxymethine group for **1**. Chemical shift arguments, $^1H-^1H$ COSY, HMQC, and HMBC NMR spectra allowed us to assign the observed ^{13}C and ^1H signals for **2** (Table 1). The additional methylene group present in this molecule was located at C-15. A NOESY correlation of H-14/H-16 indicated that H-16 was α-oriented. On the basis of all these data the structure of this compound has been established as **2** and named ptilosteroid B.

The spectral data (IR and NMR) for **3** were similar to those of **2**. After a detailed comparison of 1D and 2D NMR spectroscopic data, we observed that the only difference between these two compounds was the interchange of the C-15/C-16 group on the D ring. The hydroxy group was located at C-15 for **3**. NOESY correlations of H-14/H-15 and H-15/H-17 indicated that H-15 was α-oriented. On the basis of all these data the structure of this compound has been established as **3** and named ptilosteroid C.

NMR data of compound **4** showed similarities with those of **1**−**3** and additional typical sugar protons. Preliminary examination of the ^1H and ^{13}C NMR data revealed that the pregnane skeleton present in **1**−**3** was also present in **4**. A conspicuous group of methine resonances between δ 3.31 and 4.46 and the presence of a ^{13}C NMR acetal resonance (δ_C 104.7) suggested the presence of a cyclized hexose unit in the pyranose form. Evaluation of the ESI mass spectral fragmentation pattern of the compound showing $C_{21}H_{33}O_6S$ (*m/z* 413) [M − H − $C_6H_{10}O_8S$, aglycone unit] and $C_6H_9O_8S$ (*m/z* 241) [M − H − $C_{21}H_{34}O_6S$, sugar unit] supported this assignment. The presence of sulfate groups was suggested by the ESI mass spectrum that exhibited a molecular ion species at *m/z* 327 $[M - 2H]^{2-}$, indicating the presence of two sulfate groups. A strong IR absorption band at 1248 cm^{-1} supported the presence of sulfate esters.[13] The complete structural details of the tetracyclic core and hexose portion of the molecule were subsequently determined by NMR analysis. The ^1H and ^{13}C NMR spectra of **4** (Table 2) and a literature survey immediately suggested that the aglycone was the degraded sterol pregn-20-ene-3β,4β,19-triol (pregnenetriol).[15] According to the coupling constant values and NOESY analysis (Figure 2), the tetracyclic steroidal frame was

Table 2. NMR Spectroscopic Data for **1**−**3** in CD3OD (600 MHz for ^{1}H data of **1**, 500 MHz for ^{1}H data of **2** and **3**, 125 MHz for ^{13}C data)

	ptilosaponoside A (**4**)		ptilosaponoside B (**5**)	
position	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	34.9, CH_2	1.80, m	34.6, CH_2	1.83, m
		0.96, m		0.89, m
2	26.4, CH_2	1.90, m	28.5, CH_2	1.71, m
		1.75, m		1.64, m
3	78.9, CH	4.26, m	72.6, CH	3.53, m
4	83.0, CH	4.27, m	86.4, CH	3.89, m
5	51.2, CH	1.36, m	51.3, CH	1.34, m
6	27.9, CH_2	2.36, dddd (4.0, 12.4, 12.9, 14.2)	27.8, CH_2	2.30, dddd (4.0, 12.4, 12.9, 14.2)
		1.36, m		1.37, m
7	34.0, CH_2	0.99 m	34.0, CH_2	1.84, m
		1.83, m		0.98, m
8	37.6, CH	1.87, m	37.6, CH	1.89, m
9	57.3, CH	0.72, m	57.4, CH	0.71, m
10	40.7, qC		40.9, qC	
11	22.2, CH_2	1.52, m	22.4, CH_2	1.60, m
		1.56, m		1.54, m
12	39.3, CH_2	1.68, m	39.3, CH_2	1.70, m
		1.02, m		1.03, m
13	44.9, qC		44.9, qC	
14	58.4, CH	0.92, m	58.4, CH	0.93, m
15	26.0, CH_2	1.70, m	26.0, CH_2	1.70, m
		1.21, m		1.22, m
16	28.6, CH_2	1.76, m	28.7, CH_2	1.76, m
		1.56, m		1.57, m
17	57.1, CH	1.94, m	57.1, CH	1.94, m
18	13.7, CH_3	0.66, s	13.7, CH_3	0.66, s
19	64.8, CH	4.08, d (12.5)	64.5, CH_2	4.03, d (12.5)
		3.84, d (12.5)		3.90, d (12.5)
20	141.2, CH	5.75, ddd (8.0, 9.3, 18.0)	141.2, CH	5.75, ddd (8.0, 9.3, 18.0)
21	115.0, CH_2	4.93, m	116.0, CH	4.94, m
		4.92, m		4.93, m
1′	104.8, CH	4.46, d (7.8)	105.0, CH	4.45, d (7.8)
2′	74.6, CH	3.51, dd (7.8, 9.0)	74.4, CH	3.49, dd (7.8, 8.8)
3′	86.1, CH	4.24, t (9.0)	85.8, CH	4.25, dd (8.8, 9.2)
4′	70.5, CH	3.44, dd (9.0, 9.7)	70.1, CH	3.53, m
5′	77.9, CH	3.31, m	77.9, CH	3.37, ddd (2.2, 5.4, 8.0)
6′	63.0, CH_2	3.86, dd (2.4, 12.1)	62.5, CH_2	3.86, dd (2.2, 12.0)
		3.70, dd (6.7, 12.1)		3.67, dd (5.4, 12.0)

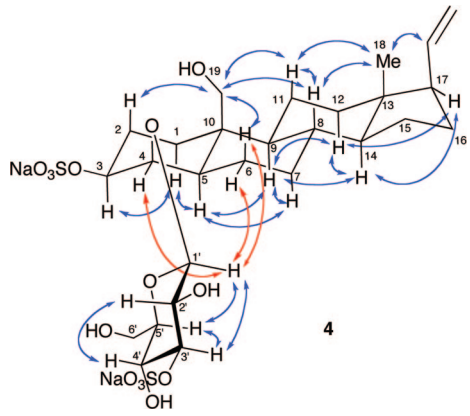

Figure 2. Selected NOE correlations for **4**.

considered to adopt an all-*trans* arrangement typical for pregnanesteroids. The downfield chemical shift at δ_H 4.26 suggested a sulfate group at C-3. The attachment of the sugar moiety to C-4 of the aglycon was deduced from the ^3J HMBC correlation between the anomeric proton (H-1′, δ_H 4.46 ppm) and C-4 (83.0 ppm) as well as from NOESY correlations between the hemiacetal proton (H-1′, δ_H 4.46 ppm) and H-4/H-6 (δ_H 4.27/δ_H 2.36; 1.36). The sugar unit in **4** was identified as glucose in a β-pyranoside configuration. The anomeric proton at C-1′ in **4** appeared at δ_H 4.46. This proton was a doublet (J = 7.8 Hz), which confirmed its axial orientation and equatorial linkage (or β position). Because H-3′ was split into a triplet (J = 9.0 Hz), it was clearly an axial proton. From this we concluded that H-2′ was *trans*-diaxial to both H-1′ and H-3′; therefore the C-2′ and C-3′ hydroxyls must be equatorial. Furthermore, H-4′ (a doublet of doublets with J = 9.0 and 9.7 Hz) had to be axial, *trans* to both H-3′ and H-5′. A strong NOESY correlation from H-1′ to H-3′ and H-5′ confirmed the 1,3-diaxial relationship of the latter protons. The downfield chemical shift to δ_H 4.24, δ_C 86.1 suggested the position of the sulfate group at C-3′, which is in agreement with the ESI mass fragmentation pattern of **4**, showing $C_6H_9O_8S$ (*m*/*z* 241) [M − H − $C_{21}H_{34}O_6S$, sulfated sugar unit]. The structure of this compound has been established as **4** and named ptilosaponoside A. The absolute configuration of the glucose in **4** could not be conclusively assigned due to the limited amount of sample available for further studies.

Compound **5** displayed NMR spectroscopic features similar to **4**, suggesting that these two compounds were related. After a detailed examination of 1D (Table 2) and 2D NMR spectroscopic data of **5**, we observed that the only difference between these compounds was the degree of sulfation on the aglycone unit with the upfield chemical shift to δ_H 3.53 suggesting no substitution at C-3. The ESI mass spectrum exhibited a molecular ion species at *m*/*z* 575, corresponding to a monocharged state [M − H]$^-$. Compound **5** was monosulfated and was consistent with $C_{27}H_{44}O_{11}S$ by HRESIMS. Through the analysis of MS spectra, ^{1}H NMR coupling constants, COSY, HMBC, and NOESY experiments, we identified the structure of this compound as **5**. However, the absolute configuration of the glucose in **5** could not be conclusively assigned due to the limited amount of sample.

In summary, we isolated five new pregnenes, ptilosteroids A (**1**), B (**2**), and C (**3**) and ptilosaponosides A (**4**) and B (**5**). All of these

polyoxygenated steroids occurred as sulfate esters. A nonsulfated polyoxygenated sterol, meristone A, was previously isolated from a Senegalese specimen of *Ptilocaulis spiculifer*.[10] Sulfated steroids from the Pacific *P. spiculifer* are described in this paper for the first time. There are few pregnane compounds isolated from sponges. They are preferentially found in soft corals.[15,16] From the natural chemodiversity point of view, the presence of pregnanes in sponges, as well as in plants, is an interesting observation. *In vitro* KB cell cytotoxicity assays of these compounds showed that they are not cytotoxic.

Experimental Section

General Experimental Procedures. Optical rotations were determined in methanol with a Jasco P1010 polarimeter (10 mm and 0.35 mL). The IR spectra were measured (neat) on a Perkin-Elmer BX-FT-IR spectrometer. The UV spectrum was recorded on a Waters 996 photodiode array detector in the HPLC solvent. NMR experiments were carried out with Bruker Avance 600 MHz and DRX 500 MHz spectrometers using CD_3OD (3.31 ppm/49.15 ppm). HRMS data were obtained with a hybrid linear trap/orbitrap mass spectrometer (LTQ-orbitrap, Thermofisher) in electrospray negative ionization mode by direct infusion of the purified compounds. Preparative HPLC was performed on an autoprep system (Waters 600 controller and Waters 600 pump with a Waters 996 photodiode array detector). Samples were injected by the Waters 2700 sample manager.

Collection and Identification of the Sponge. *Ptilocaulis spiculifer* samples were collected off New Georgia Island (North East Kolingo) in the Solomon Islands in July 2004 using scuba at a depth of 15 m. A voucher specimen is deposited in the Queensland Museum under the accession number G324820.

Extraction and Isolation. The sponge was frozen after collection and later ground, freeze-dried, and stored at −20 °C until workup. The dry powdered sponge (34 g) was extracted four times by maceration with MeOH (800 mL, 2 × 500 and 400 mL) at room temperature. After removal of the solvent under reduced pressure, the resulting crude extract (7 g) was triturated in CH_2Cl_2 two times (2 × 100 mL). Dichloromethane-insoluble extracts (6.3 g) were then partitioned between water and *n*-BuOH. After concentration, the *n*-BuOH extract (0.94 g) was purified by chromatography on Si gel (prepacked Versapack column 48 g, 45−75 μm) using a CH_2Cl_2/AcOEt/MeOH gradient (starting from CH_2Cl_2 100% to MeOH 100%) as eluent and monitored by TLC. The fractions (134.4 and 154.1 mg) containing the mixture of ptilosteroids and ptilosaponosides were eluted with AcOEt/MeOH (80:20).

After LC-MS analysis, the first mixture was purified directly by preparative reversed-phase HPLC (Waters XBridge Prep Shield, RP_{18}, 5 μm, 19 × 100 mm column, 17 mL/min) using a gradient of HCO_3NH_4 (10 mM, pH 8.1)/CH_3CN (80:20 to 50:50 over 30 min), affording ptilosteroids A (**1**) (7.2 mg), B (**2**) (1.1 mg), and C (**3**) (1.4 mg, 0.0041% of the freeze-dried sponge). The second fraction containing the mixture of ptilosteroids and ptilosaponosides was purified by chromatography on Si gel (30 mL, 35−70 μm) using a AcOEt/BuOH gradient followed by BuOH/MeOH, 1:1. Further purification on a preparative reversed-phase HPLC (Waters XBridge Prep Shield, RP_{18}, 5 μm, 19 × 100 mm column, 19 mL/min) using a gradient of HCO_3NH_4 (10 mM, pH 7.9)/CH_3CN (99:1 to 10:90 over 45 min) yielded ptilosteroids A (**1**) (1.1 mg) and B (**2**) (0.9 mg, 0.0058%) and ptilosaponosides A (**4**) (1.5 mg, 0.0044%) and B (**5**) (1.3 mg, 0.0038% of the freeze-dried sponge). The yield of compounds **1** and **2** in the sponge was 0.024% and 0.0058%, respectively.

Ptilosteroid A (1): white powder; $[\alpha]^{25.6}_D$ −2.4 (*c* 0.67, MeOH); IR (neat) ν_{max} 3388, 2931, 2844, 1637, 1214, 1072 cm^{-1}; ^1H and ^{13}C NMR see Table 1; HRESIMS *m/z* 445.1893 $[M - H]^-$ (calcd for $C_{21}H_{33}O_8S$, 445.1884).

Ptilosteroid B (2): white powder; $[\alpha]^{25}_D$ +1.9 (*c* 0.23, MeOH); IR (neat) ν_{max} 3391, 2920, 2850, 1631, 1219, 1085 cm^{-1}; ^1H and ^{13}C NMR see Table 1; HRESIMS *m/z* 429.1943 $[M - H]^-$ (calcd for $C_{21}H_{33}O_7S$, 429.1934).

Ptilosteroid C (3): white powder; $[\alpha]^{25}_D$ −21.2 (*c* 0.40, MeOH); IR (neat) ν_{max} 3388, 2933, 2852, 1632, 1218, 1071 cm^{-1}; ^1H and ^{13}C NMR see Table 1; HRESIMS *m/z* 429.1946 $[M - H]^-$ (calcd for $C_{21}H_{33}O_7S$ 429.1934).

Ptilosaponoside A (4): white powder; $[\alpha]^{25}_D$ −8.3 (*c* 0.43, MeOH); UV (HPLC solvent mixture: CH_3CN/buffer solution of 10 mM HCO_3NH_4) λ_{max} 192 nm; IR (neat) ν_{max} 3432, 2923, 2851, 1634, 1248, 1077, 1034 cm^{-1}; ^1H and ^{13}C NMR see Table 2; HRESIMS *m/z* 655.2097 $[M - H]^-$ (calcd for $C_{27}H_{43}O_{14}S_2$ 655.2100).

Ptilosaponoside B (5): white powder; $[\alpha]^{25}_D$ +0.9 (*c* 0.37, MeOH); IR (neat) ν_{max} 3392, 2923, 2851, 1633, 1256, 1077, 1039 cm^{-1}; ^1H and ^{13}C NMR see Table 2; HRESIMS *m/z* 575.2521 $[M - H]^-$ (calcd for $C_{27}H_{43}O_{11}S$, 575.2530).

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Supporting Information Available: ^1H and ^{13}C NMR for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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