Spirostanol Glycosides from *Peliosanthes sinica*

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Three new spirostanol glycosides, peliosanthosides A—C, were isolated from the whole plants of *Peliosanthes sinica*, along with two known ones. Their structures were elucidated by means of chemical and spectral evidence.

Key words *Peliosanthes sinica*; Liliaceae; spirostanol glycoside; peliosanthoside A, B, C

Peliosanthes sinica WANG *et* TANG is an herbal plant distributed in southern Yunnan and southern Guangxi, China. The genus *Peliosanthes* comprises about ten species and belongs to the *Ophiopogoneae* of Liliaceae. *Ophiopogoneae* includes three genera, *Ophiopogon*, *Liriope* and *Peliosanthes*. Although many steroidal glycosides have been found in *Ophiopogon* and *Liriope* plants,[1,2] none have been reported in the genus *Peliosanthes*. As part of our continued chemical studies on Liliaceous plants,[2e,3] we investigated the whole plants of *P. sinica*. This paper describes the isolation and structure elucidation of three new spirostanol glycosides, peliosanthosides A—C (**1**—**3**), along with glycoside J-4 (**4**) and glycoside J-3 (**5**) already found in *O. jaburan*.[2c]

Repeated column chromatography of the crude glycosides of *P. sinica* yielded glycosides **1**—**5**.

Glycoside **4**, $C_{44}H_{67}O_{20}S$ from the high resolution negative FAB-MS, was hydrolysed with acid to afford an aglycone (**6**), arabinose, rhamnose, glucose and sulfate ion. The aglycone was identified as neoruscogenin (**6**) by the analyses of positive FAB-MS, ^{13}C- and ^{1}H-NMR data.[2c,4] The ^{13}C-NMR data of **4** closely corresponded with those of glycoside J-4 isolated from *O. jaburan*,[2c] whose structure is neoruscogenin 1-*O*-α-L-rhamnopyranosyl(1→2)-4-*O*-sulfo-α-L-arabinopyranoside-3-*O*-β-D-glucopyranoside. On heating with pyridine-dioxane,[2c,5] **4** afforded a desulfated product (**7**). Partial acid hydrolysis of **7** produced compound **8**. Based on the analyses of acid hydrolysis, FAB-MS, ^{1}H- and ^{13}C-NMR spectra, **8** was readily assigned as neoruscogenin 3-*O*-β-glucopyranoside, and **7** was identified as neoruscogenin 1-*O*-α-L-rhamnopyranosyl(1→2)-α-L-arabinopyranoside-3-*O*-β-D-glucopyranoside.[2c] From the above evidence, the structure of **4** proved to be identical with that of glycoside J-4.

Glycoside **5**, $C_{45}H_{69}O_{20}S$ from the high resolution negative FAB-MS, yielded **6**, fucose, rhamnose, glucose and sulfate ion on acid hydrolysis. The ^{13}C-NMR spectrum of **5** indicated that it is a 1,3-di-*O*-glycoside of **6**. In addition, the ^{13}C-NMR signals of its sugar moiety were superimposable on those of glycoside J-3 obtained from *O. jaburan*.[2c] Desulfation of **5** yielded glycoside **9** whose structure was identified by the analyses of acid hydrolysis, negative FAB-MS and comparison of the ^{13}C-NMR signals of its sugar moiety with those of an authentic sample.[2c] Partial acid hydrolysis of **9** produced compound **8**. Therefore, the structure of **5** was neoruscogenin 1-*O*-α-L-rhamnopyranosyl(1→2)-4-*O*-sulfo-β-D-fucopyranoside-3-*O*-β-D-glucopyranoside, a glycoside J-3 which was isolated as a mixture of ruscogenin and neoruscogenin glycosides, both having the 1-*O*-α-L-rhamnopyranosyl(1→2)-4-*O*-sulfo-β-D-fucopyranosyl-3-*O*-β-D-glucopyranosyl moiety.[2c]

Glycoside **1**, designated peliosanthoside A, displayed a ^{1}H-NMR spectrum similar to **4** except for the presence of a doublet signal at δ1.13 (6H, J=6.7 Hz). The ^{13}C-NMR spectrum of **1** was also similar to that of **4** with the exception of additional signals at δ175.16 (s, carboxylic ester), 75.12 (d, methine attached with a hydroxyl group), 33.01 (d, methine), 19.32 and 17.57 (s each, methyl groups). Furthermore, in the negative FAB-MS, **1** showed a quasimolecular ion peak at m/z 1047 ($C_{49}H_{75}O_{22}S$), one hundred mass units more than **4**, indicating the presence of an acyl moiety with a molecular composition of $C_5H_8O_2$.

Alkaline hydrolysis of **1** yielded **4**, suggesting that **1** was composed of **4** and an acyl moiety. Based on the ^{13}C-NMR spectrum of **1**, the acyl moiety had two possibilities: –OCO–CH(OH)–CH(CH_3)$_2$ and –OCO–CH(CH_3)–CH(OH)(CH_3). The coupling system of the acyl moiety was established by ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY experiments. In the ^{13}C–^{1}H correlation spectroscopy (COSY) of **1**, the carbon signals at δ 75.12 and 33.01 correlated with the proton signals at δ4.35 (d, J=4.7 Hz) and 2.33 (m), respectively. The two methyl carbon signals at δ19.32 and 17.57 simultaneously correlated with the proton signal at δ1.13 (6H, d, J=6.7 Hz). In the ^{1}H–^{1}H COSY spectrum of **1**, the signal at δ2.33 showed cross peaks not only with the signal at δ4.35 but also with the signal at δ1.13. Therefore, the acyl moiety was determined to be –OCO–CH(OH)–CH(CH_3)$_2$. Such a substituent, called an α-hydroxyisovaleryl group, was reported to be present in the sesquiterpene lactones from *Ixeris stolonifera*.[6]

The remaining was the linkage position of the acyl moiety to the sugar moiety, which was determined by comparing differences between the β-glucopyranosyl ^{13}C-NMR signals of **1** and **4**. In particular was the difference between the methylene signals which appeared

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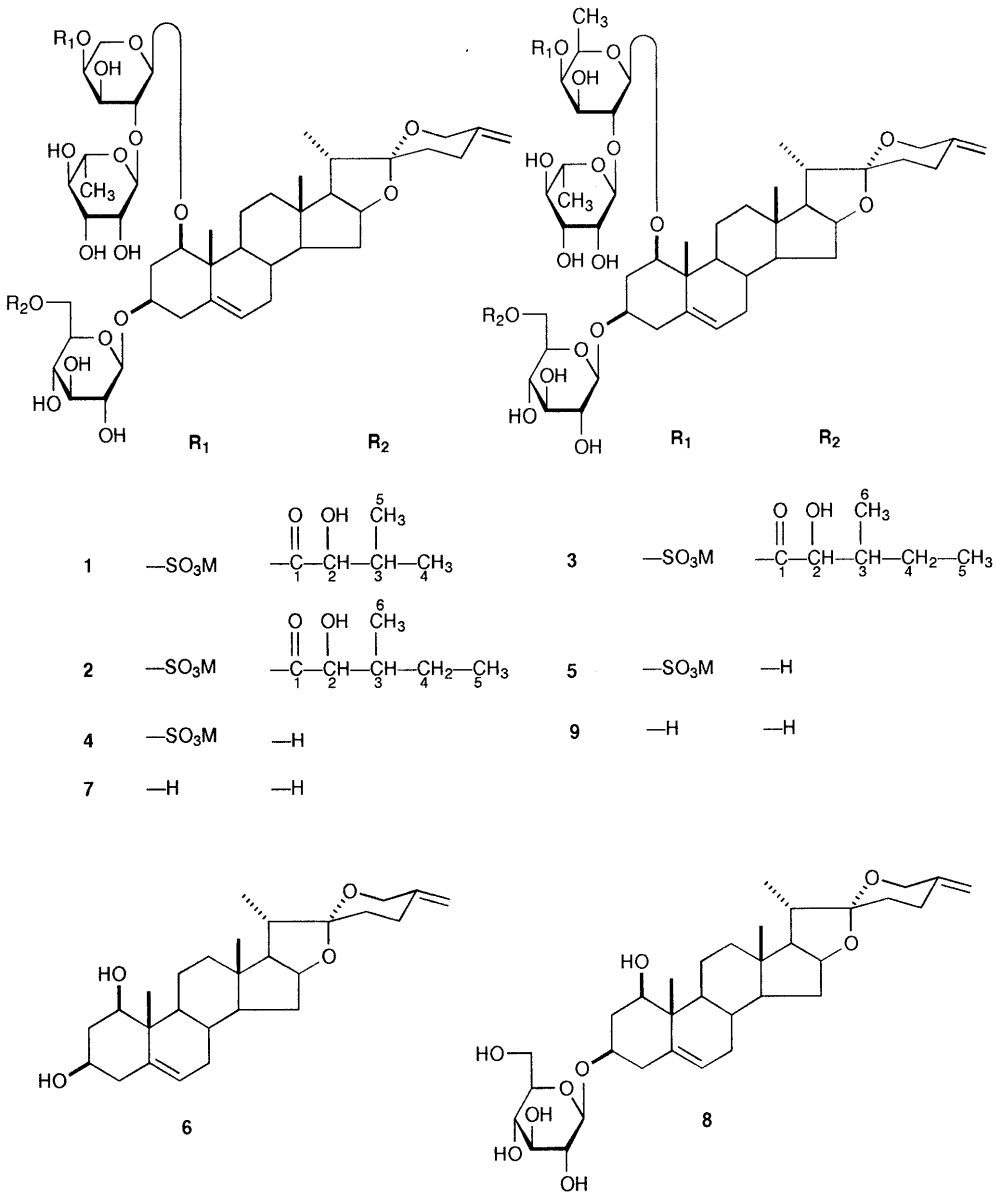

Chart 1

at δ 65.04 in **1** and δ 62.79 in **4**. The downfield shifted methylene signal could be assigned to glucosyl C-6. In addition, the glucosyl C-5 which was normally present at about δ 78.0 appeared in **1** at δ 76.07. This is characteristic of acyl substitution at glucosyl C-6. Thus, the acyl moiety was deduced to be linked at the glucosyl C-6. The ^{1}H–^{1}H COSY and ^{13}C–^{1}H COSY spectra assigned the proton and carbon signals of **1** as shown in Tables 1—3. All spectral data were self-consistent. For example, when compared to glycosides **4** and **7**, the sulfate group at the arabinosyl C-4 and the acyl group at the glucosyl C-6 led to significant downfield shift effects for both of their ^{13}C- and ^{1}H-NMR signals. Consequently, the structure of **1** was shown to be neoruscogenin 1-*O*-α-L-rhamnopyranosyl(1→2)-4-*O*-sulfo-α-L-arabinopyranoside-3-*O*-(6-*O*-α-hydroxyisovaleryl)-β-D-glucopyranoside.

Glycoside **2**, designated peliosanthoside B, showed similar ^{1}H- and ^{13}C-NMR spectra to those of **1** except for a few upfield carbon and proton signals. Its negative FAB-MS exhibited a quasimolecular ion peak at *m/z* 1061, 14 mass units more than **1**. Alkaline hydrolysis of **2** yielded glycoside **4**, suggesting that **2** might be composed of **4** and an acyl moiety. The signals of the acyl moiety were extracted from the ^{1}H–^{1}H and ^{13}C–^{1}H COSY spectra. In the ^{13}C–^{1}H COSY of **2**, carbon signals at δ 75.11 (d), 39.80 (d), 15.95 (q) and 12.01 (q) correlated with the proton signals at δ 4.42 (d, J=4.5 Hz), 2.13 (m), 1.13 (d, J=6.8 Hz) and 0.94 (t, J=7.4 Hz), respectively, while a carbon signal at d 25.14 (t) corresponded with both proton signals at δ 1.46 (m) and 1.80 (m). The ^{1}H–^{1}H COSY spectrum of **2** displayed typical cross peaks between the methyl signal at δ 0.94 and the two methylene signals at δ 1.46 (m) and 1.80 (m), and between the methyl signal at δ 1.13 and the methine signal at δ 2.13. The signal at δ 2.13 also correlated with the signal at δ 4.42. Thus, the composition of the acyl moiety was –OCO–CH(OH)–CH(CH_3)–CH_2–CH_3.

The linkage position of this acyl moiety to the sugar moiety was confirmed to be glucopyranosyl C-6 by comparing the ^{1}H- and ^{13}C-NMR signals with **1**. Tables

Table 1. ^{13}C-NMR Data for Aglycone Moieties of Compounds **1**—**9** (Pyridine-d_5, δ Values)

C	**6**	**1**	**2**	**3**	**4**	**5**	**7**	**8**	**9**
1	78.23	82.52	82.53	83.16	82.96	83.77	82.97	78.60	83.37
2	43.94[a)]	34.43	34.37	34.93	34.83	35.41	34.97	41.10	35.01
3	68.26	75.05	75.11	75.09	74.99	75.19	75.04	75.04	75.28
4	43.55[a)]	39.58	39.58	39.61	39.81	39.83	39.85	40.56[a)]	39.93
5	140.49	138.64	138.63	138.64	138.55	138.56	138.64	139.37	138.70
6	124.41	125.59	125.64	125.65	125.62	125.66	125.47	125.05	125.50
7	32.42	32.17	32.17	32.18	32.15	32.17	32.09	32.34	32.17
8	33.11	33.19	33.19	33.14	33.20	33.16	33.19	32.99	33.18
9	51.48	50.30	50.29	50.60	50.26	50.60	50.40	51.34	50.63
10	43.72	43.11	43.11	43.03	43.09	43.03	43.05	43.76	43.02
11	24.33	23.99	23.99	23.95	24.02	23.96	24.10	24.20	24.07
12	40.39	39.74	39.80	39.98	39.81	40.96	40.32	39.85[a)]	40.35
13	40.67	40.17	40.17	40.23	40.23	40.29	40.32	40.32	40.37
14	57.09	56.53	56.55	57.03	56.66	57.13	56.89	56.95	57.29
15	32.50	32.47	32.48	32.48	32.50	32.51	32.48	32.44	32.51
16	81.58	81.52	81.52	81.51	81.57	81.57	81.56	81.48	81.59
17	63.35	62.86	62.86	63.00	62.88	63.06	63.14	63.31	63.29
18	16.67	16.57	16.58	16.70	16.64	16.77	16.74	16.59	16.90
19	13.97	14.90	14.88	14.83	14.95[a)]	14.91[a)]	14.96[a)]	13.76	14.97
20	42.06	41.98	41.99	42.01	42.02	42.06	41.99	42.00	42.04
21	15.02	14.90	14.88	14.83	14.90[a)]	14.87[a)]	15.02[a)]	14.96	14.97
22	109.60	109.45	109.46	109.47	109.51	109.54	109.55	109.50	109.57
23	33.38	33.34	33.34	33.29	33.37	33.33	33.36	33.34	33.35
24	29.06	29.02	29.03	29.02	29.06	29.05	29.07	29.01	29.08
25	144.63	144.62	144.62	144.61	144.64	144.62	144.62	144.61	144.67
26	65.14	65.04	65.06	65.04	65.08	65.08	65.10	65.08	65.11
27	108.67	108.59	108.60	108.58	108.64	108.65	108.98	108.56	108.85

a) Signals can be interchangeable within each column.

Table 2. ^{13}C-NMR Data for Sugar and Acyl Moieties of Compounds **1**—**5** and **7**—**9** (Pyridine-d_5, δ Values)

C	**1**	**2**	**3**	**4**	**5**	**7**	**8**	**9**
Sugar moiety								
1-*O*-Ara								
1	99.67	99.71		99.99		100.20		
2	75.80	75.79		75.80		75.91		
3	75.00	74.94		74.99		75.18		
4	76.23	76.08		76.12		70.17		
5	65.94	65.96		65.86		67.42		
1-*O*-Fuc								
1			99.63		100.03			100.25
2			76.05		76.11			76.76
3			75.74		75.71			74.46
4			78.87		78.92			73.29
5			70.50		70.53			71.12
6			17.32		17.37			17.22
Rha								
1	101.50	101.50	101.53	101.48	101.50	101.57		101.56
2	72.34	72.34	72.34	72.41	72.39	72.57		72.59
3	72.34	72.34	72.34	72.41	72.39	72.70		72.73
4	74.12	74.12	74.20	74.09	74.17	74.20		74.23
5	69.51	69.51	69.38	69.56	69.40	69.47		69.34
6	18.98	18.98	19.03	18.99	19.00	19.05		19.07
3-*O*-Glc								
1	101.94	101.94	101.82	102.57	102.59	102.83	102.70	102.88
2	74.30	74.30	74.35	75.24	75.19	75.27	75.34	75.28
3	78.36	78.33	78.32	78.34	78.32	78.37	77.84	78.41
4	71.65	71.65	71.70	71.74	71.65	71.75	71.86	71.71
5	76.07	75.63	75.61	78.45	78.41	78.54	78.34	78.56
6	65.04	65.06	65.16	62.79	62.70	62.89	62.96	62.83
Acyl moiety								
1	175.16	175.24	175.22					
2	75.12	75.11	75.15					
3	33.01	39.80	39.80					
4	19.32[a)]	25.14	25.14					
5	17.57[a)]	12.01	12.02					
6		15.95	15.98					

a) Signals can be interchangeable within each column.

Table 3. ^{1}H-NMR Data for Glycosides **1** and **2** (Pyridine-d_5, δ Values)[a]

H	1	2
Aglycone		
1	3.77 br d (12)	3.78 br d (11)
2	2.18, 2.50	2.21, 2.58
3	4.00	4.01
4	2.47, 2.68	2.46, 2.68
6	5.54 br s	5.57 br s
7	1.55, 1.86	1.55, 1.85
8	n.d.[b]	1.75
9	n.d.[b]	1.42
11	1.54, 2.80	1.52, 2.77
12	n.d.[b]	1.36, 2.13
13	1.05	1.05
14	1.41, 2.00	1.42, 2.00
16	4.49	4.49
17	1.64	1.65
18	0.82 s	0.82 s
19	1.28 s	1.29 s
20	1.87	1.88
21	1.03 d (6.6)	1.03 d (6.7)
23	1.45, 1.74	1.45, 1.75
24	2.20, 2.70	2.21, 2.69
26	4.00, 4.44	4.01, 4.44
27	4.74 s, 4.77 s	4.75 s, 4.78 s
1-*O*-Ara		
1	4.49	4.47
2	4.30	4.30
3	4.16	4.11
4	5.23 br s	5.22 br s
5	3.65, 4.52	3.64, 4.59
Rha		
1	6.23 s	6.17 s
2	4.72	4.72
3	4.52	4.54
4	4.28	4.27
5	4.70	4.68
6	1.68 d (6.0)	1.68 d (5.7)
3-*O*-Glc		
1	5.04 d (7.7)	5.01 d (7.2)
2	4.04	4.00
3	4.29	4.30
4	4.08	4.08
5	4.48	4.46
6	4.85—4.95	4.82 br d (12) 5.00 d (12.8)
Acyl		
2	4.35 d (4.7)	4.42 d (4.5)
3	2.33 m	2.13 m
4	1.13 d (6.7)	1.46 m, 1.80 m
5	1.13 d (6.7)	0.94 t (7.4)
6		1.13 d (6.8)

a) Coupling patterns well resolved are expressed with multiplicities and coupling constants in Hz in parentheses. b) Not determined due to overlapped.

1—3 showed the signal assignments of **2** from ^{1}H–^{1}H and ^{13}C–^{1}H COSY spectra. From these results, the structure of **2** was established to be neoruscogenin 1-*O*-α-L-rhamnopyranosyl(1→2)-4-*O*-sulfo-α-L-arabinopyranoside-3-*O*-(6-*O*-α-hydroxy-β-methyl-*n*-valeryl)-β-D-glucopyranoside. The presence of such an acyl subsituent was also reported in the sesquiterpene lactones from *Ixeris stolonifera*.[6]

Glycoside **3** was designated as peliosanthoside C and displayed a quasimolecular ion peak at *m/z* 1075 in the negative FAB-MS. The ^{13}C- and ^{1}H-NMR spectra of **3** revealed that it possessed an α-hydroxy-β-methyl-*n*-valeryl moiety. The remaining signals were very similar to those of glycoside **5**. Alkaline hydrolysis of **3** afforded **5**, indicating that **3** was composed of **5** and the α-hydroxy-β-methyl-*n*-valeryl moiety. The linkage position of this acyl moiety to the sugar moiety was deduced to be glucosyl C-6, since its signal was displaced downfield at δ 65.16, while other glucosyl signals were shifted slightly upfield (see Table 2) when compared with **5**. Moreover, the proton signal at δ 4.85 (1H, br d, J=10 Hz) and 5.01 (1H, d, J=11.4 Hz) appeared in the ^{1}H-NMR spectrum of **3**, while no signal appeared in this field region in that of **5**. The two signals assignable to glucosyl H-6 resulted from esterification at the hydroxy group of glucosyl C-6. Therefore, the structure of **3** was determined to be neoruscogenin 1-*O*-α-L-rhamnopyranosyl(1→2)-4-*O*-sulfo-β-D-fucopyranoside-3-*O*-(6-*O*-α-hydroxy-β-methyl-*n*-valeryl)-β-D-glucopyranoside.

It is noted that the glycosides isolated from this plant possess a sulfate group on the sugar moiety. Sulfated steroidal glycosides are only known in *Ophiopogon jaburan*, *O. ohwii*, *O. planiscapus* and *Liriope platyphylla*[2a–d] in the Liliaceous plants. The present study is a continuing report on sulfated steroidal glycosides from the tribe of *Ophiopogoneae*. Furthermore, the steroidal glycosides obtained from this tribe show a close resemblance in structure. From the chemotaxonomic viewpoint, sulfated steroidal glycosides may be regarded as a chemical marker of *Ophiopogoneae*.

Experimental

Melting points were uncorrected. All NMR spectra were recorded in pyridine-d_5 at 400 MHz for ^{1}H-NMR, and 100 MHz for ^{13}C-NMR (including DEPT) using tetramethylsilane as an internal standard. ^{1}H–^{1}H and ^{13}C–^{1}H COSY were performed using standard pulse sequences.

Plant Material The whole plants of *Peliosanthes sinica* WANG *et* TANG were collected in Xishuanbanna, Yunnan province, China and identified by Prof. H. Li. A voucher specimen is stored in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation Fresh whole plants (2.1 kg) were extracted with hot MeOH. After removal of the solvent by evaporation, the combined extracts were dissolved in H_2O, defatted with $CHCl_3$, and then extracted with *n*-BuOH(saturated with H_2O). The combined *n*-BuOH layers were concentrated to dryness to give a residue (46 g). The residue was chromatographed on silica gel with a $CHCl_3$–MeOH–H_2O gradient (50 : 10 : 1 to 20 : 10 : 1) to give fractions 1—5 in increasing order of polarity. Fraction 4 (8.5 g) was subjected to high porous absorption resin D-101 with an aq. MeOH gradient to yield crude glycosides(1.74 g). The crude glycosides were then chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (7 : 3 : 0.5) and chromatographed again on reversed phase silica gel (RP-18) with 50%—60% MeOH to furnish glycosides **1** (45 mg), **2** (65 mg) and **3** (80 mg). Fraction 5 (7.4 g) was separated similarly as that for fr. 4 to afford glycosides **4** (350 mg) and **5** (210 mg).

Glycoside J-4 (**4**): Needles from MeOH, mp 220—222 °C, $[\alpha]_D^{20}$ −58° (c=0.52, MeOH). HRFAB-MS (neg.) *m/z*: 947.3903 (Calcd. for $[(C_{44}H_{67}O_{17}\cdot SO_3X)-X](X=K, Na, etc.)$: 947.3946). FAB-MS (neg.) *m/z*: 947 $[M-X]^-$, 802 $[947-Rha+H]^-$, 785 $[947-Glc]^-$, 429 $[947-Glc-Rha-Ara(SO_3M)]^-$. ^{1}H-NMR δ: 0.81 (3H, s, H-18), 1.03 (3H, d, J=6.7 Hz, H-21), 1.27 (3H, s, H-19), 1.68 (3H, d, J=5.8 Hz, Rha H-6), 3.65 (1H, br d, J=11.8 Hz, H-1), 4.47 (1H, d, J=5.9 Hz, Ara H-1), 4.76 and 4.79 (1H each, s, H-27), 5.04 (1H, d, J=7.7 Hz, Glc H-1), 5.23 (1H, br s, Ara H-4), 5.50 (1H, br d, J=5.2 Hz, H-6), 6.24 (1H, s, Rha H-1). ^{13}C-NMR: Tables 1, 2.

Glycoside J-3 (Neoruscogenin as Its Aglycone) (**5**): Powder from MeOH, $[\alpha]_D^{20}$ −71° (c=0.21, MeOH). HRFAB-MS (neg.) *m/z*: 961.4084 (calcd. for $[(C_{45}H_{69}O_{17}\cdot SO_3X)-X](X=K, Na, etc.)$: 961.4103). FAB-MS (neg.) *m/z*: 961 $[M-X]^-$, 815 $[961-Rha]^-$, 799 $[961-Glc]^-$.

^{1}H-NMR δ: 0.83 (3H, s, H-l8), 1.03 (3H, d, J=6.8 Hz, H-21), 1.27 (3H, s, H-19), 1.64 and 1.69 (3H each, d, J=6.2, 6.0 Hz, respectively, H-6 of Rha and Fuc), 4.73 and 4.76 (1H each, s, H-27), 5.05 (1H, d, J=7.5 Hz, Glc H-l), 5.06 (1H, br s, Fuc H-4), 5.49 (1H, br s, H-6), 6.23 (1H, s, Rha H-l). ^{13}C-NMR: Tables 1, 2.

Acid Hydrolysis of 4 and 5 A mixture of **4** (50 mg) and 5% HCl–EtOH (1:1, 5 ml) was refluxed for 5 h. After cooling, the reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O and then concentrated to dryness. The residue was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (50:10:1) yielding neoruscogenin (**6**) (5.8 mg), needles from MeOH, mp 200—202 °C, FAB-MS (pos.) m/z: 429 $[M(C_{27}H_{40}O_4)+H]^+$. ^{1}H-NMR δ: 0.90 (3H, s, H-l8), 1.04 (3H, d, J=7.0 Hz, H-21), 1.34 (3H, s, H-19), 3.81 (1H, dd, J=11.6, 4.2 Hz, H-l), 3.96 (1H, m, H-3), 4.02 and 4.45 (2H, ABq, J=12.2 Hz, H-26), 4.52 (1H, m, H-16), 4.77 and 4.80 (1H each, s, H-27), 5.61 (1H, d, J=4,3 Hz, H-6); ^{13}C-NMR: Table 1.

The H_2O layer was neutralized with Amberlite MB-3, concentrated and subjected to sugar analysis by TLC on a silica gel plate with authentic samples. $CHCl_3$–MeOH–AcOH–H_2O (7:3:1:0.5) was used as a solvent system and aniline–phthalate as the color reagent. Arabinose, rhamnose and glucose were detected as Rf values of 0.36, 0.49 and 0.25, respectively.

A part of the H_2O layer was directly used to examine the sulfate ion. A solution of 0.5% $BaCl_2$ was added to this H_2O layer. A white precipitate immediately appeared and did not dissolve after adding 5% HCl dropwise.

In the same manner, **5** (a few mg) yielded **6**, fucose, rhamnose, glucose and sulfate ion. Fucose showed an Rf value of 0.44 when using the above solvent system.

Solvolysis of 4 and 5 A solution of **4** and **5** (50 mg each) and pyridine–dioxane (4:1, 10 ml) was individually heated at 80 °C for 20 h. The reaction mixture was concentrated to dryness. After being dissolved in small amounts of 50% MeOH, the solution was passed through an Amberlite MB-3 column eluted with H_2O and then with MeOH. The MeOH eluate was concentrated to dryness to yield the desulfated product. **4** and **5** produced **7** (25 mg) and **9** (30 mg), respectively.

Compound **7**, powder from MeOH, $[\alpha]_D^{16}$ −57° (c=1.10, MeOH). FAB-MS (neg.) m/z: 867 $[M(C_{44}H_{68}O_{17})-H]^-$. ^{1}H-NMR δ: 0.85 (3H, s, H-l8), 1.05 (3H, d, J=6.8 Hz, H-21), 1.31 (3H, s, H-19), 1.69 (3H, d, J=6.0 Hz, Rha H-6), 3.72 (1H, br d, J=11 Hz, H-l), 4.78, 4.81 (1H, each, s, H-27), 5.02 (1H, d, J=7.6 Hz, Glc H-l), 5.54 (1H, br d, J=4.9 Hz, H-6), 6.24 (1H, s, Rha H-l). ^{13}C-NMR: Tables 1, 2.

Compound **9**, powder from MeOH, $[\alpha]_D^{16}$ −48° (c=0.82, MeOH). FAB-MS (neg.) m/z: 881 $[M(C_{45}H_{70}O_{17})-H]^-$. ^{1}H-NMR δ: 0.86 (3H, s, H-l8), 1.03 (3H, d, J=6.2 Hz, H-21), 1.30 (3H, s, H-19), 1.48 (3H, d, J=5.7 Hz, Fuc H-6), 1.68 (3H, d, J=5.7 Hz, Rha H-6), 4.77, 4.80 (1H, each, s, H-27), 5.03 (1H, d, J=7.8 Hz, Glc H-1), 5.53 (1H, br s, H-6), 6.27 (1H, s, Rha H-l). ^{13}C-NMR: Tables 1, 2.

Partial Acid Hydrolysis of 7 and 9 A solution of **7** and **9** (15 mg each) and 0.5 N HCl–EtOH (1:1, 2 ml) was individually heated at 90 °C for 1 h. After cooling, the reaction mixture was subjected to MCI gel CHP 20P eluted with H_2O and then MeOH. The MeOH eluate was concentrated to dryness. The residue was chromatographed on silica gel with $CHCl_3$–MeOH–H_2O (40:10:1). Both **7** and **9** afforded **8** (a total of 6.1 mg), powder from MeOH, $[\alpha]_D^{20}$ −70° (c=0.51, MeOH). FAB-MS (pos.) m/z: 591 $[M(C_{33}H_{50}O_9)+H]^+$, 429 $[591-Glc]^+$. ^{1}H-NMR δ: 0.91 (3H, s, H-18), 1.07 (3H, d, J=6.9 Hz, H-21), 1.23 (3H, s, H-19), 3.68 (1H, dd, J=11.6, 4.1 Hz, H-1), 4.78, 4.81 (1H each, s, H-27), 5.04 (1H, d, J=7.3 Hz, Glc H-1), 5.56 (1H, br d, J=4.9 Hz, H-6). ^{13}C-NMR: Tables 1, 2.

Acid Hydrolysis of 7—9 A solution of 5% HCl–dioxane (1:1, 0.5 ml) was added to each glycoside (*ca.* 2 mg) and was heated at 100 °C for 4 h. After cooling, the reaction mixture was blown to dryness with a N_2 stream and then subjected to sugar analysis as described above. **7** yielded arabinose, rhamnose and glucose, while **9** gave fucose, rhamnose and glucose. Only glucose was detected from **8**.

Peliosanthoside A (**1**): Powder from MeOH, $[\alpha]_D^{15}$ −59° (c= 0.71, MeOH). FAB-MS (neg.) m/z: 1047 $[M(C_{49}H_{75}O_{19}\cdot SO_3X)-X]^-$ (X=K, Na, *etc.*), 901 $[1047-Rha]^-$, 785 $[1047-(Glc-O-acyl)]^-$. ^{1}H- and ^{13}C-NMR: Tables 1—3.

Peliosanthoside B (**2**): Powder from MeOH, $[\alpha]_D^{16}$ −51° (c=0.64, MeOH). FAB-MS (neg.) m/z: 1061 $[M(C_{50}H_{77}O_{19}\cdot SO3X)-X]^-$ (X=K, Na, *etc.*), 785 $[1061-(Glc-O-acyl)]^-$. ^{1}H- and ^{13}C-NMR: Tables 1—3.

Peliosanthoside C (**3**): Powder from MeOH, $[\alpha]_D^{16}$ −58° (c=0.25, MeOH). FAB-MS (neg.) m/z: 1075 $[M(C_{51}H_{79}O_{19}\cdot SO_3X)-X]^-$ (X=K, Na, *etc.*), 800 $[1075-(Glc-O-acyl)+H]^-$. ^{1}H-NMR δ: 0.85 (3H, s, H-18), 0.97 (3H, t, J=7.4 Hz, acyl H-5), 1.04 (3H, d, J=6.9 Hz, H-21), 1.15 (3H, d, J=6.8 Hz, acyl H-6), 1.30 (3H, s, H-19), 1.68 and 1.71 (3H each, d, J=6.2, 6.1 Hz, respectively, H-6 of Rha and Fuc), 4.75 and 4.78 (1H each, s, H-27), 4.85 (lH, br d, J=10 Hz, Glc H-6_a), 5.01 (1H, d, J=11.4 Hz, Glc H-6_b), 5.04 (1H, br s, Fuc H-4), 5.05 (1H, d, J=7.0 Hz, Glc H-l), 5.57 (1H, br d, J=4.9 Hz, H-6), 6.19 (1H, s, Rha H-l). ^{13}C-NMR: Tables 1, 2.

Alkaline Hydrolysis of 1—3 A solution of each glycoside (15 mg) and 5% KOH–MeOH (1:1, 1 ml) was kept at room temperature for 2 h. The reaction mixture was neutralized with Amberlite MB-3 and then passed through an MCI gel CHP 20P column and eluted with aq. MeOH. The eluate was monitored by TLC. Glycosides **1** and **2** produced **4**, while **3** furnished **5**. Identification of glycosides **4** and **5** was made by comparing TLC behavior and ^{1}H-NMR spectrum with authentic samples.

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