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Steroids from the Underground Parts of *Trillium kamtschaticum*

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Two 18-norspirostanol glycosides and an 18-norspirostanol, which were new compounds as natural products, have been isolated from the underground parts of *Trillium kamtschaticum* Pall. along with eight known steroidal glycosides. Their chemical structures were determined on the basis of spectroscopic data.

Key words *Trillium kamtschaticum*; 18-norspirostanol; trillenogenin; kryptogenin; pennogenin; glycoside

In previous papers, one of the present authors reported on the constituents of *Trillium kamtschaticum* Pall.[1—6] Among the constituents, four glycosides named trillenoside A, trillenoside B, epitrillenoside C-PA, and deoxytrillenoside A were novel steroidal glycosides in that they were the first 18-norspirostanol derivatives isolated as naturally occurring sapogenins.[3—5] But their detailed NMR spectral data and biological activity have not been described. Therefore, we reexamined the constituents of the MeOH extract of the underground parts of *Trillium kamtschaticum* Pall. The present paper describes the isolation and structure elucidation of two new steroidal glycosides and a new 18-norspirostanol as natural products along with eight known steroidal glycosides.

The MeOH extract of the underground parts of *Trillium kamtschaticum* Pall. was successively subjected to Chromatorex ODS and silica gel column chromatographies as well as HPLC on ODS to afford eleven steroids (**1**—**11**).

Compounds **4**—**11** were identified as trillenoside B,[4,5] trillenoside A,[3,4] deoxytrillenoside A,[5] 3-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl kryptogenin 26-*O*-β-D-glucopyranoside,[7] anguivioside XV,[8] 3-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-β-D-glucopyranosyl furost-5-ene-3β,17α,22,26-tetraol 26-*O*-β-D-glucopyranoside,[6] 3-*O*-α-L-rhamnopyranosyl-(1→2)-[*O*-α-L-rhamnopyranosyl-(1→4)]-*O*-β-D-glcopyranosyl furost-5-ene-3β,17α,22,26-tetraol 26-*O*-β-D-glucopyranoside,[6] and 3-*O*-α-L-rhamnopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→4)-[*O*-α-L-rhamnopyranosyl-(1→2)]-*O*-β-D-glucopyranosyl furost-5-ene-3β,17α,22,26-tetraol 26-*O*-β-D-glucopyranoside,[6] respectively, based on their physical and spectral data, although the detailed NMR spectral data of **4**—**6** have not been reported in the literature.

Compound **1** was obtained as an amorphous powder. In the positive FAB-MS, **1** indicated an $[M+H]^+$ ion peak at *m/z* 477. The ^{1}H-NMR spectrum of **1** showed signals due to one tertiary methyl group (δ 1.17), one secondary methyl group (δ 1.03), and one olefinic proton (δ 5.63). The ^{13}C-NMR spectrum of **1** showed 27 carbon signals, including one carbonyl carbon (δ 204.2), four olefinic carbons (δ 175.5, 140.3, 138.9, 124.7), one acetal carbon (δ 114.6), two oxygenated methylene carbons (δ 65.1, 61.7), and five oxygenated methine carbons (δ 81.5, 78.5, 75.5, 74.5, 68.2). These ^{1}H- and ^{13}C-NMR signals were assigned with the aid of ^{1}H–^{1}H correlation spectroscopy (COSY), heteronuclear multiple quantum coherence (HMQC), heteronuclear multiple bond correlation (HMBC), and nuclear Overhauser and exchange spectroscopy (NOESY) spectra as shown in Tables 1 and 3, respectively, and they indicated **1** to be trillenogenin, which was previously[3,4] reported as a hydrolysis product of **5**.

Compound **2**, named trillenoside C, was obtained as an amorphous powder, and its positive FAB-MS showed $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 777 and 755, respectively, and fragment ion peaks at *m/z* 609 $[755-146$ (6-deoxyhexose unit)$]^+$ and 477 $[609-132$ (pentose unit)$]^+$. The ^{1}H- and ^{13}C-NMR spectra of **2** gave signals similar to those of **1** along with the additional signals due to one each of 6-deoxyhexose and pentose units, suggesting **2** to be a diglycoside of **1**. Furthermore, these NMR signals were assigned in detail by the techniques similar to those of **1**. Based on these data, **2** was defined as trillenogenin 1-*O*-α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranoside, which corresponds to a prosapogenin of **4** and **5**.

Compound **3**, named deoxytrillenoside B, was obtained as an amorphous powder, and the positive FAB-MS of **3** exhibited an $[M+H]^+$ ion peak at *m/z* 871, which was 16 mass units smaller than that of **4**, and fragment ion peaks at *m/z*

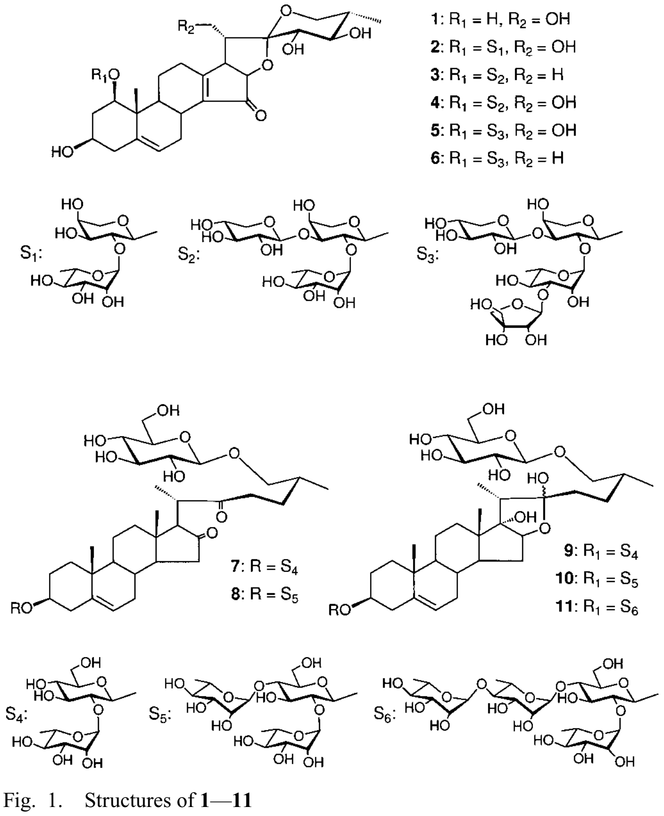

Fig. 1. Structures of **1**—**11**

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Table 1. ^{1}H-NMR Spectral Data for Compound **1** and Aglycone Moiety of Compounds **2**—**6** (in Pyridine-d_5, 500 MHz)

H	**1**	**2**	**3**	**4**	**5**	**6**
1	3.79 dd (4.5, 11.5)	3.77 dd (3.5, 12.0)	3.78 dd (3.5, 12.0)	3.74 dd (4.0, 12.0)	3.75 dd (4.0, 12.0)	3.76 dd (3.5, 12.0)
2a	2.21 ddd (11.5, 11.5, 11.5)	2.40 ddd (12.0, 12.0, 12.0)	2.45 ddd (12.0, 12.0, 12.0)	2.42 ddd (12.0, 12.0, 12.0)	2.45 ddd (12.0, 12.0, 12.0)	2.48 ddd (12.0, 12.0, 12.0)
2b	*ca.* 2.55	*ca.* 2.65	*ca.* 2.71	*ca.* 2.64	*ca.* 2.66	*ca.* 2.71
3	3.90 m	3.83 dddd (4.5, 4.5, 10.0, 10.0)	*ca.* 3.85	3.83 m	3.82 m	*ca.* 3.84
4a	*ca.* 2.57	*ca.* 2.53	2.54 dd (5.0, 12.0)	*ca.* 2.54	2.51 dd (5.5, 11.0)	*ca.* 2.53
4b	*ca.* 2.57	*ca.* 2.60	*ca.* 2.60	*ca.* 2.61	*ca.* 2.59	*ca.* 2.60
6	5.63 br d (5.5)	5.59 br d (6.0)	5.59 d (5.5)	5.58 br d (5.5)	5.59 br d (5.5)	5.59 br d (5.5)
7a	1.70 dd (11.5, 17.5)	1.66 dd (11.5, 17.0)	1.66 dd (12.0, 15.5)	*ca.* 1.65	*ca.* 1.68	*ca.* 1.66
7b	3.26 ddd (5.0, 5.0, 17.5)	3.25 ddd (5.5, 5.5, 17.0)	*ca.* 3.22	3.22 ddd (5.5, 5.5, 17.5)	3.25 ddd (4.5, 4.5, 17.5)	*ca.* 3.22
8	*ca.* 2.32	2.23 br dd (11.5, 11.5)	2.22 br dd (11.0, 11.0)	2.20 br dd (11.0, 11.0)	2.21 br dd (10.5, 10.5)	2.22 br dd (11.5, 11.5)
9	1.58 ddd (2.0, 10.5, 12.0)	*ca.* 1.72	1.72 dd (11.0, 11.0)	*ca.* 1.68	*ca.* 1.70	*ca.* 1.70
11a	1.23 dddd (4.5, 12.0, 12.0, 12.0)	1.01 dddd (4.5, 12.0, 12.0, 12.0)	*ca.* 1.01	0.95 m	0.97 m	*ca.* 1.02
11b	*ca.* 3.29	*ca.* 3.20	*ca.* 3.22	*ca.* 3.13	*ca.* 3.15	*ca.* 3.22
12a	*ca.* 2.36	*ca.* 2.58	2.30 br d (18.5)	*ca.* 2.57	*ca.* 2.63	2.32 br d (17.0)
12b	3.00 br dd (2.5, 18.0)	2.78 br d (17.0)	*ca.* 2.58	2.75 br d (18.0)	2.77 br d (18.0)	*ca.* 2.60
16	4.76 d (6.5)	4.75 d (6.5)	4.68 d (6.5)	4.74 d (6.5)	4.75 d (6.5)	4.68 d (7.0)
17	3.44 dd (6.5, 7.5)	3.32 dd (6.5, 7.5)	3.02 dd (6.5, 7.5)	3.32 dd (6.5, 7.0)	3.31 dd (6.5, 7.0)	3.03 dd (7.0, 7.5)
19	1.17 s	1.24 s	1.27 s	1.22 s	1.23 s	1.28 s
20	3.16 ddd (6.0, 7.5, 7.5)	3.14 ddd (6.0, 7.5, 7.5)	*ca.* 2.69	*ca.* 3.12	3.14 ddd (7.0, 7.0, 7.5)	*ca.* 2.70
21a	4.19 dd (7.5, 11.0)	4.18 dd (7.5, 11.0)	1.25 d (7.5)	*ca.* 4.19	4.19 dd (7.0, 11.0)	1.24 d (6.5)
21b	4.32 dd (6.0, 11.0)	*ca.* 4.32		4.33 dd (7.0, 11.0)	4.33 dd (7.5,11.0)	
23	4.16 d (9.5)	4.26 d (9.5)	3.83 d (9.5)	*ca.* 4.26	4.27 d (9.5)	3.83 d (9.5)
24	3.98 dd (9.5, 9.5)	4.01 dd (9.5, 9.5)	4.00 dd (9.5, 9.5)	3.99 dd (9.5, 9.5)	4.00 dd (9.5, 9.5)	4.00 dd (9.5, 9.5)
25	2.00 m	2.02 m	2.01 m	2.02 m	2.02 m	2.01 m
26a	3.60 dd (5.0, 11.5)	3.61 dd (5.0, 11.5)	3.60 dd (5.0, 11.5)	3.61 dd (5.0, 11.5)	3.61 dd (5.0, 11.5)	3.60 dd (5.0, 11.0)
26b	3.72 dd (11.5, 11.5)	3.73 dd (11.5, 11.5)	*ca.* 3.68	*ca.* 3.71	*ca.* 3.72	*ca.* 3.71
27	1.03 d (6.0)	1.03 d (6.5)	1.05 d (6.5)	1.02 d (6.5)	1.03 d (6.0)	1.05 d (6.0)

δ in ppm from tetramethylsilane (TMS) (coupling constants [*J*] in Hz are given in parentheses.). Assignments are based on ^{1}H–^{1}H COSY spectrum.

Table 2. ^{1}H-NMR Spectral Data for Sugar Moiety of Compounds **2**—**6** (in Pyridine-d_5, 500 MHz)

H	**2**	**3**	**4**	**5**	**6**
Ara-1	4.62 d (7.5)	4.67 d (7.5)	*ca.* 4.61	4.61 d (8.0)	*ca.* 4.64
Ara-2	4.56 dd (7.5,8.0)	*ca.* 4.66	*ca.* 4.58	4.59 dd (8.0, 8.0)	*ca.* 4.64
Ara-3	*ca.* 4.14	*ca.* 4.12	*ca.* 4.07	4.07 dd (3.5, 8.0)	*ca.* 4.11
Ara-4	*ca.* 4.15	4.44 br s	4.41 br s	*ca.* 4.42	4.44 br s
Ara-5a	3.65 d (12.0)	*ca.* 3.68	*ca.* 3.68	3.67 d (11.5)	*ca.* 3.71
Ara-5b	4.22 d (12.0)	4.24 dd (1.5,12.5)	*ca.* 4.19	4.19 d (11.5)	4.24 br d (12.0)
Rha-1	6.34 s	6.39 s	6.32 s	6.38 d (1.0)	6.42 s
Rha-2	4.75 br s	4.82 d (3.0)	4.78 br s	4.96 dd (1.0, 3.5)	*ca.* 4.96
Rha-3	4.63 br d (9.5)	4.61 dd (3.0, 9.5)	*ca.* 4.58	4.65 dd (3.5, 9.5)	*ca.* 4.64
Rha-4	4.33 dd (9.5, 9.5)	4.32 dd (9.5, 9.5)	*ca.* 4.27	4.40 dd (9.5, 9.5)	4.42 dd (9.5, 9.5)
Rha-5	4.85 dq (9.5, 6.0)	4.86 dq (9.6, 6.0)	*ca.* 4.80	*ca.* 4.84	4.89 dq (9.5, 5.5)
Rha-6	1.71 d (6.0)	1.77 d (6.0)	1.70 d (6.0)	1.68 d (6.0)	1.73 d (5.5)
Xyl-1		*ca.* 4.99	4.95 d (8.0)	4.99 d (7.5)	*ca.* 4.99
Xyl-2		3.91 dd (8.0, 8.0)	3.92 dd (8.0, 8.0)	3.92 dd (7.5, 8.0)	3.91 dd (7.5, 8.0)
Xyl-3		4.08 dd (8.0, 8.0)	*ca.* 4.09	*ca.* 4.11	*ca.* 4.11
Xyl-4		*ca.* 4.12	*ca.* 4.11	*ca.* 4.11	*ca.* 4.11
Xyl-5a		*ca.* 3.68	*ca.* 3.67	*ca.* 3.69	*ca.* 3.68
Xyl-5b		4.30 dd (5.0, 11.5)	*ca.* 4.30	*ca.* 4.30	*ca.* 4.30
Api-1				6.22 d (2.5)	6.23 s
Api-2				4.84 d (2.5)	4.85 br s
Api-4a				4.28 d (9.0)	4.28 d (9.5)
Api-4b				4.63 d (9.0)	*ca.* 4.64
Api-5a				4.14 d (11.0)	4.14 d (11.0)
Api-5b				4.17 d (11.0)	4.18 d (11.0)

δ in ppm from tetramethylsilane (TMS) (coupling constants [J] in Hz are given in parentheses.). Ara, arabinopyranosyl; Rha, rhamnopyranosyl; Xyl, xylopyranosyl; Api, apiofuranosyl.

Table 3. ^{13}C-NMR Spectral Data for Compounds **1**—**6** (in Pyridine-d_5, 125 MHz)

C	**1**	**2**	**3**	**4**	**5**	**6**	C	**2**	**3**	**4**	**5**	**6**
Ag-1	78.5	84.2	84.4	84.3	84.5	84.8[a)]	Ara-1	100.7	100.8	100.7	100.8	100.9
Ag-2	43.2	37.5	37.6	37.4	37.6	37.6	Ara-2	75.0	74.0	73.8	73.6	73.5
Ag-3	68.2	68.3	68.3	68.2	68.3	68.3	Ara-3	75.9	84.7	84.6	84.7	84.7[a)]
Ag-4	43.5	43.3	43.3	43.2	43.2	43.2	Ara-4	70.2	69.8	69.7	69.7	69.7[b)]
Ag-5	140.3	139.5	139.4	139.3	139.4	139.4	Ara-5	67.5	67.1[a)]	67.0	67.0[b)]	67.0
Ag-6	124.7	124.9	124.9	124.9	125.0	124.9	Rha-1	101.6	101.9	101.6	101.5	101.5
Ag-7	30.0	29.6	29.6	29.5	29.6	29.6	Rha-2	72.5	72.5[b)]	72.4	71.8	71.8
Ag-8	31.8	32.0	31.9	31.9	32.0	31.9	Rha-3	72.7	72.6[b)]	72.4	79.9	79.9
Ag-9	49.1	47.9	47.7	47.8	47.9	47.8	Rha-4	74.2	74.3	74.2[a)]	72.6	72.6
Ag-10	43.5	42.6	42.6	42.5	42.6	42.6	Rha-5	69.3	69.5	69.3	69.5	69.5[b)]
Ag-11	24.8	25.3	25.4	25.3	25.3	25.4	Rha-6	19.0	19.2	19.0	19.1	19.1
Ag-12	28.4	28.3	28.1	28.2	28.3	28.2	Xyl-1		106.6	106.4	106.5	106.6
Ag-13	175.5	176.4	175.8	176.5	176.4	175.8	Xyl-2		74.7	74.6[a)]	74.7[a)]	74.6
Ag-14	138.9	138.9	138.6	138.7	138.8	138.6	Xyl-3		78.3	78.2	78.4	78.4
Ag-15	204.2	204.2	204.3	204.2	204.2	204.4	Xyl-4		71.0	70.9	71.0	71.0
Ag-16	81.5	81.5	81.3	81.4	81.5	81.3	Xyl-5		67.2[a)]	67.0	67.1[b)]	67.1
Ag-17	49.5	48.9	51.9	48.8	48.9	51.9	Api-1				111.7	111.7
Ag-19	13.0	13.9	14.0	13.9	14.0	14.0	Api-2				77.8	77.8
Ag-20	49.5	49.5	41.9	49.4	49.5	42.0	Api-3				80.2	80.2
Ag-21	61.7	61.6	13.7	61.5	61.6	13.7	Api-4				75.1	75.2
Ag-22	114.6	114.6	114.6	114.5	114.6	114.7	Api-5				65.7	65.7
Ag-23	74.5	74.6	73.1	74.4[a)]	74.6[a)]	73.1						
Ag-24	75.5	75.5	75.5	75.4	75.5	75.5						
Ag-25	39.0	39.0	39.1	38.8	39.0	39.1						
Ag-26	65.1	65.1	65.1	65.0	65.1	65.1						
Ag-27	13.3	13.3	13.3	13.2	13.3	13.3						

δ in ppm from TMS. *a*, *b*) Assignments in each column may be interchangeable. Ara, arabinopyranosyl; Rha, rhamnopyranosyl; Xyl, xylopyranosyl; Api, apiofuranosyl. Assignments are based on HMQC and HMBC spectra.

739 $[871-132]^+$, 725 $[871-146]^+$, 593 $[725-132]^+$ and 461 $[593-132]^+$. The ^{1}H- and ^{13}C-NMR spectra were similar to those of **4**, except for the appearance of the signals due to one secondary methyl group and the absence of a signal assignable to one oxygenated methylene group. In the same manner as for **1**, these ^{1}H- and ^{13}C-NMR signals were examined in detail, and the structure of **3** was determined to be 21-deoxytrillenogenin 1-*O*-*α*-L-rhamnopyranosyl-(1→2)-[*β*-D-xylopyranosyl-(1→3)]-*α*-L-arabinopyranoside, which corresponds to a prosapogenin of **6**.

Although **2** and **3** were previously reported as partial hydrolysis products of **4** and **6**,[4,5] respectively, the isolation of **2** and **3** as natural products is reported here for the first time. Furthermore, this is the first example of the isolation of **7** and **8** from *T. kamtschaticum*.

18-Norspirostanol derivatives, which have unique steroidal skeletons with α,β-unsaturated ketone and hydroxyl groups at C-23 and C-24, were previously isolated from the three liliaceae plants *T. kamtschaticum*,3—5) *T. tschonoskii*,9—11) and *Paris quadrifolia*.12) However, except for two compounds, their detailed NMR spectral assignments have not been reported. We were able to assign the ^{1}H- and ^{13}C-NMR signals of six 18-norspirostanol derivatives, which are major saponins from *T. kamtschaticum*, in detail in this study.

Experimental

All the instruments and materials used were the same as those cited in a previous report,13) unless otherwise specified.

Plant Material The underground parts of *Trillium kamtschaticum* PALL. were collected in Hokkaido prefecture, Japan, in June 2002, and identified by Professor Toshihiro Nohara, Faculty of Pharmaceutical Sciences, Kumamoto University.

Extraction and Isolation The cut fresh underground parts of *Trillium kamtschaticum* PALL. (73 g) were extracted with MeOH (200 ml×2) under reflux, and the solvent was removed under reduced pressure to give a syrup (8.0 g). The MeOH extract was chromatographed over Chromatorex ODS (H$_2$O, 40% MeOH, 60% MeOH, 70% MeOH, MeOH) to give fractions (frs.) 1—5. Fraction 2 (482 mg) was subjected to HPLC (column, COSMOSIL 5C18 AR-II, Nacalai Tesque, Inc., 250 mm×20 mm i.d.; solvent, 60% MeOH) to give **1** (7 mg), **4** (67 mg), **8** (6 mg), **7** (6 mg) and fr. 6 (28 mg). Chromatography of fr. 6 over silica gel [CHCl$_3$–MeOH–H$_2$O (14 : 2 : 0.1, 7 : 3 : 0.5, 6 : 4 : 1)] furnished **2** (19 mg). Fraction 3 (412 mg) and fr. 4 (267 mg) were subjected to HPLC under the same conditions as for fr. 2 to give fr. 7 (35 mg), fr. 8 (47 mg), fr. 9 (116 mg), fr. 10 (48 mg), fr. 11 (343 mg) and **9** (51 mg). Fraction 7 was chromatographed over silica gel [CHCl$_3$–MeOH–H$_2$O (10 : 2 : 0.1, 8 : 2 : 0.2, 7 : 3 : 0.5, 6 : 4 : 1)] to give **5** (23 mg). Fraction 10 was successively subjected to silica gel [CHCl$_3$–MeOH–H$_2$O (14 : 2 : 0.1, 10 : 2 : 0.1, 8 : 2 : 0.2, 7 : 3 : 0.5)] and HPLC on YMC-pack SIL-06 [YMC, 250 mm×20 mm i.d.; solvent, CHCl$_3$–MeOH–H$_2$O (7 : 3 : 0.5)] and COSMOSIL 5C18 AR-II (60% MeOH) to afford **3** (8 mg) and **6** (11 mg). Fraction 11 was successively subjected to silica gel [CHCl$_3$–MeOH–H$_2$O (10 : 2 : 0.1, 8 : 2 : 0.2, 7 : 3 : 0.5, 6 : 4 : 1)] and HPLC under the same conditions as for fr. 2 to give fr. 12 (12 mg), fr. 13 (7 mg), **10** (118 mg), and **11** (25 mg).

Trillenogenin (**1**): Amorphous powder. $[\alpha]_D^{26}$ −221.1° (c=0.3, MeOH). Positive FAB-MS m/z: 477 $[M+H]^+$. Negative FAB-MS m/z: 475 $[M-H]^-$. ^{1}H-NMR spectral data: see Table 1. ^{13}C-NMR spectral data: see Table 3.

Trillenoside C (**2**): Amorphous powder. $[\alpha]_D^{9}$ −120.0° (c=1.8, MeOH). Positive FAB-MS m/z: 777 $[M+Na]^+$, 755 $[M+H]^+$. Negative FAB-MS m/z: 753 $[M-H]^-$. ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

Deoxytrillenoside B (**3**): Amorphous powder. $[\alpha]_D^{25}$ −92.1° (c=0.8, MeOH). Positive FAB-MS m/z: 871 $[M+H]^+$, 739 $[871-132]^+$, 725 $[871-146]^+$, 593 $[725-132]^+$, 461 $[593-132]^+$. Negative FAB-MS m/z: 869 $[M-H]^-$, 737 $[869-132]^-$, 723 $[869-146]^-$, 591 $[723-132]^-$, 459 $[591-132]^-$. ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

Trillenoside B (**4**): Amorphous powder. $[\alpha]_D^{9}$ −132.0° (c=0.8, MeOH). Positive FAB-MS m/z: 887 $[M+H]^+$, 755 $[887-132]^+$, 609 $[755-146]^+$, 477 $[609-132]^+$. Negative FAB-MS m/z: 885 $[M-H]^-$, 753 $[885-132]^-$, 607 $[753-146]^+$. ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

Trillenoside A (**5**): Amorphous powder. $[\alpha]_D^{9}$ −92.0° (c=2.7, MeOH). Positive FAB-MS m/z: 1041 $[M+Na]^+$, 887 $[M+H-132]^+$, 755 $[887-132]^+$, 609 $[755-146]^+$, 477 $[609-132]^+$. Negative FAB-MS m/z: 1017 $[M-H]^-$. ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

Deoxytrillenoside A (**6**): Amorphous powder. $[\alpha]_D^{25}$ −113.2° (c=0.8, MeOH). Positive FAB-MS m/z: 1025 $[M+Na]^+$, 1003 $[M+H]^+$, 871 $[1003-132]^+$, 739 $[871-132]^+$, 725 $[871-146]^+$, 593 $[725-132]^+$, 461 $[593-132]^+$. Negative FAB-MS m/z: 1001 $[M-H]^-$, 869 $[1001-132]^-$, 737 $[869-132]^-$, 723 $[869-146]^-$, 591 $[723-132]^-$, 459 $[591-132]^-$. ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

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