Three New Steroid Glycosides from the Underground Parts of *Trillium kamtschaticum*

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Three new steroid glycosides named trikamsterosides C, D and E were isolated from the underground parts of *Trillium kamtschaticum* PALL. (Liliaceae) along with two known 18-norspirostanol glycosides trillenosides A and B. Their chemical structures were determined on the basis of spectroscopic data and chemical evidence.

Key words *Trillium kamtschaticum*; Liliaceae; steroid glycoside; trikamsteroside; 18-norspirostanol

In preceding papers, we reported the isolation and structural elucidation of 22 steroids, two sesquiterpenoid glycosides, one phenylpropanoid, one flavonoid glycoside, and three phenylpropanoid sucrose esters from the MeOH extract of the underground parts of *Trillium kamtschaticum* PALL. (Liliaceae) and, further, that four phenolic compounds among these compounds had a stronger antioxidative activity than L-cysteine.[1,2] In a further investigation of this extract, we now report the isolation and structural elucidation of three new steroid glycosides along with two known 18-norspirostanol glycosides.

The MeOH extract of the underground parts of *T. kamtschaticum* was successively subjected to Diaion HP20 and silica gel column chromatography as well as HPLC on ODS to afford five compounds (**1**—**5**) (Fig. 1).

Compounds **4** and **5** were identified as trillenosides A and B, respectively, based on their physical and spectral data.[1]

Compound **1**, named trikamsteroside C, was obtained as an amorphous powder. The IR spectrum of **1** showed absorptions due to hydroxyl groups (3404 cm^{-1}) and an α,β-unsaturated ketone group (1693 cm^{-1}). In the positive FAB-MS, **1** exhibited an $[M+Na]^+$ ion peak at *m/z* 1041; the high-resolution (HR) positive FAB-MS indicated the molecular formula of **1** to be $C_{47}H_{70}O_{24}$. The ^{1}H-NMR spectrum of **1** showed signals due to one tertiary methyl group (δ 1.24), two secondary methyl groups [δ 1.67 (d, J=6.0 Hz), 0.94 (d, J=6.5 Hz)], one olefinic proton [δ 5.57 (br d, J=5.5 Hz)], and four monosaccharide groups. The ^{13}C-NMR spectrum of **1** gave 47 carbon signals including one carbonyl carbon (δ 204.2), four olefinic carbons (δ 176.4, 139.4, 138.7, 124.9), one acetal carbon (δ 113.7), and four anomeric carbons (δ 111.7, 106.5, 101.4, 100.8). 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), and heteronuclear multiple-bond correlation (HMBC) techniques, and **1** was characterized as a tetraglycoside of 18-norspirostanol. Further, the ^{13}C-NMR data of the aglycone moiety and the sugar moiety were superimposable on those of epitrillenoside C (**6**)[3] and **4**,[1] respectively. The structure of **1** was therefore defined as epitrillenogenin 1-*O*-β-D-apiofuranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside.

Compound **2**, named trikamsteroside D, was obtained as an amorphous powder and the molecular formula of **2** was analyzed as $C_{48}H_{74}O_{24}$ by HR-positive FAB-MS. Its IR spectrum revealed absorptions at 3386 and 1741 cm^{-1} due to hydroxyl groups and a five-membered ketone group, respectively. The ^{1}H-NMR spectrum of **2** was analogous to that of **4**, with an additional signal due to one methyl group. The ^{13}C-NMR spectrum of **2** was also similar to that of **4** except for the appearance of signals due to one each of methyl carbon, methine carbon, and quaternary carbon and the lack of signals due to two olefinic carbons. These ^{1}H- and ^{13}C-NMR signals were assigned in detail by 2D-NMR techniques similar to those of **1**. In the HMBC spectrum of **2**, key correlations were observed between H-1 of the arabinopyranosyl group and C-1, between H-17 and C-15, between H-14 and C-15, between H_2-26 and C-22, between H_3-27 and C-24, between H-24 and C-23, and between H-23 and C-24, and the planar structure of **2** was determined as illustrated in Fig. 2. Further, the ^{13}C-NMR assignments of the sugar moiety and A-ring of the aglycone moiety were quite similar to those of **4**, indicating the same sugar chain as **4** was attached to C-1 of aglycone. The configurations of the aglycone moiety were confirmed by the following evidence. On acidic hydrolysis, **2** afforded an aglycone (**2a**), named trikamsterogenin A, D-apiose, D-xylose, L-rhamnose, and L-arabinose. In the ^{1}H-NMR spectra of **2** and **2a**, the coupling constants of signals

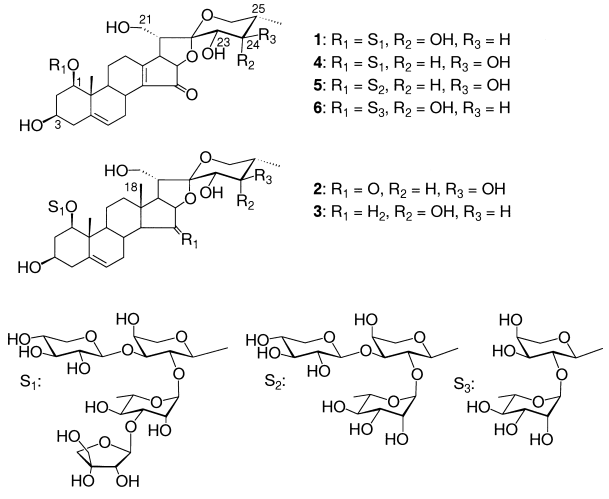

Fig. 1. Structures of **1**—**6**

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due to H-1 [δ 3.81 (dd, J=4.0, 12.0 Hz) in **2a**], H-3 [δ 3.80 (dddd, J=5.5, 5.5, 11.5, 11.5 Hz) in **2**], H-23 [δ 4.45 (d, J=9.5 Hz) in **2**; δ 4.49 (d, J=9.5 Hz) in **2a**], H-24 [δ 3.93 (dd, J=9.5, 9.5 Hz) in **2**; δ 3.96 (dd, J=9.5, 9.5 Hz) in **2a**], and H_2-26 [δ 3.68 (dd, J=11.0, 11.0 Hz), 3.65 (dd, J=5.0, 11.0 Hz) in **2a**] suggested the configurations at C-1, C-3, C-23, C-24 and C-25 to be β, β, *S*, *R* and *S*, respectively. Consequently, **2** was elucidated as 15-oxo-(23*S*,24*R*,25*S*)-spirost-5-en-1β,3β,21,23,24-pentaol 1-*O*-β-D-apiofuranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside.

Compound **3**, named trikamsteroside E, was obtained as an amorphous powder. The molecular formula of **3** was determined as $C_{48}H_{76}O_{23}$ by HR-positive FAB-MS. The IR spectrum of **3** showed absorption due to hydroxyl groups (3419 cm^{-1}), but that due to a ketone group could not be detected. The ^{1}H- and ^{13}C-NMR spectra of **3** were similar to those of **2**, although a signal due to one methylene carbon appeared and a signal due to one carbonyl carbon disappeared. These NMR signal assignments were made with the aid of similar 2D-NMR techniques as used for **1**, and the planar structure of **3** was elucidated as shown in Fig. 2. In the ^{13}C-NMR data of **3**, in comparison with those of **2**, signals due to the sugar moiety and A-ring of the aglycone moiety were al-

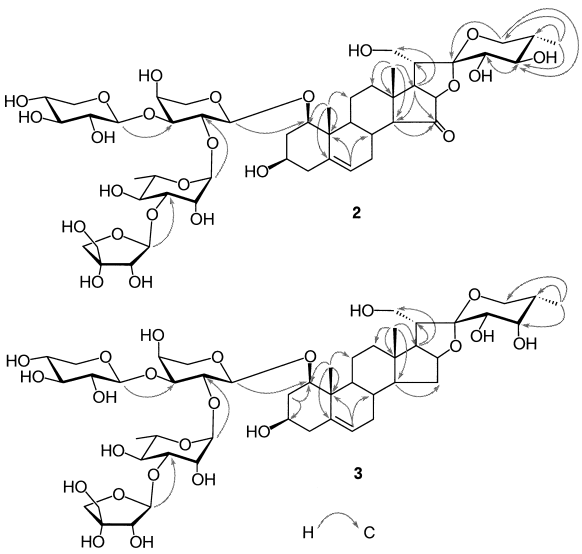

Fig. 2. ^{1}H–^{13}C Long-Range Correlations Observed for **2** and **3** in the HMBC Spectra (in C_5D_5N, 500 MHz)

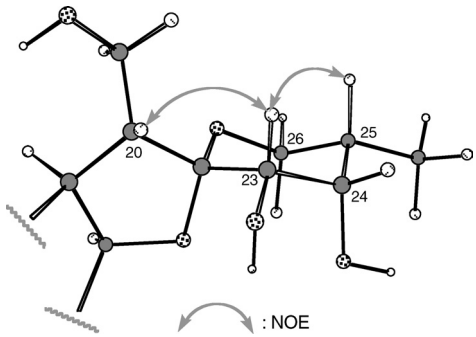

Fig. 3. Key NOEs Observed for **3a** in the NOESY Spectrum (in C_5D_5N, 500 MHz)

Table 1. ^{1}H-NMR Data for Aglycone Moiety of **1**—**3** (in C_5D_5N, 500 MHz)

H	1	2	3
1	3.72 dd (3.5, 11.5)	*ca.* 3.67	3.79 dd (3.5, 12.0)
2a	*ca.* 2.63	2.64 br d (11.5)	2.73 br d (12.0)
2b	2.43 ddd (11.5, 11.5, 11.5)	2.38 ddd (11.5, 11.5, 11.5)	2.40 ddd (12.0, 12.0, 12.0)
3	3.81 dddd (5.5, 5.5, 11.5, 11.5)	3.80 dddd (5.5, 5.5, 11.5, 11.5)	*ca.* 3.87
4a	*ca.* 2.61	2.65 dd (11.5, 11.5)	2.67 dd (12.0, 12.0)
4b	2.51 dd (5.5, 11.5)	2.50 dd (5.0, 11.5)	2.55 dd (5.0, 12.0)
6	5.57 br d (5.5)	5.53 d (6.0)	5.55 d (5.5)
7a	*ca.* 3.17	3.18 br dd (11.0, 14.5)	1.87 br dd (3.5, 14.0)
7b	*ca.* 1.64	*ca.* 1.51	*ca.* 1.55
8	2.23 br t (10.5)	1.75 m	*ca.* 1.53
9	*ca.* 1.69	*ca.* 2.05	*ca.* 1.53
11a	*ca.* 3.14	2.81 br dd (3.0, 12.5)	2.93 br d (13.5)
11b	*ca.* 0.98	*ca.* 1.47	*ca.* 1.59
12a	*ca.* 2.70	1.40 br dd (3.0, 12.5)	1.81 br d (12.5)
12b	*ca.* 2.58	1.26 ddd (5.5, 12.5, 12.5)	*ca.* 1.34
14		2.71 br s	1.17 ddd (4.5, 10.0, 12.5)
15a			*ca.* 1.99
15b			1.44 m
16	4.73 d (6.0)	*ca.* 4.25	*ca.* 4.68
17	3.22 dd (6.0, 7.5)	2.32 dd (9.0, 9.0)	1.97 dd (7.5, 8.0)
18		1.18 s	1.08 s
19	1.24 s	1.32 s	1.38 s
20	3.02 ddd (7.5, 7.5, 7.5)	3.36 ddd (3.5, 9.0, 9.0)	3.37 ddd (6.5, 6.5, 6.5)
21a	*ca.* 4.29	*ca.* 4.25	*ca.* 4.20
21b	*ca.* 4.13	*ca.* 4.13	4.02 dd (6.5,10.5)
23	*ca.* 4.27	4.45 d (9.5)	*ca.* 4.30
24	*ca.* 4.09	3.93 dd (9.5, 9.5)	*ca.* 4.09
25	1.91 m	*ca.* 2.03	1.93 m
26a	3.99 dd (11.5, 11.5)	*ca.* 3.67	*ca.* 3.87
26b	3.42 dd (5.0, 11.5)	*ca.* 3.67	3.44 dd (4.5, 11.0)
27	0.94 d (6.5)	1.06 d (6.5)	0.96 d (6.5)

δ in ppm from tetramethylsilane (TMS) (coupling constants (J) in Hz are given in parentheses).

most superimposable. To define the stereostructure of aglycone, **3** was hydrolyzed and gave an aglycone (**3a**), named trikamsterogenin B, and the same monosaccharides as the case of **2**. The coupling constants of signals due to H-1 [δ 3.79 (dd, J=4.5, 11.5 Hz)], H-3 [δ 3.95 (dddd, J=4.5, 4.5, 11.5, 11.5 Hz)], H-23 [δ 4.27 (d, J=3.0 Hz)], H-24 [δ 4.10 (dd, J=3.0, 3.0 Hz)], and H_2-26 [δ 3.89 (dd, J=11.5, 11.5 Hz); 3.45 (dd, J=4.5, 11.5 Hz)] in the ^{1}H-NMR spectrum of **3a** and key NOE correlations between H-20 and H-23 and between H-23 and H-25 in the NOESY spectrum of **3a** suggested the configurations at C-1, C-3, C-23, C-24 and C-25 to be same as those of **1** (Fig. 3). Thus, **3** was concluded to be (23*S*,24*S*,25*S*)-spirost-5-en-1β,3β,21,23,24-pentaol 1-*O*-β-D-apiofuranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-α-L-arabinopyranoside.

Compounds **1**—**3** are new steroid glycosides, and **1** corresponds to the C-24 epimer of **4**, which was previously reported as the 18-norspirostanol glycoside from the underground parts of *T. kamtschaticum*.[1] Although **2** and **3** possess an 18-methyl group, the structures of **2** and **3** were similar to those of **4** and **1**, respectively. Therefore, **2** and **3** were considered to be precursors of **4** and **1**, respectively.

Experimental

All instruments and materials used were the same as those cited in a previous report[4] unless otherwise specified.

Plant Material The underground parts of *T. kamtschaticum* were collected in Hokkaido prefecture, Japan, in May 2003 and identified by Professor Toshihiro Nohara, Faculty of Pharmaceutical Sciences, Kumamoto University.

Extraction and Isolation The cut and air-dried underground parts of *T. kamtschaticum* (279 g) were extracted with MeOH at room temperature and the solvent was removed under reduced pressure to give a syrup (87.1 g). The MeOH extract was subjected to Diaion HP20 (H_2O, MeOH, acetone) to afford fractions 1—3. A part (25.7 g) of fraction 2 (27.2 g) was chromatographed over silica gel [Merck Art. 7734; $CHCl_3$–MeOH–H_2O (10 : 2 : 0.1, 8 : 2 : 0.2, 7 : 3 : 0.5, 6 : 4 : 1, 5 : 5 : 1, 0 : 1 : 0)] to give fractions 4—12. Chromatography of fraction 10 (9.278 g) on silica gel column [Merck Art. 9385; $CHCl_3$–MeOH–H_2O (20 : 1 : 0, 14 : 2 : 0.1, 10 : 2 : 0.1, 8 : 2 : 0.2, 7 : 3 : 0.5, 6 : 4 : 1)] furnished fractions 11—20. Fractions 17

Table 2. ^{1}H-NMR Data for Sugar Moiety of **1**—**3** (in C_5D_5N, 500 MHz)

H	**1**	**2**	**3**
Ara-1	4.59 d (7.5)	4.56 d (7.5)	*ca.* 4.68
2	4.55 dd (7.5, 8.0)	4.51 dd (7.5, 8.5)	4.62 dd (7.5, 8.0)
3	4.06 dd (3.0, 8.0)	4.01 dd (3.0, 8.5)	*ca.* 4.19
4	4.39 br s	4.35 br s	4.41 br s
5a	*ca.* 4.18	*ca.* 4.12	4.23 dd (2.0, 12.5)
5b	3.67 d (12.0)	3.59 d (11.5)	*ca.* 3.68
Rha-1	6.34 br s	6.23 br s	6.35 s
2	4.94 br s	4.89 br s	4.94 br s
3	*ca.* 4.62	4.59 dd (3.0, 9.5)	4.64 dd (3.5, 9.0)
4	4.37 dd (9.5, 9.5)	4.33 dd (9.5, 9.5)	4.38 dd (9.0, 9.0)
5	*ca.* 4.82	4.76 dq (9.5, 6.0)	4.81 dq (9.0, 6.0)
6	1.67 d (6.0)	1.65 d (6.0)	1.65 d (6.0)
Xyl-1	4.97 d (7.5)	4.94 d (7.5)	4.99 d (8.0)
2	3.91 dd (7.5, 8.0)	3.87 dd (7.5, 8.5)	3.91 dd (8.0, 8.0)
3	*ca.* 4.09	*ca.* 4.07	*ca.* 4.11
4	*ca.* 4.09	*ca.* 4.07	*ca.* 4.11
5a	*ca.* 4.29	*ca.* 4.25	*ca.* 4.30
5b	*ca.* 3.67	*ca.* 3.67	*ca.* 3.68
Api-1	6.18 d (2.5)	6.16 d (2.5)	6.23 d (2.5)
2	4.80 d (2.5)	4.78 d (2.5)	4.83 d (2.5)
4a	4.62 d (9.2)	4.60 d (9.0)	4.64 d (9.0)
4b	*ca.* 4.27	*ca.* 4.24	4.29 d (9.0)
5a	4.15 d (11.5)	*ca.* 4.13	4.17 d (11.0)
5b	4.12 d (11.5)	*ca.* 4.10	4.14 d (11.0)

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

Table 3. ^{13}C-NMR Data for **1**—**4** and **6** (in C_5D_5N)

C	**1**	**2**	**3**	**4**[a]	**6**[b]	C	**1**	**2**	**3**	**4**[a]	**6**[b]
1	84.5	84.2	84.0	84.5	84.3	Ara-1	100.8	100.8	100.6	100.8	100.6
2	37.5	37.7	37.5	37.6	37.2	2	73.5	73.7	73.8	73.6	75.6
3	68.2	68.2	68.3	68.3	68.1	3	84.8	84.8	84.6	84.7	74.0
4	43.2	43.7	43.8	43.2	43.0	4	69.8[d]	69.5	69.6	69.7	69.0
5	139.4	138.1	139.6	139.4	139.2	5	67.1[e]	67.0	67.1	67.0[d]	67.2
6	124.9	125.3	124.7	125.0	124.6	Rha-1	101.4	101.4	101.4	101.5	101.3
7	29.5	28.0	32.0	29.6	29.3	2	71.7	71.7	71.8	71.8	72.2
8	31.9	30.3	33.2	32.0	31.8	3	80.0	79.9	79.8	79.9	72.2
9	47.7	43.3	50.4	47.9	47.6	4	72.5	72.5	72.6	72.6	74.8
10	42.5	42.0	42.9	42.6	42.4	5	69.4	69.3	69.5	69.5	69.4
11	25.3	25.0	24.0	25.3	25.2	6	19.0	18.9	19.0	19.1	18.8
12	28.2	39.2	40.4	28.3	28.2	Xyl-1	106.5	106.3	106.4	106.5	
13	176.4	38.4	40.9	176.4	176.5	2	74.6	74.5	74.6	74.7[c]	
14	138.7	52.8	57.1	138.8	138.6	3	78.3	78.2	78.3	78.4	
15	204.2	213.6	32.5	204.2	204.6	4	71.0	70.9	71.0	71.0	
16	82.2	81.8	83.5	81.5	82.2	5	67.0[e]	66.5	66.8	67.1[d]	
17	48.1	49.9	57.7	48.9	47.9	Api-1	111.7	111.6	111.6	111.7	
18		19.0	16.9			2	77.7	77.7	77.7	77.8	
19	14.0	15.0	15.1	14.0	13.8	3	80.1	80.1	80.2	80.2	
20	50.0	47.5	45.7	49.5	49.8	4	75.1	75.1	75.1	75.1	
21	61.5[c]	61.6	62.4	61.6	61.3	5	65.6	65.6	65.7	65.7	
22	113.7	112.8	112.7	114.6	113.6						
23	69.7[d]	74.9	70.4	74.6[c]	69.9[f]						
24	72.3	75.7	73.1	75.5	72.2[f]						
25	35.8	39.0	36.0	39.0	35.6						
26	61.3[c]	65.2	60.7	65.1	61.3						
27	12.9	13.4	13.0	13.3	12.8						

δ in ppm from TMS. **1**—**4** at 125 MHz and **6** at 50.1 MHz. *a*) Values from ref. 1. *b*) Values from ref. 3. *c*, *d*, *e*) Assignments may be interchanged in each column. *f*) Assignments in ref. 3 were interchanged. Ara, arabinopyranosyl; Rha, rhamnopyranosyl; Xyl, xylopyranosyl; Api, apiofuranosyl.

(1.288 g) and 18 (2.833 g) were each subjected to HPLC (column, COSMOSIL 5C18 AR-II, Nacalai Tesque, Inc., 250 mm×20 mm i.d.; solvent, 55% MeOH) to afford **5** (5 mg) and **3** (13 mg) from fraction 17, and **2** (76 mg), **1** (31 mg), **4** (660 mg) and **5** (54 mg) from fraction 18.

Compound **1**: Amorphous powder. $[\alpha]_D^{27}$ −125.7° (c=1.6, C_5H_5N). IR (KBr) cm^{-1}: 3404 (OH), 1693 (CO). Positive FAB-MS m/z: 1041 $[M+Na]^+$. HR positive FAB-MS m/z: 1041.4254 (Calcd for $C_{47}H_{70}O_{24}Na$: 1041.4155). ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

Compound **2**: Amorphous powder. $[\alpha]_D^{27}$ −114.4° (c=2.4, C_5H_5N). IR (KBr) cm^{-1}: 3386 (OH), 1741 (CO). Positive FAB-MS m/z: 1057 $[M+Na]^+$. HR positive FAB-MS m/z: 1057.4620 (Calcd for $C_{48}H_{74}O_{24}Na$: 1057.4468). ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

Compound **3**: Amorphous powder. $[\alpha]_D^{27}$ −81.8° (c=1.0, C_5H_5N). IR (KBr) cm^{-1}: 3419 (OH). Positive FAB-MS m/z: 1043 $[M+Na]^+$, HR positive FAB-MS m/z: 1043.4871 (Calcd for $C_{48}H_{76}O_{23}Na$: 1043.4675). ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

Acidic Hydrolysis of 2 and 3 Compounds **2** (14 mg) and **3** (12 mg) in 2 M HCl (2 ml) were each heated at 95 °C for 3 h. The reaction mixture was diluted with H_2O (20 ml) and then extracted with BuOH (20 ml). The aqueous layer was neutralized with Amberlite MB-3 (Organo Co.) and then evaporated under reduced pressure to give a monosaccharide fraction. The monosaccharide fraction was extracted with MeOH and the MeOH extract was analyzed by HPLC under the following conditions: column, Shodex RS-Pac DC-613 (6.0 mm i.d.×150 mm, Showa Denko); solvent, CH_3CN–H_2O (3 : 1); flow rate, 1.0 ml/min; column temperature, 70 °C; detector, JASCO OR-2090 plus; pump, JASCO PU-2080; and column oven, JASCO CO-2060. The retention time (t_R) and optical activity of the monsaccharides were detected as follows. **2**: L-rhamnose [t_R (min) 4.5; optical activity, negative], D-apiose [t_R (min) 5.1; optical activity, positive], D-xylose [t_R (min) 5.8; optical activity, positive] and L-arabinose [t_R (min) 6.4; optical activity, positive]; **3**: L-rhamnose [t_R (min) 4.5; optical activity, negative], D-apiose [t_R (min) 5.1; optical activity, positive], D-xylose [t_R (min) 5.8; optical activity, positive] and L-arabinose [t_R (min) 6.4; optical activity, positive]. D-Apiose was prepared by the acidic hydrolysis of benzyl β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (icariside F_2).[5] The BuOH extract was subjected to silica gel column chromatography [Merck Art. 9385; hexane–acetone (10 : 1, 5 : 1, 2 : 1, 1 : 1, 1 : 2)] to give an aglycone [**2a** (2 mg) from **2**; **3a** (1 mg) from **3**].

Compound **2a**: Amorphous powder. $[\alpha]_D^{18}$ −52.7° (c=0.17, MeOH), ^{1}H-NMR spectral data: see Table 4.

Compound **3a**: Amorphous powder. $[\alpha]_D^{18}$ −36.9° (c=0.16, MeOH), ^{1}H-NMR spectral data: see Table 4.

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Table 4. ^{1}H-NMR Data for **2a** and **3a** (in C_5D_5N, 500 MHz)

H	2a	3a
1	3.81 dd (4.0, 12.0)	3.79 dd (4.5, 11.5)
2a	2.55 m	*ca.* 2.61
2b	2.25 ddd (11.5, 11.5, 12.0)	2.22 ddd (11.5, 11.5, 11.5)
3	*ca.* 3.96	3.95 dddd (4.5, 4.5, 11.5, 11.5)
4a	2.69 ddd (1.5, 11.0, 11.0)	2.67 br dd (11.5, 11.5)
4b	2.59 ddd (2.0, 5.0, 11.0)	*ca.* 2.62
6	5.56 br d (5.0)	5.59 br d (4.0)
7a	3.17 br dddd (2.0, 5.0, 10.5, 11.5)	*ca.* 1.94
7b	1.56 m	1.57 m
8	1.81 m	1.74 m
9	1.94 ddd (4.0, 12.0, 12.0)	1.67 m
11a	*ca.* 2.78	2.89 dddd (4.0, 4.0, 4.0, 14.0)
11b	1.62 br ddd (3.0, 12.0, 12.0)	*ca.* 1.73
12a	*ca.* 1.45	*ca.* 2.04
12b	*ca.* 1.03	*ca.* 1.33
14	*ca.* 2.80	*ca.* 1.24
15a		*ca.* 2.04
15b		1.49 ddd (6.5, 12.0, 12.0)
16	4.35 d (8.0)	4.72 ddd (7.5, 7.5, 7.5)
17	2.41 dd (8.0, 8.5)	2.07 dd (6.5, 8.5)
18	1.24 s	1.16 s
19	1.26 s	1.28 s
20	3.45 ddd (3.5, 9.0, 9.0)	3.42 ddd (7.0, 7.0, 7.0)
21a	4.31 dd (9.0, 11.0)	4.24 dd (7.0, 11.0)
21b	4.19 dd (3.5, 11.0)	4.05 dd (7.0, 11.0)
23	4.49 d (9.5)	4.27 d (3.0)
24	3.96 dd (9.5, 9.5)	4.10 dd (3.0, 3.0)
25	2.06 m	*ca.* 1.93
26a	3.68 dd (11.0, 11.0)	3.89 dd (11.5, 11.5)
26b	3.65 dd (5.0, 11.0)	3.45 dd (4.5, 11.5)
27	1.06 d (7.0)	0.97 d (7.0)

δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses).

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