Four New 3,5-Cyclosteroidal Saponins from *Dracaena surculosa*

Akihito YOKOSUKA, Yoshihiro MIMAKI,* and Yutaka SASHIDA

Laboratory of Medicinal Plant Science, School of Pharmacy, Tokyo University of Pharmacy and Life Science; 1432–1 Horinouchi, Hachioji, Tokyo 192–0392, Japan. Received February 18, 2002; accepted March 25, 2002

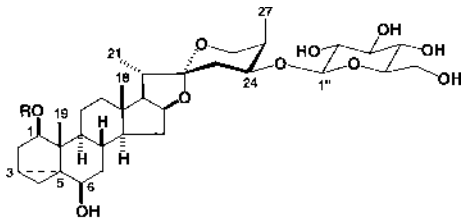
Further search for steroidal compounds contained in *Dracaena surculosa* (Agavaceae) led to the isolation of two new 3,5-cyclospirostanol saponins (1, 2) and two new 3,5-cyclofurostanol saponins (3, 4). Their structural assignment was established by spectroscopic analysis and a few chemical transformations as (24*S*,25*R*)-1β-[(β-D-fucopyranosyl)oxy]-6β-hydroxy-3α,5α-cyclospirostan-24-yl β-D-glucopyranoside (1), (24*S*,25*R*)-1β-[(β-D-glucopyranosyl)oxy]-6β-hydroxy-3α,5α-cyclospirostan-24-yl β-D-glucopyranoside (2), (25*S*)-1β-[(β-D-glucopyranosyl)oxy]-6β-hydroxy-22α-methoxy-3α,5α-cyclofurostan-26-yl β-D-glucopyranoside (3), and (25*S*)-1β-[(β-D-fucopyranosyl)oxy]-6β-hydroxy-22α-methoxy-3α,5α-cyclofurostan-26-yl β-D-glucopyranoside (4), respectively.

Key words *Dracaena surculosa*; Agavaceae; steroidal saponin; 3,5-cyclospiostanol saponin; 3,5-cyclofurostanol saponin

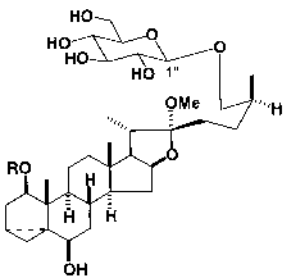
Dracaena surculosa LINDLE is an Agavaceae plant distributed in tropical regions of Asia, America, and Africa.[1] We previously made a phytochemical analysis of the whole plant of *D. surculosa* and isolated nine steroidal saponins, including three new bisdesmosidic spirostanol saponins.[2] Our further investigation of the chemical constituents of this plant has resulted in the isolation of two new 3,5-cyclospirostanol saponins (**1**, **2**) and two new 3,5-cyclofurostanol saponins (**3**, **4**). In this paper, we report the structural elucidation of the new compounds based on spectroscopic analysis and a few chemical transformations.

The plant material (fresh weight of 4.3 kg) was extracted with hot MeOH. The MeOH extract was passed through a porous-polymer polystyrene resin (Diaion HP-20) column, eluting with 30% MeOH, MeOH, and EtOAc. Column chromatography of the MeOH eluate portion over silica gel and octadecylsilanized (ODS) silica gel gave **1** (14 mg), **2** (4 mg), **3** (22 mg), and **4** (27 mg).

Compound **1** was isolated as an amorphous solid, $[\alpha]_D$ −90.0° (MeOH). The positive-ion FAB-MS of **1** showed an $[M+Na]^+$ ion at *m/z* 777, compatible with the molecular formula of $C_{39}H_{62}O_{14}$, which was confirmed by data from the ^{13}C-NMR spectrum with a total of 39 carbon signals and the results of elemental analysis. The ^{1}H-NMR spectrum of **1** (Table 1) exhibited two three-proton singlet signals at δ 1.64 and 0.88, indicating the presence of two angular methyl groups, as well as two three-proton doublet signals at δ 1.32 (J=6.9 Hz) and 1.12 (J=6.9 Hz), which were characteristic of the steroidal skeleton. In addition, two anomeric protons observed at δ 5.03 (d, J=7.7 Hz) and 4.57 (d, J=7.8 Hz) implied the presence of two monosaccharides, one of which was assumed to be 6-deoxyhexopyranose from a three-proton doublet signal at δ 1.56 (J=6.4 Hz). This ^{1}H-NMR information and one quaternary carbon signal at δ 111.2, along with two anomeric carbon signals at δ 103.4 and 101.2 in the ^{13}C-NMR spectrum were indicative of **1** being a spirostanol saponin with two monosaccharides. Comparison of the ^{1}H- and ^{13}C-NMR assignments of **1**, which were carried out by analysis of the ^{1}H–^{1}H shift correlation spectroscopy (COSY), ^{1}H-detected heteronuclear multiple quantum coherence (HMQC), and ^{1}H-detected heteronuclear multiple-bond connectivities (HMBC) spectra, with those of (24*S*,25*R*)-1β-[(β-D-fucopyranosyl)oxy]-3β-hydroxyspirost-5-en-24-yl β-D-glucopyranoside (surculoside B), a spirostanol bisdesmoside previously encountered in the same plant source,[2] revealed that the structure of the ring C—F portion of the molecule was identical to the reference compound, including the β-D-glucopyranosyloxy group attached at C-24 and the configurations of C-24 and C-25. However, significant differences were recognized in the signals from the ring A and B parts; the C-3 hydroxy-bearing methine proton and carbon could not be detected and a methylene carbon was newly observed in a very high field (δ 15.8), which was associated with the proton signals at δ 1.51 (t-like, J=4.0 Hz) and 0.56 (dd, J= 8.0, 4.0 Hz) and suggested the presence of a cyclopropane ring. The oxymethine carbon at δ 84.8 was correlated to the one-bond coupled proton at δ 4.35 (br d, J=4.0 Hz) by the HMQC spectrum. An HMBC correlation between the methyl singlet signal at δ 1.64 attributable to H_3-19 and the carbon resonance at δ 84.8 allowed the assignment of δ_H 4.35 and δ_C 84.8 as H-1 and C-1, respectively (Fig. 1). The H-1 proton thus assigned showed spin-coupling correlation with the



R
1 β-D-Fuc*p*
2 β-D-Glc*p*



R
3 β-D-Glc*p*
4 β-D-Fuc*p*

* To whom correspondence should be addressed. e-mail: mimakiy@ps.toyaku.ac.jp

Table 1. ^{1}H- and ^{13}C-NMR Chemical Shift Assignments of **1** in C_5D_5N

Position	^{1}H	J (Hz)	^{13}C
1	4.35, br d	4.0	84.8
2 (2H)	2.28, br m		33.1
3	1.14, m		23.2
4a	1.51, t-like	4.0	15.8
b	0.56, dd	8.0, 4.0	
5	—		40.0
6	3.47, br s		73.0
7eq	2.05, ddd	13.4, 3.3, 2.4	38.6
ax	1.26, ddd	13.4, 12.0, 2.4	
8	2.48, m		30.1
9	0.87, m		50.2
10	—		49.2
11eq	1.81, m		23.3
ax	1.68, m		
12eq	1.77, m		40.5
ax	1.21, m		
13	—		41.0
14	1.18, m		56.6
15a	2.08, m		32.1
b	1.44, m		
16	4.54, m		81.6
17	1.85, dd	8.5, 6.7	62.5
18	0.88, s		16.8
19	1.64, s		16.9
20	1.97, m		42.5
21	1.12, d	6.9	14.7
22	—		111.2
23 (2H)	2.05, d-like	10.8	34.1
24	4.80, ddd	10.8, 10.8, 6.1	72.8
25	2.26, m		31.7
26eq	3.93, br d	10.2	64.2
ax	3.52, br d	10.2	
27	1.32, d	6.9	9.9
1′	4.57, d	7.8	103.4
2′	4.27, dd	9.3, 7.8	72.0
3′	4.07, dd	9.3, 3.5	75.7
4′	4.04, overlapping		72.8
5′	3.77, q-like	6.4	71.4
6′	1.56, d	6.4	17.3
1″	5.03, d	7.7	101.2
2″	4.06, dd	8.6, 7.7	75.3
3″	4.27, dd	9.0, 8.6	78.7
4″	4.32, dd	9.2, 9.0	71.5
5″	3.93, ddd	9.2, 4.7, 2.2	78.4
6″a	4.50, dd	11.9, 2.2	62.5
b	4.40, dd	11.9, 4.7	

methylene protons at δ 2.28 (2H, br m), which, in turn, exhibited a correlation with the methine proton at δ 1.14. The δ 1.14 resonance had spin-coupling links with a geminal pair of protons at δ 1.51 and 0.56, which showed no additional coupling correlation. Thus, the structural fragment of $-C_{(1)}H(-O-)-C_{(2)}H_2-C_{(3)}H-C_{(4)}H_2-$ was assigned to the ring A part. The 19-methyl proton exhibited long-range correlations with not only the signal at δ 49.2 due to C-10 but also another quaternary carbon signal at δ 40.0 exclusively assignable to C-5. The remaining free bond at C-3 was rationally linked to C-5 on the basis of the above NMR data and taking into account of the acceptable distance of a linkage between C-3 and C-5. In addition, signals for a secondary hydroxyl group were identified at δ_H 3.47 (1H, br s) and δ_C 73.0, and HMBC correlations from δ 3.47 to C-5 and C-10 led to the location of the hydroxyl group at C-6. As in surculoside B, linkage of a β-D-glucopyranosyl group at C-1 was

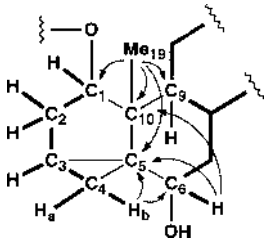


Fig. 1. HMBC Correlations of the Ring A and B Moieties of **1**

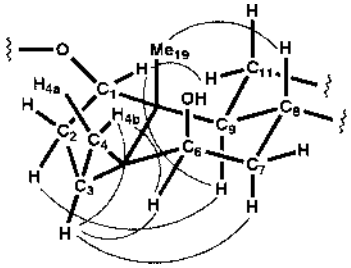


Fig. 2. NOE Correlations of the Ring A and B Moieties of **1**

confirmed by a long-range correlation between the signals of the anomeric proton at δ 4.57 and the C-1 carbon. Accordingly, the ring A and B parts were shown to include a 3,5-cyclo-1-fucosyloxy-6-hydroxyl structure. In the phase-sensitive NOE correlation spectroscopy (PHNOESY) spectrum of **1**, an NOE correlation between H-8 [δ 2.48 (m)] and H_3-19 indicated the B/C *trans* ring fusion. Further NOEs from H-1 to H-9 [δ 0.87 (m)] and H-11α(eq) [δ 1.81 (m)], H-3 to H-4b (δ 0.56), H-6, and H-7α(ax) [δ 1.26 (ddd, J=13.4, 12.0, 2.4 Hz)], and from H-4b to H-6 were consistent with the 1β, 3α, 5α, and 6β configurations (Fig. 2). Finally, the structure of **1** was ascertained by converting **1** to surculoside B; the solution of **1** dissolved in dioxane–H_2O (8 : 1) containing *p*-toluenesulfonic acid (*p*-TsOH) as catalyst was heated at 95°C for 3 h to give surculoside B. All of these data allowed the structural elucidation of **1** as (24*S*,25*R*)-1β-[(β-D-fucopyranosyl)oxy]-6β-hydroxy-3α,5α-cyclospirostan-24-yl β-D-glucopyranoside.

Compound **2** ($C_{39}H_{62}O_{15}$) was obtained as an amorphous solid. The ^{1}H-NMR spectrum of **2** showed signals characteristic of the 1,24-bisdesmosidic spirostanol saponin with a 3α,5α-cyclo ring system and a 6β-hydroxyl group as observed in that of **1**. Analysis of the ^{13}C-NMR spectrum of **2** and comparison with that of **1** suggested that the structure of the aglycon moiety of **2** was completely identical to that of **1**, but differed from **1** in terms of the monosaccharide constituent. Instead of the signals for a fucosyl moiety, six signals assignable to a β-D-glucopyranosyl group were observed at δ 103.1 (C-1), 74.9 (C-2), 78.9 (C-3), 72.0 (C-4), 78.2 (C-5), and 63.1 (C-6). In the HMBC spectrum, the anomeric proton signal at δ 4.78 (d, J=7.9 Hz) corresponding to the carbon signal at δ 103.1 showed a long-range correlation with the aglycon C-1 carbon signal at δ 85.0, while the anomeric proton signal of another glucosyl residue at δ 5.04 had a correlation with C-24 at δ 72.8. Thus, the structure of **2** was formulated as (24*S*,25*R*)-1β-[(β-D-glucopyranosyl)-oxy]-6β-hydroxy-3α,5α-cyclospirostan-24-yl β-D-glucopyranoside.

Compound **3** ($C_{40}H_{66}O_{15}$) was suggested to be a 22-methoxyfurostanol saponin by a positive color reaction with Ehrlich's reagent,[3,4] and the ^{1}H-NMR [δ 3.25 (3H, s)] and ^{13}C-NMR [δ 112.7 (C-22) and 47.3 (Me)] spectra.[5] The ^{1}H-NMR spectrum showed signals for four steroid methyl groups at δ 1.64 (s), 1.17 (d, J=6.9 Hz), 1.05 (d, J=6.7 Hz), and 0.85 (s), a pair of cyclopropane methylene protons at δ 1.58 (t-like, J=4.0 Hz) and 0.60 (dd, J=7.9, 4.0 Hz), and two anomeric protons at δ 4.85 (d, J=7.8 Hz) and 4.77 (d, J=7.8 Hz). The ^{1}H- and ^{13}C-NMR assignments of **3**, which were carried out by analysis of the COSY spectrum followed by HMQC and HMBC data, suggested that the structure of the ring A and B parts included a 3,5-cyclo-1-glucosyloxy-6-hydroxyl structure. In the PHNOESY spectrum, an NOE correlation between H-8 [δ 2.48 (m)] and H_3-19 [1.64 (s)] confirmed the B/C *trans* ring fusion. Furthermore, NOE correlations were observed from H-1 [δ 4.41 (br d, J=4.9 Hz)] to H-9 [δ 0.82 (m)] and H-11α(eq) [δ 1.80 (m)], H-3 [δ 1.13 (m)] to H-4b [δ 0.60 (dd, J=7.9, 4.0 Hz)], H-6 [δ 3.48 (br s)], and H-7α(ax) [δ 1.25 (ddd, J=13.0, 11.8, 2.5 Hz)], and from H-4b to H-6, which corresponded to the 1β, 3α, 5α, and 6β configurations. When the dioxane–H_2O solution of **3** was treated in the presence of *p*-TsOH at 95°C for 1 h, **3** was converted to (25*S*)-1β-[(β-D-glucopyranosyl)oxy]-3β-hydroxy-22α-methoxyfurost-5-en-26-yl β-D-glucopyranoside.[2] Thus, the structure of **3** was assigned as (25*S*)-1β-[(β-D-glucopyranosyl)oxy]-6β-hydroxy-22α-methoxy-3α,5α-cyclofurostan-26-yl β-D-glucopyranoside.

Compound **4** ($C_{40}H_{66}O_{14}$) was also a 22α-methoxy-3α,5α-cyclofurostanol saponin closely related to **3**. The ^{1}H- and ^{13}C-NMR spectra clearly indicated the presence of a terminal β-D-fucopyranosyl unit [δ_H 4.58 (d, J=7.8 Hz); δ_C 103.4 (C-1), 72.0 (C-2), 75.7 (C-3), 72.8 (C-4), 71.4 (C-5), and 17.3 (C-6)] and a terminal β-D-glucopyranosyl unit [δ_H 4.85 (d, J=7.8 Hz); δ_C 105.1 (C-1), 75.2 (C-2), 78.6 (C-3), 71.8 (C-4), 78.5 (C-5), and 62.9 (C-6)]. In the HMBC spectrum, the anomeric proton signal at δ 4.58 showed a long-range correlation with the aglycon C-1 carbon signal at δ 84.8, while another anomeric proton signal at δ 4.85 had a correlation with C-26 at δ 74.9. The structure of **4** was shown to be (25*S*)-1β-[(β-D-fucopyranosyl)oxy]-6β-hydroxy-22α-methoxy-3α,5α-cyclofurostan-26-yl β-D-glucopyranoside.

Recently, Nohara and his co-workers reported four new 3,5-cyclosteroidal compounds with the withanolide skeleton, called cilistol p, cilistol pm, cilistol pl, and cilistol u, respectively, from *Solanum cilistum*.[6] Compounds **1**—**4** are the first 3,5-cyclosteroidal glycosides with the spirostanol or furostanol skeleton.

Experimental

Optical rotations were measured using a JASCO DIP-360 (Tokyo, Japan) automatic digital polarimeter. IR spectra were recorded on a JASCO FT-IR 620 spectrophotometer. NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^{1}H-NMR, Karlsruhe, Germany) spectrophotometer using standard Bruker pulse programs. Chemical shifts were given as δ values with reference to tetramethylsilane (TMS) as internal standard. FAB-MS were recorded on a Finnigan MAT TSQ-700 (San Jose, CA, U.S.A.) and high resolution matrix-assisted laser desorption ionization time-of-flight (HR-MALDI-TOF) MS on a Micromass Q-TOF-2 (Manchester, U.K.) mass spectrometer. Elemental analysis was carried out using an Elementar Vario EL (Hanau, Germany) elemental analyzer. Diaion HP-20 (Mitsubishi-Kasei, Tokyo, Japan), silica gel (Fuji-Silysia Chemical, Aichi, Japan), and ODS silica gel (Nacalai Tesque, Kyoto, Japan) were used for column chromatography. TLC was carried out on precoated Kieselgel 60 F_{254} (0.25 mm thick, Merck, Darmstadt, Germany) and $RP_{18}F_{254}S$ plates (0.25 mm thick, Merck), and spots were visualized by spraying the plates with 10% H_2SO_4 solution, followed by heating. All chemicals used were of biochemical reagent grade.

Plant Material *D. surculosa* was purchased from a nursery in Exotic Plants (Chiba, Japan) in October 1997, and identified by one of the authors (Y. S). A voucher of the plant is on file in our laboratory (voucher no. DS-97-007., Laboratory of Medicinal Plant Science).

Extraction and Isolation The plant material (fresh weight, 4.3 kg) was extracted with hot MeOH twice (10 l each time). The MeOH extract was concentrated under reduced pressure, and the extract was passed through a Diaion HP-20 column, eluting with 30% MeOH, MeOH, and EtOAc. Column chromatography of the MeOH eluate portion on silica gel and elution with a stepwise gradient mixture of $CHCl_3$–MeOH (9 : 1; 4 : 1; 3 : 1; 2 : 1; 1 : 1), and finally with MeOH alone, gave five fractions (I—V). Fraction III was subjected to column chromatography on silica gel eluting with $CHCl_3$–MeOH–H_2O (60 : 10 : 1; 50 : 10 : 1; 40 : 10 : 1) and ODS silica gel with MeOH–H_2O (8 : 5) and MeCN–H_2O (1 : 3; 2 : 5) to give **1** (14 mg), **2** (4 mg), **3** (22 mg), and **4** (27 mg).

Compound **1**: Amorphous solid, $[\alpha]_D^{26}$ −90.0° (c=0.10, MeOH). FAB-MS (positive mode) m/z: 777 $[M+Na]^+$. *Anal.* Calcd for $C_{39}H_{62}O_{14}\cdot 3H_2O$: C, 57.90; H, 8.47. Found: C, 57.54; H, 8.45. IR ν_{max} (film) cm^{-1}: 3388 (OH), 2928 (CH), 1074. ^{1}H- and ^{13}C-NMR, see Table 1.

Transformation of 1 into Surculoside B A solution of **1** (7.8 mg) in a mixture of dioxane–H_2O (8 : 1, 3 ml) containing a catalytic amount of *p*-TsOH was heated at 95°C for 3 h. After cooling, the reaction mixture was chromatographed on silica gel eluting with $CHCl_3$–MeOH–H_2O (40 : 10 : 1) and ODS silica gel with MeCN–H_2O (1 : 3) to yield surculoside B (2.0 mg).[2]

Compound **2**: Amorphous solid, $[\alpha]_D^{26}$ −42.0° (c=0.10, MeOH). FAB-MS (positive mode) m/z: 793 $[M+Na]^+$. HR-MALDI-TOF-MS m/z: 793.3990 (Calcd for $C_{39}H_{62}O_{15}Na$: 793.3986). IR ν_{max} (film) cm^{-1}: 3388 (OH), 2926 (CH), 1077. ^{1}H-NMR (C_5D_5N) δ: 5.04 (1H, d, J=7.8 Hz, H-1″), 4.79 (1H, ddd, J=10.9, 10.8, 6.4 Hz, H-24), 4.78 (1H, d, J=7.9 Hz, H-1′), 4.52 (1H, m, H-16), 4.41 (1H, br d, J=5.3 Hz, H-1), 3.47 (1H, br s, H-6), 1.65 (3H, s, H_3-19), 1.58 (1H, t-like, J=3.9 Hz, H-4a), 1.32 (3H, d, J=6.9 Hz, H_3-27), 1.14 (1H, m, H-3), 1.11 (3H, d, J=7.0 Hz, H_3-21), 0.83 (3H, s, H_3-18), 0.56 (1H, dd, J=7.9, 3.9 Hz, H-4b). ^{13}C-NMR (C_5D_5N) δ: 85.0 (C-1), 33.0 (C-2), 23.2 (C-3), 15.9 (C-4), 39.9 (C-5), 73.0 (C-6), 38.6 (C-7), 30.0 (C-8), 50.0 (C-9), 49.1 (C-10), 23.3 (C-11), 40.5 (C-12), 40.9 (C-13), 56.5 (C-14), 32.0 (C-15), 81.6 (C-16), 62.4 (C-17), 16.7 (C-18), 16.9 (C-19), 42.5 (C-20), 14.7 (C-21), 111.2 (C-22), 34.1 (C-23), 72.8 (C-24), 31.7 (C-25), 64.2 (C-26), 9.9 (C-27), 103.1 (C-1′), 74.9 (C-2′), 78.9 (C-3′), 72.0 (C-4′), 78.2 (C-5′), 63.1 (C-6′), 101.2 (C-1″), 75.3 (C-2″), 78.7 (C-3″), 71.5 (C-4″), 78.4 (C-5″), 62.5 (C-6″).

Compound **3**: Amorphous solid, $[\alpha]_D^{26}$ −42.0° (c=0.10, MeOH). FAB-MS (negative mode) m/z: 785 $[M-H]^-$. *Anal.* Calcd for $C_{40}H_{66}O_{15}\cdot 3H_2O$: C, 58.23; H, 8.80. Found: C, 58.56; H, 8.62. IR ν_{max} (film) cm^{-1}: 3387 (OH), 2927 (CH), 1076. ^{1}H-NMR (C_5D_5N) δ: 4.85 (1H, d, J=7.8 Hz, H-1″), 4.77 (1H, d, J=7.8 Hz, H-1′), 4.50 (1H, q-like, J=7.0 Hz, H-16), 4.41 (1H, br d, J=4.9 Hz, H-1), 3.48 (1H, br s, H-6), 3.25 (3H, s, OMe), 2.48 (1H, m, H-8), 1.80 (1H, m, H-11α), 1.64 (3H, s, H_3-19), 1.58 (1H, t-like, J=4.0 Hz, H-4a), 1.25 (1H, ddd, J=13.0, 11.8, 2.5 Hz, H-7α), 1.17 (3H, d, J=6.9 Hz, H_3-21), 1.13 (1H, m, H-3), 1.05 (3H, d, J=6.7 Hz, H_3-27), 0.85 (3H, s, H_3-18), 0.82 (1H, m, H-9), 0.60 (1H, dd, J=7.9, 4.0 Hz, H-4b). ^{13}C-NMR (C_5D_5N) δ: 85.0 (C-1), 33.0 (C-2), 23.2 (C-3), 15.8 (C-4), 40.0 (C-5), 73.0 (C-6), 38.5 (C-7), 30.0 (C-8), 50.0 (C-9), 49.1 (C-10), 23.2 (C-11), 40.4 (C-12), 41.3 (C-13), 56.5 (C-14), 32.2 (C-15), 81.4 (C-16), 64.3 (C-17), 16.7 (C-18), 16.9 (C-19), 40.4 (C-20), 16.2 (C-21), 112.7 (C-22), 30.9 (C-23), 28.2 (C-24), 34.4 (C-25), 74.9 (C-26), 17.6 (C-27), 47.3 (OMe), 103.1 (C-1′), 74.9 (C-2′), 78.9 (C-3′), 72.0 (C-4′), 78.2 (C-5′), 63.1 (C-6′), 105.1 (C-1″), 75.2 (C-2″), 78.6 (C-3″), 71.7 (C-4″), 78.5 (C-5″), 62.9 (C-6″).

Transformation of 3 into (25*S*)-1β-[(β-D-Glucopyranosyl)oxy]-3β-hydroxy-22α-methoxyfurost-5-en-26-yl β-D-Glucopyranoside A solution of **3** (12 mg) in a mixture of dioxane–H_2O (8 : 1, 3 ml) containing a catalytic amount of *p*-TsOH was heated at 95°C for 1 h. After cooling, the reaction mixture was chromatographed on silica gel eluting with $CHCl_3$–MeOH–H_2O (40 : 10 : 1) and ODS silica gel with MeCN–H_2O (1 : 3) to yield (25*S*)-1β-[(β-D-glucopyranosyl)oxy]-3β-hydroxy-22α-methoxyfurost-5-en-26-yl β-D-glucopyranoside (1.0 mg).[2] An aliquot of 4 mg of **3** did not react and was recovered.

Compound **4**: Amorphous solid, $[\alpha]_D^{26}$ −56.0° (c=0.10, MeOH). FAB-MS (negative mode) m/z: 769 $[M-H]^-$. *Anal.* Calcd for $C_{40}H_{66}O_{14}\cdot 3/2H_2O$: C, 59.02; H, 8.54. Found: C, 59.10; H, 8.63. IR ν_{max} (film) cm^{-1}: 3388 (OH), 2930 (CH), 1074. ^{1}H-NMR (C_5D_5N) δ: 4.85 (1H, d, J=7.8 Hz, H-1″), 4.58 (1H, d, J=7.8 Hz, H-1′), 4.52 (1H, q-like, J=7.2 Hz, H-16), 4.37 (1H, br d,

J=5.0 Hz, H-1), 3.47 (1H, br s, H-6), 3.26 (3H, s, OMe), 1.64 (3H, s, H_3-19), 1.56 (3H, d, J=6.4 Hz, H_3-6′), 1.51 (1H, t-like, J=3.9 Hz, H-4a), 1.19 (3H, d, J=6.9 Hz, H_3-21), 1.14 (1H, m, H-3), 1.06 (3H, d, J=6.7 Hz, H_3-27), 0.90 (3H, s, H_3-18), 0.57 (1H, dd, J=7.9, 3.9 Hz, H-4b). ^{13}C-NMR (C_5D_5N) δ: 84.8 (C-1), 33.0 (C-2), 23.3 (C-3), 15.8 (C-4), 40.0 (C-5), 73.0 (C-6), 38.6 (C-7), 30.0 (C-8), 50.2 (C-9), 49.2 (C-10), 23.3 (C-11), 40.5 (C-12), 41.4 (C-13), 56.5 (C-14), 32.2 (C-15), 81.4 (C-16), 64.3 (C-17), 16.7 (C-18), 16.9 (C-19), 40.5 (C-20), 16.3 (C-21), 112.7 (C-22), 30.9 (C-23), 28.2 (C-24), 34.5 (C-25), 74.9 (C-26), 17.6 (C-27), 47.3 (OMe), 103.4 (C-1′), 72.0 (C-2′), 75.7 (C-3′), 72.8 (C-4′), 71.4 (C-5′), 17.3 (C-6′), 105.1 (C-1″), 75.2 (C-2″), 78.6 (C-3″), 71.8 (C-4″), 78.5 (C-5″), 62.9 (C-6″).

Acknowledgments We are grateful to Mr. Akira Higuchi, Medicinal Research Laboratories, Taisho Pharmaceutical Co., Ltd. for the measurement of the HR-MALDI-TOF-MS.

References and Notes

1) Tsukamoto Y. (executive ed.), "The Grand Dictionary of Horticulture," Shogakukan, Tokyo, 1989, Vol. 1, pp. 148—149.
2) Yokosuka A., Mimaki Y., Sashida Y., *J. Nat. Prod.*, **63**, 1239—1243 (2000).
3) Kiyosawa S., Hutoh M., Komori T., Nohara T., Hosokawa I., Kawasaki T., *Chem. Pharm. Bull.*, **16**, 1162—1164 (1968).
4) Nohara T., Miyahara K., Kawasaki T., *Chem. Pharm. Bull.*, **23**, 872—885 (1975).
5) The furostanol saponins (**3**, **4**) were obtained as a mixture of the C-22 hydroxyl and C-22 methoxyl forms, which could not be separated because of their readily convertible nature in dissolved solvent. The furostanols are presumed to exist in the C-22 hydroxyl form and the C-22 methoxyl saponins may be produced through the extraction and purification procedures. The C-22 hydroxyl form present in the mixture was completely converted to the C-22 methoxyl form by treatment with hot MeOH, and the structural elucidation of **3** and **4** was carried out with the C-22 methoxyl form. The configuration of C-22 was determined to be α by an NOE correlation between the signals of the C-22 methoxyl protons and the H-16 proton.
6) Zhu X.-H., Ando J., Takagi M., Ikeda T., Yoshimitu A., Nohara T., *Chem. Pharm. Bull.*, **49**, 1440—1443 (2001).