Steroidal Saponins from *Disporopsis pernyi*

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Four new steroidal saponins, named disporosides A–D (**1**–**4**), corresponding to (3*β*,25*R*)-3-[(*β*-D-glucopyranosyl-(1→2)-[*β*-D-glucopyranosyl-(1→6)]-*β*-D-glucopyranosyl)oxy]-5*β*-spirostan (**1**), (3*β*,25*R*)-3-[(*β*-D-glucopyranosyl-(1→2)-[6-*O*-hexadecanoyl-*β*-D-glucopyranosyl-(1→6)]-*β*-D-glucopyranosyl)oxy]-5*β*-spirostan (**2**), (3*β*,22*R*,25*R*)-26-[(*β*-D-glucopyranosyl)oxy]-3-[(*β*-D-glucopyranosyl-(1→2)-*β*-D-glucopyranosyl)-oxy]-5*β*-furostan (**3**), and (3*β*,22*R*,25*R*)-26-[(*β*-D-glucopyranosyl)oxy]-3-[(*β*-D-glucopyranosyl-(1→2)-[*β*-D-glucopyranosyl-(1→6)]-*β*-D-glucopyranosyl)oxy]-5*β*-furostan (**4**), have been isolated from the fresh rhizomes of *Disporopsis pernyi*, together with the three known compounds Ys-I, agavoside B, and (3*β*,25*R*)-3-[(*β*-D-xylopyranosyl-(1→3)-*β*-D-glucopyranosyl-(1→4)-*β*-D-galactopyranosyl)oxy]-5*α*-spirostan-12-one. Their structures were elucidated by spectroscopic analyses, chemical transformations (acid hydrolysis), and comparison with literature data.

Introduction. – Our previous studies on the chemical constituents of the family Liliaceae has shown that plants belonging to the tribe *polygonateae*, such as *Polygonatum kingianum* [1] or *P. pratii* [2], are rich in steroidal saponins. The genus *Disporopsis*, which is taxonomically close to the genus *Polygonatum*, is endemic to Southeast Asia. It comprises four known species, all of which are distributed in the Yunnan province of China. Until now, no chemical investigation has been performed on this genus.

Disporopsis pernyi (HUA) DIELS, a Chinese folk medicine, is a remedy to rheumatism, coughing, tonsillitis, and conjunctivitis, and is often being used as a tonic [3]. As a part of our continuing work to discover novel secondary metabolites from liliaceous plants [4–11], we investigated the rhizomes of *D. pernyi* and isolated seven steroidal saponins, among which disporosides A–D (**1**–**4**) are unknown natural products. In the present paper, we report the structural characterization of these compounds.

Results and Discussion. – The MeOH extracts of the fresh rhizomes of *D. pernyi* were suspended in H_2O and extracted with BuOH. The BuOH fraction was purified by column chromatography (CC) on silica gel and *RP-8* gel to afford compounds **1**–**4**, in addition to three known compounds. The latter were identified as the steroidal saponins Ys-I [12], agavoside B [13], and (3*β*,25*R*)-3-[(*β*-D-xylopyranosyl-(1→3)-*β*-D-glucopyranosyl-(1→4)-*β*-D-galactopyranosyl)oxy]-5*α*-spirostan-12-one[1]) [14], on the basis of their spectroscopic data and by comparison with literature data.

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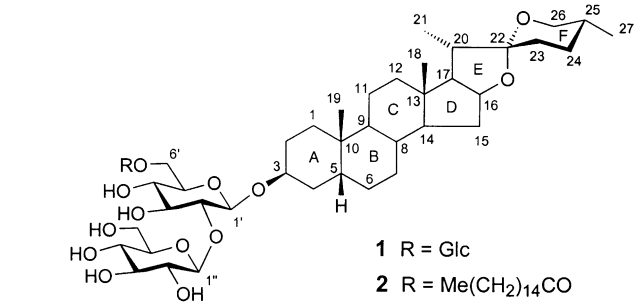
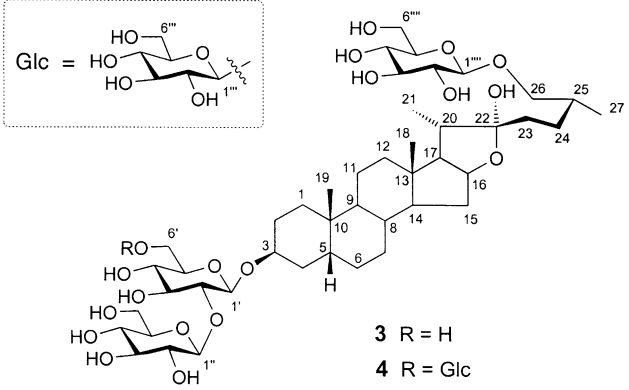
[1]) Alternative name: 3*β*-*O*-(*β*-D-xylopyranosyl-(1→3)-*β*-D-glucopyranosyl-(1→4)-*β*-D-galactopyranosyl)hecogenin (hecogenin = (3*β*,25*R*)-3-hydroxy-5*α*-spirostan-12-one).





Compounds **1**–**4**, obtained as white amorphous powders, belong to steroidal saponins of the smilagenin[2]) type, as indicated by four characteristic Me signals at δ_H 0.67–1.33 ppm in the ^{1}H-NMR spectrum, and a quaternary C-atom signal at *ca.* δ_C 110 ppm in the ^{13}C-NMR spectrum. Their molecular formulae were assigned to be $C_{45}H_{74}O_{18}$ (**1**), $C_{55}H_{94}O_{14}$ (**2**), $C_{45}H_{76}O_{19}$ (**3**), and $C_{51}H_{86}O_{24}$ (**4**) on the basis of the negative-ion HR-FAB mass spectra.

The ^{1}H- and ^{13}C-NMR spectra of **1** (*Table*) exhibited four characteristic Me signals at δ_H 0.80 (*s*), 0.97 (*s*), 0.68 (*d*, $J = 5.5$ Hz), and 1.14 ppm (*d*, $J = 6.7$ Hz), and a quaternary-C-atom resonance at δ_C 109.3 ppm (C(22)), indicating the presence of a steroidal skeleton. In addition, the signals at δ_C 37.0 (C(5)), 40.4 (C(9)), and 24.1 ppm (C(19)) suggested that **1** was a 5β-steroidal spirostanol [15]. The ^{13}C- and ^{1}H-NMR spectral features of **1** were in good agreement with those of smilagenin[2]) [16], except for the chemical shifts of C(2) (δ_C 27.1), C(3) (δ_C 75.4), and C(4) (δ_C 30.9) of the aglycone, as well as the appearance of three sets of sugar units (three anomeric H-atoms at δ_H 5.34 (*d*, $J = 7.6$ Hz), 5.11 (*d*, $J = 7.7$ Hz), and 4.89 (*d*, $J = 7.4$ Hz)). Acid hydrolysis of **1** afforded D-glucose (Glc) exclusivley, indicating the presence of three β-D-glucopyranosyl units. The downfield shift of C(3) and the upfield shifts of both C(2) and C(4) suggested that the carbohydrate moiety was linked to C(3) of the steroidal aglycone, which was confirmed by the long-range correlation of the anomeric H-atom

[2]) Trivial name for (3β,25*R*)-5β-spirostan-3-ol.

at δ_H 4.89 ppm (H−C(1′)) with the aglycone-C(3) resonance at δ_C 75.4 ppm in the HMBC spectrum. The ^{13}C-NMR resonances of the sugar units were assigned by HMQC and HMQC/TOCSY experiments (see the *Table*). The sugar sequence was determined by the HMBC correlations of the remaining two anomeric H-atoms at δ_H 5.34 (H−C(1″)) and 5.11 ppm (H−C(1‴)) with the ^{13}C-NMR resonances at δ_C 83.0 (C(2′)) and 70.1 ppm (C(6′)). In the IR spectrum of compound **1**, the absorption at 898 cm^{-1} was stronger than the one at 922 cm^{-1}, indicating (*R*)-configuration at C(25) [17]. On the basis of the above evidence, disporoside A (**1**) was determined to be (3*β*,25*R*)-3-[(*β*-D-glucopyranosyl-(1→2)-[*β*-D-glucopyranosyl-(1→6)]-*β*-D-glucopyranosyl)oxy]-5*β*-spirostan.

Table 1. *^{13}C-NMR Data of Compounds* **1**–**4**. At 125 MHz in (D_5)pyridine; *δ* in ppm.

	1	**2**	**3**	**4**		**1**	**2**	**3**	**4**
CH_2(1)	31.1	30.7	30.8	31.1	H−C(1′)	101.9	102.3	101.9	101.9
CH_2(2)	27.1	27.1	27.1	27.5	H−C(2′)	83.0	83.4	83.2	82.9
H_α−C(3)	75.4	74.9	75.3	75.3	H−C(3′)	77.1	77.0	78.0	77.2
CH_2(4)	32.2	32.2	32.5	32.5	H−C(4′)	71.6	71.9	71.7	71.6
H_β−C(5)	37.0	37.1	36.9	37.0	H−C(5′)	78.0	78.0	78.2	78.0
CH_2(6)	26.9	26.9	26.9	26.9	CH_2(6′)	70.1	64.5	62.9	70.1
CH_2(7)	26.9	26.9	27.1	26.9	H−C(1″)	105.9	106.1	105.9	105.9
H_β−C(8)	35.6	35.4	35.3	35.7	H−C(2″)	77.1	76.2	77.0	77.0
H_α−C(9)	40.4	40.5	40.4	40.9	H−C(3″)	78.5	78.7	78.5	78.5
C(10)	35.4	35.7	35.6	35.4	H−C(4″)	71.8	71.6	71.8	71.9
CH_2(11)	21.2	21.3	21.3	21.3	H−C(5″)	77.9	78.6	78.5	78.1
CH_2(12)	40.4	40.5	40.4	40.8	CH_2(6″)	62.9	62.9	62.9	62.9
C(13)	41.0	41.0	41.3	41.4	H−C(1‴)	105.4	–	–	105.4
H_α−C(14)	56.6	56.6	56.5	56.6	H−C(2‴)	75.3	–	–	75.3
CH_2(15)	31.9	31.9	31.0	32.5	H−C(3‴)	78.5	–	–	78.7
H_α−C(16)	81.3	81.4	81.3	81.4	H−C(4‴)	71.8	–	–	71.9
H_α−C(17)	63.3	63.3	64.1	64.1	H−C(5‴)	78.0	–	–	78.5
β-Me(18)	16.6	16.7	16.8	16.8	CH_2(6‴)	62.9	–	–	62.9
β-Me(19)	24.1	24.1	24.1	24.2	H−C(1⁗)	–	–	104.9	104.9
H_β−C(20)	42.1	42.1	40.7	40.9	H−C(2⁗)	–	–	75.3	75.3
α-Me(21)	15.1	15.1	16.5	16.5	H−C(3⁗)	–	–	78.6	78.7
C(22)	109.3	109.3	110.7	110.8	H−C(4⁗)	–	–	71.7	71.6
CH_2(23)	30.9	31.3	31.0	31.0	H−C(5⁗)	–	–	78.5	78.1
CH_2(24)	29.3	29.4	28.4	28.5	CH_2(6⁗)	–	–	62.9	62.9
CH_2(23)	30.7	30.7	34.5	34.4	CH_2*C*OO	–	173.6	–	–
H−C(25)	67.0	67.0	75.5	75.5	*C*H_2COO	–	34.6	–	–
CH_2(26)	17.3	17.4	17.5	17.6	Me*C*H_2	–	29.7	–	–
					Et(*C*H_2)$_{11}$	–	29.6	–	–
					C$H_2$$CH_2$COO	–	25.5	–	–
					MeCH_2	–	14.3	–	–

Comparing the ^{1}H- and ^{13}C-NMR spectra of compound **2** with those of Ys-I, isolated previously from *Yucca gloriosa* [12], suggested that the new compound had the same aglycone and sugar moieties as Ys-I. Compound **2** showed four steroidal Me signals at δ_H 0.84 (*s*, Me(18)), 1.00 (*s*, Me(19)), 1.20 (*d*, J = 6.8 Hz, Me(21)), and 0.69 ppm (*d*, J = 5.3 Hz, Me(27)), a quaternary C-atom at δ_C 109.3 (C(22), three resonances at δ_C 37.1 (C(5)), 40.5 (C(9)), and 24.1 ppm (Me(19)), as well as two

anomeric H-atom signals at δ_H 5.40 (*d*, $J = 7.7$ Hz) and 4.94 ppm (*d*, $J = 7.4$ Hz). Moreover, compound **2** exhibited one set of additional signals at δ_C 173.6 (C=O), 14.3 (Me), 25.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), and 34.6 ppm ($(CH_2)_n$), corresponding to a long-chain fatty-acid moiety. The fragment-ion peak at *m/z* 255 in the negative-ion FAB mass spectrum of **2** suggested the presence of a palmitoyl ($Me(CH_2)_{14}COO-$) group. In the HMBC spectrum of **2**, correlations of the $CH_2(6')$ resonances at δ_H 4.98 and 4.75 ppm with that of the palmitoyl C=O group at δ_C 173.6 ppm indicated that the fatty acid was attached at C(6′) of the 'inner' glucose unit of the Ys-I portion of **2**. Moreover, HMBC correlations of the signal at δ_H 4.94 ppm (H–C(1′)) with that at δ_C 75.0 ppm (C(3)), and of the one at δ_H 5.40 (H–C(1″)) with that at δ_C 83.4 (C(2′)) confirmed the $(1 \rightarrow 2)$ sugar linkage of **2**. Consequently, disporoside B (**2**) corresponds to (3*β*,25*R*)-3-[(*β*-D-glucopyranosyl-$(1 \rightarrow 2)$-[6-*O*-hexadecanoyl-*β*-D-glucopyranosyl-$(1 \rightarrow 6)$]-*β*-D-glucopyranosyl)oxy]-5*β*-spirostan.

Compounds **3** and **4** tested positive to the *Ehrlich* reagent, suggesting that they belong to the furostanol glycosides. The ^{13}C-NMR data (*Table*) of **3** and **4** arising from the steroidal rings *A*–*D* were in good accordance with those of **1** and **2**, with the exception of the signals of the furostanol ring *F*. In addition, **3** showed one and **4** showed two more *β*-D-glucopyranosyl units than Ys-I. When treated with 1M aqueous HCl solution, both compounds afforded exclusively D-glucose as the sugar residue and smilagenin as the aglycone, as verified by NMR and IR spectroscopy [16]. The ^{13}C-NMR data of the sugar units of **3** and **4** were assigned by HMQC and HMQC/TOCSY experiments (*Table*). The location and sequence of the sugar moieties were determined by HMBC experiments. In the case of **3**, long-range correlations of the resonances at δ_H 4.80 ppm (H–C(1‴) with δ_C 75.5 ppm (C(26)), at δ_H 4.95 (H–C(1′)) with δ_C 75.3 (C(3)), and at δ_H 5.40 (H–C(1″)) with δ_C 83.2 (C(2′)) were observed. And in the case of **4**, there was, besides the above mentioned correlations, an additional one for the anomeric signal at δ_H 5.11 ppm (H–C(1‴)) and the resonance at δ_C 70.1 ppm (C(6′)). On the basis of these evidences, disporosides C (**3**) and D (**4**) were determined to be (3*β*,22*R*,25*R*)-26-[(*β*-D-glucopyranosyl)oxy]-3-[(*β*-D-glucopyranosyl-$(1 \rightarrow 2)$-*β*-D-glucopyranosyl)oxy]-5*β*-furostan and (3*β*,22*R*,25*R*)-26-[(*β*-D-glucopyranosyl)oxy]-3-[(*β*-D-glucopyranosyl-$(1 \rightarrow 2)$-[*β*-D-glucopyranosyl-$(1 \rightarrow 6)$]-*β*-D-glucopyranosyl)oxy]-5*β*-furostan, respectively.

Experimental Part

General. Thin-layer chromatography (TLC): precoated silica-gel plates (*Qingdao Haiyang Chemical Co.*); detection by spraying with 5% anisaldehyde in H_2SO_4, followed by heating. Optical rotations: *HORIBA SEPA-300* high-sensitive polarimeter. IR Spectra: *Bio-Rad FTS-135* spectrophotometer, KBr disks; in cm^{-1}. NMR Spectra: *Bruker DRX-500* instrument (500/125 MHz), in (D_5)pyridine at 25°; δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz. FAB-MS: *VG AutoSpec-3000* mass spectrometer, glycerol matrix; in *m/z*.

Plant Material. The fresh rhizomes of *Disporopsis pernyi* (HUA) DIELS were collected at Jinping, southeast of Yunnan province, China. The plants were identified by Prof. *H. Li*. A voucher specimen was deposited at the Herbarium of the Kunming Institute of Botany, Chinese Academy of Sciences, China.

Extraction and Isolation. The fresh rhizomes of *D. pernyi* (10.0 kg) were extracted with hot MeOH. The extract was concentrated under reduced pressure, suspended in H_2O, and extracted with BuOH. The BuOH fraction (40.0 g after evaporation) was chromatographed (SiO_2; $CHCl_3$/MeOH/H_2O 7:2:1, lower layer) to give 4 fractions (Fr.). *Fr. 1* was subjected to CC (1. SiO_2; $CHCl_3$/MeOH/H_2O 7:3:1, lower layer; 2. *RP-8* gel; MeOH/H_2O 1:1) to afford two mixtures. The mixtures were refluxed in 30% aq. acetone for 10 h to furnish **3** (100 mg)

and **4** (140 mg), resp. *Fr. 2* was separated by CC (1. SiO_2; $CHCl_3$/MeOH/H_2O 7:2:1, lower layer; 2. *RP-8* gel, MeOH/H_2O 7:3) to afford agavoside B (200 mg) and **1** (110 mg). *Fr. 3* was also purified by CC (1. SiO_2; $CHCl_3$/MeOH/H_2O 8:2:1; 2. *RP-8* gel, MeOH/H_2O 4:1) to give Ys-I (80 mg) and **2** (150 mg). *Fr. 4* was purified by CC (*RP-8* gel; MeOH/H_2O 7:3) to afford (3*β*,25*R*)-3-[(*β*-D-xylopyranosyl-(1 → 3)-*β*-D-glucopyranosyl-(1 → 4)-*β*-D-galactopyranosyl)oxy]-5*α*-spirostan-12-one[1]) (50 mg).

*(3β,25*R*)-3-[(β-*D*-Glucopyranosyl-(1 → 2)-[β-*D*-glucopyranosyl-(1 → 6)]-β-*D*-glucopyranosyl)oxy]-5β-spirostan* (*disporoside A*; **1**). White amorphous powder. $[\alpha]_D^{23} = -0.5$ ($c = 0.4$, pyridine). IR (KBr): 3403, 2930, 1453, 1075, 986, 922, 898. ^{1}H-NMR ((D$_5$)pyridine)[3]): 5.34 (*d*, *J* = 7.6, H−C(1″)); 5.11 (*d*, *J* = 7.7, H−C(1‴)); 4.89 (*d*, *J* = 7.4, H−C(1′)); 4.54 (*m*, H−C(16)); 1.14 (*d*, *J* = 6.7, Me(21)); 0.97 (*s*, Me(19)); 0.80 (*s*, Me(18)); 0.68 (*d*, *J* = 5.5, Me(27)). ^{13}C-NMR: see *Table*. FAB-MS: 902 (M^-), 739 ($[M - H - 162]^-$). HR-FAB-MS: 901.4793 ($[M - H]^-$, $[C_{45}H_{74}O_{18} - H]^-$; calc. 901.4797).

Acid Hydrolysis of **1**. A soln. of **1** (5 mg) in HCl/MeOH 1:1 (1M, 1 ml) was heated at 95° for 5 h. The mixture was neutralized with aq. $NaHCO_3$ soln. (1M) and evaporated to dryness. TLC Analysis (R_F 0.1 ($CHCl_3$/MeOH/H_2O 7:3:0.5)) and optical rotation dispersion ($[\alpha]_D^{23} = +23.5$ ($c = 0.17$, H_2O)) indicated the presence of D-glucose.

*(3β,25*R*)-3-[(β-*D*-Glucopyranosyl-(1 → 2)-[6-O-hexadecanoyl-β-*D*-glucopyranosyl-(1 → 6)]-β-*D*-glucopyranosyl)oxy]-5β-spirostan* (*Disporoside B*; **2**). White amorphous powder. $[\alpha]_D^{23} = -54.2$ ($c = 0.4$, pyridine). ^{1}H-NMR ((D$_5$)pyridine)[3]): 5.40 (*d*, *J* = 7.7, H−C(1″)); 4.98 (br. *d*, *J* = 10.9, H_a−C(6′)); 4.94 (*d*, *J* = 7.4, H−C(1′)); 4.75 (*dd*, *J* = 4.0, 10.9, H_b−C(6′)); 3.59 (br. *d*, *J* = 11.0, H_a−C(6″)); 3.53 (br. *d*, *J* = 11.0, H_b−C(6″)); 2.40 (*m*, CH_2COO); 1.20 (*d*, *J* = 6.4, Me(21)); 1.00 (*s*, Me(19)); 0.87 (*t*, *J* = 6.4, *Me*$(CH_2)_{14}$); 0.84 (*s*, Me(18)); 0.69 (*d*, *J* = 5.3, Me(27)). ^{13}C-NMR: see *Table*. FAB-MS: 977 ($[M - H]^-$), 255 ($[M - H - 398 - 2 \times 162]^-$). HR-FAB-MS: 977.6515 ($[M - H]^-$; $[C_{55}H_{94}O_{14} - H]^-$; calc. 977.6565).

Acid Hydrolysis of **2**. Compound **2** (2 mg) was subjected to acid hydrolysis as described for **1**. TLC analysis and optical rotation dispersion indicated the presence of D-glucose.

*(3β,22*R*,25*R*)-26-[(β-*D*-Glucopyranosyl)oxy]-3-[(β-*D*-glucopyranosyl-(1 → 2)-β-*D*-glucopyranosyl)oxy]-5β-furostan* (*Disporoside C*; **3**). White amorphous powder. $[\alpha]_D^{23} = -40.9$ ($c = 0.2$, pyridine). IR (KBr): 3414, 2930, 1453, 1078, 1038. ^{1}H-NMR ((D$_5$)pyridine)[3]): 5.40 (*d*, *J* = 7.7, H−C(1″)); 4.96 (*m*, H−C(16)); 4.95 (*d*, *J* = 7.5, H−C(1′)); 4.80 (*d*, *J* = 7.8, H−C(1‴)); 4.00 (*t*, *J* = 12.1, H_a−C(26)); 3.60 (*dd*, *J* = 2.5, 12.1, H_b−C(26)); 1.33 (*d*, *J* = 6.8, Me(21)); 1.00 (*d*, *J* = 5.0, Me(27)); 0.98 (*s*, Me(19)); 0.87 (*s*, Me(18)). ^{13}C-NMR: see *Table*. FAB-MS: 919 ($[M - H]^-$), 757 ($[M - H - 162]^-$). HR-FAB-MS: 919.4870 ($[M - H]^-$, $[C_{45}H_{76}O_{19} - H]^-$; calc. 919.4903).

Acid Hydrolysis of **3**. A soln. of **3** (30 mg) in 1M aq. HCl soln. (10 ml) was heated at 95° for 5 h. The mixture was neutralized with aq. $NaHCO_3$ soln. (1M) and extracted with $CHCl_3$ (3×). The org. phase was concentrated and subjected to CC (SiO_2; $CHCl_3$/MeOH 20:1 → 10:1) to afford smilagenin[2]) (8.0 mg), as identified by NMR and IR [16]. The above aq. phase was concentrated to dryness and then chromatographed (SiO_2; $CHCl_3$/MeOH/H_2O 7:3:0.5) to yield D-glucose (3.2 mg), as identified by TLC and optical rotation dispersion (see acid hydrolysis of **1**).

*(3β,22*R*,25*R*)-26-[(β-*D*-Glucopyranosyl)oxy]-3-[(β-*D*-glucopyranosyl-(1 → 2)-[β-*D*-glucopyranosyl-(1 → 6)]-β-*D*-glucopyranosyl)oxy]-5β-furostan* (*Disporoside D*; **4**). White amorphous powder. $[\alpha]_D^{23} = -43.7$ ($c = 0.4$, pyridine). IR (KBr): 3415, 2930, 1453, 1076, 1040, 907. ^{1}H-NMR ((D$_5$)pyridine)[3]): 5.35 (*d*, *J* = 7.6, H−C(1″)); 5.11 (*d*, *J* = 7.4, H−C(1‴)); 5.00 (*m*, H−C(16)); 4.89 (*d*, *J* = 7.4, H−C(1′)); 4.79 (*d*, *J* = 7.7, H−C(1⁗)); 1.33 (*d*, *J* = 7.0, Me(21)); 1.01 (*d*, *J* = 6.7, Me(27)); 0.97 (*s*, Me(19)); 0.84 (*s*, Me(18)). ^{13}C-NMR: see *Table*. FAB-MS: 1082 (M^-), 919 ($[M - H - 162]^-$), 757 ($[M - H - 2 \times 162]^-$), 595 ($[M - H - 3 \times 162]^-$). HR-FAB-MS: 1081.5367 ($[M - H]^-$, $[C_{51}H_{86}O_{24} - H]^-$; calc. 1081.5431).

Acid Hydrolysis of **4**. Compound **4** (30 mg) was subjected to acid hydrolysis, as described for **3**, to afford smilagenin[2]) (5.0 mg), and D-glucose (6.0 mg; identified as described for the hydrolysis of **1**).

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