Three New Cycloartane (= 9,19-Cyclolanostane) Glycosides from *Cimicifuga foetida*

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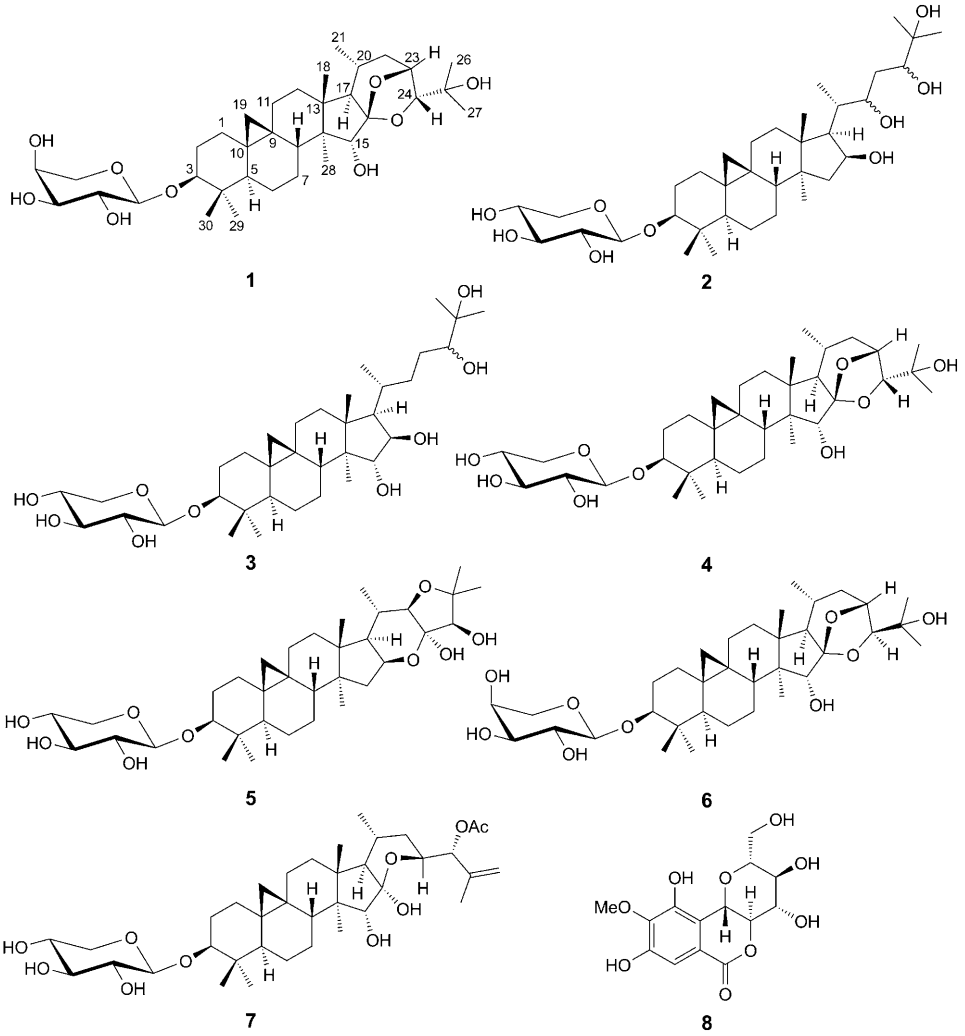
Three new cycloartane glycosides, 24-epicimigenol 3-(α-L-arabinopyranoside) (**1**), (3β,16β)-cycloartane-3,16,22,24,25-pentol 3-(β-D-xylopyranoside) (**2**), and (3β,15α,16β)-cycloartane-3,15,16,24,25-pentol 3-(β-D-xylopyranoside) (**3**), together with five known compounds, including four cycloartane glycosides and bergenin, were isolated from the rhizomes of *Cimicifuga foetida*. Their structures were elucidated by spectroscopic methods.

Introduction. – The rhizomes of *Cimicifuga foetida*, *C. Dahurica*, and *C. Heracleifolia* (Ranunculaceae) are a source of a popular herbal medicine in China, which have been used as an antipyretic and analgesic agent since ancient times [1]. In Europe and the United States, *C. racemosa*, commonly called black cohosh, has a long and diverse history of medicinal use. The alcoholic extracts of black cohosh are the active ingredient of numerous popular phytomedicines and dietary supplements, which have been used in women's health in reducing menstrual pain and menopausal disorders [2]. The roots/rhizomes have traditionally been used to treat a variety of medical conditions including colds, kidney ailments, malaise, rheumatism, and women's conditions such as uterine disorders and menstrual complaints [3]. According to previous chemical and pharmacological investigations on *Cimicifuga* species, three main classes of constituents have been isolated: 9,19-cycloartane triterpene glycosides, chromenones, and cinnamic acid derivatives, of which triterpene glycosides are considered to be the bioactive components [4]. Previously, our research group has studied *C. foetida* collected from Lijiang and Dali Counties in Yunnan Province and Heze County in Guizhou Province, and reported a series of new cycloartane triterpene glycosides including a novel triterpene alkaloid [5], as well as their antitumor and anticomplement activities [6–8].

Our further chemical investigation on the rhizomes of *C. foetida* collected from Dali County, Yunnan Province, led to the isolation of the three new 9,19-cycloartane triterpene glycosides **1**–**3**, together with five known compounds, 24-epicimigenol 3-(β-D-xylopyranoside) (**4**) [9], cimiaceroside B (=(3β,16β,22*R*,23*R*,24*R*)-16,23:22,25-diepoxy-23,24-dihydroxy-9,19-cyclolanostan-3-yl β-D-xylopyranoside; **5**) [10], cimigenol 3-(α-L-arabinopyranoside) (**6**) [11], 24-*O*-acetyl-25-anhydroshengmanol 3-(β-D-xylopyranoside) (=(3β,15α,16β,23*S*,24*R*)-24-(acetyloxy)-16,23-epoxy-15,16-dihy-

droxy-9,19-cyclolanos-25-en-3-yl β-D-xylopyranoside; **7**) [12], and bergenin (**8**) [13] which was isolated for the first time from the genus *Cimicifuga*.



Results and Discussion. – Compound **1** was isolated as a white powder. The combination of the HR-FAB-MS (*m/z* 643.3837 ($[M+Na]^+$)) and ^{13}C-NMR data led to the determination of its formula as $C_{35}H_{56}O_9$. The IR spectrum showed absorption at 3412 cm^{-1} for OH groups. In the ^{1}H-NMR spectrum (*Table*), the characteristic cyclopropane CH_2 signals at δ(H) 0.28 (*d*, $J=3.9$ Hz) and 0.53 (*d*, $J=3.4$ Hz), six tertiary Me groups at δ(H) 1.04, 1.07, 1.18, 1.26, 1.29, and 1.42 (6*s*), a secondary Me group at δ(H) 0.95 (*d*, $J=6.0$ Hz), and an anomeric H-atom at δ(H) 4.80 (*d*, $J=7.1$ Hz) were observed. The ^{13}C-NMR spectrum (*Table*) showed five O-bearing C-atoms assignable to a glycosidic moiety at δ(C) 107.5 (*d*, C(1′)), 73.0 (*d*, C(2′)), 74.7 (*d*, C(3′)),

69.6 (*d*, C(4′)), and 66.8 (*t*, C(5′)), and six O-bearing C-atoms at δ(C) 112.2 (*s*), 88.7 (*d*), 84.1 (*d*), 80.8 (*d*), 73.7 (*d*), and 68.6 (*s*). All of the above evidences suggested that **1** was a highly oxygenated 9,19-cycloartane triterpene monoglycoside. A comparison of the ^{1}H- and ^{13}C-NMR data of **1** with those of the known 24-epicimigenol 3-(β-D-xylopyranoside) (**4**) [9] showed that, structurally, **1** closely resembles **4**, except for the presence of an α-L-arabinose [11] moiety instead of a β-D-xylose moiety. Acid hydrolysis of **1**, transformation of the hydrolyzed monosaccharide to the methyl (4*R*)-2-(polyhydroxyalkyl)thiazolidine-4-carboxylate and trimethylsilylation followed by gas chromatography (GC) of the product showed that the sugar of **1** was L-arabinose. In the HMBC spectrum of **1** (*Fig. 1*), a correlation was observed between the signal at δ(H) 4.80 (*d*, $J = 7.1$ Hz, H–C(1′)) and δ(C) 88.7 (*d*, C(3)), suggesting that the sugar moiety was located at C(3). Unambiguous ROESY correlations (*Fig. 2*) of H–C(15) with H–C(8) and Me(18) revealed an α-orientation of the OH group at C(15). The relative configurations of C(23) and C(24) were assigned as *rel*-(23*R*,24*R*), respectively, by comparing the coupling constants of the H–C(23) and H–C(24) signals of **1** with those of 24-epicimigenol 3-(β-D-xylopyranoside) (**4**) [9]. Therefore, compound **1** was identified as 24-epicimigenol 3-(α-L-arabinopyranoside).

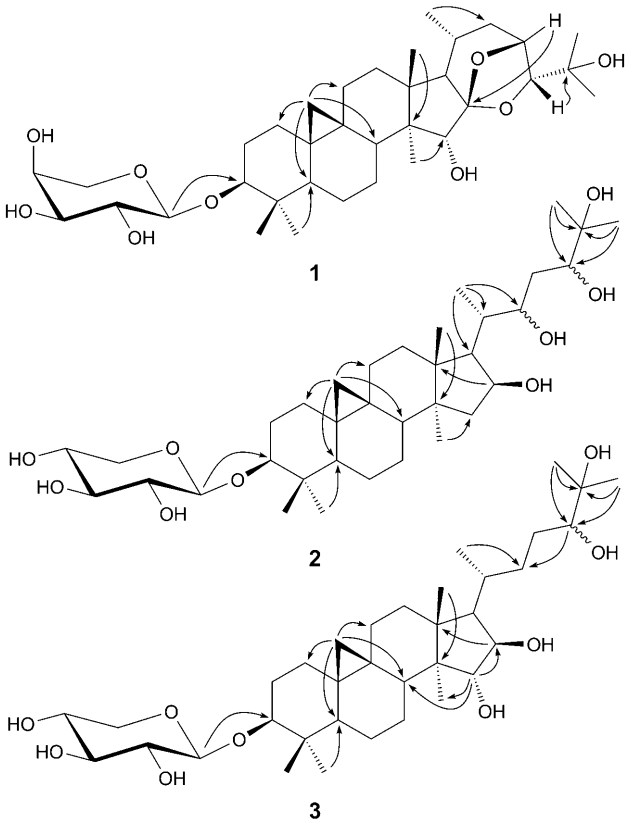


Fig. 1. *Major HMBCs of compounds* **1**–**3**

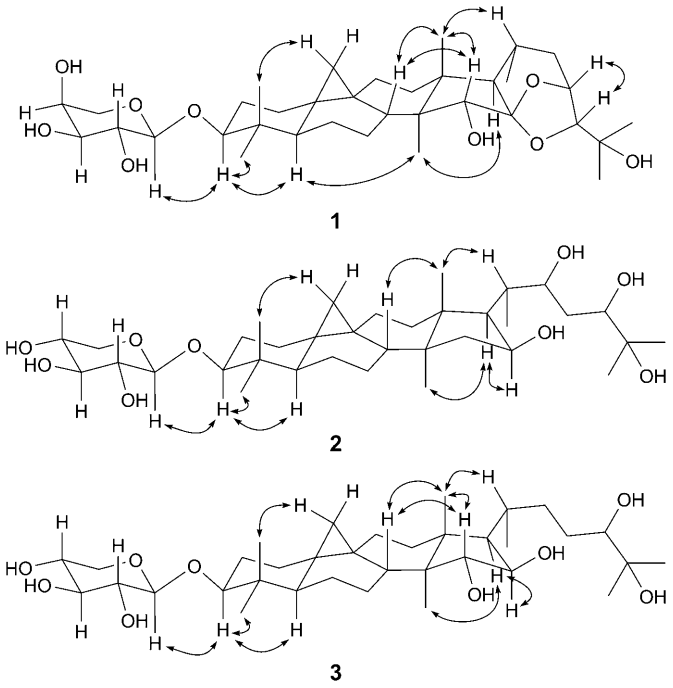


Fig. 2. *Key ROESY correlations of compounds* **1**–**3**

Compound **2**, a white powder, showed a *quasi*-molecular ion at *m*/*z* 623 ([*M* – H]$^-$) in the FAB-MS (negative-ion mode). The ^{13}C-NMR spectrum and HR-FAB-MS (*m*/*z* 623.4143 ([*M* – H]$^-$)) determined its molecular formula as $C_{35}H_{60}O_9$, corresponding to six degrees of unsaturation. The IR spectrum showed absorption of OH groups at 3477 cm^{-1}. The ^{1}H-NMR spectrum exhibited characteristic cyclopropane CH_2 signals at δ(H) 0.26 (*d*, *J* = 3.8 Hz) and 0.51 (*d*, *J* = 3.3 Hz), six tertiary Me groups at δ(H) 0.90, 1.06, 1.34, 1.46, 1.56, and 1.58 (6 *s*), a secondary Me group at δ(H) 1.22 (*d*, *J* = 6.9 Hz), and an anomeric H-atom at δ(H) 4.87(*d*, *J* = 7.4 Hz). The ^{13}C-NMR spectrum (*Table*) showed data consistent with a β-D-xylose moiety at δ(C) 107.6 (*d*, C(1′)), 75.6 (*d*, C(2′)), 78.7 (*d*, C(3′)), 71.3 (*d*, C(4′)), and 67.2 (*t*, C(5′)) [9], and five O-bearing C-atoms at δ(C) 88.6 (*d*), 71.9 (*d*), 72.6 (*d*), 76.4 (*d*), and 72.8 (*s*). The ^{1}H- and ^{13}C-NMR data of **2** resembled those of the known compound cimiaceroside B (**5**) [10], except for signals of ring *D* and the C(17) side chain. A HMBC (*Fig. 1*) between δ(H) 4.89 (overlapped, H–C(16)) and δ(C) 46.0 (*s*, C(13)) was observed. Moreover, ^{1}H,^{1}H-COSY cross-peaks between δ(H) 4.89 (overlapped, H–C(16)) and 2.36 (overlapped, H–C(17)), revealed that one OH group was attached at C(16). An OH group located at C(22) was based on the unambiguous HMBC between δ(H) 1.22 (*d*, *J* = 6.9 Hz, Me(21)) and δ(C) 72.6 (*d*, C(22)). The vicinal relationship of the OH groups at C(24) and C(25) were concluded from the HMBCs Me(26)/C(24), Me(26)/C(25), Me(26)/C(27), Me(27)/C(24), Me(27)/C(25), and Me(27)/C(26) (*Fig. 1*). The HMBC between δ(H) 4.87 (*d*, *J* = 7.4 Hz, H–C(1′)) and δ(C) 88.6 (*d*, C(3)) suggested that the sugar moiety was attached

Table. *The ^{1}H- and ^{13}C-NMR Data* (C_5D_5N) *of Compounds* **1**–**3**. δ in ppm, J in Hz. Assignments were confirmed by HSQC, HMBC, and ^{1}H,^{1}H-COSY experiments.

	1		**2**		**3**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
CH_2(1)	32.5 (*t*)	1.20[a]), 1.54[a])	32.2 (*t*)	1.55[a]), 1.23[a])	32.5 (*t*)	1.26[a]), 1.62[a])
CH_2(2)	30.1 (*t*)	2.35–2.40 (*m*)	30.2 (*t*)	1.94[a]), 2.34[a])	30.0 (*t*)	1.96[a]), 2.35[a])
H–C(3)	88.7 (*d*)	3.50 (*dd*, *J* = 4.2, 11.6)	88.6 (*d*)	3.50 (*dd*, *J* = 4.2, 11.4)	88.6 (*d*)	3.51 (*dd*, *J* = 4.0, 11.6)
C(4)	41.4 (*s*)		41.4 (*s*)		41.4 (*s*)	
H–C(5)	47.8 (*d*)	1.33[a])	47.7 (*s*)	1.33[a])	47.7 (*d*)	1.38[a])
CH_2(6)	21.2 (*t*)	0.69–0.78, 1.54–1.58 (2*m*)	21.2 (*t*)	0.66–0.75 (*m*), 1.53[a])	21.4 (*t*)	0.69–0.79 (*m*), 1.59[a])
CH_2(7)	26.4 (*t*)	1.05[a]), 2.02[a])	26.4 (*t*)	1.08[a]), 1.98[a])	26.6 (*t*)	2.06–2.16 (*m*)
H–C(8)	48.7 (*d*)	1.70[a])	48.4 (*d*)	1.66[a])	49.4 (*d*)	1.81[a])
C(9)	20.1 (*s*)		20.1 (*s*)		20.5 (*s*)	
C(10)	26.7 (*s*)		26.5 (*s*)		26.3 (*s*)	
CH_2(11)	26.6 (*t*)	1.16[a]), 2.09–2.12 (*m*)	26.4 (*t*)	1.08[a]), 1.98[a])	26.3 (*t*)	1.10[a])
CH_2(12)	34.0 (*t*)	1.59[a])	33.5 (*t*)	1.66[a])	34.2 (*t*)	1.65–1.74 (*m*)
C(13)	41.8 (*s*)		46.0 (*s*)		46.1 (*s*)	
C(14)	47.5 (*s*)		47.3 (*s*)		48.7 (*s*)	
H–C(15) or CH_2(15)	80.8 (*d*)	4.23 (*s*)	48.6 (*t*)	1.75–1.80 (*m*), 2.12[a])	88.7 (*d*)	4.46 (br. *s*)
C(16) or H–C(16)	112.2 (*s*)		71.9 (*d*)	4.89[a])	81.8 (*d*)	4.62–4.64 (*m*)
H–C(17)	60.8 (*d*)	1.76[a])	53.4 (*d*)	2.36[a])	55.6 (*d*)	1.98[a])
Me(18)	19.6 (*q*)	1.18 (*s*)	19.7 (*q*)	1.46 (*s*)	19.7 (*q*)	1.46 (*s*)
CH_2(19)	31.0 (*t*)	0.28 (*d*, *J* = 3.9), 0.53 (*d*, *J* = 3.4)	30.2 (*t*)	0.26 (*d*, *J* = 3.8), 0.51 (*d*, *J* = 3.3)	30.4 (*t*)	0.29 (*d*, *J* = 3.5), 0.51 (*d*, *J* = 2.9)
H–C(20)	23.5 (*d*)	1.70[a])	37.0 (*d*)	2.66–2.70 (*m*)	28.8 (*d*)	2.32–2.38 (*m*)
Me(21)	19.6 (*q*)	0.95 (*d*, *J* = 6.0)	15.2 (*q*)	1.22 (*d*, *J* = 6.9)	18.4 (*q*)	1.08 (*d*, *J* = 6.2)
CH_2(22) or H–C(22)	29.7 (*t*)	1.95[a]), 2.63–2.69 (*m*)	72.6 (*d*)	4.81[a])	33.3 (*t*)	1.49[a]), 2.24–2.30 (*m*)
H–C(23) or CH_2(23)	73.7 (*d*)	4.57–4.60 (*m*)	36.8 (*t*)	2.40[a]), 2.06[a])	28.1 (*t*)	1.79–1.83 (*m*), 2.00[a])
H–C(24)	84.1 (*d*)	3.68 (*d*, *J* = 4.2)	76.4 (*d*)	4.35[a])	77.3 (*d*)	3.91–3.93 (*m*)
C(25)	68.6 (*s*)		72.8 (*s*)		72.6 (*s*)	
Me(26)	30.8 (*q*)	1.42 (*s*)	26.1 (*q*)	1.56 (*s*)	25.9 (*q*)	1.47 (*s*)
Me(27)	26.0 (*q*)	1.26 (*s*)	26.5 (*q*)	1.58 (*s*)	26.5 (*q*)	1.44 (*s*)
Me(28)	11.8 (*q*)	1.07 (*s*)	20.6 (*q*)	0.90 (*s*)	12.9 (*q*)	1.27 (*s*)
Me(29)	25.8 (*q*)	1.29 (*s*)	25.8 (*q*)	1.34 (*s*)	25.8 (*q*)	1.30 (*s*)
Me(30)	15.4 (*q*)	1.04 (*s*)	15.5 (*q*)	1.06 (*s*)	15.6 (*q*)	1.05 (*s*)
H–C(1′)	107.5(*d*)	4.80 (*d*, *J* = 7.1)	107.6 (*d*)	4.87 (*d*, *J* = 7.4)	107.6 (*d*)	4.86 (*d*, *J* = 7.5)
H–C(2′)	73.0 (*d*)	4.44 (*d*, *J* = 7.9)	75.6 (*d*)	4.04 (*t*, *J* = 8.0)	75.6 (*d*)	4.03 (*t*, *J* = 7.9)
H–C(3′)	74.7 (*d*)	4.17 (*t*, *J* = 8.7)	78.7 (*d*)	4.17 (*t*, *J* = 8.6)	78.7 (*d*)	4.16 (*t*, *J* = 8.6)
H–C(4′)	69.6 (*d*)	4.30–4.33 (*m*)	71.3 (*d*)	4.23[a])	71.3 (*d*)	4.22[a])
CH_2(5′)	66.8 (*t*)	3.78 (*d*, *J* = 10.9), 4.28[a])	67.2 (*t*)	3.71–3.79 (*m*), 4.38[a])	67.2 (*t*)	3.74 (*t*, *J* = 10.5), 4.36 (*dd*, *J* = 5.0, 11.1)

[a]) Signals overlapped.

to C(3). Significant ROESY correlations (*Fig. 2*) between H–C(16) and H–C(17) indicated β-orientation of the OH group at C(16). The configurations of C(22) and C(24) are still unknown. Thus, **2** was elucidated as (3β,16β)-cycloartane-3,16,22,24,25-pentol 3-(β-D-xylopyranoside).

Compound **3**, a white powder, showed a *quasi*-molecular ion at *m*/*z* 623 ($[M-H]^-$) in the FAB-MS (negative-ion mode). The ^{13}C-NMR and HR-FAB-MS (*m*/*z* 623.4154 ($[M-H]^-$)) indicated the molecular formula as $C_{35}H_{60}O_9$, which was identical to that of compound **2**. The IR and NMR spectroscopic data of **3** were also similar to those of **2**. The major difference between **3** and **2** in the ^{13}C-NMR spectrum revealed that an OH group was located at C(15) in **3** rather than at C(22) in **2**. The conclusion was confirmed by the HMBCs (*Fig. 1*) between δ(H) 4.46 (br. *s*, H–C(15)) and δ(C) 49.4 (*d*, C(8)), 81.8 (*d*, C(16)), and 12.9 (*q*, C(28)). Further supportive evidence were obtained from the ^{1}H,^{1}H-COSY plot, which showed the correlations H–C(15)/H–C(16) and H–C(16)/H–C(17). The ROESY correlations (*Fig. 2*) H–C(15)/H–C(8) and Me(18), and H–C(16)/H–C(17) suggested that the OH groups at C(15) and C(16) were in α- and β-orientation, respectively. Therefore, **3** was characterized as (3β,15α,16β)-cycloartane-3,15,16,24,25-pentol 3-(β-D-xylopyranoside).

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Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Marine Chemical*, P. R. China); *Lichroprep RP-18* (40–63 μm; *Merck*, Darmstadt, Germany). TLC: detection by heating the plates after being sprayed with 10% aq. H_2SO_4 soln. Optical rotations: *Horiba-SEAP-300* spectropolarimeter. IR Spectra: *Bio-Rad-FTS-40* instrument; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker-AV-400* or *-DRX-500* instrument; chemical shifts δ in ppm rel. to Me_4Si as the internal standard, *J* in Hz. FAB-MS (glycerol matrix) and HR-FAB-MS: *VG-Autospec-3000* spectrometer; in *m*/*z*.

Plant Material. Cimicifuga foetida L. rhizomes were collected from Dali County, Yunnan Province, P. R. China, in September 2008. The plant was identified by Prof. *Z.-Y. Wang*, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (KUN No. 200809021) has been deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Kunming, P. R. China.

Extraction and Isolation. The dried and milled rhizomes *C. foetida* (8 kg) were extracted with MeOH (3 × 15 l, 3 h each) under reflux and the extracts concentrated to give a residue (1 kg) which was suspended in H_2O (2 l) and then extracted successively with petroleum ether (3 × 2 l), AcOEt (3 × 2 l), and BuOH (3 × 2 l). The AcOEt extract (500 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 100:0, 50:1, 20:1, 10:1, and 5:1): *Fractions I–V. Fr. IV* (23 g) was subjected to CC (SiO_2, $CHCl_3$/MeOH 30:1): *Fr. IV.1* and *IV.2*. *Fr. IV.1* (5 g) was subjected to CC (SiO_2, petroleum ether/^{i}PrOH 6:1; then *RP-18*, MeOH/H_2O 70:30): **1** (35 mg) and **4** (13 mg). *Fr. IV.2* (12 g) was subjected to CC (SiO_2, petroleum ether/^{i}PrOH 6:1; then *RP-18*, MeOH/H_2O 65:35): **5** (15 mg) and **6** (79 mg). From *Fr. V* (15 g), **8** (1000 mg) was precipitated and crystallized from MeOH. The residue of the mother liquor of *Fr. V* (mixture after filtering compound **8**) was subjected to CC (SiO_2, petroleum ether/PrOH 6:1): *Fr. V.1* and *V.2*. Separation of *Fr. V.1* (4 g) by CC (*RP-18*, MeOH/H_2O 55:45) yielded **2** (10 mg) and **3** (30 mg). Compound **7** (18 mg) was obtained similarly from *Fr. V.2* (1.5 g) by CC (*RP-18*, MeOH/H_2O 85:15).

Acid Hydrolysis. Each of compounds **1**–**3** (1 mg each) in 1N HCl/MeOH 1:1 (1 ml) was heated at 90° for 6 h in a water bath. After cooling to r.t., the mixture was neutralized with 2N NaOH , and then extracted with $CHCl_3$ (3 × 1 ml). The aq. layer was lyophilized to give a sugar residue.

Identification of the Sugar Component of Compounds **1**–**3** *and Determination of the Absolute Configuration.* The pyridine soln. (0.5 ml each) of the sugar residue and of L-cysteine methyl ester hydrochloride (0.3 mg) were mixed and heated at 60° for 1 h. The trimethylsilylation reagent 1-(trimethylsilyl)-1*H*-imidazole (0.3 ml) was added, and heating at 60° was continued for another 30 min. The precipitate was centrifuged off, and the supernatant (4 µl) was subjected to GC analysis (*Shimadzu-GC-17A* gas chromatography, equipped with an H_2 flame-ionization detector; *DB-1* column (25 m × 0.32 mm i.d., film thickness 0.25 µm); oven temp. 120–250°, programmed increase 4°/min, injection-port temp. 250°, detector temp. 280°; carrier gas He, 10 psi; injection volume 4 µl, split ratio 1:50): L-arabinose, t_R 7.17 min; D-xylose, t_R 9.30 min.

24-Epicimigenol 3-(α-L-Arabinopyranoside) (=*(3β,15α,16α,23R,24R)-16,23:16,24-Diepoxy-15,25-dihydroxy-9,19-cyclolanostan-3-yl α-L-Arabinopyranoside*; **1**): White powder. $[\alpha]_D^{19} = +17.61$ ($c = 0.95$, $CHCl_3$/MeOH 1:1). IR (KBr): 3412, 2937, 1063. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (pos.): 621 ($[M+H]^+$). HR-FAB-MS: 643.3837 ($[M+Na]^+$, $C_{35}H_{56}NaO_9^+$; calc. 643.3822).

(3β,16β)-Cycloartane-3,16,22,24,25-pentol 3-(β-D-Xylopyranoside) (=*(3β,16β)-16,22,24,25-Tetrahydroxy-9,19-cyclolanostan-3-yl β-D-Xylopyranoside*; **2**): White powder. $[\alpha]_D^{20} = -24.07$ ($c = 1.00$, $CHCl_3$/MeOH 1:1). IR (KBr): 3477, 2929, 1046. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 623 ($[M-H]^-$). HR-FAB-MS: 623.4143 ($[M-H]^-$, $C_{35}H_{59}O_9^-$; calc. 623.4159).

(3β,15α,16β)-Cycloartane-3,15,16,24,25-pentol 3-(β-D-Xylopyranoside) (=*(3β,15α,16β)-15,16,24,25-Tetrahydroxy-9,19-cyclolanostan-3-yl β-D-Xylopyranoside*; **3**): White powder. $[\alpha]_D^{20} = +7.87$ ($c = 1.00$, $CHCl_3$/MeOH 1:1). IR (KBr): 3478, 2927, 1061. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 623 ($[M-H]^-$). HR-FAB-MS: 623.4154 ($[M-H]^-$, $C_{35}H_{59}O_9^-$; calc. 623.4159).

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