Four New 9,19-Cyclolanostane Derivatives from the Rhizomes of *Cimicifuga yunnanensis* HSIAO

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Four new 9,19-cyclolanostane-type triterpenes, 24-*O*-acetyl-25-anhydroshengmanol-3-*O*-*β*-D-xylopyranoside (**1**), 25-*O*-butylcimigenol-3-*O*-*β*-D-xylopyranoside (**2**), 12-*β*-hydrocimigenol-3-one (**3**), and 12-*β*-hydrocimigenol-1-en-3-one (**4**), together with 15 known analogues were isolated from the rhizome of *Cimicifuga yunnanensis* HSIAO. Their structures were determined by spectroscopic and chemical methods.

Introduction. – The rhizome of several *Cimicifuga* species (Ranunculaceae), called 'Shengma' in China, is a source of a popular herbal medicine, which has been used as an antipyretic and analgesic agent since ancient times. In Europe and the United States, a dietary supplement made from the alcoholic extract of *Cimicifuga racemosa*, also called black cohosh, has been reputed to reduce the frequency and intensity of hot flashes and other menopause symptoms. *Cimicifuga yunnanensis* is a rare species indigenous to the north-west of Yunnan Province of China [1]. The rhizome of *C. yunnanensis* is a very famous herb drug, which is used by local people such as Tibetan and Naxi people to relieve fever, headache, and some menopause symptoms. Chemical constituents of *Cimicifuga* species like *C. racemosa*, *C. dahurica*, *C. simplex*, and *C. foetida* have been investigated, and a series of highly oxygenated triterpene glycosides and aglycons have been isolated and identified [2–25]. However, no work has been reported so far on the chemical constituents of *C. yunnanensis*.

The present study on *C. yunnanensis* resulted in the isolation of four new 9,19-cyclolanostane triterpenes **1**–**4** (see *Fig. 1*). The present article deals with the isolation and structural elucidation of the new 9,19-cyclolanostane triterpenes, based on spectroscopic analyses and chemical correlations.

Results and Discussion. – Compound **1** was isolated as a white powder. In the negative-ion HR-ESI-MS, it showed a quasi-molecular ion at *m*/*z* 661.3958 ($[M-H]^-$), consistent with a molecular formula $C_{37}H_{58}O_{10}$. The IR spectrum showed absorptions of OH and C=O groups at 3433 and 1709 cm^{-1}, respectively. The assignment of the ^1H- and ^{13}C-NMR spectroscopic data of **1** (*Table*) was based on HMQC, HMBC data (*Fig. 2*), and a $^1H,^1H$-COSY spectrum. The ^1H- and ^{13}C-NMR spectra displayed characteristic signals for a cyclopropane CH_2 at δ(H/C) 0.26, 0.51; 30.8 (CH_2(19)). The ^{13}C-NMR spectrum exhibited 37 signals, of which 30 were attributed to a triterpene

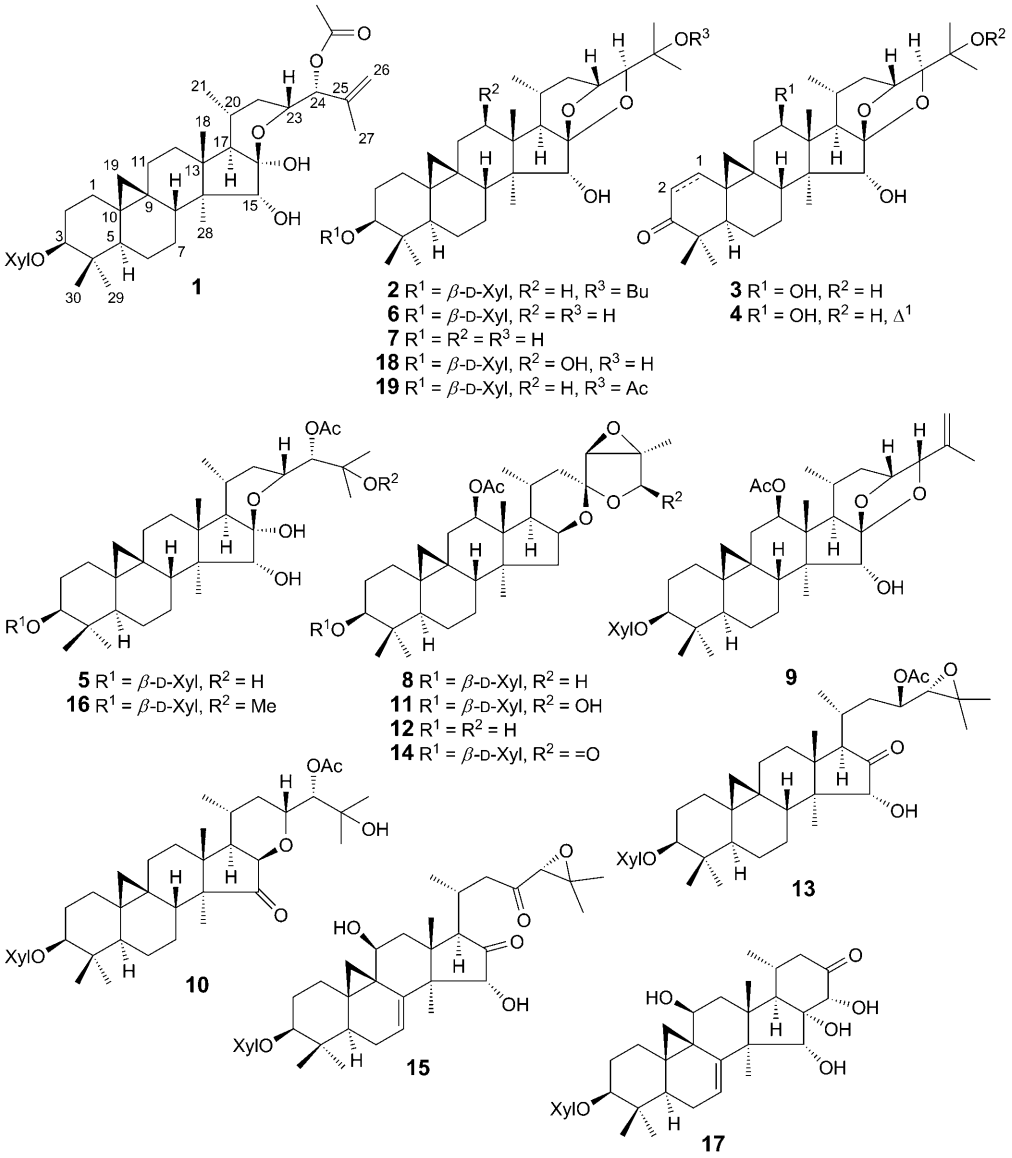
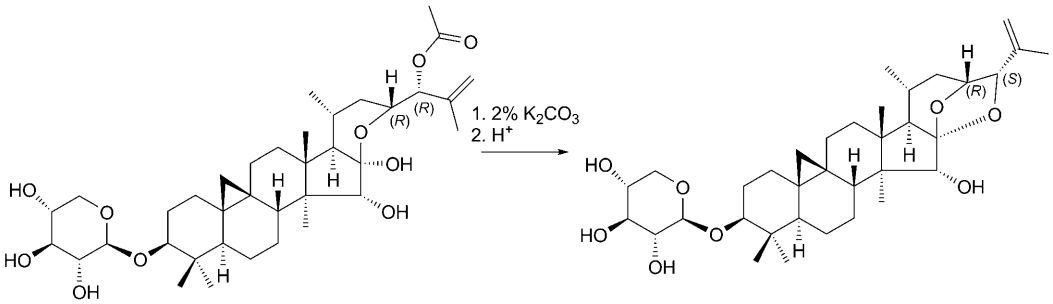


Fig. 1. *Structures of compounds* **1**–**19**

skeleton, five to a pentose unit, and two to an AcO group. A DEPT experiment permitted differentiation of the 37 ^{13}C-NMR resonances into eight quaternary C-atoms, 13 CH, nine CH_2, and seven Me groups. All these data suggested that **1** is a 9,19-cyclolanostane triterpene monoglycoside [16]. The NMR spectroscopic data of **1** showed a close resemblance with those of compound **5** [20], except for the presence of two downfield signals at δ(C) 115.9 and 142.2, and the absence of a quaternary C-atom

and a Me signal due to C(25) and C(26), respectively. On the basis of these observations, it was reasonable to assume that **1** is a 25-dehydrated derivative of **5**, which was supported by the upfield shift of C(27) by 7.2 ppm. The HMBC spectrum showed correlations of δ(H) 1.79 (H–C(27)) with δ(C) 142.2 (C(25)), 115.9 (C(26)), and 82.8 (C(24)), and a pair of *singlet*s at δ(H) 5.18 (H_a–C(26)) and 4.98 (H_b–C(26)) with δ(C) 82.8 (C(24)) and 18.3 (C(27)) further supported the deduction. The monosaccharide obtained after acid hydrolysis was identified as D-xylose by comparing its R_f value and optical rotation with an authentic sample. Significant NOESY (*Fig. 3*) correlations of H–C(3) with H–C(5) suggested a β-orientation of the substituent at C(3), whereas the associations of H–C(15) with H–C(8) and Me(18), revealed an α-orientation of the OH group at C(15). Compound **1** was converted to 25-anhydrocimigenol-3-*O*-β-D-xylopyranoside (**1a**), which was identified by comparison of its spectral data with those reported in the literature [12], on 2% K_2CO_3 treatment, followed by 5% AcOH treatment (*Scheme*). This conversion suggested the (23*R*,24*R*) configuration for **1**. Therefore, the structure of compound **1** was elucidated as 24-*O*-acetyl-25-anhydroshengmanol-3-*O*-β-D-xylopyranoside.

Scheme. *Conversion of* **1** *into* **1a**



Compound **2** was isolated as a white powder. The negative-ion HR-ESI-MS of **2** showed a quasimolecular ion at *m*/*z* 675.3672 ([*M* – H]$^-$), corresponding to the molecular formula $C_{39}H_{64}O_9$. The IR spectrum showed a strong absorption band at 3398 cm^{-1} for OH groups. The ^{1}H-NMR spectra (*Table*) showed diagnostic signals due to a cyclopropane CH_2 at δ(H) 0.28 and 0.52 (each 1 H, *d*, *J* = 3.6, CH_2(19)), and an anomeric H-atom at δ(H) 4.86 (*d*, *J* = 7.6). The ^{13}C-NMR spectrum (*Table*) displayed five C-atoms of a glycosidic moiety (δ(C) 107.6, 75.6, 78.7, 71.3, and 67.2). The ^{1}H- and ^{13}C-NMR data of **2** were similar to those of **6** [16][18], except for an additional *O*-butyl (δ(H/C) 3.38/61.1 (C(1″)), 1.47/32.9 (C(2″)), 1.34/19.7 (C(3″)), 0.87/14.1 (C(4″)) functionality in **2**, which was positioned at C(25), based on the HMBC correlation of H–C(1″) to C(25). The deduction was also confirmed by the downfield shift of C(25) by 4.9 ppm. The relative configuration of **2** was assigned on the basis of a NOESY experiment (*Fig. 3*). The configurations of C(23) and C(24) were ascribed as (*R*) and (*S*), respectively, by comparing the spectral data of the C(23) signal and the coupling constants of the H–C(24) signal of **2** with those of known 9,19-cyclolanostane triterpene glycosides [11][23]. Therefore, the structure of compound **2** was identified as 25-*O*-butylcimigenol-3-*O*-β-D-xylopyranoside.

Table. *The [1]H- and [13]C-NMR Data for Compounds* **1**–**4**. In C_5D_5N; δ in ppm, J in Hz. Assignements were confirmed by HMQC, HMBC, and $^1H,^1H$-COSY experiments.

	1		**2**		**3**		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
1	32.4 (*t*)	1.57–1.60 (*m*), 1.22–1.24 (*m*)	32.4 (*t*)	1.58 (overlapped), 1.22 (overlapped)	33.7 (*t*)	1.73 (*ddd*, *J* = (4.5), 1.42 (*m*)	154.1 (*d*)	6.80 (*d*, *J* = 10.0)
2	30.2 (*t*)	2.35–2.38 (*m*), 1.93–1.96 (*m*)	30.0 (*t*)	2.36 (br. *d*, *J* = 11), 1.95 (br. *d*, *J* = 11)	37.6 (*t*)	2.62 (*ddd*, *J* = 6.5), 2.29 (br. *d*, *J* = 10.0)	126.7 (*d*)	6.08 (*d*, *J* = 10.0)
3	88.5 (*d*)	3.49 (*dd*, *J* = 4.0, 11.5)	88.6 (*d*)	3.51 (*dd*, *J* = 4.0, 11.4)	215.0 (*s*)		204.2 (*s*)	
4	41.4 (*s*)		41.4 (*s*)		50.2 (*s*)		46.2 (*s*)	
5	47.6 (*d*)	1.32–1.34 (*m*)	47.6 (*d*)	1.34 (overlapped)	48.2 (*d*)	1.58 (*dd*, *J* = 4.0, 12.3)	45.0 (*d*)	2.02–2.04 (*m*)
6	21.0 (*t*)	0.71–0.74 (*m*)	21.1 (*t*)	0.71 (br. *d*, *J* = 12.4)	21.4 (*t*)	0.79–0.81 (*m*)	29.9 (*t*)	1.22–1.24 (*m*)
7	26.6 (*t*)	2.01–2.04 (*m*), 1.07–1.09 (*m*)	26.5 (*t*)	2.10 (overlapped), 1.19 (overlapped)	26.0 (*t*)	2.14 (br. *d*, *J* = 12.5), 1.14 (overlapped)	19.8 (*t*)	1.41 (overlapped), 1.89 (overlapped)
8	49.1 (*d*)	1.73–1.76 (*m*)	48.7 (*d*)	1.65–1.67 (*m*)	47.4 (*d*)	1.81 (*dd*, *J* = 5, 12.2)	44.6 (*d*)	2.09–2.12 (*m*)
9	20.0 (*s*)		20.0 (*s*)		21.7 (*s*)		25.1 (*s*)	
10	26.7 (*s*)		26.7 (*s*)		26.2 (*s*)		30.1 (*s*)	
11	26.7 (*t*)	2.05–2.09 (*m*), 1.32–1.34 (*m*)	26.4 (*t*)	2.10 (overlapped), 1.05 (overlapped)	41.1 (*t*)	2.80 (*dd*, *J* = 9.0, 9.0), 1.48 (overlapped)	41.3 (*t*)	2.70 (*dd*, *J* = 8.0, 8.0), 1.75–1.77 (*m*)
12	34.1 (*t*)	1.71–1.73 (*m*), 1.55–1.58 (*m*)	34.1 (*t*)	1.65–1.68 (*m*), 1.52–1.54 (*m*)	72.7 (*d*)	4.21 (br. *s*)	71.7 (*d*)	4.21 (br. *s*)
13	42.1 (*s*)		41.9 (*s*)		41.1 (*s*)		47.9 (*s*)	
14	46.7 (*s*)		47.3 (*s*)		47.9 (*s*)		48.5 (*s*)	
15	79.6 (*s*)	4.14 (overlapped)	80.1 (*d*)	4.24 (*s*)	79.9 (*d*)	4.45 (*d*, *J* = 8.0)	79.3 (*d*)	4.41 (*d*, *J* = 8.0)
16	103.5 (*s*)		111.9 (*s*)		112.3 (*s*)		112.1 (*s*)	
17	60.6 (*d*)	1.79 (overlapped)	59.5 (*d*)	1.44–1.47 (*m*)	59.9 (*d*)	1.85 (*s*)	59.5 (*s*)	1.85 (br. *s*)
18	20.5 (*q*)	1.23 (*s*)	19.5 (*q*)	1.13 (*s*)	12.2 (*q*)	1.45 (*s*)	11.7 (*s*)	1.36 (*s*)
19	30.8 (*t*)	0.26 (*d*, *J* = 3.3), 0.51 (*d*, *J* = 3.2)	30.9 (*t*)	0.52 (*d*, *J* = 3.6), 0.28 (*d*, *J* = 3.6)	30.3 (*t*)	0.59 (*d*, *J* = 4.0), 0.73 (*d*, *J* = 4.0)	31.1 (*t*)	0.78 (*d*, *J* = 4.0), 1.21 (*d*, *J* = 4.8)
20	27.3 (*d*)	1.79 (overlapped)	24.1 (*d*)	1.65–1.68 (*m*)	24.1 (*d*)	1.86 (overlapped)	23.9 (*d*)	1.83 (overlapped)
21	21.3 (*q*)	0.97 (*d*, *J* = 3.5)	19.6 (*q*)	0.84 (br. *d*, *J* = 7.2)	21.0 (*q*)	1.39 (*d*, *J* = 6.0)	21.2 (*q*)	1.39 (*d*, *J* = 6.0)
22	32.2 (*t*)	1.73–1.75 (*m*), 1.99–2.02 (*m*)	38.2 (*t*)	0.97–0.99 (*m*), 2.22–2.26 (*m*)	38.8 (*t*)	1.14 (overlapped), 2.39–2.43 (*m*)	38.6 (*t*)	1.11 (overlapped), 2.38–2.41 (*m*)
23	74.6 (*d*)	4.13 (overlapped)	71.7 (*d*)	4.64 (*d*, *J* = 8.8)	71.8 (*d*)	4.78 (*d*, *J* = 9.0)	71.7 (*d*)	4.79 (*d*, *J* = 8.8)

Table (cont.)

	1		**2**		**3**		**4**	
	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)
24	82.8 (*d*)	6.04 (*d*, *J* = 9)	88.2 (*d*)	3.67 (*s*)	90.1 (*d*)	3.83 (*s*)	89.9 (*d*)	3.83 (*s*)
25	142.2 (*s*)		75.9 (*s*)		71.0 (*s*)		70.9 (*s*)	
26	115.9 (*t*)	5.18 (*s*), 4.98 (*s*)	22.9 (*q*)	1.28 (br. *s*)	27.1 (*q*)	1.51 (*s*)	27.1 (*q*)	1.51 (*s*)
27	18.3 (*q*)	1.79 (*s*)	20.2 (*q*)	1.29 (br. *s*)	25.6 (*q*)	1.49 (*s*)	25.6 (*q*)	1.49 (*s*)
28	11.9 (*q*)	1.24 (*s*)	11.8 (*q*)	1.18 (*s*)	11.9 (*q*)	1.19 (*s*)	11.4 (*q*)	1.17 (*s*)
29	25.8 (*q*)	1.30 (*s*)	25.8 (*q*)	1.31 (br. *s*)	22.6 (*q*)	1.09 (*s*)	21.8 (*q*)	1.16 (*s*)
30	15.5 (*q*)	1.02 (*s*)	15.5 (*q*)	1.05 (*s*)	20.8 (*q*)	0.99 (*s*)	19.2 (*q*)	0.93 (*s*)
Ac	170.4 (*s*)							
	21.5 (*q*)	1.90 (*s*)						
1″			61.1 (*t*)	3.38 (*dd*, *J* = 6, 11.8)				
2″			32.9 (*t*)	1.47 (overlapped)				
3″			19.7 (*t*)	1.34 (overlapped)				
4″			14.1 (*q*)	0.87 (br. *s*)				
1′	107.6 (*d*)	4.86 (*d*, *J* = 7.5)	107.6 (*d*)	4.86 (*d*, *J* = 7.6)				
2′	75.6 (*d*)	4.03 (*t*, *J* = 8.0)	75.6 (*d*)	4.03 (*t*, *J* = 8)				
3′	78.6 (*d*)	4.15 (overlapped)	78.7 (*d*)	4.17 (overlapped)				
4′	71.3 (*d*)	4.22 (*dd*, *J* = 5.5, 9.3)	71.3 (*d*)	4.20–4.24 (*m*)				
5′	67.1 (*t*)	3.75 (*t*, *J* = 11), 4.37 (*dd*, *J* = 5.0, 11.5)	67.2 (*t*)	3.73 (*t*, *J* = 10.4), 4.34 (*dd*, *J* = 5.0, 11.0)				

Compound **3** was obtained as colorless needles. In the negative-ion HR-ESI-MS, it showed a quasi-molecular ion at *m*/*z* 501.3217 ($[M-H]^-$), consistent with the molecular formula $C_{30}H_{46}O_6$. The IR spectrum showed OH and C=O absorptions at 3456 and 1688 cm^{-1}. In the ^{1}H-NMR spectrum of **3** (*Table*), there were six tertiary Me at δ(H) 0.99, 1.09, 1.19, 1.45, 1.49, and 1.51, a secondary Me at δ(H) 1.39 (*d*, *J* = 6.0), and the cyclopropane CH_2 at δ(H) 0.59 and 0.73 (each 1 H, *d*, *J* = 4.0, CH_2(19)). The ^{13}C-NMR spectrum showed 30 signals, including a C=O group at δ(C) 215.0, and six O-bearing C-atom signals at δ(C) 90.1 (*d*), 79.9 (*d*), 72.7 (*d*), 71.8 (*d*), 112.3 (*s*), and 71.0 (*s*). The above evidence suggested that compound **3** was a highly oxygenated 9,19-cyclolanostane triterpene aglycone. The NMR spectrum of **3** resembled the one of 12β-hydroxycimigenol [4], except that a hydroxymethine C-atom (δ(C) 77.7) at C(3) in 12β-hydroxycimigenol was replaced by a C=O group (δ(C) 215.0) in **3**, which was in accordance with the downfield shifts of C(2) and C(4) by 6.7 and 9.4 ppm respectively. HMBC Correlations of δ(H) 1.73 and 1.42 (CH_2(1)) and δ(H) 2.62 and 2.29 (CH_2(2)) with δ(C) 215.0 (C(3)) also confirmed above deduction. The relative configuration of **3** was determined to be the same as that of **2** by an analysis of the NOESY data (*Fig. 3*). Accordingly, compound **3** was characterized as 12β-hydroxycimigenol-3-one.

Compound **4** was isolated as colorless needles. The negative-ion HR-ESI-MS established the molecular formula of **4** as $C_{30}H_{44}O_6$. Its NMR data (*Table*) were similar to those of **3** except for the signals in ring *A*. C=C Signals at δ(C) 154.1 and 126.7 were observed in **4**, whereas the signals of two CH_2 groups due to C(1) and C(2) were absent.

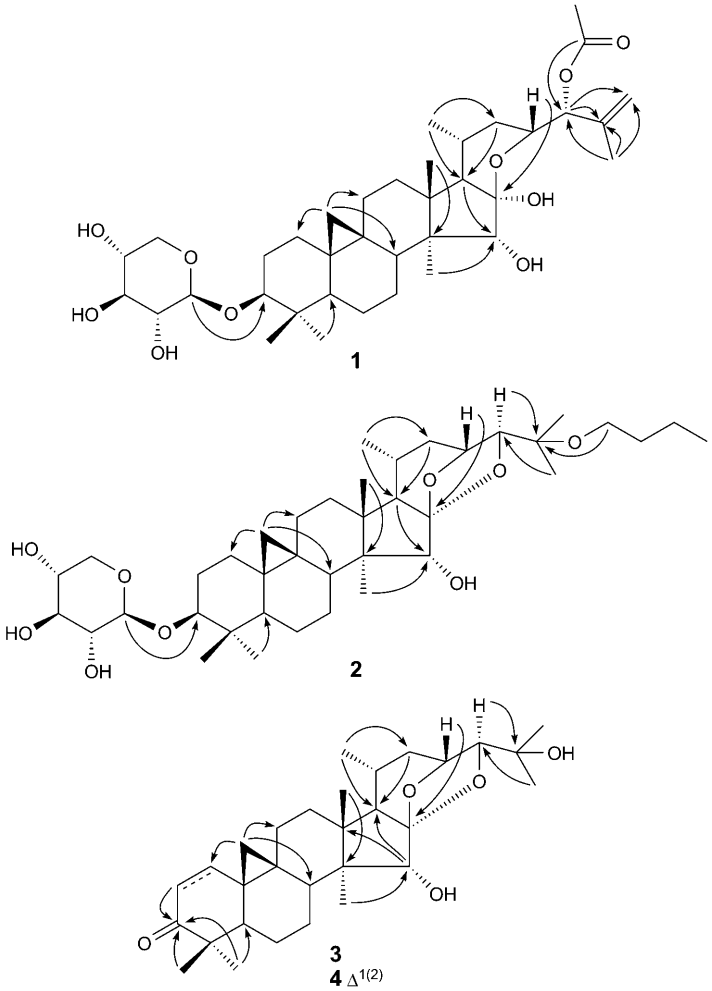


Fig. 2. *Major HMBC correlations of compounds* **1**–**4**

Significant HMBC correlations (*Fig. 2*) were observed between the C=O group at δ(C) 204.2 and the olefinic H-atoms at δ(H) 6.08 and 6.80 (each 1 H, d, $J = 10.0$). This evidence suggested that compound **4** could be transformed from **3** through dehydrogenation between C(1) and C(2). Therefore, compound **4** was characterized as 12β-hydroxycimigenol-1-en-3-one.

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), and *Sephadex LH-20* (*Pharmacia Fine Chemical Co. Ltd.*). Fractions were monitored by TLC, and spots were visualized by heating TLC plates sprayed with 10% H_2SO_4. Optical rotations: *Horiba SEAP-300* spectropolarimeter.

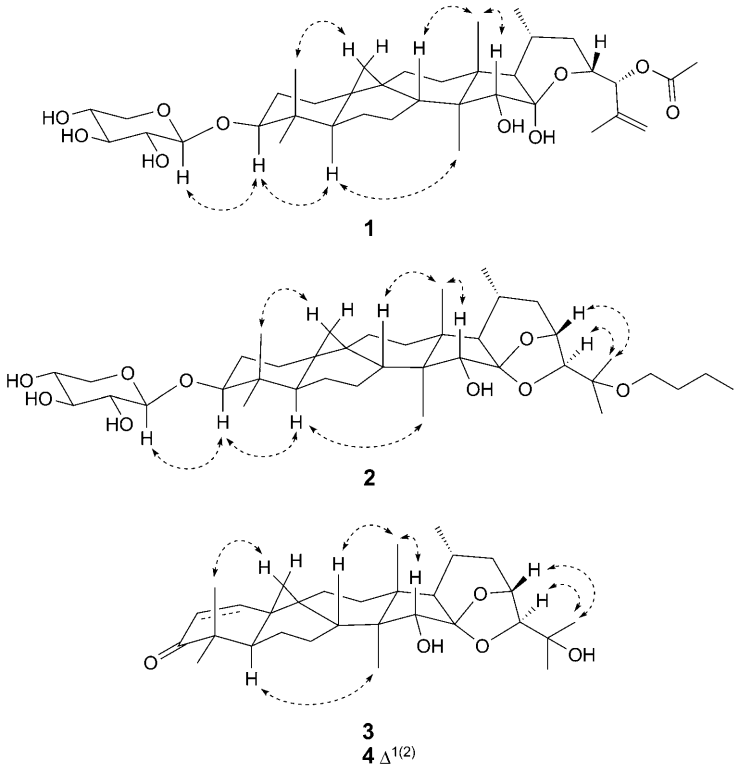


Fig. 3. *Key NOESY correlations of compounds* **1**–**4**

IR Spectra: *Shimadzu IR-450* instrument; in cm^{-1}; KBr pellets. NMR Spectra: *Bruker AV-400,* or *DRX-500* instruments; chemical shifts (δ) in ppm; Me_4Si as the internal standard; *J* in Hz. FAB-MS and HR-FAB-MS: *VG-AUTOSPEC-3000* spectrometer; in *m/z* (rel. int. in % of the base peak).

Plant Material. Cimicifuga yunnanensis HSIAO rhizomes were collected from Napa lake, Xianggelila County, Yunnan Province, China, in August 2005. The plant was identified by Prof. *Bao-Gui Li*, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Science. A Voucher specimen (KUN No. 200508025) 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 of *C. yunnanensis* (9 kg) were extracted with MeOH (3 × 20 l, 2 d, each) at r.t. to give a residue (903 g) after evaporating *in vacuo* at 50°. This residue was suspended in H_2O and then extracted successively with petroleum ether (PE), AcOEt, and BuOH. The AcOEt extract (308 g) was chromatographed on SiO_2 (CH_3Cl/MeOH 1:0 → 0:1) to afford fractions *Fr. 1–4*. *Fr. 2* (13 g) was re-subjected to repeated CC (SiO_2; CH_3Cl/MeOH 60:1 → 40:1, then *RP-18*, MeOH/H_2O 60:40) to afford **7** [8] (1460 mg), **12** [3] (22 mg), **3** (9 mg), and **4** (12 mg). *Fr. 3* (92 g) was subjected to CC (SiO_2; CH_3Cl/MeOH, 30:1 → 10:1) to give *Fr. 3.1–3.3*. *Fr. 3.1* (13.6 g) was subjected to CC (SiO_2; CH_3Cl/MeOH, 40:1 → 30:1, then *RP-18*, MeOH/H_2O 60:40 → 70:30) to yield **9** [12] (22 mg), **10** [22] (17 mg), **14** [17] (7 mg), and **2** (19 mg). *Fr. 3.2* (9.8 g) was subjected to CC (*RP-18*; MeOH/H_2O 60:40 → 70:30, then *Sephadex LH-20*) to afford **8** [21] (3560 mg), **19** [3] (2576 mg), and **13** [2][9][10][16] (1933 mg). *Fr. 3.2* (58.9 g) was separated into *Fr. 3.2.1–3.2.3* by CC (SiO_2; $CHCl_3$/Me_2CO, 2.5:1 to 1:2). Compound **11** [21] (20800 mg) was crystallized in MeOH from *Fr. 3.2.1* (28.6 g). The residue of *Fr. 3.2.1* (mixture after filtering compound **11**) was subjected to CC (*RP-18*; MeOH/H_2O,

65:35) to yield **15** [14] (37 mg), **16** [20] (42 mg), and **1** (83 mg). Separation of *Fr. 3.2.2* (5.2 g) on *RP-18* gel ($MeOH/H_2O$, 62:38) to give **6** [25] (1673 mg) and **5** [20] (2365 mg). Compounds **17** [3] (403 mg) and **18** [4] (36 mg) were obtained from *Fr. 3.2.3* (2.0 g) in a similar manner (*RP-18*; $MeOH/H_2O$, 60:40).

Acid Hydrolysis and Identification of the Sugar Moieties in Compounds **1** *and* **2**. Compounds **1** and **2** (15 mg) were separately refluxed with 0.5N HCl (3 ml) for 2 h. Each reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The H_2O layer was evaporated to dryness under reduced pressure to give a monosaccharide, which had an R_f value ($AcOEt/CHCl_3/MeOH/H_2O$, 3:2:2:1) and a specific rotation ($[\alpha]_D^{15} = +52.1$ ($c = 0.16$, H_2O) of **1** and $[\alpha]_D^{15} = +24.3$ ($c = 0.10$, H_2O) of **2**) comparable to those of D-xylose (*Sigma–Aldrich*).

Conversion of **1** *to* **1a**. **1** (6 mg) was dissolved in MeOH (5 ml), 2% K_2CO_3 (5 ml) was added, and then the soln. was stirred at r.t. overnight. The soln. was neutralized with 5% AcOH, and extracted with AcOEt (25 ml × 3). After removal of the solvent, the residue was dissolved in THF (3 ml) and 5% AcOH (3 ml), and heated on a boiling water bath for 3 h. After evaporation of the solvent *in vacco,* the products were chromatographed over SiO_2 (30 g). The fractions eluted with $CHCl_3$/MeOH (30:1) gave **1a** (4.6 mg), which was identified by comparison of the spectral data with the reported data [12].

*(3β,9β,15α,16β,23*R*,24*R*)-15,16-Dihydroxy-3-(β-*D*-xylopyranosyloxy)-16,23-epoxy-9,19-cyclolanost-25-en-24-yl Acetate* (**1**). White powder. M.p. 226–228°. $[\alpha]_D^{24} = +17.4$ ($c = 0.10$, MeOH). IR (KBr): 3433, 2941, 1709, 1632, 1044. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 661 ($[M-H]^-$). HR-ESI-MS: 661.3958 ($[M-H]^-$, $C_{37}H_{57}O_{10}^-$; calc. 661.3952).

*(3β,15α,23*R*,24*S*)-15-Hydroxy-25-butyl-16,23:16,24-diepoxy-9,19-cyclolanosta-3-*O*-β-*D*-xylopyranoside* (=*(2*S*,4a*R*,5a*S*,7a*R*,7b*R*,11*R*,12a*S*,13*R*,13a*S*)-11-(2-Butoxypropan-2-yl)-13-hydroxy-1,1,7a,8,13a-pentamethyloctadecahydro-10,12a-epoxycyclopropa[1′,8a′]naphtho[2′,1′:4,5]indeno[2,1-*b*]oxepin-2-yl β-*D*-xylopyranoside*; **2**). White powder. M.p. 223–225°. $[\alpha]_D^{24} = +9.5$ ($c = 0.10$, MeOH). IR (KBr): 3398, 2927, 1164, 1086, 1043. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 675 ($[M-H]^-$). HR-ESI-MS: 675.3672 ($[M-H]^-$, $C_{39}H_{63}O_9^-$; calc. 675.4472).

*(12β,15α,23*R*,24*S*)-12,15,25-Trihydroxy-16,23:16,24-diepoxy-9,19-cyclolanostan-3-one* (=*(4a*R*,5a*S*,7a*R*,7b*R*,11*R*,12a*S*,13*R*,13a*S*)-13-Hydroxy-11-(2-hydroxypropan-2-yl)-1,1,7a,8,13a-pentamethylhexadecahydro-10,12a-epoxycyclopropa[1′,8a′]naphtho[2′,1′:4,5]indeno[2,1-*b*]oxepin-2(1*H*)-one*; **3**). Colorless needles. M.p. 325–327°. $[\alpha]_D^{24} = +22.5$ ($c = 0.12$, MeOH). IR (KBr): 3456, 2938, 1688, 1379, 1032. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 501 ($[M-H]^-$). HR-ESI-MS: 501.3217 ($[M-H]^-$, $C_{30}H_{45}O_6^-$; calc. 501.3216).

*(12β,15α,23*R*,24*S*)-12,15,25-Trihydroxy-16,23:16,24-diepoxy-9,19-cyclolanosta-1-en-3-one* (=*(4a*S*,5a*S*,7a*R*,7b*R*,11*R*,12a*S*,13*R*,13a*S*)-13-Hydroxy-11-(2-hydroxypropan-2-yl)-1,1,7a,8,13a-pentamethyl-6,7,7a,7b,8,9,10,11,13,13a,13b,14,15,15a-tetradecahydro-10,12a-epoxycyclopropa[1′,8a′]naphtho[2′,1′:4,5]-indeno[2,1-*b*]oxepin-2(1*H*)-one*; **4**). Colorless needles. M.p. 334–336°. $[\alpha]_D^{24} = +20.5$ ($c = 0.10$, MeOH). IR (KBr): 3432, 2929, 1652, 1383, 1031. ^{1}H- and ^{13}C-NMR: *Table.* FAB-MS (neg.): 499 ($[M-H]^-$). HR-ESI-MS: 499.3055 ($[M-H]^-$, $C_{30}H_{43}O_6^-$; calc. 499.3059).

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