Four New Germine Esters from *Veratrum dahuricum*

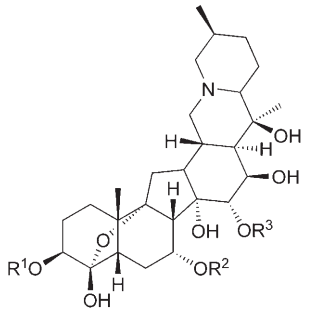
by **Jian Tang**[a]), **Hui-Liang Li**[b]), **Yun-Heng Shen**[b]), **Hui-Zi Jin**[a]), **Shi-Kai Yan**[a]), **Run-Hui Liu**[b]), and **Wei-Dong Zhang***[a])[b])

[a]) School of Pharmacy, Shanghai Jiao Tong University, Shanghai 200240, P. R. China
[b]) Department of Phytochemistry, School of Pharmacy, Second Military Medical University, Shanghai 200433, P. R. China
(phone: +86-21-25070386; fax: +86-21-25070386; e-mail: wdzhangY@hotmail.com)

Four new alkaloids, compounds **1**–**4**, based on the germine (=4,9-epoxycevane-3,4,7,14,15,16,20-heptol; **5**) framework, were isolated from the rhizomes of *V. dahuricum*, together with germine proper. The X-ray crystal structure of germine (**5**) was solved, and all compounds were characterized by circular dichroism, 1D- and 2D-NMR (^{1}H,^{1}H-COSY, DEPT, HSQC, HMBC), as well as HR-MS analyses.

Introduction. – The genus *Veratrum* (Liliaceae) consists of more than 40 species, including 14 species in China [1], several of which have been used in traditional Chinese medicine (TCM) against diseases such as apoplexy or epilepsy [2]. The investigation of *V. dahuricum* started in the 1980s, and 13 steroidal alkaloids, mainly including ceveratrum and jerveratrum frameworks, have been reported from this species [2–4]. Some of these alkaloids display significant hypotensive, analgesic, and antitumor activities [5]. Especially cyclopamine, an analogue of jervine, isolated from *V. dahuricum*, showed significant antitumor activity [6][7].

Based on these previous results, it was thought worthwhile to investigate the alkaloids of *V. dahuricum*. This led to the isolation of four new alkaloidal germine esters, compounds **1**–**4**, from the $CHCl_3$-soluble part of the aqueous-EtOH extract of the rhizomes of *V. dahuricum*, together with germine (**5**). Herein, we report the isolation and structure elucidation of these compounds.



	R^1	R^2	R^3
1	Ac	Ac	Ang
2	Ver	H	H
3	Ac	H	Ang
4	Ver	H	Ang
5	H	H	H

Ang = angeloyl
Ver = veratroyl

Results and Discussion. – Compound **5** was identified as germine by comparison of its spectroscopic data with those previously reported in the literature [8]. Its

configuration was confirmed by X-ray crystal-structure analysis (*Fig. 1*)[1]), and by circular dichroism (CD; see *Fig. 2* below). Compounds **1**–**4** were found to be germine derivatives not reported previously.

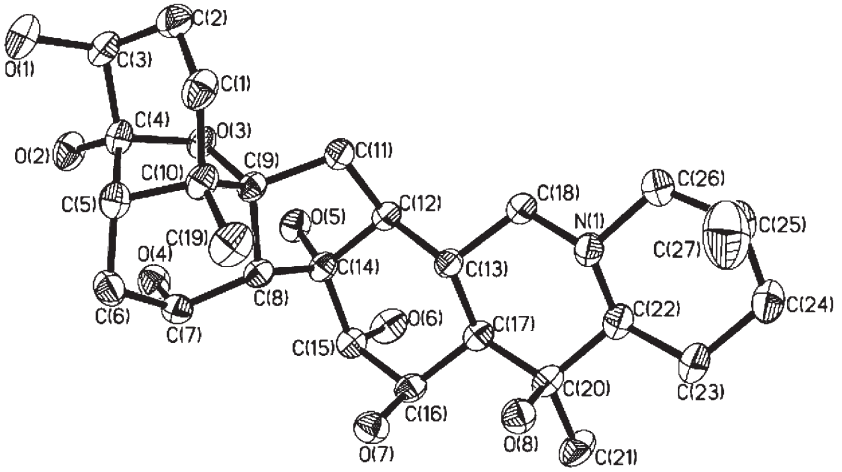


Fig. 1. *X-Ray crystal structure of germine* (**5**)[1])

Compound **1** showed the $[M+H]^+$ ion peak at *m*/*z* 676.3691 by HR-ESI-TOF-MS, and its molecular formula was deduced as $C_{36}H_{53}NO_{11}$. The ^{1}H-NMR resonances (*Table 1*) at δ(H) 1.99 (*s*, Me), 1.98 (*s*, Me), 1.81 (*q*, J = 1.8 Hz, Me), 1.89 (*dd*, J = 7.8, 1.8 Hz, Me), and 6.01 (*dd*, J = 7.2, 1.8 Hz, 1 H) showed HSQC correlations with δ(C) 20.7, 20.7, 20.8, 16.7, and 137.7, respectively (*Table 2*). The ^{13}C-NMR spectrum of **1** showed five signals in the downfield region at δ(C) 170.2, 170.1, 167.5, 137.7, and 127.5. These data indicated two AcO groups and an *O*-angeloyl (Ang)[2]) moiety in **1** [9]. Based on the observed ^{1}H-NMR chemical-shift differences between germine (**5**) and **1**, from δ(H) 3.77 (*d*, H–C(3)) to 4.94 (*d*), from 3.83 (*d*, H–C(15)) to 5.05 (*d*), and from 4.38 (*d*, H–C(7)) to 5.54 (*d*), respectively, the two AcO groups and the AngO function were connected to C(3), C(15), and C(7), respectively. The HMBC long-range correlations between δ(H) 4.94 and both δ(C) 170.2 (Me*C*O) and 104.2 (C(4)), between δ(H) 5.05 and δ(C) 170.1 (Me*C*O), 79.8 (C(14)), and 68.7 (C(16)), and between δ(H) 5.54 and δ(C) 167.5 (C=O of Ang), 32.0 (C(6)), and 45.9 (C(8)), respectively, further confirmed the above deduction (see *Exper. Part*).

The CD spectrum of **1** (*Fig. 2*) exhibited great similarity to that of **5**, indicating identical absolute configurations. Thus, from the above data, the structure of compound **1** was deduced as (3β,4*S*,7α,9*R*,14α,15α,16β)-3,7-diacetoxy-4,9-epoxy-15-{[(2*Z*)-2-methylbut-2-enoyl]oxy}cevane-4,14,16,20-tetrol.

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[1]) The crystallographic data of **5** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication number CCDC-635769. Copies of the data can be obtained, free of charge, at http://www.ccdc.cam.ac.uk/data_request/cif.

[2]) Angeloyl = (2*Z*)-2-methylbut-2-enoyl.

Table 1. *^{1}H-NMR Data of* **1**–**5**. At 600 MHz in $CDCl_3$; δ in ppm, J in Hz.

Atom	**1**	**2**	**3**	**4**	**5**
CH_2(1)	1.59–1.65 (*m*)	1.60–1.65 (*m*)	1.65–1.71 (*m*)	1.59–1.66 (*m*)	1.58–1.64 (*m*)
	1.50–1.56 (*m*)	1.50–1.53 (*m*)	1.58–1.62 (*m*)		1.50–1.56 (*m*)
CH_2(2)	2.07–2.14 (*m*)	2.01–2.07 (*m*)	2.19–2.23 (*m*)	1.80–1.84 (*m*)	1.92–1.98 (*m*)
	1.66–1.71 (*m*)	1.67–1.71 (*m*)	1.68–1.72 (*m*)	1.68–1.74 (*m*)	1.52–1.58 (*m*)
H–C(3)	4.94 (*d*, J = 4.2)	5.20 (*d*, J = 4.8)	4.86 (*d*, J = 4.2)	5.09 (*d*, J = 4.8)	3.77 (*d*, J = 4.2)
H–C(5)	2.18 (*t*, J = 3.6)	2.16 (*t*, J = 2.4)	2.30 (br. *s*)	2.35 (br. *s*)	2.31 (*t*, J = 3.0)
CH_2(6)	2.14–2.17 (*m*)	2.15–2.19 (*m*)	2.06–2.10 (*m*)	2.55–2.59 (*m*)	2.05–2.09 (*m*)
	2.01–2.06 (*m*)	2.01–2.07 (*m*)	1.98–2.03 (*m*)	2.16–2.20 (*m*)	1.98–2.03 (*m*)
H–C(7)	5.54 (*d*, J = 3.0)	4.49 (*d*, J = 3.0)	4.49 (*d*, J = 4.8)	4.57 (*d*, J = 4.2)	4.38 (*d*, J = 3.0)
H–C(8)	2.84 (*d*, J = 6.0)	2.34 (*d*, J = 3.0)	2.73 (*d*, J = 3.6)	2.67 (*d*, J = 3.6)	2.48 (*d*, J = 3.0)
CH_2(11)	2.17 (*dd*,	2.29 (*dd*,	2.30 (*dd*,	2.59 (*dd*,	2.19 (*dd*,
	J = 7.2, 4.2)	J = 15.0, 9.0)	J = 15.0, 8.4)	J = 15.0, 8.4)	J = 7.2, 3.0)
	1.53–1.58 (*m*)	1.70–1.74 (*m*)	1.65–1.71 (*m*)	1.65–1.71 (*m*)	1.56–1.60 (*m*)
H–C(12)	1.67–1.71 (*m*)	1.50–1.54 (*m*)	1.70–1.74 (*m*)	1.71–1.76 (*m*)	1.67–1.71 (*m*)
H–C(13)	1.48–1.52 (*m*)	1.48–1.52 (*m*)	1.51–1.57 (*m*)	1.54–1.58 (*m*)	1.50–1.56 (*m*)
H–C(15)	5.05 (*d*, J = 3.6)	3.72 (*d*, J = 7.2)	5.35 (*d*, J = 3.6)	5.40 (*d*, J = 3.0)	3.83 (*d*, J = 3.0)
H–C(16)	4.18 (*d*, J = 4.2)	4.49 (*d*, J = 4.2)	4.37 (*d*, J = 3.6)	4.31 (*d*, J = 1.8)	4.38 (*d*, J = 4.2)
H–C(17)	1.23 (*dd*,	1.25 (*dd*,	1.27 (*dd*,	1.25 (*d*, J = 12.0)	1.35 (*dd*,
	J = 12.0, 1.8)	J = 12.0, 1.8)	J = 12.0, 1.8)		J = 12.0, 1.8)
CH_2(18)	2.66 (*d*, J = 7.8)	2.67 (*d*, J = 7.2)	2.93 (*d*, J = 7.2)	2.89 (*d*, J = 7.2)	2.62 (*d*, J = 7.2)
	1.61–1.65 (*m*)	1.79–1.83 (*m*)	1.70–1.74 (*m*)	1.67–1.72 (*m*)	1.58–1.62 (*m*)
H–C(22)	1.66 (*dd*,	1.66 (*dd*,	1.67 (*dd*,	1.70 (*dd*,	1.65 (*dd*,
	J = 9.0, 3.0)	J = 9.0, 3.0)	J = 9.0, 3.0)	J = 8.4, 3.0)	J = 9.0, 2.4)
CH_2(23)	1.52–1.58 (*m*)	1.55–1.59 (*m*)	1.58–1.64 (*m*)	1.58–1.62 (*m*)	1.51–1.57 (*m*)
		1.51–1.55 (*m*)		1.52–1.56 (*m*)	
CH_2(24)	1.46–1.53 (*m*)	1.52–1.56 (*m*)	1.58–1.64 (*m*)	1.56–1.60 (*m*)	1.46–1.53 (*m*)
		1.32–1.38 (*m*)	1.48–1.53 (*m*)	1.48–1.53 (*m*)	
H–C(25)	2.02–2.07 (*m*)	2.10–2.14 (*m*)	1.73–1.77 (*m*)	1.82–1.86 (*m*)	1.84–1.88 (*m*)
CH_2(26)	2.59 (*d*,	2.60 (*d*,	2.84 (*d*,	2.62 (*d*, J = 12.0)	2.58 (*d*,
	J = 12.0)	J = 12.0)	J = 12.0)		J = 12.0)
	2.15–2.21 (*m*)	2.27–2.33 (*m*)	2.26–2.32 (*m*)	2.28–2.34 (*m*)	2.10–2.14 (*m*)
Me(19)	0.95 (*s*)	1.00 (*s*)	1.03 (*s*)	1.02 (*s*)	0.88 (*s*)
Me(21)	1.13 (*s*)	1.19–1.23 (*m*)	1.27–1.31 (*m*)	1.20–1.24 (*m*)	1.15–1.19 (*m*)
Me(27)	1.03 (*d*, J = 7.2)	1.09 (*d*, J = 6.0)	1.14 (*d*, J = 7.8)	1.09 (*d*, J = 7.2)	1.01 (*d*, J = 7.2)
3-Ester:					
Ac	1.99 (*s*)		2.02–2.06 (*m*)		
H–C(2′)		7.55 (*s*)		7.47 (*s*)	
3′-MeO		3.93 (*s*)		3.84 (*s*)	
4′-MeO		3.94 (*s*)		3.85 (*s*)	
H–C(5′)		6.89 (*d*, J = 8.4)		6.81 (*d*, J = 8.4)	
H–C(6′)		7.66 (*dd*,		7.59 (*dd*,	
		J = 8.4, 1.8)		J = 8.4, 1.8)	
7-AcO	1.98 (*s*)				
15-*O*-Ang:					
H–C(3‴)	6.01 (*dd*,		6.10 (*dd*,	6.10 (*dd*,	
	J = 7.2, 1.8)		J = 7.2, 1.2)	J = 7.2, 1.2)	
Me(4‴)	1.89 (*dd*,		1.96 (*dd*,	1.96 (*dd*,	
	J = 7.8, 1.8)		J = 7.2, 1.2)	J = 7.2, 1.2)	
Me(5‴)	1.81 (*q*, J = 1.8)		1.89 (*s*)	1.89 (*s*)	

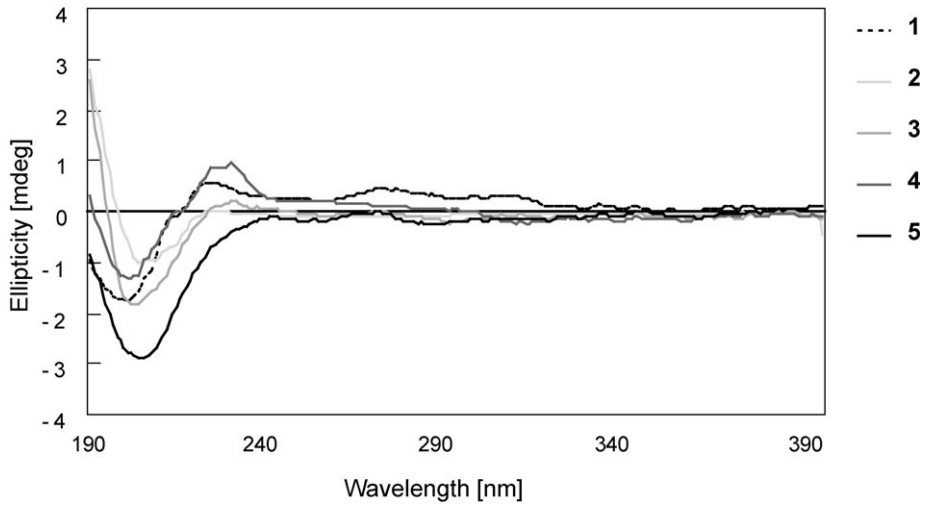

Fig. 2. *Circular-dichroism spectra of* **1**–**5**. In MeOH at 20°.

Compound **2** showed the $[M+H]^+$ peak at *m/z* 674.3544 by HR-ESI-TOF-MS, in accord with the molecular formula $C_{36}H_{51}NO_{11}$. The resonances at δ(H) 3.93 (*s*, Me), 3.94 (*s*, Me), 6.89 (*d*, $J = 8.4$ Hz, 1 H), 7.55 (*s*, 1 H), and 7.66 (*dd*, $J = 8.4$, 1.8 Hz, 1 H) were correlated with δ(C) 56.0, 56.1, 110.4, 112.6, and 123.8, respectively, in the HSQC spectrum. The ^{13}C-NMR data of **2** (*Table 2*) showed seven signals in the downfield region at δ(C) 166.7, 153.5, 148.9, 123.8, 122.6, 112.6, and 110.4, as well as two signals at δ(C) 56.1 and 56.0, indicating a veratroyl (Ver)[3]) group [10]. The other notable difference between the ^{1}H-NMR spectra of **2** and **5** was the signal for H–C(3), which appeared at δ(H) 5.20 (*d*, $J = 4.8$ Hz) for **2**, instead at δ(H) 3.77 (*d*, $J = 4.2$ Hz) for **5**. Further, this signal was HMBC-correlated with δ(C) 166.7 (C=O of Ver) and 105.6 (C(4)). Thus, the *O*-Ver group was attached at C(3) in compound **2**. The similarity of the CD spectra of **2** and **5** (*Fig.* 2) again confirmed the same relative configuration. Thus, compound **2** was identified as (3β,4*S*,7α,9*R*,14α,15α,16β)-3-[(3,4-dimethoxybenzoyl)oxy]-4,9-epoxycevane-4,7,14,15,16,20-hexol.

Compound **3** showed the $[M+H]^+$ signal at *m/z* 634.3595 by HR-ESI-TOF-MS, and its molecular formula was deduced as $C_{34}H_{51}NO_{10}$. The ^{1}H- and ^{13}C-NMR spectra of **3** (*Tables 1* and *2*, resp.) were similar to those of **1**, except for the disappearance of the 7-AcO resonance in **3**. The HMBC correlations between δ(H) 4.86 (*d*, $J = 4.2$ Hz, H–C(3)) and both δ(C) 172.1 (Me*C*O) and 105.7 (C(4)), and between δ(H) 5.35 (*d*, $J = 3.6$ Hz, H–C(15)) and both δ(C) 168.6 (C=O of Ang) and 70.2 (C(16)) confirmed that the AcO and Ang groups were attached to C(3) and C(15), respectively. Again, similar CD spectra were obtained for **3** and **1**. Thus, the structure of **3** was elucidated as (3β,4*S*,7α,9*R*,14α,15α,16β)-3-acetoxy-4,9-epoxy-15-{[(2*Z*)-2-methylbut-2-enoyl]oxy}-cevane-4,7,14,16,20-pentol.

Compound **4** showed the $[M+H]^+$ ion peak at *m/z* 756.3958 by HR-ESI-TOF-MS, and its molecular formula was deduced as $C_{41}H_{57}NO_{12}$. The ^{1}H- and ^{13}C-NMR spectra

[3]) Veratroyl = 3,4-dimethoxybenzoyl.

Table 2. *^{13}C-NMR Data of* **1**–**5**. At 150 MHz in $CDCl_3$; δ in ppm.

Atom	**1**	**2**	**3**	**4**	**5**
C(1)	32.5	32.7	33.3	32.7	32.0
C(2)	26.8	26.7	28.0	28.8	28.1
C(3)	74.3	75.3	75.9	74.9	72.5
C(4)	104.2	105.6	105.7	105.6	106.4
C(5)	47.3	47.8	47.3	46.6	44.5
C(6)	32.0	28.9	30.1	28.9	28.9
C(7)	68.0	67.4	68.5	66.8	67.1
C(8)	45.9	46.2	47.6	48.1	47.5
C(9)	92.5	93.9	94.5	93.0	92.9
C(10)	45.2	44.1	45.8	45.8	46.4
C(11)	32.0	33.2	34.4	33.2	33.0
C(12)	44.7	44.6	46.1	46.0	45.7
C(13)	32.4	33.5	33.5	33.8	33.2
C(14)	79.8	82.9	82.1	81.2	82.3
C(15)	70.2	70.0	73.0	70.1	69.5
C(16)	68.7	69.6	70.2	69.4	69.9
C(17)	45.8	45.7	47.3	46.6	43.9
C(18)	61.6	61.3	62.3	61.4	61.4
C(19)	18.3	19.2	19.3	19.2	19.0
C(20)	72.3	73.2	73.5	73.0	73.1
C(21)	20.2	19.2	22.7	20.6	20.1
C(22)	70.3	73.1	72.2	69.8	70.1
C(23)	18.2	18.4	19.5	18.4	18.3
C(24)	28.9	29.7	30.7	29.7	29.1
C(25)	27.2	27.4	28.7	27.3	27.3
C(26)	61.2	61.4	62.7	61.6	61.5
C(27)	16.7	17.1	17.6	17.0	16.9
3-Ester:					
C(1′)	170.2	122.6	172.1	123.1	
C(2′)	20.7	112.6	21.2	112.6	
C(3′)		148.9		148.8	
C(4′)		153.5		153.2	
C(5′)		110.4		110.3	
C(6′)		123.8		123.6	
C=O		166.7		165.8	
3′-MeO		56.1		56.1	
4′-MeO		56.1		56.0	
7-Me*C*O	170.1				
7-*Me*CO	20.7				
15-*O*-Ang:					
C(1″)	167.5		168.6	167.2	
C(2″)	127.5		129.4	128.0	
C(3″)	137.7		138.7	137.6	
C(4″)	16.7		16.1	15.5	
C(5″)	20.8		20.9	20.6	

of **4** (*Tables 1* and *2*, resp.) were comparable to those of **2**, except for the presence of an additional Ang group [δ(H) 1.89 (*s*, Me); 1.96 (*dd*, J = 7.2, 1.2 Hz, Me); 6.10 (*dd*, J = 7.2, 1.2 Hz, 1 H)]. The HMBC correlation between δ(H) 5.40 (*d*, J = 3.0 Hz, H–C(15)) and the C=O resonance at δ(C) 167.2 (C(1″)) demonstrated that the AngO group was attached to C(15). The similarity of the CD spectra of **4** and **2** (*Fig. 2*) confirmed the same relative configurations. Thus, the structure of compound **4** was deduced as (3β,4*S*,7α,9*R*,14α,15α,16β)-3-[(3,4-dimethoxybenzoyl)oxy]-4,9-epoxy-15-{[(2*Z*)-2-methylbut-2-enoyl]oxy}cevane-4,7,14,16,20-pentol.

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Experimental Part

General. TLC Analyses were performed on *HSG* F_{254} silica-gel plates (10–40 μm; *Yantai*, China); visualization under UV light (254, 365 nm) and by spraying with *Dragendorff* reagent. Column chromatography (CC) was performed on silica gel (200–300 mesh; *Yantai*), silica gel *H* (10–40 μm; *Qingdao Marine Chemical Factory*, China), and *Sephadex LH-20* (*Pharmacia*). Melting points (m.p.) were measured on an *XT-4-100X* micro-melting-point apparatus; uncorrected. Optical rotations were determined on a *Perkin-Elmer-341* polarimeter. CD Spectra were obtained on a *JASCO J-810* instrument. ^{1}H- and ^{13}C-NMR Spectra were recorded in $CDCl_3$ on a *Bruker Avance*^{II}*-600* apparatus at 600/150 MHz, resp.; δ in ppm rel. to Me_4Si, J in Hz. ESI and HR-ESI-TOF mass spectra were recorded on *Varian MAT-212* and *Q-Tof micro-YA019* machines; in *m*/*z*.

Plant Material. The plants were collected in Yanbian, Jilin Province, P. R. China, in September 2005, and authenticated as *V. dahuricum* by Prof. *Yong-Zhen Liu*, School of Pharmacy, Yanbian University, China. A voucher specimen (No. 211) was deposited at the Herbarium of the School of Pharmacy, Shanghai Jiao Tong University, Shanghai, China.

Extraction and Isolation. The air-dried, powdered rhizomes of *V. dahuricum* (25 kg) were heated at reflux with 75% aq. EtOH (2 × 3 h). The extract was concentrated *in vacuo* to afford an aq. residual, which was successively extracted with petroleum ether (PE), $CHCl_3$, AcOEt, and BuOH. The $CHCl_3$-soluble extract (125 g) was subjected to CC (SiO_2, 200–300 mesh; $CHCl_3$/MeOH 20:0, 20:1, 10:1, 5:1, 2:1, 0:1) to yield six subfractions, which were further fractioned by CC (1. silica gel *H*, 10–40 μm; $CHCl_3$/acetone gradient; 2. *Sephadex LH-20*). This afforded a mixture of alkaloids, which were further purified by repeated CC (silica gel *H*) to afford compounds **1**–**4** ($CHCl_3$/acetone 20:1, 10:1, 5:1, 2:1) and **5** ($CHCl_3$/acetone 6:1, 4:1, 2:1, 1:1).

(3β,4S,7α,9R,14α,15α,16β)-3,7-Diacetoxy-4,9-epoxy-15-{[(2Z)-2-methylbut-2-enoyl]oxy}cevane-4,14,16,20-tetrol (**1**). Colorless, amorphous powder. M.p. 231–233° (acetone). $[\alpha]_D^{20} = +2.8$ (c = 0.0785, $CHCl_3$). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. 2D-NMR (HMBC; 600 MHz, $CDCl_3$): H–C(3)/C(4), H–C(3)/Me*C*O, H–C(7)/C(5), H–C(7)/C(9), H–C(7)/Me*C*O, H–C(15)/C(14), H–C(15)/C(16), H–C(15)/(C=O of Ang, H–C(16)/C(20), H–C(19)/C(10), H–C(25)/C(24), H–C(25)/C(26). ESI-MS: 676 ([M+H]$^+$), 658 ([M+H−H_2O]$^+$), 616 ([M+H−H_2O−Ac]$^+$). HR-ESI-TOF-MS: 676.3691 ([M+H]$^+$, $C_{36}H_{54}NO_{11}^+$; calc. 676.3697).

(3β,4S,7α,9R,14α,15α,16β)-3-[(3,4-Dimethoxybenzoyl)oxy]-4,9-epoxycevane-4,7,14,15,16,20-hexol (**2**). Colorless, amorphous powder. M.p. 280–283° (MeOH). $[\alpha]_D^{20} = +13.0$ (c = 0.0812, $CHCl_3$). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. 2D-NMR (HMBC; 600 MHz, $CDCl_3$): H–C(3)/C(4), H–C(3)/C=O of Ver, H–C(7)/C(5), H–C(7)/C(9), H–C(15)/C(14), H–C(15)/C(16), H–C(16)/C(20), H–C(19)/C(10), H–C(25)/C(24), H–C(25)/C(26). ESI-MS: 674 ([M+H]$^+$), 656 ([M+H−H_2O]$^+$), 492 ([M+H−H_2O−Ang]$^+$). HR-ESI-TOF-MS: 674.3544 ([M+H]$^+$, $C_{36}H_{52}NO_{11}^+$; calc. 674.3540).

*(3β,4*S*,7α,9*R*,14α,15α,16β)-3-Acetoxy-4,9-epoxy-15-{[(2*Z*)-2-methylbut-2-enoyl]oxy}cevane-4,7,14,16,20-pentol* (**3**). Colorless, amorphous powder. M.p. 198–200° (acetone). $[\alpha]_D^{20} = -8.0$ (c = 0.0935, $CHCl_3$). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. 2D-NMR (HMBC; 600 MHz, $CDCl_3$): H–C(3)/C(4), H–C(3)/Me*C*O; H–C(7)/C(5), H–C(7)/C(9), H–C(15)/C(14), H–C(15)/C(16), H–C(15)/C=O of Ang, H–C(16)/C(20), H–C(19)/C(10), H–C(25)/C(24), H–C(25)/C(26). ESI-MS: 634 ($[M+H]^+$), 616 ($[M+H-H_2O]^+$), 598 ($[M+H-2H_2O]^+$), 556 ($[M+H-2H_2O-Ac]^+$). HR-ESI-TOF-MS: 634.3595 ($[M+H]^+$, $C_{34}H_{52}NO_{10}^+$; calc. 634.3591).

*(3β,4*S*,7α,9*R*,14α,15α,16β)-3-[(3,4-Dimethoxybenzoyl)oxy]-4,9-epoxy-15-{[(2*Z*)-2-methylbut-2-enoyl]oxy}cevane-4,7,14,16,20-pentol* (**4**). Colorless, amorphous powder. M.p. 281–283° (acetone). $[\alpha]_D^{20} = +18.0$ (c = 0.0855, $CHCl_3$). ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. 2D-NMR (HMBC; 600 MHz, $CDCl_3$): H–C(3)/C(4), H–C(3)/C=O of Ver, H–C(7)/C(5), H–C(7)/C(9), H–C(15)/C(14), H–C(15)/C(16), H–C(15)/C=O of Ang, H–C(16)/C(20), H–C(19)/C(10), H–C(25)/C(24), H–C(25)/C(26). ESI-MS: 756 ($[M+H]^+$), 738 ($[M+H-H_2O]^+$), 638 ($[M+H-H_2O-Ang]^+$), 474 ($[M+H-H_2O-Ang-Ver]^+$). HR-ESI-TOF-MS: 756.3958 ($[M+H]^+$, $C_{41}H_{58}NO_{12}^+$; calc. 756.3959).

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