Two Glycosides and Other Constituents from *Anemone tomentosa* Roots

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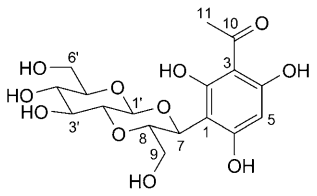
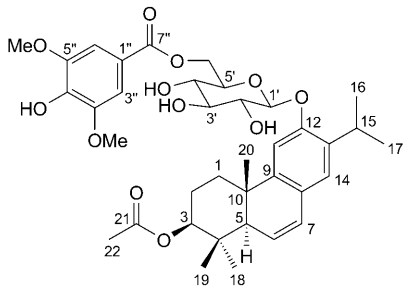
Two new natural products, *i.e.*, 1-*O*,2-*O*-[(1*S*,2*S*)-1-(3-acetyl-2,4,6-trihydroxyphenyl)-3-hydroxypropane-1,3-diyl]-β-D-glucopyranose (=tomentoside I; **1**) and (3β)-3-(acetyloxy)ferruginol 12-[6-*O*-(4-hydroxy-3,5-dimethoxybenzoyl)-β-D-glucopyranoside] (=tomentoside II; **2**), were isolated from the EtOH extract of the root of *Anemone tomentosa*, together with five known compounds. Their structures were characterized by means of spectroscopic methods, especially by ^{1}H-, ^{13}C-, and 2D-NMR and HR-MS, as well as by chemical methods and comparison with literature data.

Introduction. – The genus *Anemone* (Ranunculaceae) comprises *ca.* 150 species, of which 52 are distributed in northern China. As the main effective components of the genus *Anemone*, triterpenoid saponins have extensive biological activities, such as antitumor, antibacterial, and insect-antifeeding properties. *Anemone tomentosa* (MAXIM.) PEI is a perennial herb that is commonly called 'Dahuocao' in China [1][2]. Its roots have been used as traditional Chinese medicine for the treatment of dysentery, malaria, infantile malnutrition, carbuncles, and so on. [3]. Previous phytochemical studies on *A. tomentosa* have led to the isolation of coumarins [4], triterpenoids, and sterols [5][6]. To further study its active constituents and provide the reference for effective utilization of *A. tomentosa*, our continuing phytochemical investigation has led to the isolation of seven compounds of which **1** and **2** were two novel compounds. Herein, we describe the isolation of these compounds and the structural elucidation of the two new compounds.



1[1])



2[1])

[1]) Arbitrary atom numbering; for systematic names, see *Exper. Part.*

Results and Discussion. – The crystalline compound **1** was assigned the molecular formula $C_{17}H_{22}O_{11}$ with seven indices of hydrogen deficiency (IHD), based on HR-FAB-MS at *m/z* 401.1089 ($[M-H]^-$) in combination with NMR data (*Table 1*). The IR spectrum of **1** showed characteristic absorptions for OH (3405 cm^{-1}), conjugated C=O (1662 cm^{-1}), and phenyl groups (1601 and 1508 cm^{-1}). The ^{13}C-NMR and DEPT spectra of **1** indicated 17 C-atoms comprising one Me, two CH_2OH, and eight CH groups (seven of them O-bearing) and six quaternary C-atoms, including one C=O and five aromatic C-atoms. Analysis of the ^{1}H- and ^{13}C-NMR and DEPT spectra revealed the presence of one pentasubstituted benzene ring (δ(H) 7.01 (*s*, 1 H); δ(C) 135.8 (C), 148.3 (C), 132.1 (C), 150.6 (C), 116.9 (CH), and 152.2 (C)), one β-glucopyranosyl unit (δ(H) 4.78 (*d*, *J* = 7.8 Hz, 1 H); δ(C) 99.8 (CH), 78.7 (CH), 73.2 (CH), 70.4 (CH), 78.3 (CH), and 60.5 (CH_2)), one Ac group (δ(H) 2.48 (*s*, 3 H); δ(C) 194.6 (C) and 26.5 (Me)), one *CH*$_2$OH group (δ(H) 3.47 (*dd*, *J* = 12.2, 4.3 Hz) and 3.68–3.70 (*m*); δ(C) 61.3 (CH_2)), three phenolic OH groups (δ(H) 9.16, 10.12, and 10.38 (3 br. *s*)), and two CH–O groups (δ(H) 4.23 (*d*, *J* = 7.5 Hz) and 3.73 (*m*); δ(C) 78.4 (CH) and 80.5 (CH)). Taking into account the NMR data and the seven degrees of unsaturation calculated from the empirical formula of **1**, it was suggested that **1** had one alicyclic ring in addition to one Ac group, one benzene moiety, and one glucose ring. The D-glucose was also confirmed by co-TLC and GC analysis with a standard sample after acid hydrolysis of **1** [7]. The linkage site of the rings and substituents was determined by analysis of the

Table 1. *^{1}H-, ^{13}C-, and 2D-NMR Data* (400 and 100 MHz, resp.; (D_6)DMSO) *of* **1**[1]). δ in ppm, *J* in Hz.

	δ(H)	δ(C) (DEPT)	HMBC (H → C)	NOESY
C(1)		135.8 (C)		
C(2)		148.3 (C)		
C(3)		132.1 (C)		
C(4)		150.6 (C)		
H–C(5)	7.01 (*s*)	116.9 (CH)	C(1), (3)	
C(6)		152.2 (C)		
H–C(7)	4.23 (*d*, *J* = 7.5)	78.4 (CH)	C(1), C(2), C(6), C(9), C(1′)	H–C(1′), CH_2(9)
H–C(8)	3.71–3.75 (*m*)	80.5 (CH)	C(1), C(9), C(2′)	H–C(2′)
CH_2(9)	3.47 (*dd*, *J* = 12.2, 4.3), 3.68–3.70 (*m*)	61.3 (CH_2)	C(7), C(8)	H–C(7)
C(10)		194.6 (C)		
Me(11)	2.48 (*s*)	26.5 (Me)	C(3), C(10)	
H–C(1′)	4.78 (*d*, *J* = 7.8)	99.8 (CH)	C(7), C(3′), C(5′)	H–C(7), H–C(3′), H–C(5′)
H–C(2′)	2.96 (*d*, *J* = 7.8, 1.5)	78.7 (CH)	C(8)	H–C(8), H–C(4′)
H–C(3′)	3.33–3.38 (*m*)[a])	73.2 (CH)		H–C(1′), H–C(5′)
H–C(4′)	3.15–3.19 (*m*)[a])	70.4 (CH)		H–C(2′)
H–C(5′)	3.23–3.27 (*m*)[a])	78.3 (CH)		H–C(1′), H–C(3′)
CH_2(6′)	3.41–3.56 (*m*)[a])	60.5 (CH_2)		
OH–C(2)	10.38 (br. *s*)			
OH–C(4)	10.12 (br. *s*)			
OH–C(6)	9.16 (br. *s*)			

[a]) Overlapped signals.

HMBC and ^{13}C-NMR data. The HMBCs Me(11) (δ(H) 2.48)/C(10) (δ(C) 194.6) and C(3) (δ(C) 132.1), CH_2(9) (δ(H) 3.47 and 3.68 – 3.70)/C(7) (δ(C) 78.4) and C(8) (δ(C) 80.5) suggested that the Ac and CH_2OH groups were located at C(3) and C(8), and the correlations H–C(5) (δ(H) 7.01)/C(3) (δ(C) 132.1) and C(1) (δ(C) 135.8) indicated that three OH groups were attached to C(2), C(4), and C(6), respectively (*Fig. 1*). The presence of an *O*-glycosyl bond and an ether bond was confirmed to be at C(1′) and C(2′) of the glucose because the chemical shifts of C(1′) and C(2′) were shifted downfield by *ca*. 3.3 and 3.8 ppm [8], respectively. This conclusion was further supported by the HMBCs H–C(2′) (δ(H) 2.96)/C(8), H–C(1′) (δ(H) 4.78)/C(7), H–C(8) (δ(H) 3.71 – 3.75)/C(2′) (δ(C) 78.7), H–C(7) (δ(H) 4.23)/C(1′) (δ(C) 99.8), as well as the NOESY correlations H–C(7)/H–C(1′), and H–C(8)/H–C(2′). The connection of the alicyclic and phenyl rings (C(7) → C(1)) was established by the correlations H–C(7)/C(2) (δ(C) 148.3) and C(6) (δ(C) 152.2). The relative configuration of **1** was established by the coupling constants and NOESY correlations (*Fig. 1*). The correlations H–C(1′)/H–C(7), H–C(3′) (δ(H) 3.35), and H–C(5′) (δ(H) 3.25), H–C(3′)/H–C(5′), H–C(2′)/H–C(8) and H–C(4′) (δ(H) 3.18) indicated that the glucopyranose and alicyclic rings all had a chair conformation with *trans*-fused ring junctions. In the ^{1}H-NMR spectrum, the *d* at δ(H) 4.78 (J = 7.8 Hz, H–C(1′)) suggested that the glucose was in β-configuration, and the large coupling constant (J = 7.5 Hz) also indicated that H–C(7) and H–C(8) were, similarly to H–C(1′) and H–C(2′), in *trans*-axial orientation. The NMR assignments were based on the combination of HMBC and NOESY data analysis and comparison with literature values [9]. Therefore, the structure of compound **1** was elucidated as 1-*O*,2-*O*-[(1*S*,2*S*)-1-(3-acetyl-2,4,6-trihydroxyphenyl)-3-hydroxypropane-1,3-diyl]-β-D-glucopyranose and named tomentoside I.

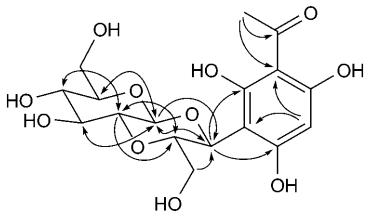


Fig. 1. *Key HMBC* (H → C) *and NOESY* (H ↔ H) *correlations of* **1**

Compound **2**, obtained as yellowish amorphous powder from MeOH, had the molecular formula $C_{37}H_{48}O_{12}$ with 14 degrees of unsaturation, based on the HR-FAB-MS (*m*/*z* 683.3059 ([*M* – H]$^-$)) and NMR data (*Table 2*). The IR spectrum displayed characteristic absorptions for OH (3410 cm^{-1}), C=O (1712 and 1689 cm^{-1}), disubstituted C=C (1637 cm^{-1}), and phenyl groups (1608 and 1500 cm^{-1}). The ^{13}C-NMR and DEPT spectra showed only 34 C-atom signals suggesting the presence of seven Me, three CH_2, and thirteen CH groups (including two olefinic and six O-bearing C-atoms), and eleven quaternary C-atoms (including two C=O and three O-bearing aryl C-atoms). These spectral features suggested **2** to be a diterpenoid glycoside containing a symmetrical structure moiety. Of the 37 C-atoms, 22 were assigned to the aglycone part

Table 2. *^{1}H-, ^{13}C-, and 2D-NMR Data* (400 and 100 MHz, resp.; CD_3OD) *of* **2**[1]). δ in ppm, J in Hz.

	δ(H)	δ(C) (DEPT)	HMBC (H → C)	NOESY
CH_2(1)	1.44–1.47 (*m*, H_α)	36.3 (CH_2)	C(3), C(5), C(20)	H–C(3), H–C(5), Me(18)
	2.00–2.03 (*m*, H_β)			H–C(11), Me(20)
CH_2(2)	1.65–1.68 (*m*, H_α)	24.9 (CH_2)	C(4), C(10)	
	1.79–1.82 (*m*, H_β)			Me(19), Me(20)
H–C(3)	4.76 (*dd*,	73.9 (CH)	C(1), C(5), C(18),	H_α–C(1), H–C(5),
	J = 10.6, 4.8)		C(19), C(21)	Me(18)
C(4)		41.1 (C)		
H–C(5)	2.06 (*d*, *J* = 3.1)	51.0 (CH)	C(1), C(3), C(7),	H_α–C(1), H–C(3),
			C(18), C(19), C(20)	Me(18)
H–C(6)	6.03 (*dd*, *J* = 9.8, 3.1)	130.6 (CH)	C(4), C(7), C(8), C(10)	
H–C(7)	6.78 (*dd*, *J* = 9.5, 3.1)	125.1 (CH)	C(5), C(9), C(14)	H–C(14)
C(8)		131.9 (C)		
C(9)		142.4 (C)		
C(10)		39.2 (C)		
H–C(11)	6.89 (*s*)	118.9 (CH)	C(8), C(13)	H_β–C(1), Me(20)
C(12)		145.1 (C)		
C(13)		132.9 (C)		
H–C(14)	6.71 (*s*)	123.6 (CH)	C(7), C(9), C(12), C(15)	H–C(7)
H–C(15)	3.28 (*sept.* *J* = 7.0)	28.4 (CH)	C(12), C(13), C(14),	
			C(16), C(17)	
Me(16)	1.22 (*d*, *J* = 7.0)	22.8 (Me)	C(13), C(15), C(17)	
Me(17)	1.25 (*d*, *J* = 7.0)	22.5 (Me)	C(13), C(15), C(16)	
Me(18)	1.02 (*s*)	23.2 (Me)	C(3), C(5), C(19)	H_α–C(1), H–C(3),
				H–C(5)
Me(19)	1.07 (*s*)	29.6 (Me)	C(3), C(5), C(18)	H_α–C(2), Me(20)
Me(20)	1.32 (*s*)	20.1 (Me)	C(1), C(5), C(9)	H_β–C(1), H_α–C(2),
				H–C(11), Me(19)
C(21)		170.6 (C)		
Me(22)	2.08 (*s*)	21.3 (Me)	C(21)	
H–C(1′)	5.01 (*d*, *J* = 7.4)	99.2 (CH)	C(12), C(3′)	H–C(3′), H–C(5′)
H–C(2′)	3.23–3.26 (*m*)[a])	72.6 (CH)		H–C(4′)
H–C(3′)	3.29–3.34 (*m*)[a])	77.1 (CH)		H–C(1′), H–C(5′)
H–C(4′)	3.18–3.22 (*m*)[a])	69.1 (CH)		H–C(2′)
H–C(5′)	3.41–3.45 (*m*)[a])	74.7 (CH)		H–C(1′), H–C(3′)
CH_2(6′)	4.23–4.26 (*m*),	64.1 (CH_2)	C(7″)	
	4.51–4.55 (*m*)			
C(1″)		122.9 (C)		
H–C(2″)	7.15 (*s*)	107.2 (CH)	C(4″)	
C(3″)		147.6 (C)		
C(4″)		141.0 (C)		
C(5″)		147.6 (C)		
H–C(6″)	7.15 (*s*)	107.2 (CH)	C(4″)	
C(7″)		165.7 (C)		
*Me*O–C(3″,5″)	3.75 (*s*, 6 H)	55.8 (Me)	C(3″), C(5″)	

[a]) Overlapped signals.

and 15 to the glycosyl moiety. The ^{1}H-NMR spectrum of **2** indicated the presence of two olefinic H-atoms (δ(H) 6.03 (*dd*, $J = 9.8, 3.1$ Hz) and 6.78 (*dd*, $J = 9.5, 3.1$ Hz)), two aromatic H-atoms (δ(H) 6.89 and 6.71 (2*s*)), one CH–O (δ(H) 4.76 (*dd*, $J = 10.6$, 4.8 Hz)), an i-Pr (δ(H) 3.28 (*sept.* $J = 7.0$ Hz, 1 H); δ(H) 1.22 and 1.25 (2*d*, $J = 7.0$ Hz, 3 H each)), three additional tertiary Me (δ(H) 1.02, 1.07, and 1.32 (3*s*)), and one Ac Me group (δ(H) 2.08 (*s*)). The ^{13}C-NMR and DEPT spectra also displayed the presence of two olefinic C-atoms at δ(C) 130.6 (CH) and 125.1 (CH), and six aromatic C-atoms at δ(C) 131.9 (C), 142.4 (C), 118.9 (CH), 145.1 (C), 132.9 (C), and 123.6 (CH). The above NMR data were typical of an abietane-type diterpenoid having one aromatic ring [10] and quite similar to those of hinokiol [11] and totarol [12]. The ^{1}H-NMR spectrum of **2** also displayed an aromatic signal at δ(H) 7.15 (*s*, 2 H), which demonstrated one 1,3,4,5-tetrasubstituted aromatic ring, and one *s* due to two MeO groups at δ(H) 3.75 (*s*, 6 H). The above information, together with the observation of an ester C=O signal at δ(C) 165.7, indicated the presence of a 4-hydroxy-3,5-dimethoxybenzoyl unit in the molecule. Furthermore, seven sugar H-atoms (δ(H) 5.01 (*d*, $J = 7.4$ Hz, 1 H), 3.18 – 4.55 (*m*, 6 H)) were observed in the ^{1}H-NMR spectrum of **2**. By means of HMBC and NOESY NMR experiments, these seven sugar H-atoms could be assigned. In addition, the anomeric C-atom signal at δ(C) 99.2 (CH), the CH signals at δ(C) 72.6, 77.1, 69.1, and 74.7, and the CH_2 signal at δ(C) 64.1 in the ^{13}C-NMR spectrum indicated that the monosaccharide unit was glucose, which was also confirmed by co-TLC and GC analysis with a standard sample after acid hydrolysis [7]. The positions of the substituents were determined by the HMBC experiment (*Fig. 2*). The correlations showed three-bond coupling from H–C(1′) (δ(H) 5.01) to C(12) (δ(C) 145.1) and from H–C(6′) (δ(H) 4.51 – 4.55) to C(7″) (δ(C) 165.7), which indicated that C(12) of the aglycone and C(7″) of the substituted benzoyl moiety were attached to C(1′) and C(6′) of the glucose unit, respectively. The location of the Ac unit at C(3) by an ester linkage was evident from the HMBC H–C(3) (δ(H) 4.76)/C(21) (δ(C) 170.6). In addition, the observed correlations H–C(14) (δ(H) 6.71)/C(15) (δ(C) 28.4), H–C(15) (δ(H) 3.28)/C(12) (δ(C) 145.1), C(13) (δ(C) 132.9), and C(14) (δ(C) 123.6), as well as Me(16) (δ(H) 1.22) and Me(17) (δ(H) 1.25)/C(13) (δ(C) 132.9) confirmed the location of the glycosyl moiety at C(12) and of the i-Pr group at C(13). The relative configuration of **2** was deduced by the analysis of the coupling constants

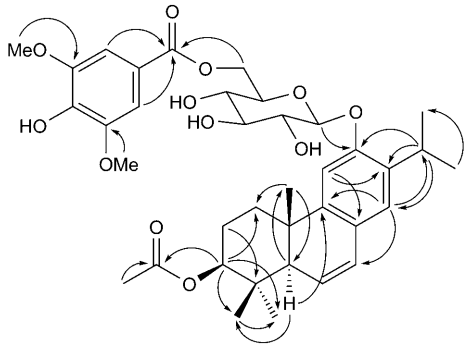


Fig. 2. *Key HMBCs* (H → C) *of* **2**

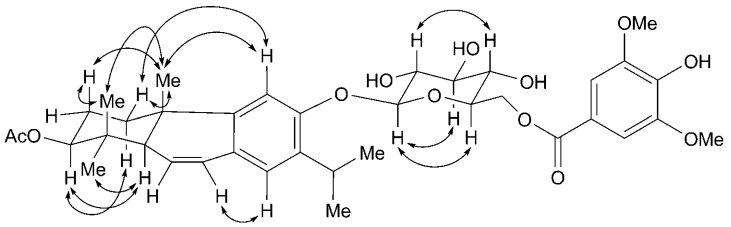


Fig. 3. *Key NOESY* (H ↔ H) *correlations of* **2**

and NOESY correlations (*Fig. 3*). The correlations Me(20) (δ(H) 1.32)/H_β–C(2) (δ(H) 1.79–1.82), H–C(11) (δ(H) 6.89), and Me(19) (δ(H) 1.07), Me(19)/H_β–C(2), Me(18) (δ(H) 1.02)/H–C(5) (δ(H) 2.06) indicated that ring *A* has a chair conformation and is *trans*-fused with ring *B*. The glucose was proposed to have β-configuration on the basis of the coupling constant ($J = 7.4$ Hz) between H–C(1′) and H–C(2′) (δ(H) 3.23–3.26) in the ^{1}H-NMR spectrum. Similarly, a large coupling constant ($J = 10.6$ Hz) between H–C(3) and H_β–C(2) (δ(H) 1.79–1.82) [13] and the NOESY correlations H–C(3)/H–C(5) and H_α–C(1) (δ(H) 1.44–1.47) indicated the α-orientation of H–C(3). From the above data, the structure of compound **2** was, thus, elucidated as (3β)-3-(acetyloxy)ferruginol 12-[6-*O*-(4-hydroxy-3,5-dimethoxybenzoyl)-β-D-glucopyranoside] and named tomentoside II (ferruginol = (4b*S*,8a*S*)-4b,5,6,7,8,8a,9,10-octahydro-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-3-ol).

The five known compounds were identified as 4,5-dimethoxy-7-methylcoumarin (coumarin = 2*H*-1-benzopyran-2-one) [4], 4,7-dimethoxy-5-methylcoumarin [14], betulinic acid (= (3β)-3-hydroxylup-20(29)-en-8-oic acid) [15][16], oleanolic acid (= (3β)-3-hydroxyolean-12-en-28-oic acid) [17][18], and oleanolic acid 3-α-L-arabinopyranoside [19], respectively, by detailed spectroscopic analysis and comparison of their spectral data (^{1}H- and ^{13}C-NMR and MS) with the literature values. These five known compounds were obtained for the first time from *A. tomentosa*.

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Experimental Part

General. All solvents were of anal. grade (*Xi'an Chemical Plant*, China). Thin-layer chromatography (TLC): precoated silica-gel GF_{254} plates (SiO_2; *Qingdao Haiyang Chemical Plant*, China). Column Chromatography (CC): SiO_2 (100–200 or 200–300 mesh; *Qingdao*) and *Sephadex LH-20* gel (*Amersham Biosciences*). M.p.: *X-4* micro melting-point apparatus; uncorrected. Optical rotations: *Perkin-Elmer-341* digital polarimeter. UV Spectra: *Shimadzu-UV-2401* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Perkin-Elmer-1700* spectrometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker-DRX-400* spectrometer; in $CDCl_3$, CD_3OD, or (D_6)DMSO solns.; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. FAB-MS: *VG-Autospec-3000* mass spectrometer; in *m*/*z*, glycerol matrix. GC/MS: *GC6890N-MSD5973N* (*Agilent*); *HP-5* MS fused SiO_2 cap. column (30 m × 0.25 mm; film thinkness 0.25 μm).

Plant Material. The root of *A. tomentosa* were collected from the Ziwuling mountain areas of Gansu Province in China, in September 2007, and identified by Prof. *Xiao-Qiang Guo* (Department of Life

Sciences, Longdong University, P. R. China). A voucher specimen (No. 2007-18) was deposited with the Herbarium of the Department of Life Sciences, Longdong University.

Extraction and Isolation. Ground air-dried roots of *A. tomentosa* (5.0 kg) were extracted 3 × with 80% aq. EtOH at r.t. (with 25 l for 7 d each time), and then the extracts were combined and concentrated under reduced pressure at 60°: 448 g of a brown viscous residue. The EtOH extract was suspended in dist. H_2O (1500 ml) and partitioned successively with petroleum ether (450 ml), $CHCl_3$ (450 ml), AcOEt (450 ml), and BuOH (sat. with H_2O, 450 ml). The conc. AcOEt-soluble extract (103 g) was subjected to CC (SiO_2 (100–200 mesh), gradient hexane/$CHCl_3$ and $CHCl_3$/MeOH (pure or mixtures)): *Frs.* E_1–E_{13}. *Fr.* E_3 (1.6 g; $CHCl_3$/MeOH 4:1) was repeatedly subjected to CC (SiO_2 (200–300 mesh), stepwise elution with $CHCl_3$/MeOH 5:1 → 1:1; then *Sephadex LH-20*, MeOH): *4,5-dimethoxy-7-methylcoumarin* (11 mg) and *4,7-dimethoxy-5-methylcoumarin* (15 mg). *Fr.* E_5 (2.3 g; $CHCl_3$/MeOH 7:2) was subjected to CC (SiO_2 (200–300 mesh), $CHCl_3$/MeOH 4:1 → 2:1): *betulinic acid* (27 mg) and *oleanolic acid* (14 mg). *Fr.* E_6 (10.0 g; $CHCl_3$/MeOH 3:1) was subjected to CC (SiO_2 (200–300 mesh), $CHCl_3$/MeOH 4:1 → 1:2): *Frs.* $E_{6.1}$–$E_{6.5}$. *Fr.* $E_{6.2}$ was subjected to CC (*Sephadex LH-20*, MeOH): **1** (10 mg). *Fr.* $E_{6.4}$ was further purified by prep. TLC (MeOH/$CHCl_3$/hexane 1:3:1): **2** (8 mg). *Fr.* E_{10} (13.9 g) was subjected to CC (SiO_2 (200–300 mesh), AcOEt/MeOH 8:1 → 2:1; then *Sephadex LH-20*, MeOH), and recrystallized from MeOH: oleanolic acid 3-α-L-arabinopyranoside (16 mg).

*1-O,2-O-[(1*S*,2*S*)-1-(3-Acetyl-2,4,6-trihydroxyphenyl)-3-hydroxypropane-1,3-diyl]-β-*D*-glucopyranose* (**1**): White plate crystal. M.p. 185–187. $[\alpha]_D^{21} = +21.2$ ($c = 0.54$, MeOH). UV (MeOH): 210 (2.12), 268 (3.57). IR (KBr): 3405, 1662, 1601, 1508, 1468, 1203, 1044, 875. ^{1}H- and ^{13}C-NMR (DEPT): *Table 1*. HR-FAB-MS: 401.1089 ($[M-H]^-$, $C_{17}H_{21}O_{11}^-$; calc. 401.1084).

*(3β)-3-(Acetyloxy)ferruginol 12-[6-O-(4-Hydroxy-3,5-dimethoxybenzoyl)-β-*D*-glucopyranoside]* (= *(4b*S*,7*S*,8a*R*)-7-(Acetyloxy)-4b,5,6,7,8,8a-hexahydro-4b,8,8-trimethyl-2-(1-methylethyl)phenanthren-3-yl β-*D*-Glucopyranoside 6-(4-Hydroxy-3,5-dimethoxybenzoate)*; **2**): Yellowish amorphous powder. M.p. 205–208. $[\alpha]_D^{21} = +32.4$ ($c = 0.11$, MeOH). UV (MeOH): 208 (2.85), 238 (3.89), 324 (3.61). IR (KBr): 3410, 2935, 1712, 1689, 1637, 1608, 1500, 1347, 1208, 1140, 1032, 714. ^{1}H- and ^{13}C-NMR (DEPT): *Table 2*. HR-FAB-MS: 683.3059 ($[M-H]^-$, $C_{37}H_{47}O_{12}^-$; calc. 683.3068).

Acid Hydrolysis of Compounds **1** *and* **2** *and Determination of the Absolute Configuration of the Glucose.* Compound **1** or **2** (2 mg) was dissolved in MeOH (1 ml) and 2N HCl (1 ml), resp. The mixture was refluxed (magnetic stirring) in a water bath at 90° for 2 h. After cooling, the mixture was diluted with H_2O (2 ml) and extracted twice with AcOEt (2 ml). The aq. layer was neutralized by passing it through an ion-exchange resin (*Amberlite MB-3*) column by elution with H_2O. The eluent was concentrated and the residue dissolved in pyridine (0.1 ml). To this soln., 0.10M D-cysteine methyl ester hydrochloride in pyridine (0.1 ml) was added. The mixture was kept at 60° for 1.5 h and then dried *in vacuo*. The residue was trimethylsilylated with 1-(trimethylsilyl)-1*H*-imidazole (0.1 ml) for 2 h. The mixture was partitioned between hexane and H_2O (each 1 ml), and the hexane extract was analyzed by GC (*HP-5* MS fused SiO_2 cap. column, column temp. 230°, injection temp. 250°, N_2 as carrier gas). In the acid hydrolysate of **1** and **2**, D-glucose was confirmed by comparison of the retention times of their derivatives with those of D-glucose (t_R 24.5 min) and L-glucose (t_R 21.7 min) [7], resp.

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