Three Novel 24,30-Dinortriterpenoids, Paeonenoides A – C, from *Paeonia veitchii*

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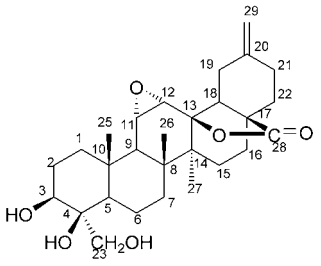
Three novel 24,30-dinortriterpenoids named paeonenoides A – C (**1** – **3**) and the four related acetonide derivatives **4** – **7**, most likely artifacts of isolation, together with a known triterpenoid, akebonic acid (**8**), were isolated from the root cortex of *Paeonia veitchii*. Their structures were established by spectroscopic means. The 24,30-dinor skeleton of triterpenoids occurs rarely in nature.

Introduction. – The root cortex of *Paeonia veitchii* LYNCH. is one of the most important crude drugs in Chinese traditional medicine and has been used as an analgesic, sedative, and anti-inflammatory agent. It is also frequently used as a remedy for cardiovascular, extravasated blood, stagnated blood, and female diseases in traditional oriental medicine [1]. Previous chemical studies of this plant led to the isolation of the monoterpene glycosides, paeoniflorin, and related compounds [2][3]. In this paper, we describe the isolation and structural elucidation of three novel 24,30-dinortriterpenoids named paeonenoides A – C (**1** – **3**) and the four related acetonide derivatives **4** – **7**, together with a known triterpenoid, akebonic acid (**8**) [4][5], from the AcOEt fraction of the root cortex of *P. veitchii*. The 24,30-dinor skeleton of oleanane-type triterpenoids occurs rarely in nature. We already reported a new 24,30-dinortriterpenoid isolated from another species (*P. delavayi*) for the first time during our previous work [6]. This is only the second time that 24,30-dinortriterpenoids were isolated from natural sources.

Results and Discussion. – Paeonenoide A (**1**), obtained as white amorphous powder, gave a molecular-ion peak at *m/z* 472 in the EI-MS, in accordance with the molecular formula $C_{28}H_{40}O_6$ determined by the HR-EI-MS, which suggested that compound **1** is a dinortriterpenoid. This deduction was confirmed by the ^{13}C- and DEPT-NMR spectra exhibiting signals for 28 C-atoms (see the *Table*). The mass spectrum of **1** exhibited the characteristic fragment-ion peaks at *m/z* 247 and 253, typical for a 11α,12α-epoxyoleanane γ-lactone. The IR spectrum of **1** showed absorption bands for an exocyclic CH_2 group (1645 and 903 cm^{-1}), an epoxide ring (872 cm^{-1}), and a γ-lactone (1775 cm^{-1}). According to further spectral data, the structure of **1** was determined to be (3β,4β,11α,12α,13β)-11,12-epoxy-3,4,13,23-tetrahydroxy-24,30-dinorolean-20(29)-en-28-oic acid 28,13-lactone.



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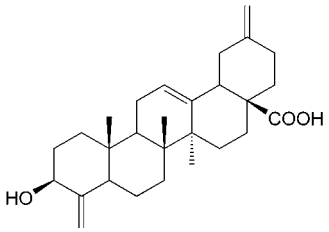

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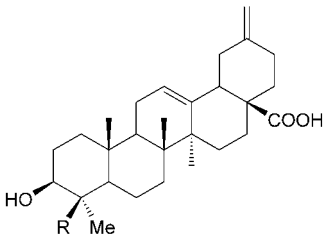

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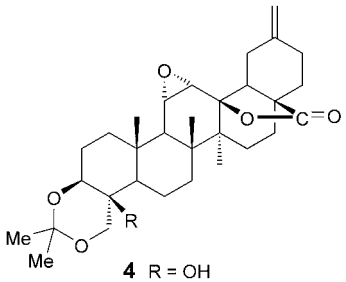

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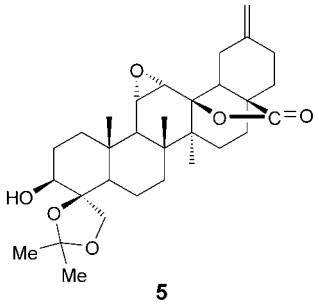

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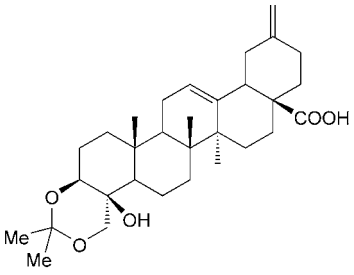

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The presence of the exocyclic CH_2 group of **1** was supported by the signals of two olefinic H-atoms at δ (H) 4.73 (*s*, 1 H) and 4.75 (*s*, 1 H) and an olefinic CH_2 at δ (C) 110.3 in the NMR spectra. The ^{1}H- and ^{13}C-NMR spectra of **1** showed similarities to those of (3β,11α,12α,13β)-11,12-epoxy-3,13,23-trihydroxy-30-norolean-20(29)-en-28-oic acid 28,13-lactone [7], except for the absence of the Me group at δ *ca.* 12 (C(24)) and a quaternary C-atom at δ *ca.* 43 (C(4)); instead an additional O-bearing quaternary C-atom was present at δ 74.1. The HMBC experiment showed the expected long-range correlations between the quaternary C-atom at δ 74.1 and H–C(3) (δ 3.67 (*dd*, $J = 11.2, 5.4$ Hz)) and CH_2(23) (δ 3.62 and 3.82 (each *d*, $J = 10.8$ Hz, each 1 H)). So, the quaternary C-atom at δ 74.1 was assigned to C(4), substituted by an OH group. The NOESY experiment revealed the correlation H–C(3)/CH_2(23), indicating the β-orientation of OH–C(4).

Paeonenoide B (**2**), obtained as white amorphous powder, gave a molecular-ion peak at *m/z* 424 in the EI-MS, in accordance with the molecular formula $C_{28}H_{40}O_3$ determined by the HR-EI-MS, suggesting a dinor skeleton also for compound **2**. The structure of **2** was determined to be (3β)-3-hydroxy-24,30-dinoroleana-4(23),12,20(29)-trien-28-oic acid by its spectroscopic data.

Table. *^{13}C-NMR Data for Compounds* **1**–**8**. **2**, **3**, and **8** in C_5D_5N; **1** and **4**–**7** in $CDCl_3$; δ in ppm.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
C(1)	37.7 (*t*)	38.4 (*t*)	38.8 (*t*)	38.1 (*t*)	38.0 (*t*)	38.6 (*t*)	38.2 (*t*)	38.9 (*t*)
C(2)	27.0 (*t*)	28.4 (*t*)	28.3 (*t*)	22.8 (*t*)	26.8 (*t*)	23.2 (*t*)	27.7 (*t*)	27.9 (*t*)
C(3)	74.6 (*d*)	73.3 (*d*)	79.8 (*d*)	75.4 (*d*)	71.0 (*d*)	77.5 (*d*)	75.3 (*d*)	78.0 (*d*)
C(4)	74.1 (*s*)	154.8 (*s*)	75.3 (*s*)	68.3 (*s*)	85.0 (*s*)	36.7 (*s*)	68.2 (*s*)	39.2 (*s*)
C(5)	49.1 (*d*)	51.0 (*d*)	56.4 (*d*)	49.0 (*d*)	52.2 (*d*)	50.8 (*d*)	49.2 (*d*)	55.7 (*d*)
C(6)	17.6 (*t*)	17.4 (*t*)	17.9 (*t*)	16.8 (*t*)	18.6 (*t*)	17.0 (*t*)	22.9 (*t*)	18.7 (*t*)
C(7)	31.1 (*t*)	32.7 (*t*)	32.8 (*t*)	31.0 (*t*)	30.8 (*t*)	30.8 (*t*)	32.2 (*t*)	33.1 (*t*)
C(8)	41.1 (*s*)	39.2 (*s*)	39.9 (*s*)	41.1 (*s*)	40.8 (*s*)	40.7 (*s*)	39.5 (*s*)	39.7 (*s*)
C(9)	50.2 (*d*)	48.1 (*d*)	48.1 (*d*)	50.4 (*d*)	49.9 (*d*)	51.1 (*d*)	47.1 (*d*)	48.0 (*d*)
C(10)	36.5 (*s*)	36.8 (*s*)	38.0 (*s*)	37.0 (*s*)	36.9 (*s*)	36.9 (*s*)	37.4 (*s*)	37.3 (*s*)
C(11)	52.9 (*d*)	23.7 (*t*)	23.9 (*t*)	52.8 (*d*)	52.6 (*d*)	52.6 (*d*)	23.3 (*t*)	23.7 (*t*)
C(12)	57.3 (*d*)	123.1 (*d*)	123.0 (*d*)	57.3 (*d*)	57.0 (*d*)	57.0 (*d*)	123.2 (*d*)	123.0 (*d*)
C(13)	87.1 (*s*)	144.2 (*s*)	144.2 (*s*)	87.1 (*s*)	86.9 (*s*)	86.6 (*s*)	142.9 (*s*)	144.0 (*s*)
C(14)	41.5 (*s*)	42.1 (*s*)	42.2 (*s*)	41.8 (*s*)	41.4 (*s*)	41.6 (*s*)	41.9 (*s*)	42.0 (*s*)
C(15)	26.2 (*t*)	28.3 (*t*)	28.6 (*t*)	27.0 (*t*)	28.1 (*t*)	26.8 (*t*)	29.9 (*t*)	28.2 (*t*)
C(16)	21.9 (*t*)	23.9 (*t*)	23.9 (*t*)	21.9 (*t*)	21.9 (*t*)	21.7 (*t*)	23.3 (*t*)	23.7 (*t*)
C(17)	44.2 (*s*)	47.2 (*s*)	47.1 (*s*)	44.1 (*s*)	43.9 (*s*)	43.9 (*s*)	46.8 (*s*)	46.9 (*s*)
C(18)	54.8 (*d*)	47.5 (*d*)	48.1 (*d*)	54.9 (*d*)	54.6 (*d*)	54.6 (*d*)	46.8 (*d*)	47.8 (*d*)
C(19)	34.7 (*t*)	41.6 (*t*)	42.0 (*t*)	34.7 (*t*)	34.5 (*t*)	34.4 (*t*)	41.4 (*t*)	41.9 (*t*)
C(20)	146.3 (*s*)	149.2 (*s*)	149.2 (*s*)	146.4 (*s*)	146.1 (*s*)	146.1 (*s*)	147.8 (*s*)	149.0 (*s*)
C(21)	32.0 (*t*)	38.4 (*t*)	38.4 (*t*)	32.1 (*t*)	31.8 (*t*)	31.8 (*t*)	37.2 (*t*)	38.2 (*t*)
C(22)	30.2 (*t*)	30.5 (*t*)	30.4 (*t*)	30.2 (*t*)	30.0 (*t*)	30.0 (*t*)	29.7 (*t*)	30.2 (*t*)
C(23)	68.4 (*t*)	102.9 (*t*)	17.9 (*q*)	69.4 (*t*)	69.6 (*t*)	72.3 (*t*)	69.5 (*t*)	28.6 (*q*)
C(24)						12.0 (*q*)		16.3 (*q*)
C(25)	16.8 (*q*)	16.1 (*q*)	15.2 (*q*)	17.7 (*q*)	16.1 (*q*)	18.5 (*q*)	15.6 (*q*)	15.4 (*q*)
C(26)	19.2 (*q*)	17.4 (*q*)	17.4 (*q*)	18.7 (*q*)	18.9 (*q*)	18.9 (*q*)	17.2 (*q*)	17.3 (*q*)
C(27)	20.4 (*q*)	26.3 (*q*)	26.1 (*q*)	20.4 (*q*)	20.0 (*q*)	20.1 (*q*)	26.1 (*q*)	26.0 (*q*)
C(28)	178.9 (*s*)	179.6 (*s*)	179.4 (*s*)	178.5 (*s*)	178.3 (*s*)	178.3 (*s*)	180.6 (*s*)	179.1 (*s*)
C(29)	110.3 (*t*)	107.2 (*t*)	107.1 (*t*)	110.3 (*t*)	110.1 (*t*)	110.1 (*t*)	107.2 (*t*)	106.8 (*t*)
Me_2C				99.3 (*s*)	110.6 (*s*)	99.0 (*s*)	99.1 (*s*)	
Me				30.0 (*q*)	26.8 (*q*)	29.9 (*q*)	29.8 (*q*)	
Me				19.2 (*q*)	26.5 (*q*)	19.3 (*q*)	18.5 (*q*)	

In the ^{13}C-NMR spectrum of **2** (*Table*), the signals of a COOH group (δ 179.6), three olefinic quaternary C-atoms (δ 154.8, 149.2, and 144.2), one olefinic CH (δ 123.1), two olefinic CH_2 (δ 102.9 and 107.2), one OCH (δ 73.3), four quaternary C-atoms bearing no O-substituents, three saturated CH, ten saturated CH_2, and three Me groups were present. The ^{1}H- and ^{13}C-NMR data of **2** were similar to those of akebonic acid (**8**) [4][5], suggesting that they have the same skeleton. The differences consisted in the absence of two Me groups at δ(C) *ca.* 28 and 16 and in the presence of two additional olefinic C-atoms at δ 102.9 (*t*) and 154.8 (*s*), indicating one more exocyclic C=C bond in compound **2**. The HMQC spectrum showed that the two exocyclic CH_2 H-atoms at δ 5.69 (*s*, 1 H) and 4.83 (*s*, 1 H) corresponded to the C-atom at δ 102.9. The HMBC experiment displayed correlations of the signals at δ 5.69 and 4.83 with those at δ 73.4 (C(3)), 154.8 (C(4)), and 51.0 (C(5)). Therefore, the additional exocyclic C=C bond was placed between C(4) and C(23). The CH_2(29)=C(20) moiety was also confirmed by the long-range correlations between the signals at δ 4.80 and 4.75 (CH_2(29)) and those at δ 41.6 (C(19)), 149.2 (C(20)), and 30.5 (C(21)) in the HMBC experiment.

Paeonenoide C (**3**), obtained as white amorphous powder, gave a molecular-ion peak at *m/z* 442 in the EI-MS, in accordance with the molecular formula $C_{28}H_{42}O_4$ determined by the HR-EI-MS, also suggesting the dinor skeleton for compound **3**. The ^{1}H- and ^{13}C-NMR data (*Table*) were also similar to those of akebonic acid (**8**) [4][5].

The structure of **3** was determined to be (3*β*,4*β*)-3,4-dihydroxy-24,30-dinoroleana-12,20(29)-dien-28-oic acid.

Compared to the data of **8**, the ^{13}C-NMR spectrum of **3** revealed the absence of a Me group at δ(C) *ca.* 28 and the presence of an additional O-bearing quaternary C-atom at δ 75.3. The HMBC experiment showed that the signal at δ 3.91 (H–C(3)) correlated with δ(C)75.3, and the signal at δ 1.42 (Me(23)) correlated with δ(C) 75.3, 79.8 (C(3)), and 56.4 (C(5)). Therefore, the quaternary C-atom at δ 75.3 was assigned to C(4), substituted by an OH group instead of a normal Me group, thus forming the 24,30-dinor skeleton. The *β*-orientation of OH–C(4) was confirmed by the NOE interaction between H–C(3) (δ 3.91) and Me(23) (δ 1.42) in the NOESY experiment.

Compound **4**, obtained as a white amorphous powder, exhibited a molecular-ion peak at *m/z* 512 in the EI-MS, in accordance with the molecular formula $C_{31}H_{44}O_6$, confirmed by its HR-EI-MS and ^{13}C-NMR spectrum (*Table*). Compound **4** was determined to be (3*β*,4*β*,11*α*,12*α*,13*β*)-11,12-epoxy-4,13-dihydroxy-3,23-(isopropylidenedioxy)-24,30-dinorolean-20(29)-en-28-oic acid 28,13-lactone.

Comparison of the ^{1}H- and ^{13}C-NMR data of **4** and **1** showed that the presence of a further acetal C-atom at δ(C) 99.3 and two additional tertiary Me groups at δ(H) 1.43 and 1.46 and δ(C) 19.2 and 30.0 was the main difference. The HMBC experiment showed that the acetal C-atom (δ 99.3) was correlated with CH_2(23) (δ 3.65 and 3.69 (each *d*, *J* = 10.5 Hz, each 1 H), H–C(3) (δ 3.61 (*dd*, *J* = 11.0, 4.0 Hz)) and two Me groups at δ 1.43 and 1.46. So, the acetal C-atom was connected with C(3) and C(23) through O-atoms forming a six-membered 1,3-dioxane moiety.

Compound **5**, obtained as white amorphous powder, gave a molecular-ion peak at *m/z* 512 in the EI-MS, in accordance with the molecular formula $C_{31}H_{44}O_6$, determined by its HR-EI-MS and ^{13}C-NMR spectrum, which is identical with that of **4**. Comparison of the ^{1}H- and ^{13}C-NMR spectra (*Table*) of **5** with those of **4** suggested that these two molecules possess the same substitution patterns along rings B–E and differ only in ring A. Compound **5** was determined to be (3*β*,4*β*,11*α*,12*α*,13*β*)-11,12-epoxy-3,13-dihydroxy-4,23-(isopropylidenedioxy)-24,30-dinorolean-20(29)-en-28-oic acid 28,13-lactone. Compounds **4** and **5** represent acetonide derivatives of **1** whose structures corroborated the structure assigned to **1**.

The ^{13}C-NMR signals of C(4) and the acetal C-atom of **5** were shifted downfield to δ 85.0 and 110.6 from δ 68.3 and 99.3 in **4**, respectively. In the HMBC experiment, the long-range correlations were clearly observed only between the acetal C-atom (δ 110.6) and CH_2(23) (δ 3.75 and 4.14 (each *d*, *J* = 8.5 Hz, each 1 H)) and two tertiary Me groups at δ 1.39 and 1.47, while the correlation between the acetal C-atom and H–C(3) (δ 3.24 (*dd*, *J* = 8.6, 3.5 Hz)) was not observed. Therefore, the acetal C-atom of **5** was connected with C(4) and C(23) through O-atoms forming a five-membered 1,3-dioxolane moiety instead of the 1,3-dioxolane moiety of **4**. The downfield shift of C(4) and the acetal C-atom was attributed to the strain effect in the five-membered ring.

Compound **6**, obtained as white amorphous powder, showed a molecular-ion peak at *m/z* 510 in the EI-MS, in accordance with the molecular formula $C_{32}H_{46}O_5$, confirmed by its HR-EI-MS and ^{13}C-NMR spectrum (*Table*). The structure of **6** was determined to be (3*β*,4*α*,11*α*,12*α*,13*β*)-11,12-epoxy-13-hydroxy-3,23-isopropylidenedioxy)-30-norolean-20(29)-en-28-oic acid 28,13-lactone, which represents the acetonide derivative of (3*β*,4*α*,11*α*,12*α*,13*β*)-11,12-epoxy-3,13,23-trihydroxy-30-norolean-20(29)-en-28-oic acid 28,13-lactone [7].

Comparison of the ^{1}H- and ^{13}C-NMR data of **6** with those of (3*β*,4*α*,11*α*,12*α*,13*β*)-11,12-epoxy-3,13,23-trihydroxy-30-norolean-20(29)-en-28-oic acid 28,13-lactone [7] showed that the acetal C-atom at *δ* 99.0 and two additional tertiary Me groups at *δ*(H) 1.40 and 1.43 and *δ*(C) 19.3 and 29.9 were present in **6**. The HMBC spectrum showed the long-range correlations between the acetal C-atom (*δ* 99.0) and H−C(3) (*δ* 3.53 (*dd*, *J* = 11.8, 3.9 Hz), CH_2(23) (*δ* 3.42 and 3.49 (each *d*, *J* = 10.6 Hz, each 1 H)) and two tertiary Me groups at *δ* 1.40 and 1.43.

Compound **7**, obtained as white amorphous powder, showed a molecular-ion peak at *m/z* 498 in the EI-MS, in accordance with the molecular formula $C_{31}H_{46}O_5$, confirmed by its HR-EI-MS and ^{13}C-NMR spectrum (*Table*). Further spectral data suggested that **7** is the acetonide derivative of (3*β*,4*β*)-3,4,23-trihydroxy-24,30-dinoroleana-12,20(29)-dien-28-oic acid, which was isolated previously from *P. delavayi* [6]. The structure of **7** was finally determined to be (3*β*,4*β*)-4-hydroxy-3,23-(isopropylidenedioxy)-24,30-dinoroleana-12,20(29)-dien-28-oic acid.

The ^{1}H- and ^{13}C-NMR spectra of **7** were analogous to those of (3*β*,4*β*)-3,4,23-trihydroxy-24,30-dinoroleana-12,20(29)-dien-28-oic acid. The main difference was the presence of an additional acetal C-atom at *δ* 99.1 and two tertiary Me groups at *δ*(H) 1.44 and 1.47 and *δ*(C) 18.5 and 29.8. Long-range correlations were observed between the acetal C-atom (*δ* 99.1) and H−C(3) (*δ* 3.60 (*dd*, *J* = 13.8, 4.2 Hz)), CH_2(23) (*δ* 3.65 and 3.71 (each *d*, *J* = 11.3 Hz, each 1 H)), and two Me groups at *δ* 1.44 and 1.47 in the HMBC spectrum.

The acetonides **4-7** are most likely artifacts, derived from acetalization of native diols with acetone present during the chromatographic operation procedures.

Experimental Part

General. Optical rotations: *Jasco DIP-370* digital polarimeter. IR Spectra: *Bio-Rad FtS-135* spectrometer with KBr pellets; in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker AM-400* and *DRX-500* spectrometers; *δ* in ppm, *J* in Hz; Me_4Si as internal standard; measured in C_5D_5N and $CDCl_3$. Mass spectra: *VG Autospec-3000* spectrometer; 70 eV for EI; *m/z* (rel. %).

Plant Material. The root cortex of *P. veitchii* was bought from *Yunnan Province Crude Drug Company*, in August 1999. It was identified by Mr. *Z. W. Lu*, and a voucher specimen was deposited in the Herbarium of Kunming Institute of Botany, The Chinese Academy of Sciences.

Extraction and Isolation. The air-dried and powdered root cortex (5.0 kg) was extracted three times with 95% EtOH at r.t. The crude extract was evaporated and the resulting residue partitioned between H_2O and AcOEt. The AcOEt extract (56 g) was separated by CC (silica gel (200–300 mesh; 1.5 kg), $CHCl_3$/Me_2CO 1:0 → 0:1): *Fractions 1–8. Fr. 2* (1.8 g) was purified by repeated CC (silica gel, petroleum ether/Me_2CO 9:1 and $CHCl_3$/Me_2CO 95:5 and 9:1): **4** (10 mg), **5** (9 mg), and **6** (11 mg). *Fr. 3* (2.5 g) was purified by CC (silica gel, $CHCl_3$/Me_2CO 9:1 and 8:2); then *Sephadex LH-20*, MeOH): **2** (13 mg), **7** (14 mg), and **8** (22 mg). *Fr. 4* (3.2 g) was purified by CC (silica gel, $CHCl_3$/Me_2CO 8:2 and 7:3); then *RP-18*, MeOH/H_2O 50:50 and 60:40): **1** (13 mg) and **3** (12 mg).

Paeonenoide A (=(3*β*,4*β*,11*α*,12*α*,13*β*)-*11,12-Epoxy-3,4,13,23-tetrahydroxy-24,30-dinorolean-20(29)-en-28-oic Acid 28,13-Lactone*; **1**). White amorphous powder. $[\alpha]_D^{21} = +137.50$ (*c* = 0.20, $CHCl_3$). IR (KBr): 3325, 2933, 1775, 1645, 1473, 1441, 1391, 1356, 1222, 1188, 1147, 1049, 1022, 929, 903, 872. ^{1}H-NMR ($CDCl_3$, 400 MHz): 4.75, 4.73 (2 *s*, each 1 H, CH_2(29)); 3.82, 3.62 (2 *d*, *J* = 10.8, CH_2(23)); 3.67 (*dd*, *J* = 11.2, 5.4, H_α−C(3)); 3.08 (*d*, *J* = 5.0, overlapped, H−C(11), H−C(12)); 2.70 (*t*, *J* = 13.5, H_α−C(19)); 2.59 (*dd*, *J* = 13.5, 3.6, H_β−C(19)); 2.24 (overlapped, H−C(18)); 1.58 (*d*, *J* = 5.0, H−C(9)); 1.50 (*dd*, *J* = 13.3, 5.3, H_α−C(16)); 1.21 (*s*, Me(25)); 1.16 (*s*, Me(27)); 1.11 (*s*, Me(26)); 0.91 (*dd*, *J* = 12.2, 2.1, H−C(5)). ^{13}C-NMR: *Table.* EI-MS (70 eV): 472 (5, M^+), 457 (5, $[M - Me]^+$), 441 (100, $[M - CH_2OH]^+$), 423 (5), 253 (6), 247 (7), 233 (6), 189 (17), 173 (27), 159 (20), 147 (24), 105 (33), 91 (35). HR-EI-MS: 472.2863 ($C_{28}H_{40}O_6^+$; calc. 472.2825).

Paeonenoide B (=*(3β)-3-Hydroxy-24,30-dinoroleana-4(23),12,20(29)-trien-28-oic Acid*; **2**). White amorphous powder. $[\alpha]_D^{21} = +104.51$ (*c* = 0.27, MeOH). IR (KBr): 3429, 2932, 2865, 1695, 1654, 1560, 1509, 1459, 1387, 1295, 1127, 1048, 887. ^{1}H-NMR (C_5D_5N, 400 MHz): 5.69, 4.83 (2 *s*, each 1 H, CH_2(23)); 5.51 (br. *s*,

H–C(12)); 4.80, 4.75 (2 *s*, each 1 H, CH_2(29)); 3.99 (*dd*, *J* = 11.5, 5.7, H_α–C(3)); 3.24 (*dd*, *J* = 11.7, 4.5, H–C(18)); 2.65 (*t*, *J* = 14.9, H_β–C(19)); 2.33 (overlapped, H_α–C(19)); 1.28 (*s*, Me(27)); 1.02 (*s*, Me(26)); 0.84 (*s*, Me(25)). ^{13}C-NMR: *Table*. EI-MS (70 eV): 424 (10, M^+), 380 (90, $[M - CO_2]^+$), 232 (49), 218 (18), 204 (20), 188 (100), 173 (65), 159 (43), 145 (40), 131 (65), 119 (58), 105 (77), 91 (74). HR-EI-MS: 424.5214 ($C_{28}H_{40}O_3^+$; calc. 424.5261).

Paeonenoide C (*=(3β,4β)-3,4-Dihydroxy-24,30-dinoroleana-12,20(29)-dien-28-oic Acid*; **3**). White amorphous powder. $[\alpha]_D^{21} = +120.24$ (*c* = 0.21, MeOH). IR (KBr): 3437, 2937, 1693, 1649, 1461, 1385, 1294, 1202, 1101, 1067, 1046, 1016, 886, 758. ^{1}H-NMR (C_5D_5N, 400 MHz): 5.49 (br. *s*, H–C(12)); 4.79, 4.74 (2 *s*, each 1 H, CH_2(29)); 3.91 (*dd*, *J* = 11.9, 4.5, H_α–C(3)); 3.22 (*dd*, *J* = 13.5, 4.6, H–C(18)); 2.61 (*t*, *J* = 13.4, H_β–C(19)); 2.31 (overlapped, H_α–C(19)); 1.70 (*dd*, *J* = 10.5, 4.3, H–C(9)); 1.42 (*s*, Me(23)); 1.14 (*s*, Me(27)); 0.99 (*s*, Me(26)), 0.85 (*s*, Me(25)). ^{13}C-NMR: *Table*. EI-MS (70 eV): 442 (14, M^+), 424 (10, $[M - H_2O]^+$), 396 (12), 378 (9), 248 (20), 232 (94), 219 (26), 204 (22), 187 (100), 173 (34), 159 (27), 131 (40), 119 (32), 105 (42), 91 (34). HR-EI-MS: 442.3101 ($C_{28}H_{42}O_4^+$; calc. 442.3083).

(3β,4β,11α,12α,13β)-11,12-Epoxy-4,13-dihydroxy-3,23-(isopropylidenedioxy)-24,30-dinorolean-20(29)-en-28-oic Acid 28,13-Lactone (**4**). White amorphous powder. $[\alpha]_D^{21} = +65.50$ (*c* = 0.50, $CHCl_3$). IR (KBr): 3500, 2983, 2934, 2868, 1778, 1454, 1385, 1363, 1268, 1201, 1142, 1110, 1050, 929, 860. ^{1}H-NMR ($CDCl_3$, 400 MHz): 4.74, 4.72 (2 *s*, each 1 H, CH_2(29)); 3.69, 3.65 (2 *d*, *J* = 10.5, each 1 H, CH_2(23)); 3.61 (*dd*, *J* = 11.0, 4.0, H_α–C(3)); 3.06 (*d*, *J* = 3.8, overlapped, H–C(11), H–C(12)); 2.70 (*t*, *J* = 13.6, H_α–C(19)); 2.58 (*dd*, *J* = 13.6, 3.5, H_β–C(19)); 2.23 (overlapped, H–C(18)); 1.60 (*d*, *J* = 5.0, H–C(9)); 1.46, 1.43 (2 *s*, each 3 H, 2 Me); 1.19 (*s*, Me(25)); 1.13 (*s*, Me(27)); 1.09 (*s*, Me(26)); 0.84 (*dd*, *J* = 12.6, 2.0, H–C(5)). ^{13}C-NMR: *Table*. EI-MS (70 eV): 512 (20, M^+), 497 (45, $[M - Me]^+$), 481 (100, $[M - CH_2OH]^+$), 423 (11), 293 (7), 265 (4), 247 (16), 232 (8), 201 (14), 189 (25), 173 (45), 159 (30), 147 (37), 105 (49), 72 (92). HR-EI-MS: 512.3133 ($C_{31}H_{44}O_6^+$; calc. 512.3138).

(3β,4β,11α,12α,13β)-11,12-Epoxy-3,13-dihydroxy-4,23-(isopropylidenedioxy)-24,30-dinorolean-20(29)-en-28-oic Acid 28,13-Lactone (**5**). White amorphous powder. $[\alpha]_D^{21} = +92.14$ (*c* = 0.35, $CHCl_3$). IR (KBr): 3528, 3063, 2946, 1775, 1647, 1396, 1365, 1257, 1230, 1146, 1079, 1051, 985, 927, 873. ^{1}H-NMR ($CDCl_3$, 400 MHz): 4.72, 4.70 (2 *s*, each 1 H, CH_2(29)); 4.14, 3.75 (2 *s*, each 1 H, CH_2(23)); 3.24 (*dd*, *J* = 8.6, 3.5, H_α–C(3)); 3.04 (br. *s*, overlapped, H–C(11), H–C(12)); 2.68 (*t*, *J* = 13.5, H_α–C(19)); 2.55 (*dd*, *J* = 13.5, 3.8, H_β–C(19)); 2.23 (*dd*, *J* = 13.2, 7.2, H–C(18)); 1.55 (*d*, *J* = 5.4, H–C(9)); 1.47, 1.39 (2 *s*, each 3 H, 2 Me); 1.10 (*s*, Me(27)); 1.08 (*s*, Me(26)); 1.06 (*s*, Me(25)); 0.83 (*t*, *J* = 7.6, H–C(5)). ^{13}C-NMR: *Table*. EI-MS (70 eV): 512 (49, M^+), 497 (100, $[M - Me]^+$), 468 (8, $[M - CO_2]^+$), 453 (77), 437 (38), 293 (28), 265 (10), 247 (31), 232 (17), 221 (34), 203 (21), 189 (32), 173 (49), 159 (42), 147 (49), 105 (57), 91 (59). HR-EI-MS: 512.3136 ($C_{31}H_{44}O_6^+$; calc. 512.3138).

(3β,4β,11α,12α,13β)-11,12-Epoxy-13-hydroxy-3,23-(isopropylidenedioxy)-30-norolean-20(29)-en-28-oic Acid 28,13-Lactone (**6**). White amorphous powder. $[\alpha]_D^{21} = +71.13$ (*c* = 0.24, $CHCl_3$). IR (KBr): 2938, 2859, 1777, 1466, 1391, 1361, 1256, 1220, 1167, 1133, 1114, 1067, 1024, 932, 895, 872, 863. ^{1}H-NMR ($CDCl_3$, 400 MHz): 4.73, 4.71 (2 *s*, each 1 H, CH_2(29)); 3.53 (*dd*, *J* = 11.8, 3.9, H_α–C(3)); 3.49, 3.42 (2 *d*, *J* = 10.6, each 1 H, CH_2(23)); 3.03 (*d*, *J* = 3.8, overlapped, H–C(11), H–C(12)); 2.71 (*t*, *J* = 13.5, H_α–C(19)); 2.58 (*dd*, *J* = 13.5, 3.5, H_β–C(19)); 2.23 (overlapped, H–C(18)); 1.67 (*d*, *J* = 5.0, H–C(9)); 1.43, 1.40 (2 *s*, each 3 H, 2 Me); 1.08 (*s*, Me(27)); 1.05 (*s*, Me(24)); 1.04 (*s*, Me(25)); 1.03 (*s*, Me(26)); 0.76 (*dd*, *J* = 12.7, 2.0, H–C(5)). ^{13}C-NMR: *Table*. EI-MS (70 eV): 510 (13, M^+), 495 (100, $[M - Me]^+$), 435 (8), 291 (7), 263 (7), 247 (13), 233 (10), 219 (13), 201 (18), 189 (21), 173 (36), 159 (23), 147 (25), 119 (22), 105 (30), 95 (25). HR-EI-MS: 510.3350 ($C_{32}H_{46}O_5^+$; calc. 510.3345).

(3β,4α)-4-Hydroxy-3,23-(isopropylidenedioxy)-24,30-dinoroleana-12,20(29)-dien-28-oic Acid (**7**). White amorphous powder. $[\alpha]_D^{21} = +123.68$ (*c* = 0.28, $CHCl_3$). IR (KBr): 3562, 2935, 1693, 1460, 1382, 1275, 1250, 1203, 1117, 1053, 1023, 885, 861, 75. ^{1}H-NMR ($CDCl_3$, 400 MHz): 5.34 (br. *s*, H–C(12)); 4.63 (*s*, CH_2(29)); 3.71, 3.65 (2 *d*, *J* = 11.3, each 1 H, CH_2(23)); 3.60 (*dd*, *J* = 13.8, 4.2, H_α–C(3)); 2.72 (*dd*, *J* = 13.3, 4.4, H–C(18)); 2.51 (*t*, *J* = 13.6, H_β–C(19)); 1.73 (*t*, *J* = 12.0, H–C(9)); 1.47, 1.44 (2 *s*, each 3 H, 2 Me); 1.17 (*s*, Me(27)); 1.12 (*s*, Me(25)); 0.80 (*s*, Me(26)). ^{13}C-NMR: *Table*. EI-MS (70 eV): 498 (11, M^+), 483 (21, $[M - Me]^+$), 467 (17, $[M - CH_2OH]^+$), 452 (7), 440 (10), 266 (12), 248 (10), 232 (98), 219 (17), 209 (25), 187 (100), 173 (32), 159 (27), 131 (36), 105 (40), 72 (51). HR-EI-MS: 498.3340 ($C_{31}H_{46}O_5^+$; calc. 498.3345).

Akebonic acid (=(3β)-3-Hydroxy-30-noroleana-12,20(29)-dien-28-oid Acid; **8**). White amorphous powder. $[\alpha]_D^{21} = +49.38$ (*c* = 0.40, C_5H_5N). IR (KBr): 3424, 2935, 1691, 1653, 1463, 1384, 1297, 1212, 1102, 996, 886. ^{1}H-NMR (C_5D_5N, 400 MHz): 5.50 (br. *s*, H–C(12)); 4.80, 4.75 (2 *s*, each 1 H, CH_2(29)); 3.45 (*dd*, *J* = 9.8, 6.5, H_α–C(3)); 3.25 (*dd*, *J* = 13.6, 4.7, H–C(18)); 2.64 (*t*, *J* = 13.6, H_β–C(19)); 1.24 (*s*, Me(23), Me(24)); 1.02 (*s*, Me(27)); 1.00 (*s*, Me(26)); 0.87 (*s*, Me(25)). ^{13}C-NMR: *Table*. EI-MS (70 eV): 440 (40, M^+), 422 (10, $[M - H_2O]^+$), 394 (29, $[M - HCOOH]^+$), 248 (58), 232 (84), 219 (34), 207 (65), 187 (78), 175 (53), 145 (44), 131 (55), 107 (54), 91 (64), 69 (77).

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