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

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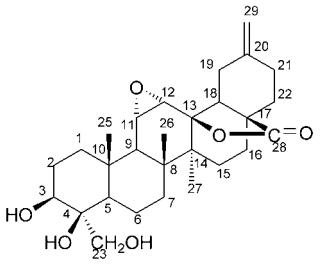
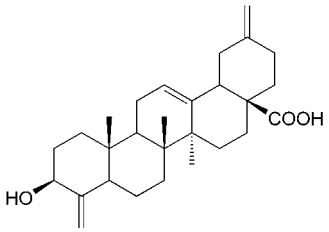
Three novel 24,30-dinortriterpenoids named paeonenoides A – C (**1** – **3**) and the four related acetonide derivatives **4** – **7**, most likely artifacts of isolation, together with a known triterpenoid, akebonic acid (**8**), were isolated from the root cortex of *Paeonia veitchii*. Their structures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

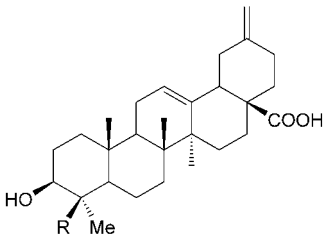
**Results and Discussion.** – Paeonenoide A (**1**), obtained as white amorphous powder, gave a molecular-ion peak at *m/z* 472 in the EI-MS, in accordance with the molecular formula $C_{28}H_{40}O_6$ determined by the HR-EI-MS, which suggested that compound **1** is a dinortriterpenoid. This deduction 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 11$\alpha$,12$\alpha$-epoxyoleanane $\gamma$-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 $\gamma$-lactone (1775 $cm^{-1}$). According to further spectral data, the structure of **1** was determined to be (3$\beta$,4$\beta$,11$\alpha$,12$\alpha$,13$\beta$)-11,12-epoxy-3,4,13,23-tetrahydroxy-24,30-dinorolean-20(29)-en-28-oic acid 28,13-lactone.



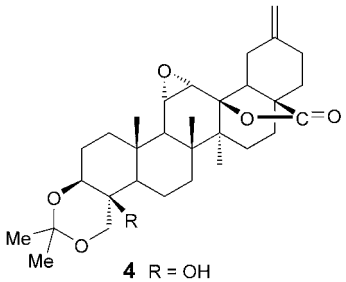

**1**



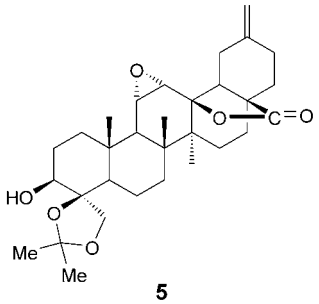

**2**



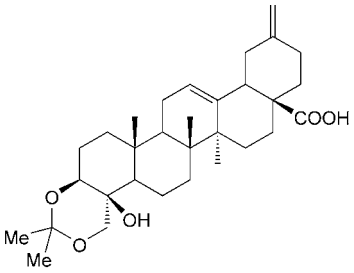

**3** R = OH
**8** R = Me




**4** R = OH
**6** R = Me




**5**




**7**

The presence of the exocyclic $CH_2$ group of **1** was supported by the signals of two olefinic H-atoms at $\delta$ (H) 4.73 (*s*, 1 H) and 4.75 (*s*, 1 H) and an olefinic $CH_2$ at $\delta$ (C) 110.3 in the NMR spectra. The $^1$H- and $^{13}$C-NMR spectra of **1** showed similarities to those of (3$\beta$,11$\alpha$,12$\alpha$,13$\beta$)-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 $\delta$ *ca.* 12 (C(24)) and a quaternary C-atom at $\delta$ *ca.* 43 (C(4)); instead an additional O-bearing quaternary C-atom was present at $\delta$ 74.1. The HMBC experiment showed the expected long-range correlations between the quaternary C-atom at $\delta$ 74.1 and H–C(3) ($\delta$ 3.67 (*dd*, $J$ = 11.2, 5.4 Hz)) and $CH_2$(23) ($\delta$ 3.62 and 3.82 (each *d*, $J$ = 10.8 Hz, each 1 H)). So, the quaternary C-atom at $\delta$ 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 $\beta$-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 (3$\beta$)-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 $CDCl_3$; $\delta$ 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 ($\delta$ 179.6), three olefinic quaternary C-atoms ($\delta$ 154.8, 149.2, and 144.2), one olefinic CH ($\delta$ 123.1), two olefinic $CH_2$ ($\delta$ 102.9 and 107.2), one OCH ($\delta$ 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 $\delta$(C) *ca.* 28 and 16 and in the presence of two additional olefinic C-atoms at $\delta$ 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 $\delta$ 5.69 (*s*, 1 H) and 4.83 (*s*, 1 H) corresponded to the C-atom at $\delta$ 102.9. The HMBC experiment displayed correlations of the signals at $\delta$ 5.69 and 4.83 with those at $\delta$ 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 $\delta$ 4.80 and 4.75 ($CH_2$(29)) and those at $\delta$ 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 $\delta$(C) *ca.* 28 and the presence of an additional O-bearing quaternary C-atom at $\delta$ 75.3. The HMBC experiment showed that the signal at $\delta$ 3.91 (H–C(3)) correlated with $\delta$(C)75.3, and the signal at $\delta$ 1.42 (Me(23)) correlated with $\delta$(C) 75.3, 79.8 (C(3)), and 56.4 (C(5)). Therefore, the quaternary C-atom at $\delta$ 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) ($\delta$ 3.91) and Me(23) ($\delta$ 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 $\delta$(C) 99.3 and two additional tertiary Me groups at $\delta$(H) 1.43 and 1.46 and $\delta$(C) 19.2 and 30.0 was the main difference. The HMBC experiment showed that the acetal C-atom ($\delta$ 99.3) was correlated with $CH_2$(23) ($\delta$ 3.65 and 3.69 (each *d*, *J* = 10.5 Hz, each 1 H), H–C(3) ($\delta$ 3.61 (*dd*, *J* = 11.0, 4.0 Hz)) and two Me groups at $\delta$ 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 $\delta$ 85.0 and 110.6 from $\delta$ 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 ($\delta$ 110.6) and $CH_2$(23) ($\delta$ 3.75 and 4.14 (each *d*, *J* = 8.5 Hz, each 1 H)) and two tertiary Me groups at $\delta$ 1.39 and 1.47, while the correlation between the acetal C-atom and H–C(3) ($\delta$ 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, $H_\alpha$–C(3)); 3.08 (*d*, *J* = 5.0, overlapped, H–C(11), H–C(12)); 2.70 (*t*, *J* = 13.5, $H_\alpha$–C(19)); 2.59 (*dd*, *J* = 13.5, 3.6, $H_\beta$–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, $H_\alpha$–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, $H_\alpha$–C(3)); 3.24 (*dd*, *J* = 11.7, 4.5, H–C(18)); 2.65 (*t*, *J* = 14.9, $H_\beta$–C(19)); 2.33 (overlapped, $H_\alpha$–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, $H_\alpha$–C(3)); 3.22 (*dd*, *J* = 13.5, 4.6, H–C(18)); 2.61 (*t*, *J* = 13.4, $H_\beta$–C(19)); 2.31 (overlapped, $H_\alpha$–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, $H_\alpha$–C(3)); 3.06 (*d*, *J* = 3.8, overlapped, H–C(11), H–C(12)); 2.70 (*t*, *J* = 13.6, $H_\alpha$–C(19)); 2.58 (*dd*, *J* = 13.6, 3.5, $H_\beta$–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, $H_\alpha$–C(3)); 3.04 (br. *s*, overlapped, H–C(11), H–C(12)); 2.68 (*t*, *J* = 13.5, $H_\alpha$–C(19)); 2.55 (*dd*, *J* = 13.5, 3.8, $H_\beta$–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, $H_\alpha$–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, $H_\alpha$–C(19)); 2.58 (*dd*, *J* = 13.5, 3.5, $H_\beta$–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, $H_\alpha$–C(3)); 2.72 (*dd*, *J* = 13.3, 4.4, H–C(18)); 2.51 (*t*, *J* = 13.6, $H_\beta$–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, $H_\alpha$–C(3)); 3.25 (*dd*, *J* = 13.6, 4.7, H–C(18)); 2.64 (*t*, *J* = 13.6, $H_\beta$–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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