# Three New 24-Noroleanane Triterpenoids from *Quercus aliena* var. *acuteserrata*

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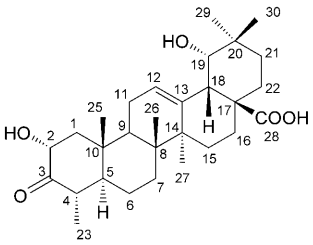
Three new 24-noroleanane triterpenoids, *i.e.*, 2$\alpha$,19$\alpha$-dihydroxy-3-oxo-24-norolean-12-en-28-oic acid (**1**) and 19$\alpha$-hydroxy-3-oxo-24-norolean-12-en-28-oic acid (**2**), and 2$\alpha$,3$\beta$,19$\alpha$-trihydroxy-24-norolean-12-en-28-oic acid (**3**) were isolated from *Quercus aliena* var. *acuteserrata*, together with three known compounds, bartogenic acid (**4**), ilexgenin A (**5**), and aophitolic acid (**6**). Their structures were established by spectroscopic methods, especially 2D-NMR and MS analyses.

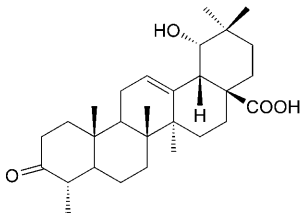
**Introduction.** – The plants of *Quercus aliena* Bl. (Fagaceae) – with its three variations *Q. aliena* Bl. var. *acuteserrata* MAXIM. ex WENZ., var. *pekingensis* SCHOTT. f. *pekingensis*, and var. *pekingensis* SCHOTT. f. *jeholensis* – are widely distributed in China [1], and are commonly used as haemostatic agents in traditional Chinese medicine (TCM) [2]. The acorns of this plant containing rich amylum (55.8%) [1] are eatable in local. A recent study showed that the aqueous extract of *Q. aliena* acorn displays significant superoxide-radical-scavenging activity ($IC_{50}$ = 4.92 μg/ml) as well as hepatoprotective action against $CCl_4$-induced liver injury [3]. In pioneering chemical investigations on *Q. aliena*, a series of tannins [4], two triterpenoids, and a sterol [2] were reported. However, as far as we know, no phytochemical study on *Q. aliena* var. *acuteserrata* has been conducted previously.

In the present work, we report three new 24-noroleanane triterpenoids, *i.e.*, 2$\alpha$,19$\alpha$-dihydroxy-3-oxo-24-norolean-12-en-28-oic acid (**1**), 19$\alpha$-hydroxy-3-oxo-24-norolean-12-en-28-oic acid (**2**), and 2$\alpha$,3$\beta$,19$\alpha$-trihydroxy-24-norolean-12-en-28-oic acid (**3**), along with three known constituents, bartogenic acid (**4**), ilexgenin A (**5**), and aophitolic acid (**6**). These compounds were isolated from the seeds of *Q. aliena* var. *acuteserrata*, and their structures were established by spectroscopic methods, especially 2D-NMR.

**Results and Discussion.** – Compound **1** was isolated as a colorless amorphous powder. The HR-EI mass spectrum indicated the molecular formula $C_{29}H_{44}O_5$ (*m*/*z* 472.3182 ($M^+$; calc. 472.3189)), as corroborated by positive-mode ESI-MS (*m*/*z* 495.3 ($[M+Na]^+$), 967.6 ($[2M+Na]^+$)). A total of 29 signals were observed in the $^{13}$C-NMR spectrum of **1** (*Table 1*), with six Me, eight $CH_2$, six sp$^3$ CH, a trisubstituted C=C ($\delta$(C) 124.7, 142.9), and two C=O groups ($\delta$(C) 213.2, 184.2), as well as five quaternary sp$^3$ C-atoms. The IR spectrum revealed the presence of OH (3521), C=O




**1**

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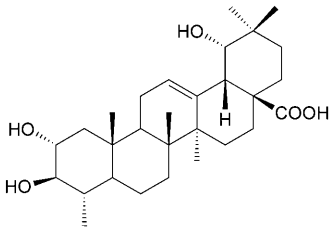


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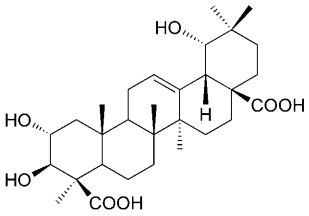


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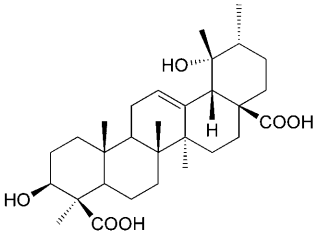
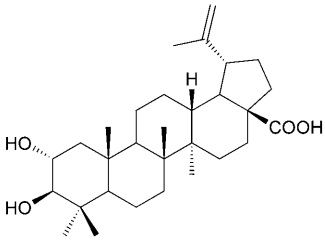



**5**




**6**

Table 1. *[13]C-NMR Data for Compounds* **1**–**3**. At 50 MHz; $\delta$ in ppm.

| Atom | **1**[a]) | **1**[b]) | **2**[a]) | **3**[b]) | Atom | **1**[a]) | **1**[b]) | **2**[a]) | **3**[b]) |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 49.9 | 50.2 | 39.9 | 47.0 | C(16) | 27.4 | 28.0 | 27.4 | 28.4 |
| C(2) | 72.1 | 72.5 | 37.3 | 71.8 | C(17) | 45.2 | 45.8 | 45.2 | 46.0 |
| C(3) | 213.2 | 213.4 | 213.5 | 82.3 | C(18) | 43.4 | 44.6 | 43.4 | 44.9 |
| C(4) | 42.9 | 42.9 | 44.7 | 37.6 | C(19) | 81.5 | 81.0 | 81.5 | 81.8 |
| C(5) | 54.9 | 54.5 | 53.5 | 52.1 | C(20) | 34.7 | 35.4 | 34.6 | 35.7 |
| C(6) | 22.2 | 21.9 | 22.2 | 21.4 | C(21) | 28.0 | 28.8 | 27.9 | 29.2 |
| C(7) | 31.5 | 31.8 | 31.4 | 32.5 | C(22) | 32.4 | 33.3 | 32.4 | 33.6 |
| C(8) | 39.5 | 39.4 | 39.3 | 39.8 | C(23) | 11.2 | 11.3 | 11.5 | 16.0 |
| C(9) | 45.5 | 45.6 | 45.5 | 46.2 | C(25) | 14.4 | 14.0 | 12.9 | 15.1 |
| C(10) | 37.7 | 37.5 | 36.9 | 38.2 | C(26) | 17.3 | 17.3 | 17.1 | 17.7 |
| C(11) | 24.4 | 24.4 | 24.2 | 24.7 | C(27) | 25.0 | 24.5 | 24.9 | 24.8 |
| C(12) | 124.7 | 123.3 | 124.8 | 123.5 | C(28) | 184.2 | 181.1 | 184.3 | 180.9 |
| C(13) | 142.9 | 145.1 | 142.8 | 145.0 | C(29) | 28.0 | 28.5 | 27.9 | 28.8 |
| C(14) | 41.5 | 42.0 | 41.4 | 42.3 | C(30) | 28.0 | 24.4 | 27.9 | 29.1 |
| C(15) | 28.0 | 28.8 | 27.9 | 29.1 | | | | | |

[a]) In $CDCl_3$ solution. [b]) In $C_5D_5N$ solution.

(1720), and COO (1707 $cm^{-1}$) groups. In the $^1$H-NMR spectrum (*Table 2*), five Me *singlet*s ($\delta$(H) 1.22, 1.20, 0.98, 0.97, 0.79) and one Me *doublet* ($\delta$(H) 1.07) were distinguished. These data suggested that **1** is a nortriterpenoid.

A direct comparison of the $^{13}$C-NMR data of **1** (in ($D_6$)pyridine; *Table 1*) with those of the known compound ilexolic acid B [5] indicated that these two compounds have the same rings *B*–*E*, as confirmed by HMBC correlations (*Fig. 1*). In the HMBC spectrum, Me(27) and $CH_2$(11) correlated with an olefinic quaternary C-atom at $\delta$(C) 142.9,

Table 2. *$^1$H-NMR Data for Compounds* **1**–**3**. At 400 and 50 MHz, resp.; $\delta$ in ppm, $J$ in Hz.

| | **1**[a]) | **1**[b]) | **2**[a]) | **3**[b]) |
|---|---|---|---|---|
| $H_\alpha$–C(1) | 1.10–1.16 (*m*) | 1.32–1.37 (*m*) | 1.32–1.37 (*m*) | 1.27–1.30 (*m*) |
| $H_\beta$–C(1) | 2.45–2.51 (*m*) | 2.55 (*dd, J* = 12.4, 7.1) | 1.93–1.97 (*m*) | 2.29 (*dd*, *J* = 12.6, 5.1) |
| $H_\alpha$–C(2) | | | 2.30–2.35 (*m*) | |
| $H_\beta$–C(2) | 4.28 (*dd*, *J* = 11.9, 7.2) | 4.54 (*dd*, *J* = 12.0, 6.9) | 2.46 (*dd*, *J* = 14.1, 6.4) | 4.01–4.14 (*m*) |
| $H_\alpha$–C(3) | | | | 3.32 (*t*, *J* = 9.4) |
| H–C(4) | 2.45–2.51 (*m*) | 2.35–2.43 (*m*) | 2.27–2.33 (*m*) | 1.66–1.70 (*m*) |
| H–C(5) | 1.10–1.16 (*m*) | 1.00–1.05 (*m*) | 1.13–1.16 (*m*) | 0.90–0.91 (*m*) |
| $H_\alpha$–C(6) | 1.53–1.63 (*m*) | 1.42–1.44 (*m*) | 1.59–1.61 (*m*) | 1.59–1.62 (*m*) |
| $H_\beta$–C(6) | 1.53–1.63 (*m*) | 1.44–1.46 (*m*) | 1.28–1.32 (*m*) | 1.05–1.08 (*m*) |
| $H_\alpha$–C(7) | 1.43–1.49 (*m*) | 1.37–1.40 (*m*) | 1.45–1.50 (*m*) | 1.46–1.53 (*m*) |
| $H_\beta$–C(7) | 1.28–1.35 (*m*) | 1.24–1.28 (*m*) | 1.30–1.32 (*m*) | 1.31–1.33 (*m*) |
| H–C(9) | 1.73–1.78 (*m*) | 1.83–1.87 (*m*) | 1.71–1.77 (*m*) | 1.94 (*dd*, *J* = 7.7, 9.7) |
| $CH_2$(11) | 2.10 (*dd*, *J* = 8.6, 2.7) | 2.01–2.24 (*m*) | 2.07 (*dd*, *J* = 9.1, 2.2) | 2.10–2.16 (*m*) |
| H–C(12) | 5.45 (*t*, *J* = 3.4) | 5.55 (*s*) | 5.45 (*s*) | 5.55 (*t*, *J* = 3.3) |
| $H_\alpha$–C(15) | 0.94–0.98 (*m*) | 1.15–1.19 (*m*) | 0.95–0.97 (*m*) | 1.11–1.16 (*m*) |
| $H_\beta$–C(15) | 1.50–1.58 (*m*) | 2.01–2.24 (*m*) | 1.52–1.57 (*m*) | 2.11–2.16 (*m*) |
| $H_\alpha$–C(16) | 2.29 (*td*, *J* = 13.8, 3.7) | 2.83 (*td*, *J* = 13.6, 4.5) | 2.25–2.30 (*m*) | 2.84 (*td*, *J* = 14.1, 3.5) |
| $H_\beta$–C(16) | 1.63–1.71 (*m*) | 2.01–2.24 (*m*) | 1.67–1.69 (*m*) | 2.11–2.15 (*m*) |
| H–C(18) | 3.08 (br. *s*) | 3.63 (br. *s*) | 3.09 (br. *s*) | 3.63 (*s*) |
| H–C(19) | 3.34 (*d*, 3.9) | 3.63 (*s*) | 3.34 (br. *s*) | 3.63 (*s*) |
| $H_\alpha$–C(21) | 1.03–1.10 (*m*) | 1.18–1.25 (*m*) | 1.07–1.12 (*m*) | 1.15–1.20 (*m*) |
| $H_\beta$–C(21) | 1.79–1.83 (*m*) | 2.01–2.24 (*m*) | 1.79–1.85 (*m*) | 2.14–2.20 (*m*) |
| $H_\alpha$–C(22) | 1.63–1.71 (*m*) | 2.01–2.24 (*m*) | 1.72–1.75 (*m*) | 2.02–2.05 (*m*) |
| $H_\beta$–C(22) | 1.79–1.93 (*m*) | 2.01–2.24 (*m*) | 1.78–1.84 (*m*) | 2.14–2.20 (*m*) |
| Me(23) | 1.07 (*d*, *J* = 6.5) | 1.13 (*d*, *J* = 7.2) | 0.99 (*d*, *J* = 6.5) | 1.28 (*d*, *J* = 6.4) |
| Me(25) | 1.20 (*s*) | 1.12 (*s*) | 1.11 (*s*) | 1.20 (*s*) |
| Me(26) | 0.79 (*s*) | 1.08 (*s*) | 0.80 (*s*) | 0.93 (*s*) |
| Me(27) | 1.22 (*s*) | 1.57 (*s*) | 1.25 (*s*) | 1.64 (*s*) |
| Me(29) | 0.98 (*s*) | 1.21 (*s*) | 0.98 (*s*) | 1.12 (*s*) |
| Me(30) | 0.97 (*s*) | 1.13 (*s*) | 0.97 (*s*) | 1.07 (*s*) |

[a]) In $CDCl_3$ solution. [b]) In $C_5D_5N$ solution.

which indicated a trisubstituted C=C bond in 12-position. This was confirmed by the HMBC correlations of H–C(18)/C(12) and H–C(12)/C(11). Further, the HMBC correlations from H–C(18), $CH_2$(16), and $CH_2$(22) to the carbon signal at $\delta$(C) 184.2 suggested that C(28) was part of a COOH group, as further supported by a broad IR band at 3000–2500 $cm^{-1}$. An oxygenated CH ($\delta$(H) 3.34, $\delta$(C) 81.5) was located in 19-position bearing an OH group on the basis of the HMBC correlations between H–C(19) and C(13), C(17), C(20), and C(29), resp. The strong HMBC correlations from the Me group at $\delta$(H) 1.07 to C(3), C(4), and C(5) indicated that it was attached to C(4), which, in turn, suggested that **1** has a 24-noroleanane-type skeleton. As judged from the chemical shift, the remaining C=O group at $\delta$(C) 213.2 was assigned to C(3) on the ground of HMBC correlations of Me(23)/C(3) and $CH_2$(1)/C(3). The mutual HMBC correlations from the $^1$H-NMR signal of an oxygenated CH ($\delta$(H) 4.28, $\delta$(C) 72.1) to both C(3) and C(1), as well as from H–C(4) to this oxygenated CH, indicated an OH function at C(2).

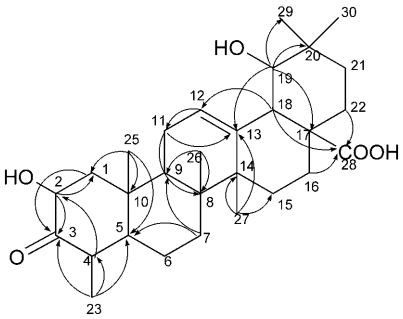



Fig. 1. *Selected HMBC* (H → C) *correlations for* **1**

The relative configuration of **1** was determined by extensive analysis of the $^1$H-NMR (*Table 2*) and ROESY data (*Fig. 2*). The large coupling constant ($J = 11.9$ Hz) between H–C(2) and $H_\alpha$–C(1) clearly indicated that the 2-OH group is in equatorial $\alpha$-position, as further supported by the ROESY correlation of H–C(2)/Me(25). In the ROESY spectrum, H–C(4) correlated with $H_\beta$–C(6) and Me(25), which indicated 1,3-diaxial relationships for H–C(2)/Me(25) and H–C(2)/$H_\beta$–C(6). Thus, the $\beta$-configuration was assigned to H–C(4). The observed ROESY correlations confirmed that the configurations of rings *B*–*E* in **1** were the same as in ilexolic acid B. The *A*–*E* rings of **1** were assigned to be in chair, chair, half-chair, chair, and chair conformations, respectively. The ROESY correlation between $H_\alpha$–C(22) and $H_\alpha$–C(16) indicated that the COOH group (C(28)) was $\beta$-oriented. Finally, H–C(18), correlating with Me(30) and H–C(12) were assigned $\beta$-orientations. Thus, the ROESY correlation of H–C(19)/H–C(18) revealed $\alpha$-configuration for the 19-OH group. From these data, the structure of compound **1** was established.

The molecular formula $C_{29}H_{44}O_4$ for **2**, as determined by HR-EI-MS (*m*/*z* 456.3256 ($M^+$; calc. 456.3240)), showed one O-atom less than that of **1**. The IR absorptions revealed the presence of OH (3458), C=O (1720), and COO (1699 cm$^{-1}$) groups. The broad IR absorption band at 3000–2500 cm$^{-1}$ also indicated the presence of a carboxylic acid. Comparison of the $^1$H- and $^{13}$C-NMR spectra of **1** and **2** (both recorded in $CDCl_3$) indicated closely related structures, the only difference being the absence of the 2-OH function in compound **2**. This structural deduction was confirmed by HMBC

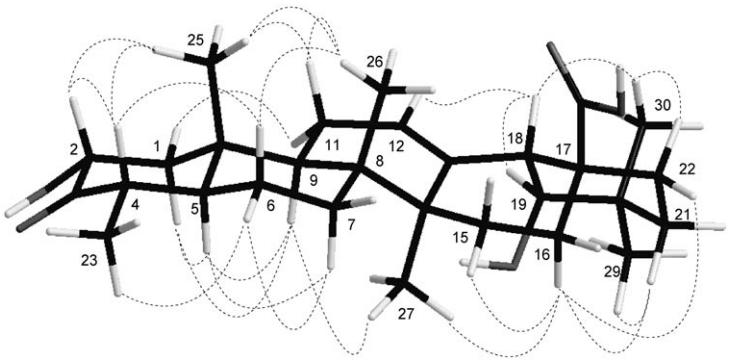



Fig. 2. *Key ROESY correlations* (dashed lines) *for* **1**

experiments (*Fig. 3,a*): two H-atoms of a $CH_2$ unit ($\delta$(H) 2.46, 2.30–2.35) showed strong correlations with C(1), C(3), and C(4), and were, thus, assigned to $CH_2$(2). Complete $^1$H- and $^{13}$C-NMR assignment was achieved on the basis of HSQC, HMBC, and ROESY spectra.

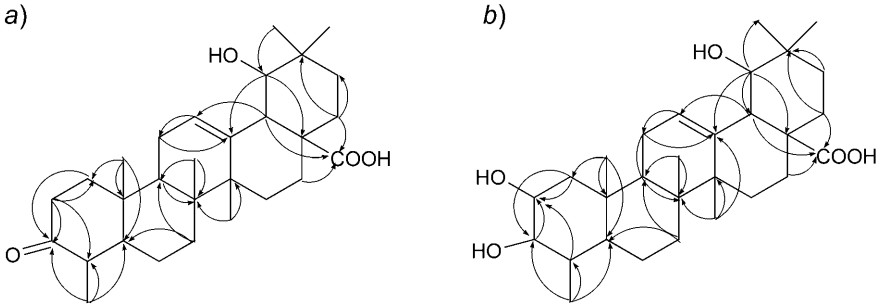



Fig. 3. *Selected HMBC* (H → C) *correlations for* **2** (*a*) *and* **3** (*b*)

Compound **3**, an amorphous solid, was assigned the molecular formula $C_{29}H_{46}O_5$, as determined by HR-EI-MS (*m*/*z* 474.3358 ($M^+$; calc. 474.3345)). Again, the IR spectrum revealed OH (3446), C=O (1697), and COOH (3000–2500 cm$^{-1}$) groups. Comparison of the $^1$H- and $^{13}$C-NMR data of **3** (spectra recorded in ($D_5$)pyridine) with those of **1** (same solvent) indicated very similar structures, the only difference being a 3-OH group ($\delta$(C) 82.3, $\delta$(H) 3.32) in **3** replacing the C=O function ($\delta$(C) 213.2) in **1**. The presence of HO–C(3) was further confirmed by the HMBC correlations of H–C(3)/C(5), H–C(1)/C(3), and Me(23)/C(3) (*Fig. 3,b*) . The relative configuration and conformation of **3** were established by ROESY analyses (*Fig. 4*). The ROESY cross-peaks from H–C(3) to Me(23) and H–C(5) indicated 1,3-diaxial relationships for H–C(3)/Me(23) and H–C(3)/H–C(5), suggesting that the 3-OH group is $\beta$-configured. From these data, the structure of **3** was established.

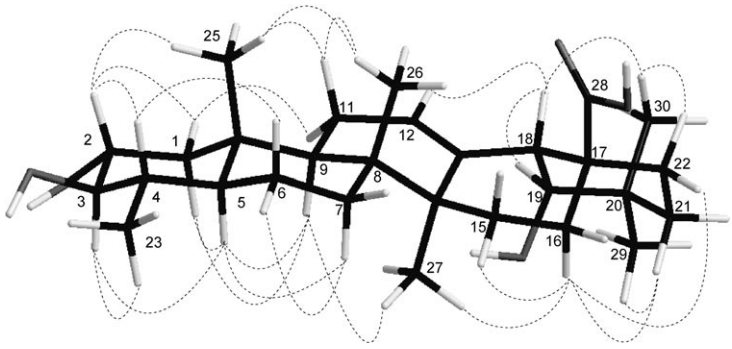



Fig. 4. *Key ROESY correlations* (dashed lines) *for* **3**

The three known compounds, bartogenic acid (**4**) [6], ilexgenin A (**5**) [7], and aophitolic acid (**6**) [8] were identified by comparison of their $^1$H- and $^{13}$C-NMR as well as MS data with those reported in the literature.

## Experimental Part

*General*. All solvents used were of anal. grade (*Shanghai Chemical Plant*, Shanghai, P. R. China.). Column chromatography (CC): silica gel (200–300 mesh), silica gel *H60*, *$C_{18}$* reverse-phase (RP) silica gel (250 mesh; *Merck*), or *MCI CHP20P* gel (75–150 μm; *Mitsubishi Chemical Industries, Ltd.*). Optical rotation: *Perkin-Elmer 341* polarimeter. IR spectra: *Perkin-Elmer 577* spectrometer; in $cm^{-1}$. NMR spectra: *Bruker AM-400* spectrometer; $\delta$ in ppm rel. to $Me_4Si$, *J* in Hz. EI-MS (70 eV) and ESI-MS: *Finnigan MAT 95* and *Finnigan LCQ-DECA* instruments, resp.; in *m*/*z* (rel. %).

*Plant Material.* The seeds of *Quercus aliena* Bl. were collected in September 2004 in Shanxi Province, Qinling Mountains, P. R. China. The plant material was authenticated by Prof. *Xiao-An Wang*, School of Biology, Shanxi Normal University. A voucher specimen (No. QA-var-A-2004-1Y) has been deposited at the Shanghai Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences, P. R. China.

*Extraction and Isolation*. The powdered seeds of *Q. aliena* var. *acuteserrata* MAXIM. ex WENZ. (2 kg) were percolated with 95% EtOH. Removal of the solvent under reduced pressure gave rise to a crude extract (280 g), which was purified by CC ($SiO_2$; petroleum ether (PE)/$Me_2CO$ 50:1 → 0:1): fractions *Fr. A–D*. *Fr. A* (1.5 g) was separated by CC ($SiO_2$; PE/AcOEt 2:1) to afford **1** (40 mg). *Fr. B* (20 g) was purified by CC ($SiO_2$; PE/AcOEt 15:1 → 4:1): *Fr. B.1* and *Fr. B.2*. The latter fraction (1.5 g) was separated by CC ($SiO_2$; $CHCl_3$/MeOH 100:1), and the resulting major component was further purified on *Sephadex LH-20* eluting with MeOH/$H_2O$ 8:2 to afford **2** (22 mg). *Fr. C* (5.5 g) was purified by CC (*RP-18*; 80% MeOH in $H_2O$) to give one major fraction, which was further separated by CC ($SiO_2$; PE/AcOEt 3:1 → 1:1): *Fr. C.1* and *Fr. C.2*. *Fr. C.1* (1.2 g) was purified by CC ($SiO_2$; PE/AcOEt 1:1) to afford **4** (840 mg). *Fr. D* (20 g) was purified by CC ($SiO_2$; PE/AcOEt 2:1 → 1:1): *Fr. D.1* and *Fr. D.2*. *Fr. D.1* (100 mg) was further purified on *Sephadex LH-20* eluting with MeOH to afford **3** (32 mg). *Fr. D.2* (3 g) was also separated on *Sephadex LH-20* (70–90% MeOH in $H_2O$) to obtain two major subfractions, *Fr. D.2.1* and *Fr. D.2.2*. The former (50 mg) was resubjected to CC (*Sephadex LH-20*, MeOH) to afford **6** (20 mg). *Fr. D.2.2* (100 mg) was purified by CC (*RP-18*; 80% MeOH in $H_2O$) to afford **5** (15 mg).

*(2α,19α)-2,19-Dihydroxy-3-oxo-24-norolean-12-en-28-oic Acid* (**1**). Colorless powder. M.p. 212–213°. $[\alpha]_D^{23} = +75.6$ ($c = 0.64$, $CHCl_3$). IR (KBr): 3521, 3396, 2939, 2875, 1720, 1707, 1454, 1389, 1340, 1263, 1173, 1101, 1030, 978, 725. $^1$H- and $^{13}$C-NMR: see *Tables 2* and *1*, resp. ESI-MS (pos.): 967.6 ($[2M+Na]^+$), 495.3 ($[M+Na]^+$). ESI-MS (neg.): 966.5 ($[2M+Na-H]^-$), 471.2 ($[M-H]^-$). EI-MS: 472 (2, $M^+$), 426 (6), 354 (7), 264 (52), 246 (62), 231 (56), 219 (17), 201 (100), 185 (32), 159 (9), 145 (15), 131 (33), 119 (26), 91 (16), 79 (10), 55 (12). HR-EI-MS: 472.3182 ($M^+$, $C_{29}H_{44}O_5^+$; calc. 472.3189).

*(19α)-19-Hydroxy-3-oxo-24-norolean-12-en-28-oic Acid* (**2**). Colorless powder. M.p. 171–172°. $[\alpha]_D^{20} = +44.2$ ($c = 0.16$, $CHCl_3$). IR (KBr): 3458, 2937, 2873, 1699, 1454, 1387, 1171, 1067, 756. $^1$H- and $^{13}$C-NMR: see *Tables 2* and *1*, resp. EI-MS: 456 (10, $M^+$), 264 (68), 246 (70), 231 (50), 219 (13), 201 (100), 185 (18), 146 (19), 131 (27), 119 (23), 105 (16), 81(16), 55(16). HR-EI-MS: 456.3256 ($M^+$, $C_{29}H_{44}O_4^+$; calc. 456.3240).

*(2α,3β,19α)-2,3,19-Trihydroxy-24-norolean-12-en-28-oic Acid* (**3**). Colorless powder. M.p. 195–196°. $[\alpha]_D^{20} = +16.6$ ($c = 0.54$, $C_5H_5N$). IR (KBr): 3446, 2943, 2870, 1697, 1551, 1454, 1387, 1211, 1043, 974, 760. $^1$H- and $^{13}$C-NMR: see *Tables 2* and *1*, resp. EI-MS: 474 (6, $M^+$), 264 (66), 456 (21), 264 (70), 246 (79), 231 (54), 219 (16), 201 (100), 185 (22), 131 (22), 119 (16), 105 (11), 81 (10), 55 (14). HR-EI-MS: 474.3358 ($M^+$, $C_{29}H_{46}O_5^+$; calc. 474.3345).

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