# Phenolic and Triterpenoid Glycosides from *Pyrola calliantha*

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Pyrocallianthasides A (**1**) and B (**2**), a new dimer and a new mono-deglucosyl trimer of homoarbutin (=4-hydroxy-3-methylphenyl $\beta$-glucopyranoside), and callianthaside A (**3**), a new ursane-type triterpene glycoside, together with three known phenolic glycosides and three known ursane-type triterpenoids, were isolated from the whole plants of *Pyrola calliantha*. The structures of **1**–**3** were elucidated by chemical and spectroscopic methods.

**Introduction.** – As a traditional Chinese medicine, *Pyrola calliantha* H. Andr. (Pyrolaceae) has been used for the treatment of rheumatoid arthritis and gastric or pulmonary hemorrhage [1]. In previous studies on this plant, several compounds were obtained from its AcOEt extract, including homoarbutin, renifolin, hyperin and its glycosides [2], hydroxylrenifolin, ursolic acid [3], chimaphilin, and quercetin [4]. Our phytochemical investigation of the 50% EtOH extract of the title plant led to the isolation of nine compounds, comprising two new phenolic glycosides, *i.e.*, pyrocallianthasides A (**1**) and B (**2**), a new triterpenoid glycoside, *i.e.*, callianthaside A (**3**), and six known compounds, *i.e.*, homoarbutin and isohomoarbutin [5], pyrolaside A [6], asiatic acid [7], ($2\alpha$,$3\beta$)-2,3,23,24-tetrahydroxyurs-12-en-28-oic acid [8], and ($2\alpha$,$3\beta$,$4\alpha$,$19\alpha$)-2,3,19,23-tetrahydroxyurs-12-en-28-oic acid $\beta$-glucopyranosyl ester [9]. In this paper, we report the isolation and structural elucidation of **1**–**3**.

**Results and Discussion.** – Pyrocallianthaside A[1]) (**1**) was obtained as white amorphous powder. Its HR-ESI-MS showed a quasi-molecular-ion peak $[M+Na]^+$ at $m/z$ 593.1841, in accord with the molecular formula $C_{26}H_{34}O_{14}$. The acid-hydrolysis experiment gave glucose as the sugar moiety. The $^1$H-NMR spectrum (*Table 1*) revealed two individual $\beta$-glucopyranosyl groups in the molecule of **1**. The detailed NMR studies and biogenetic considerations allowed us to elucidate the structure of **1** as 4-*O*,5′-didehydrobis[4-hydroxy-3-methylphenyl $\beta$-glucopyranoside].

The $^1$H-NMR spectrum of **1** displayed signals for a 1,3,4-trisubstituted aromatic ring ($\delta$ 6.96 (*d*, $J$ = 3.0 Hz, H−C(2)), 6.78 (*d*, $J$ = 9.0 Hz, H−C(5)), and 6.86 (*dd*, $J$ = 9.0, 3.0 Hz, H−C(6)), a 1,3,4,5-tetrasubstituted aromatic ring ($\delta$ 6.54 and 6.03, each *d*, $J$ = 2.4 Hz, H−C(2′) and H−C(6′)), two Me groups ($\delta$ 2.12 and 2.14 (each *s*)), and two glucopyranose moieties ($\delta$ 4.77 (*d*, $J$ = 4.77 Hz) and 4.53 (*d*, $J$ = 7.8 Hz)). In the $^{13}$C-NMR spectrum of **1** (*Table 1*), twelve aromatic C-atoms (5 CH and 7 C), two Me

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

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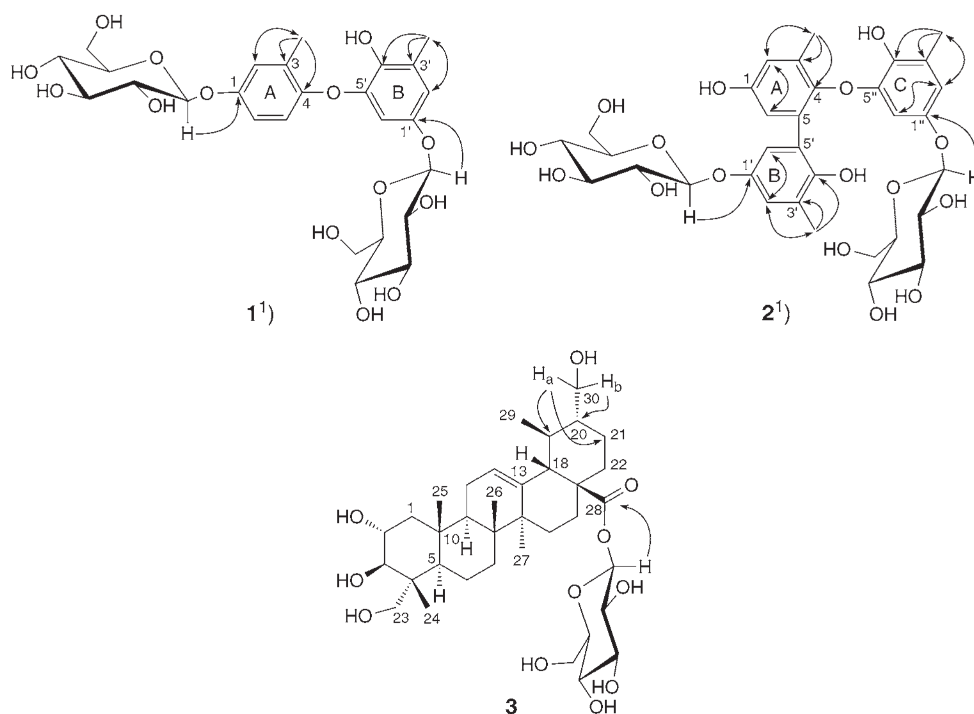


Figure. *Key HMBC correlations* (H → C) *and structures of* **1**–**3**

groups, and two $\beta$-glucopyranose units were observed. The above NMR evidences indicated **1** to be a homoarbutin (=4-hydroxy-3-methylphenyl $\beta$-D-glucopyranoside) dimer. The HMQC and HMBC (*Figure*) experiments allowed to unambiguously assign all $^{1}$H- and $^{13}$C-NMR signals of the two homoarbutin units. The linkage position of the dimer was suggested at 4-*O*,5′ on the basis of biogenetic consideration (assuming that **1** was biosynthesized through OH–C(4) of unit A attacking C(5′) of ring B), and which was also supported by the chemical shift of C(4) ($\delta$ 148.6), C(5′) ($\delta$ 145.7) and C(4′) ($\delta$ 139.9).

Pyrocallianthaside B[1]) (**2**) was obtained as white amorphous powder. The HR-ESI-MS gave the molecular formula $C_{33}H_{40}O_{16}$ ($[M+Na]^{+}$ at *m/z* 715.2209). The acid hydrolysis and HPLC analysis, as well as the $^{1}$H- and $^{13}$C-NMR data (*Table 1*) indicated the presence of two individual $\beta$-glucopyranose moieties. Further NMR data and biogenetic considerations concluded the structure of **2** to be 1-*O*-de($\beta$-glucopyranosyl)pyrolaside B.

The $^{1}$H-NMR spectrum of **2** exhibited six *d* of aromatic protons ($\delta$ 6.73, 6.64, 6.76, 6.70, 6.41, and 6.04), and three *s* of Me groups ($\delta$ 2.18, 2.11, and 2.09) for the aglycone, demonstrating a mono-deglucosylated homoarbutin trimer, which was consistent with the $^{13}$C-NMR data (18 sp$^{2}$ C-atoms and 3 Me) for the aglycone. The two $\beta$-glucopyranose units were established by the anomeric-proton signals at $\delta$ 4.52 (*d*, $J=7.8$ Hz) and 4.54 (*d*, $J=7.8$ Hz). The HMBC analysis (*Figure*) elucidated the assignments of the $^{1}$H- and $^{13}$C-NMR signals for the three phenolic units; however, no significant HMBC correlations among the three fragments were observed. The linkage between rings A and B was deduced to be C(5)–C(5′) based on two quaternary C-signals at $\delta$ 128.0 and 134.5. Two deshielded $^{13}$C signals at $\delta$ 144.5

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1** *and* **2**[1]). $\delta$ in ppm, $J$ in Hz.

| | **1** ((D$_6$)DMSO) | | **2** (CD$_3$OD) | |
|---|---|---|---|---|
| | $\delta$(H) | $\delta$(C) | $\delta$(H) | $\delta$(C) |
| C(1) | – | 153.9 | – | 155.6 |
| H–C(2) | 6.96 (*d*, $J$ = 3.0) | 119.2 | 6.73 (*d*, $J$ = 2.8) | 118.4 |
| C(3) | – | 130.4 | – | 134.0 |
| C(4) | – | 148.6 | – | 144.5 |
| H–C(5) or C(5) | 6.78 (*d*, $J$ = 9.0) | 120.4 | – | 128.0 |
| H–C(6) | 6.86 (*dd*, $J$ = 9.0, 3.0) | 115.0 | 6.64 (*d*, $J$ = 2.8) | 116.9 |
| Me–C(3) | 2.12 (*s*) | 16.1 | 2.11 (*s*) | 16.7 |
| C(1′) | – | 149.9 | – | 152.0 |
| H–C(2′) | 6.54 (*d*, $J$ = 2.4) | 112.2 | 6.76 (*d*, $J$ = 2.4) | 121.0 |
| C(3′) | – | 126.1 | – | 128.2 |
| C(4′) | – | 139.9 | – | 148.0 |
| C(5′) | – | 145.7 | – | 134.5 |
| H–C(6′) | 6.03 (*d*, $J$ = 2.4) | 103.6 | 6.70 (*d*, $J$ = 2.4) | 118.0 |
| Me–C(3′) | 2.14 (*s*) | 16.5 | 2.18 (*s*) | 17.0 |
| C(1″) | – | – | – | 151.5 |
| H–C(2″) | | | 6.41 (*d*, $J$ = 2.4) | 113.1 |
| C(3″) | | | – | 126.2 |
| C(4″) | | | – | 140.5 |
| C(5″) | | | – | 147.2 |
| H–C(6″) | | | 6.04 (*d*, $J$ = 2.4) | 102.8 |
| Me–C(3″) | | | 2.09 (*s*) | 16.1 |
| Glc-1[a]): | | | | |
| H–C(1) | 4.77 (*d*, $J$ = 7.8) | 101.2 | 4.52 (*d*, $J$ = 7.8) | 103.9 |
| H–C(2) | 3.30–3.33 (*m*) | 76.9 | 3.31–3.33 (*m*) | 77.7 |
| H–C(3) | 3.19–3.22 (*m*) | 73.3 | 3.34–3.36 (*m*) | 74.8 |
| H–C(4) | 3.27–3.30 (*m*) | 69.6 | 3.39–3.41 (*m*) | 71.0 |
| H–C(5) | 3.11–3.13 (*m*) | 77.0 | 3.44–3.46 (*m*) | 77.8 |
| CH$_2$(6) | 3.43–3.46 (*m*), 3.57 (*dd*, $J$ = 12.0, 1.8) | 60.6 | 3.63–3.67 (*m*), 3.81 (*d*, $J$ = 11.4) | 62.5 |
| Glc-2[a]): | | | | |
| H–C(1) | 4.53 (*d*, $J$ = 7.8) | 101.6 | 4.54 (*d*, $J$ = 7.8) | 103.2 |
| H–C(2) | 3.24–3.27 (*m*) | 76.4 | 3.22–3.24 (*m*) | 77.6 |
| H–C(3) | 3.07–3.09 (*m*) | 73.2 | 3.29–3.31 (*m*) | 74.9 |
| H–C(4) | 3.13–3.15 (*m*) | 69.8 | 3.24–3.26 (*m*) | 71.4 |
| H–C(5) | 3.14–3.16 (*m*) | 76.5 | 3.38–3.40 (*m*) | 77.8 |
| CH$_2$(6) | 3.38–3.42 (*m*), 3.68 (*dd*, $J$ = 12.0, 1.8) | 60.7 | 3.67–3.69 (*m*), 3.70 (*dd*, $J$ = 12.6, 2.4) | 62.1 |

[a]) ^{1}H and [13]C Assignments may be interchanged for the corresponding sites of both glucosyl moieties.

(C(4)) and 147.2 (C(5″)) in rings A and C suggested the presence of a C(4)–*O*–C(5″) moiety. Such a structure was very similar to that of pyrolaside B [6]. The most important difference of the ^{13}C-NMR data between **2** and pyrolaside B was that the latter had additional glucose signals. Therefore, the structure of **2** was determined to be 1-*O*-de($\beta$-glucopyranosyl)pyrolaside B.

Callianthaside A (**3**), obtained as colorless amorphous powder, was shown to have the molecular formula $C_{36}H_{58}O_{11}$ based on the HR-ESI-MS ($[M+Na]^+$ at $m/z$

689.3871). The structure of **3** was established to be (2$\alpha$,3$\beta$,4$\alpha$)-2,3,23,30-tetrahydroxyurs-12-en-28-oic acid $\beta$-glucopyranosyl ester by NMR studies (*Table 2*), acid hydrolysis, and HPLC analysis.

Table 2. *$^1$H- and $^{13}$C-NMR Data* ($CD_3OD$) *of* **3**. $\delta$ in ppm, $J$ in Hz.

| | $\delta$(H) | $\delta$(C) | | $\delta$(H) | $\delta$(C) |
|---|---|---|---|---|---|
| $CH_2$(1) | 1.95–1.97 (*m*), 0.88–0.90 (*m*) | 48.1 | $CH_2$(21) | 1.49–1.52 (*m*), 1.64–1.67 (*m*) | 25.9 |
| H–C(2) | 3.67–3.69 (*m*) | 69.7 | $CH_2$(22) | 1.60–1.61 (*m*), 1.78–1.82 (*m*) | 37.3 |
| H–C(3) | 3.35–3.36 (*m*) | 78.3 | | | |
| C(4) | – | 44.1 | $CH_2$(23) | 3.25 (*d*, $J$ = 11.4), 3.49 (*d*, $J$ = 11.4) | 66.4 |
| H–C(5) | 1.26 (br. *s*) | 48.3 | | | |
| $CH_2$(6) | 0.79–0.81 (*m*) | 19.1 | Me(24) | 0.69 (*s*) | 13.9 |
| $CH_2$(7) | 1.28–1.30 (*m*), 1.59–1.63 (*m*) | 33.7 | Me(25) | 1.04 (*s*) | 18.0 |
| | | | Me(26) | 0.84 (*s*) | 17.8 |
| C(8) | – | 41.0 | Me(27) | 1.13 (*s*) | 24.0 |
| H–C(9) | 3.32–3.33 (*m*) | 49.0 | C(28) | – | 177.9 |
| C(10) | – | 39.0 | Me(29) | 0.91 (*d*, $J$ = 6.4) | 17.1 |
| $CH_2$(11) | 1.96–1.98 (*m*) | 24.5 | $CH_2$(30) | 3.51–3.54 (*m*), 3.64 (*dd*, $J$ = 10.8, 3.0) | 65.9 |
| H–C(12) | 5.32 (br. *s*) | 127.3 | | | |
| C(13) | – | 139.1 | Glc: | | |
| C(14) | – | 43.4 | H–C(1) | 5.34 (*d*, $J$ = 7.8) | 95.7 |
| $CH_2$(15) | 1.25–1.28 (*m*) | 29.2 | H–C(2) | 3.32–3.34 (*m*) | 78.6 |
| $CH_2$(16) | 1.73–1.75 (*m*) | 25.2 | H–C(3) | 3.30–3.33 (*m*) | 71.2 |
| C(17) | – | 49.5 | H–C(4) | 3.37–3.40 (*m*) | 78.3 |
| H–C(18) | 2.27 (*d*, $J$ = 11.6) | 54.1 | H–C(5) | 3.28–3.30 (*m*) | 73.9 |
| H–C(19) | 1.67–1.68 (*m*) | 34.4 | $CH_2$(6) | 3.79 (*dd*, $J$ = 12.0, 1.8), 3.64–3.67 (*m*) | 62.5 |
| H–C(20) | 0.90–1.03 (*m*) | 47.6 | | | |

The $^1$H- and $^{13}$C-NMR spectra, together with acid hydrolysis and HPLC analysis, showed the presence of a $\beta$-glucopyranose in the molecule of **3** ($\delta$(H) 5.34 (*d*, $J$ = 7.8 Hz)). The $^1$H-NMR spectrum displayed four Me *s* at $\delta$ (H) 0.69, 0.84, 1.04, and 1.13, one Me *d* at $\delta$ (H) 0.91 ($J$ = 6.4 Hz), and an olefinic proton at $\delta$ (H) 5.32 (br. *s*, H–C(12)) for the aglycone. The $^{13}$C-NMR spectrum displayed 30 C-signals (5 Me, 10 $CH_2$, 8 CH, and 7 C), including the diagnostic C=O group ($\delta$(C) 177.9) and C=C bond ($\delta$(C) 127.3 and 139.1) for the aglycone. The above-mentioned evidences indicated a ursane-type triterpene glycoside. The $^1$H- and $^{13}$C-NMR data of **3** were nearly superposed with those of quadranoside IV (=(2$\alpha$,3$\beta$,4$\alpha$)-2,3,23-trihydroxyurs-12-en-28-oic acid $\beta$-glucopyranosyl ester) [10], except for one $CH_2$ ($\delta$ (C) 65.9; $\delta$ (H) 3.53 and 3.64) in **3** replacing the Me–C(20) of quadranoside IV, demonstrating **3** to be 30-hydroxylated quadranoside IV. The assumption was supported by the HMBC cross-peaks $H_a$–C(30)/C(19) and C(21), and $H_b$–C(30)/C(20) (*Figure*). The relative configuration of **3** was established to be the same as that of quadranoside IV, based on the similar NMR data.

## Experimental Part

*General*. Column chromatography (CC): silica gel (200–300 mesh; *Qingdao Haiyang, Co.*, China), *D1400* macroporous resin (*Yangzhou Pharmaceutical Factory,* China), *Sephadex LH-20* (*Pharmacia Biotech AB*, Uppsala, Sweden), *MCI* gel *CHP-20P* (*Mitsubishi Chemical Industries Co., Ltd.*, Japan),

and *ODS-A* gel (*Greenberbs Science & Technology Development Co., Ltd.*, Beijing, China); percentage *v*/*v*. TLC: silica gel $HSGF_{254}$ (*Yantai Jiangyou Guijiao Kaifa Co.*, China). HPLC: *Waters* HPLC system, *Waters-51-HPLC* pump, *PL-ELS-1000* detector; column *Prevail Carbohydrate ES 5μ* (5 μm, i.d. 4.6 × 250 mm). Optical rotation: *Perkin-Elmer 341* polarimeter. UV Spectra: *Shimadzu UV-240* spectrometer; $\lambda_{max}$ (log $\varepsilon$) in nm. IR Spectra: *Nicolet Magna-750-FTIR* spectrometer; KBr pellets; in $cm^{-1}$. NMR Spectra: *Bruker AV-400* instrument; at 400 ($^1H$) and 100 MHz ($^{13}C$); in $CD_3OD$ or ($D_6$)DMSO solns.; $\delta$ in ppm rel. to $SiMe_4$, *J* in Hz. ESI-MS and HR-ESI-MS: *Finnigan LCQ-Deca* and *Waters/Micromass Q-Tof-Ultima* mass spectrometers, resp.; in *m*/*z* (rel. int.).

*Plant Material.* The fresh whole plant of *Pyrola calliantha* (Pyrolaceae) was collected in Taibai County of Shanxi Province, P. R. China, in February 2006. The plant was identified by Prof. *D. Y. Zhu*. A voucher specimen (No. 0077) was deposited in our laboratory.

*Extraction and Isolation.* The dry whole herbs of *P. calliantha* (10 kg) were extracted with 50% EtOH (20 l) for 3 days at r.t. and for three times. The concentrated extract was subjected to CC (*D1400* macroporous resin, 10 × 65 cm column; $H_2O$, then 20, 40, 60% EtOH). The 20% EtOH fraction (78 g) was subjected to CC ($SiO_2$ (2.0 kg), $CHCl_3$/MeOH 30 : 1, 20 : 1, 15 : 1, 10 : 1, 8 : 1, 6 : 1, 4 : 1, 7 : 3, and 1 : 1): *Fr. 1–9. Fr. 8* was subjected to CC (*MCI* gel *CHP-20P*, $H_2O$, then 10, 20, 30, 40, 50, and 60% MeOH): *Fr. 8.1–8.7.* From *Fr. 8.3*, **1** (35 mg) and pyrolaside A (12 mg) were obtained, after two CC (1. *Sephadex LH-20*, $H_2O$; 2. *LiChrospher RP-C18*, 20 and 30% MeOH/$H_2O$). From *Fr. 8.4*, **2** (16 mg) was obtained, after two CC (1. *Sephadex LH-20*, $H_2O$; 2. *LiChrospher RP-C18*, 25% MeOH/$H_2O$). The 40% EtOH fraction (60 g) was subjected to CC ($SiO_2$ (2.0 kg), $CHCl_3$/MeOH 30 : 1, 20 : 1, 15 : 1, 10 : 1, 5 : 1, 5 : 2, 5 : 3, 5 : 4, and 1 : 1): *Fr. A–Fr. I.* Then *Fr. G* was subjected to CC (*LiChrospher RP-C18*, $H_2O$, then 10, 20, 30, 40, 50, 60, 70, and 80% MeOH): *Fr. G.1–G.9. Fr. G.4* was subjected to CC (*Sephadex LH-20*, $H_2O$): *Fr. G.4a–G.4f.* From *Fr. G.4d*, **3** (8 mg) was obtained and purified by CC (*LiChrospher RP-C18*, 30% MeOH/$H_2O$). From *Fr. G.5*, (2$\alpha$,3$\beta$,4$\alpha$,19$\alpha$)-2,3,19,23-tetrahydroxyurs-12-en-28-oic acid $\beta$-glucopyranosyl ester (20 mg) was obtained, after two CC (1. *Sephadex LH-20*, $H_2O$; 2. *LiChrospher RP-C18*, 40% MeOH/$H_2O$). The 60% EtOH fraction (13 g) was subjected to CC ($SiO_2$ (0.5 kg), $CHCl_3$/MeOH 40 : 1, 30 : 1, 20 : 1, 10 : 1, 5 : 1, and 1 : 1): *Fr. I–Fr. VI. Fr. III* was subjected to CC (*Sephadex LH-20*, $H_2O$): *Fr. III.1–III.7.* From *Fr. III.4*, homoarbutin (60 mg) and isohomoarbutin (40 mg) were obtained, after CC (*LiChrospher RP-C18*, 10, and 20% MeOH/$H_2O$). From *Fr. III.5*, asiatic acid (10 mg) and (2$\alpha$,3$\beta$)-2,3,23,24-tetrahydroxyurs-12-en-28-oic acid (13 mg) were obtained, after CC (*LiChrospher RP-C18*, 30, and 40% MeOH/$H_2O$).

*Pyrocallianthaside A* (*=4-*O*,5′-Didehydrobis[4-hydroxy-3-methylphenyl β-Glucopyranoside]=4-[5-(β-Glucopyranosyloxy)-2-hydroxy-3-methylphenoxy]-3-methylphenyl β-Glucopyranoside*; **1**): White amorphous powder. $[\alpha]_D^{25} = -47.8$ ($c = 0.450$, MeOH). UV (MeOH): 202 (3.20), 283 (3.65). IR: 3473, 2891, 1630, 1606, 1497, 1365, 1202, 1101, 1070, 1016. $^1H$- and $^{13}C$-NMR: *Table 1.* ESI-MS (pos.): 593.1 ($[M+Na]^+$). ESI-MS (neg.): 569.3 ($[M-H]^-$). HR-ESI-MS: 593.1841 ($[M+Na]^+$, $C_{26}H_{34}NaO_{14}^+$; calc. 593.1846).

*Pyrocallianthaside B* (*=1-*O*-De(β-glucopyranosyl)pyrolaside B=1-*O*-De(β-glucopyranosyl)-5,5′:4-*O*,5″-tetradehydrotris[4-hydroxy-3-methylphenyl β-Glucopyranoside]=3-{[5′-(β-*D*-Glucopyranosyloxy)-2′,5-dihydroxy-3,3′-dimethyl[1,1′-biphenyl]-2-yl]oxy}-4-hydroxy-5-methylphenyl β-Glucopyranoside*; **2**): White amorphous powder. $[\alpha]_D^{25} = -53$ ($c = 0.175$, MeOH). UV (MeOH): 205 (4.17), 288 (4.00). IR: 2924, 1624, 1601, 1497, 1427, 1356, 1196, 1072, 1032. $^1H$- and $^{13}C$-NMR: *Table 1.* ESI-MS (pos.): 715.1 ($[M+Na]^+$). ESI-MS (neg.): 691.3 ($[M-H]^-$), 1383.6 ($[2M-H]^-$). HR-ESI-MS: 715.2209 ($[M+Na]^+$, $C_{33}H_{40}NaO_{16}^+$; calc. 715.2214).

*Callianthaside A* (*=(2α,3β,4α)-2,3,23,30-Tetrahydroxyurs-12-en-28-oic Acid β-Glucopyranosyl Ester*; **3**): White amorphous powder. $[\alpha]_D^{25} = +34$ ($c = 0.200$, MeOH). IR: 3421, 2921, 2875, 1736, 1637, 1460, 1385, 1074, 1051. $^1H$- and $^{13}C$-NMR: *Table 2.* ESI-MS (pos.): 689.3 ($[M+Na]^+$). ESI-MS (neg.): 711.5 ($[M-COOH]^-$). HR-ESI-MS: 689.3871 ($[M+Na]^+$, $C_{36}H_{58}NaO_{11}^+$; calc. 689.3877).

*Acid Hydrolysis of* **1**–**3**. Each sample (2 mg) was treated with 2N aq. HCl at 90° for 4 h. The mixture was neutralized with $NaHCO_3$, then extracted with BuOH. The aq. soln. was analyzed by ELSD-HPLC (column *Prevail Carbohydrate ES 5μ* (5 μm, i.d. 4.6 × 250 mm), 80% MeCN/$H_2O$, flow rate 1.0 ml/min, r.t.). Glucose (standard, $t_R$ 17.5 min; **1**, $t_R$ 17.3 min; **2**, $t_R$ 17.4 min; **3**, $t_R$ 17.5 min) was detected from **1**–**3**.

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