Triterpenoids and Saponins from the Leaves of *Uncaria hirsuta*

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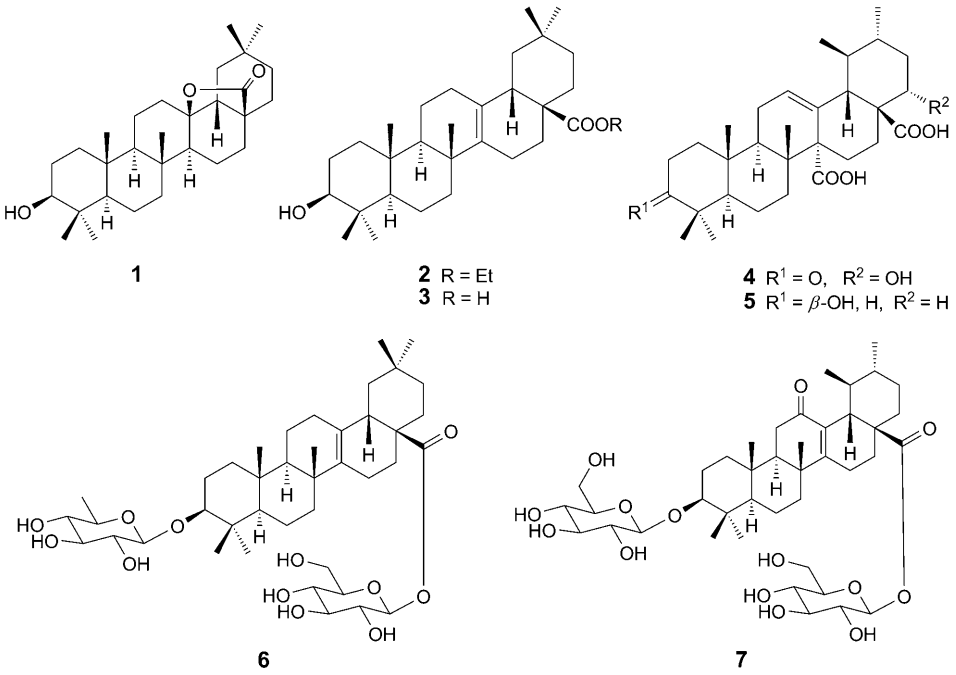
Three new triterpenoids, (3β)-3-hydroxy-27-noroleano-13(28)-lactone (**1**), (22α)-22-hydroxy-3-oxo-urs-12-ene-27,28-dioic acid (**4**), and (3β)-3-(β-D-glucopyranosyloxy)-12-oxopyroquinovic acid β-D-glucopyranosyl ester (**7**), together with four known compounds, pyrocincholic acid ethyl ester (**2**), pyrocincholic acid (**3**), quinovic acid (**5**), and (3β)-3-(β-D-quinovopyranosyloxy)pyrocincholic acid β-D-glucopyranosyl ester (**6**), were isolated from the EtOH extract of the leaves of *Uncaria hirsuta* HAVILAND. Their structures were determined by means of spectroscopic analyses, including HR-ESI-MS and 2D-NMR techniques. The configuration of **1** was confirmed by X-ray analysis; **2** is an artefact, as verified by the HPLC and LC/MS analysis.

Introduction. – *Uncaria hirsuta* HAVILAND (family Rubiaceae) grows wild in southern China, mainly in the Guangxi Zhuang Autonomous Region. The leaves of this plant are used as a folk medicine for treating ailments in the cardiovascular and central nervous systems, such as lightheadedness, convulsions, numbness, and hypertension, *etc.* [1]. So far, two alkaloids (uncarine-A and -B), four flavones (rutin, neohesperidin, quercetrin, and afzelin), ursolic acid, umbelliferone, chlorogenic acid, and daucosterin have been reported from *U. hirsuta* in previous studies [2][3].

In the present investigation, the two new triterpenoids **1** and **4** and the novel 12-oxo-27-nortriterpenoid glycoside **7** were isolated from the leaves of *U. hirsuta* and their structures elucidated, together with four known compounds, *i.e.*, pyrocincholic acid ethyl ether [4] (**2**), pyrocincholic acid [4] (**3**), quinovic acid [5] (**5**), and (3β)-3-(β-D-quinovopyranosyloxy)pyrocincholic acid β-D-glucopyranosyl ester [6] (**6**). To the best of our knowledge, this is the first report of the isolation of a 12-oxo-27-nortriterpenoid glycoside.

Results and Discussion. – Compound **1** was obtained as colorless prismatic crystals. The HR-ESI-MS of **1** exhibited its $[M+H]^+$ peak at m/z 443.3528, consistent with the molecular formula $C_{29}H_{46}O_3$. The IR spectrum of **1** indicated the existence of an OH (3520 cm^{-1}) and a γ-lactone moiety (1762 cm^{-1}). The ^{1}H-NMR spectrum of **1** (*Table 1*) showed six Me *s* at δ(H) 0.76, 0.88, 0.91, 0.96, 0.97, and 1.02 (each 3 H) and one OCH signal at δ(H) 3.19 (*dd*, $J=11.3$, 4.8 Hz, H_α–C(3)). The ^{13}C-NMR spectrum of **1** (*Table 2*) displayed the signals of 29 C-atoms, including a C=O group of a γ-lactone moiety at δ(C) 180.23 and two oxygenated C-atoms at δ(C) 78.85 and 86.94. Judging



from the DEPT and HMQC spectra of **1**, the remaining δ(C) were due to 5 quaternary C-atoms and 4 CH, 11 CH_2, and 6 Me groups. Comparison of the ^{13}C-NMR spectrum of **1** with that of pyrocincholic acid [4] (=(3β)-3-hydroxy-27-norolean-13-en-28-oic acid; **3**) revealed that the olefinic C-atoms present in **3** had disappeared in **1**; instead, a quaternary C-atom signal was observed at δ(C) 86.94, arising from the γ-lactone moiety. In the HMBC spectrum, the correlations of Me(23) (δ(H) 0.96) and Me(24) (δ(H) 0.76) with a C-atom bearing an OH group at δ(C) 78.85 (*d*) placed this OH group at C(3) (*Fig. 1*). The *m* of H–C(16) (δ(H) 1.92–1.98) correlated with the C=O

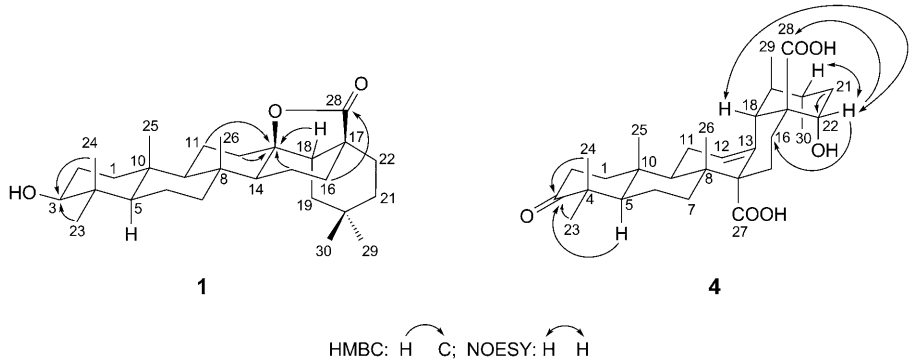


Fig. 1. *Selected HMBC and NOESY correlations of* **1** *and* **4**

signal at δ(C) 180.23, and the *m* of H–C(11) (δ(H) 1.42–1.50), H–C(12) (δ(H) 1.75–1.81), H–C(15) (δ(H) 1.67–1.75), and H–C(18) (δ(H) 1.80–1.82) correlated with the *s* of the C-atom bearing a lactone O-atom at δ(C) 86.94 in the HMBC spectrum. The above results suggested that the C(=O)–O unit of a γ-lactone moiety was connected to C(17) and C(13) (*Fig. 1*). Therefore, the structure of **1** was elucidated to be (3β)-3-hydroxy-27-noroleano-13(28)-lactone, which was confirmed by an X-ray crystal-structure analysis (*Fig. 2*).

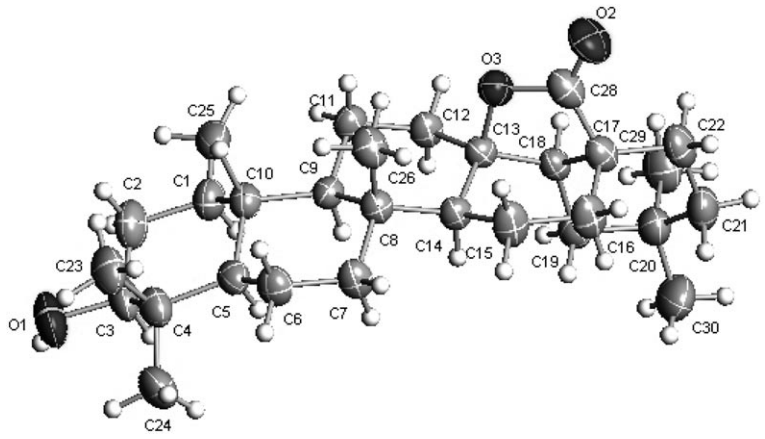


Fig. 2. *X-Ray single crystal structure of* **1**

Compound **4**, obtained as a white amorphous powder, had the molecular formula $C_{30}H_{44}O_6$ as deduced from its HR-ESI-MS (*m*/*z* 523.3016 ($C_{30}H_{44}NaO_6^+$)). Absorptions for OH (3436 cm^{-1}) and C=O groups (1700 cm^{-1}) were observed in the IR spectrum. The presence of a quinovic acid (=(3β)-3-hydroxyurs-12-ene-27,28-dioic acid; **5**) skeleton and the substitution pattern followed from the NMR data (*Table 1* and *2*) [5]. The ^{13}C-NMR spectrum of **4** (*Table 2*) revealed the presence of a C=O group (δ(C) 216.41, C), C-atom signals due to the *B*, *C*, and *D* rings typical of quinovic acid, and strongly deshielded signals for C(2) (δ(C) 34.35, CH_2) and C(4) (δ(C) 47.22, C). Thus, the C=O group is located at C(3). This was confirmed by the HMBCs of Me(23) (δ(H) 1.04) and Me(24) (δ(H) 1.08) with the C=O group (δ(C) 216.41) (*Fig. 1*). The OH group was placed at C(22) to account for the correlations of CH_2(21) (δ(H) 2.02–2.04 and 1.84–1.90) with the oxygenated CH (δ(C) 74.53) in the HMBC spectrum. These bindings were corroborated by the ^{1}H,^{1}H-COSY plot of **4**, which displayed correlations of H–C(22) (δ(H) 4.58 (*dd*, *J* = 11.6, 3.9 Hz)) with H–C(21) (*Exper. Part*). A NOESY experiment was carried out for the assignment of the configuration of the OH group of **4**. The NOESY correlations H–C(22)/H–C(18) (δ(H) 2.80) and H–C(20) (δ(H) 1.35–1.42) established the relative α-configuration of the OH group. Thus, **4** was determined to be (22α)-22-hydroxy-3-oxours-12-ene-27,28-dioic acid.

Compound **7** was found to possess the molecular formula $C_{41}H_{64}O_{14}$ by HR-ESI-MS (*m*/*z* 781.4385 ($[M+H]^+$)). In the ^{1}H-NMR spectrum of **7** (*Table 1*), 6 Me signals (4*s* and 2*d*) assignable to the aglycone, 1*d* ascribable to H–C(18) at δ(H) 3.74 (*J* =

Table 1. *^{1}H-NMR Data* (500 MHz) *of* **1**, **4**, *and* **7**. δ in ppm, J in Hz.

	1	**4**	**7**
CH_2(1)	1.75–1.81, 0.90–0.93 (2*m*)	1.81–1.83, 1.60–1.63 (2*m*)	1.91 (br. *d*, *J* = 12.3), 1.35–1.39 (*m*)
CH_2(2)	1.61–1.63 (*m*)	2.50–2.53, 2.40–2.48 (2*m*)	2.25–2.28, 1.82–1.85 (2*m*)
H–C(3)	3.19 (*dd*, *J* = 11.3, 4.8)		3.46 (*dd*, *J* = 11.2, 5.0)
H–C(5)	0.75–0.77 (*m*)	1.57–1.58 (*m*)	0.83 (br. *d*, *J* = 10.3)
CH_2(6)	1.38–1.40, 1.42–1.50 (2*m*)	1.42–1.45 (*m*)	1.82–1.85, 1.45–1.48 (2*m*)
CH_2(7)	0.97–1.00, 1.75–1.81 (2*m*)	2.00–2.01, 1.76–1.81 (2*m*)	1.42–1.44, 0.77–0.79 (2*m*)
H–C(9)	0.66–0.68 (*m*)	2.92 (br. *s*)	1.63 (*dd*, *J* = 14.1, 4.0)
CH_2(11)	1.57–1.60, 1.42–1.50 (2*m*)	2.13–2.17, 2.00–2.04 (2*m*)	2.68–2.72 (*m*), 2.62 (*dd*, *J* = 17.9, 3.9)
CH_2(12) or H–C(12)	1.77–1.80 (*m*)	6.08 (*d*, *J* = 2.8)	
H–C(14)	1.15–1.21 (*m*)		
CH_2(15)	1.67–1.75 (*m*)	2.82–2.83 (*m*)	2.81–2.84, 2.49–2.51 (2*m*)
CH_2(16)	1.92–1.98, 1.22–1.28 (2*m*)	3.03 (br. *d*, *J* = 12.9), 2.56–2.58 (*m*)	2.23–2.25 (*m*)
H–C(18)	1.80–1.82 (*m*)	2.80 (br. *s*)	3.74 (*d*, *J* = 10.3)
CH_2(19) or H–C(19)	1.17–1.21, 1.40–1.42 (2*m*)	1.60–1.63 (*m*)	1.11–1.14 (*m*)
H–C(20)		1.35–1.42 (*m*)	1.09–1.12 (*m*)
CH_2(21)	1.28–1.31 (*m*)	2.02–2.04, 1.84–1.90 (2*m*)	1.45–1.48, 1.32–1.35 (2*m*)
CH_2(22) or H–C(22)	1.57–1.60 (*m*)	4.58 (*dd*, *J* = 11.6, 3.9)	2.05 (*td*, *J* = 13.4, 4.5), 1.82–1.85 (*m*)
Me(23)	0.96 (*s*)	1.04 (*s*)	1.39 (*s*)
Me(24)	0.76 (*s*)	1.08 (*s*)	1.04 (*s*)
Me(25)	0.88 (*s*)	1.00 (*s*)	0.89 (*s*)
Me(26)	0.97 (*s*)	1.26 (*s*)	1.29 (*s*)
Me(29)	1.02 (*s*)	1.29 (*d*, *J* = 6.0)	1.06 (*d*, *J* = 6.1)
Me(30)	0.91 (*s*)	0.96 (*d*, *J* = 6.4)	0.92 (*d*, *J* = 6.0)
H–C(1′)			5.02 (*d*, *J* = 7.7)
H–C(2′)			4.12 (*t*, *J* = 8.1)
H–C(3′)			3.95–4.01 (*m*)
H–C(4′)			4.25–4.34 (*m*)
H–C(5′)			4.25–4.34 (*m*)
CH_2(6′)			4.67 (*dd*, *J* = 11.5, 2.1), 4.47 (*dd*, *J* = 11.8, 5.6)
H–C(1″)			6.21 (*d*, *J* = 7.7)
H–C(2″)			4.25–4.34 (*m*)
H–C(3″)			4.07–4.09 (*m*)
H–C(4″)			4.25–4.34 (*m*)
H–C(5″)			4.25–4.34 (*m*)
CH_2(6″)			4.42–4.44 (*m*)

10.3 Hz), and 1*dd* due to H–C(3) at δ(H) 3.46 (J = 11.2, 5.0 Hz) were observed. Two anomeric H-atom signals at δ(H) 6.21 (*d*, J = 7.6 Hz) and 5.02 (*d*, J = 7.7 Hz) indicated β-D-linkage of the sugar moieties in **7**. The ^{13}C-NMR spectrum of **7** (*Table 2*) revealed

Table 2. *^{13}C-NMR Data* (125 MHz) *of* **1**, **4**, *and* **7**. δ in ppm.

	1	**4**	**7**		**1**	**4**	**7**
C(1)	38.59 (*t*)	39.61 (*t*)	38.24 (*t*)	C(22)	26.82 (*t*)	74.53 (*d*)	34.38 (*t*)
C(2)	27.27 (*t*)	34.35 (*t*)	26.60 (*t*)	C(23)	27.98 (*q*)	27.04 (*q*)	28.13 (*q*)
C(3)	78.85 (*d*)	216.41 (*s*)	88.79 (*d*)	C(24)	15.27 (*q*)	21.57 (*q*)	16.83 (*q*)
C(4)	38.83 (*s*)	47.22 (*s*)	39.61 (*s*)	C(25)	16.73 (*q*)	16.27 (*q*)	16.08 (*q*)
C(5)	55.45 (*d*)	55.01 (*d*)	55.34 (*d*)	C(26)	15.90 (*q*)	19.03 (*q*)	18.68 (*q*)
C(6)	17.88 (*t*)	20.12 (*t*)	18.51 (*t*)	C(27)		178.19 (*s*)	
C(7)	41.75 (*t*)	36.83 (*t*)	38.02 (*t*)	C(28)	180.23 (*s*)	179.15 (*s*)	176.02 (*s*)
C(8)	36.71 (*s*)	40.21 (*s*)	40.38 (*s*)	C(29)	33.05 (*q*)	18.35 (*q*)	17.60 (*q*)
C(9)	59.50 (*d*)	46.36 (*d*)	53.91 (*d*)	C(30)	25.61 (*q*)	21.28 (*q*)	20.34 (*q*)
C(10)	37.21 (*s*)	36.95 (*s*)	36.91 (*s*)	C(1′)			107.08 (*d*)
C(11)	17.64 (*t*)	23.62 (*t*)	34.62 (*t*)	C(2′)			75.92 (*d*)
C(12)	35.00 (*t*)	128.75 (*d*)	197.65 (*s*)	C(3′)			78.90 (*d*)
C(13)	86.94 (*s*)	134.54 (*s*)	134.97 (*s*)	C(4′)			72.08 (*d*)
C(14)	46.88 (*d*)	57.35 (*s*)	165.82 (*s*)	C(5′)			78.66 (*d*)
C(15)	18.25 (*t*)	24.71 (*t*)	22.47 (*t*)	C(6′)			63.26 (*t*)
C(16)	21.90 (*t*)	20.26 (*t*)	23.33 (*t*)	C(1″)			95.86 (*d*)
C(17)	44.88 (*s*)	55.00 (*s*)	47.15 (*s*)	C(2″)			74.11 (*d*)
C(18)	49.02 (*d*)	56.36 (*d*)	39.30 (*d*)	C(3″)			78.98 (*d*)
C(19)	33.65 (*t*)	37.39 (*d*)	41.39 (*d*)	C(4″)			71.23 (*d*)
C(20)	31.16 (*s*)	37.90 (*d*)	38.57 (*d*)	C(5″)			78.51 (*d*)
C(21)	34.09 (*t*)	39.83 (*t*)	30.71 (*t*)	C(6″)			62.50 (*t*)

12 C-atoms for the sugar moieties and 29 C-atoms for the aglycone portion (6 Me, 9 CH_2, 6 CH, and 8 C), including the diagnostic C=O group (δ(C) 197.65), one ester COO group (δ(C) 176.02), and one tetrasubstituted C=C moiety (δ(C) 134.97 and 165.82). The above-mentioned evidences indicated a 27-norursane-type triterpene glycoside. The ^{1}H- and ^{13}C-NMR data of the aglycone of **7** were nearly superposed with those of pyroquinovic acid (=(3β)-3-hydroxy-27-norurs-13-en-28-oic acid) [7], except for a ketone C=O signal (δ(C) 197.65) of **7** replacing the CH_2(12) signal of pyroquinovic acid. This suggested that the aglycone of **7** was 12-oxopyroquinovic acid which was supported by the HMBC cross-peaks C(12)/H–C(9) (δ(H) 1.63, *dd*, J = 14.1, 4.0 Hz), CH_2(11) (δ(H) 2.68–2.72 and 2.62), and H–C(18) (δ(H) 3.74, *d*, J = 10.3 Hz) (*Fig. 3*). The HMBCs of H–C(9), CH_2(15) (δ(H) 2.81–2.84 and 2.49–2.51), CH_2(16) (δ(H) 2.23–2.25), H–C(18), and Me(26) (δ(H) 1.29) with one olefinic C-atom at δ(C) 165.82, and of H–C(15) and H–C(18) with the other olefinic C-atom at δ(C) 134.97 confirmed their attribution to C(14) and C(13), respectively. The attachment of the glucose residue to C(3) of the aglycone was determined by the HMBC of the anomeric H-atom at δ(H) 5.02 with the C-atom at δ(C) 88.79. The upfield shift of the anomeric atom C(1″) of the second β-D-glucose moiety (δ(C) 95.86) indicated that it is involved in an ester with the C(28) carboxyl group of the aglycone, as confirmed by the HMBC H–C(1″) (δ(H) 6.21)/C(28) (δ(C) 176.02). ^{1}H,^{1}H-COSY and NOESY experiments were carried out to further elucidate the structure of **7** (*Fig. 3* and *Exper. Part*). From these results, the structure of **7** was established as (3β)-3-(β-D-glucopyranosyloxy)-12-oxopyroquinovic acid β-D-glucopyranosyl ester and named uncariaside A.

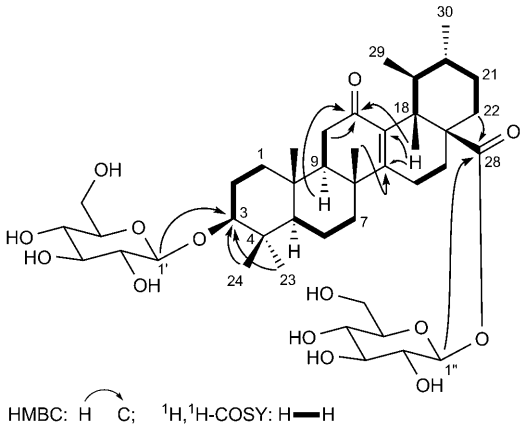


Fig. 3. *Key HMBC and ^{1}H,^{1}H-COSY correlations of* **7**

Experimental Part

General. TLC: *HSGF254* SiO_2 TLC plates (*Yantai Chemical Industrial Institute*, P. R. China). Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Marine Chemical Inc.*, Qingdao, P. R. China), *MCI* gel *CHP20P* (75–150 μm; *Mitsubishi Chemical Industries*), and *Sephadex LH-20* (*Pharmacia Biotech AB*, Uppsala, Sweden) as packing materials. M.p.: *Büchi Melting-Point-B-540* apparatus; uncorrected. Optical rotations: *Krüss P800-T* polarimeter. IR Spectra: *Nicolet*™*-380* spectrometer from *Thermo Electron*; $\tilde{\nu}$ in cm^{-1}. 1D- and 2D-NMR Spectra: *Bruker AV-500* instrument. ESI-MS: *Finnigan LCQ-DECAXP^{plus}* mass spectrometer; in *m*/*z*. HR-ESI-MS: *APEXIII-7.0-Tesla*-FT mass spectrometer (*Bruker Daltonics, Inc.*); in *m*/*z*.

Plant Material. The leaves of *U. hirsuta* were collected in Ningming Guangxi, China, and identified by Dr. *Li-Hong Wu*. A voucher specimen (No. 20050828) was deposited with the laboratory of Shanghai R&D Center for Standardization of Chinese Medicines.

Extraction and Isolation. Air-dried leaves (30 kg) of *U. hirsuta* were extracted with hot 80% EtOH (200 l, 3 × 2 h). After evaporation of the solvent, part of the residue (2.5 kg) was suspended in H_2O (2 l) and extracted successively with CH_2Cl_2 (4 × 2 l) and BuOH (4 × 2 l). The CH_2Cl_2 part (410 g) was subjected to CC (SiO_2, gradient petroleum ether/AcOEt 0 → 100%, then MeOH): *Fractions 1–20*. *Fr. 10* (10.2 g) was further submitted to CC: **1** (52.5 mg), **3** (43.0 mg), and one new fraction. *Fr. 10.1* (53 mg) was further purified by repeated CC (SiO_2): **2** (26.9 mg)[1]). *Fr. 11* (22.5 g) was subjected to CC: **5** (100.4 mg) and two new fractions. *Fr. 11.1* (42 mg) was further purified by repeated CC (SiO_2, *Sephadex LH-20*): **4** (8.4 mg).

The BuOH extract (500 g) was subjected to CC (SiO_2, AcOEt, then successively AcOEt/MeOH 19:1, 9:1, 4:1, and 1:1, then MeOH). The fraction eluted with AcOEt/MeOH 1:1 was submitted to CC (SiO_2, $CHCl_3$/MeOH 9:1, 4:1, and 1:1, then MeOH): *Fractions A–D*. *Fr. A* (20 g) was subjected to CC (SiO_2, *Sephadex LH-20* with MeOH): **6** (12.4 mg) and **7** (8.3 mg).

(3β)-3-Hydroxy-27-noroleano-13(28)-lactone (*=(3β)-3,13-Dihydroxy-27-norolean-28-oic Acid γ-Lactone*; **1**): Colorless crystals. M.p. 252.6–254.7°. $[\alpha]_D^{25} = +1.7$ ($c = 0.05$, MeOH). IR (KBr): 3520.7, 2297.9, 1762.0, 1467.0, 1383.5, 1242.1, 1143.1. ^{1}H- and ^{13}C-NMR ($CDCl_3$): *Tables 1* and *2*. ESI-MS (pos.): 443.4 ($[M+H]^+$). HR-ESI-MS (pos.): 443.3528 ($[M+H]^+$, $C_{29}H_{47}O_3^+$; calc. 443.3525).

(22α)-22-Hydroxy-3-oxours-12-ene-27,28-dioic Acid (**4**). Amorphous powder. $[\alpha]_D^{25} = +115$ ($c =$ 0.02, MeOH). IR (KBr): 3436.2, 1700.6, 1458.6, 1386.9, 1204.5. ^{1}H- and ^{13}C-NMR (C_5D_5N): *Tables 1*

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[1]) Compound **2** was subsequently shown to be an artefact of isolation, arising through esterification of pyrocincholic acid (**3**) with EtOH.

and *2*. ^{1}H,^{1}H-COSY: H–C(1)/H–C(2); H–C(6)/H–C(5), H–C(7); H–C(9)/H–C(11), H–C(12); H–C(15)/H–C(16); H–C(19)/H–C(18), Me(29); H–C(20)/H–C(19), Me(30); H–C(21)/H–C(20), H–C(22). NOESY: H–C(5)/H–C(9), Me(23); H–C(18)/H–C(20), Me(29), H–C(22); H–C(19)/Me(30); H–C(22)/H–C(18), H–C(20). ESI-MS (pos.): 523.31 ($[M+Na]^+$). HR-ESI-MS: 523.3016 ($[M+Na]^+$, $C_{30}H_{44}NaO_6^+$; calc. 523.3036).

*Uncariaside A (=(3β)-3-(β-*D*-Glucopyranosyloxy)-12-oxopyroquinovic Acid β-*D*-Glucopyranosyl Ester=(3β)-3-(β-*D*-Glucopyranosyloxy)-27-norurs-13-en-28-oic Acid β-*D*-Glucopyranosyl Ester*; **7**): Amorphous powder. $[\alpha]_D^{25} = -52$ ($c = 0.05$, MeOH). IR (KBr): 3421.1, 2927.6, 1734.7, 1647.0, 1457.3, 1076.3. ^{1}H- and ^{13}C-NMR (C_5D_5N): *Tables 1* and *2*. ^{1}H,^{1}H-COSY: H–C(2)/H–C(1), H–C(3); H–C(5)/CH_2(6); H–C(9)/CH_2(11); H–C(19)/H–C(18), Me(29); H–C(20)/Me(30). NOESY: H–C(3)/H–C(1′), H–C(5); H–C(5)/H–C(3), H–C(9), Me(23); H–C(9)/H–C(5), Me(23); H–C(18)/H–C(22), Me(29). ESI-MS (pos.): 781.4 ($[M+H]^+$). HR-ESI-MS: 781.4385 ($[M+H]^+$, $C_{41}H_{65}O_{14}^+$; calc. 781.4374).

X-Ray Crystal-Structure Analysis of **1**[2]). Single crystals suitable for X-ray analysis were obtained by recrystallization from petroleum ether/AcOEt 1:1. A colorless prismatic crystal with approximate dimensions 0.496 mm × 0.418 mm × 0.327 mm was used for analysis. All measurements were recorded on a *Bruker-SMART CCD* area-detector diffractometer employing graphite-monochromated MoK_α radiation (λ 0.71073 Å) at 293 K and operating in the $\varphi-\omega$ mode. Data collection and cell refinement: *Bruker SMART*. Program used to refine structure: SHELXL-97; refinement on F^2, full-matrix least-squares calculations. Crystal data and experimental details: $C_{29}H_{46}O_3$, M_r 442.66; orthorhombic, space group $P2_12_12_1$ ($Z=4$), $a = 11.4632$ (10), $b = 14.5388$ (12), $c = 15.3259$ (13) Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$; independent data, 3124 ($R_{int} = 0.1385$); θ range 1.93–26.99°, $R(I > 2\sigma(I)) = 0.0552$, $wR_2 = 0.1285$; largest peak and hole in difference map: 0.309 and −0.287 e Å^{-3}.

Acid Hydrolysis of **7***: Determination of the Absolute Configuration of the Sugar Components*. The absolute configuration of glucose was determined as described by *Cases et al.* [8]: Uncariaside A (**7**; 2 mg) was heated with 1N HCl (2 ml) for 4 h at 105°. The mixture was cooled, neutralized, and partitioned between AcOEt (2 ml) and H_2O (2 ml). The aq. layer was evaporated and contained in a vial. The following solns. were added: *a*) (2*S*)-1-aminopropan-2-ol/MeOH 1:8 (20 µl); *b*) AcOH/MeOH 1:4 (17 µl); *c*) 3% Na[BH_3CN] in MeOH (13 µl). The vial was capped, and the mixture was allowed to react for 2 h at 65°. After cooling, 3M aq. CF_3COOH was added dropwise until the pH dropped to pH 1–2. The mixture was evaporated and co-evaporated with H_2O (3 × 0.5 ml) and MeOH (5 × 0.5 ml). The residue was dried overnight in a desiccator and treated with pyridine/Ac_2O 1:1 for 1 h at 100°. After cooling, the mixture was extracted with $CHCl_3$ and the extract washed with H_2O (3 × 1 ml) and sat. $NaHCO_3$ soln. (3 × 1 ml). The org. phase was dried (Na_2SO_4) and subjected to GC/MS (*Thermo TR-5MS* column (60 m × 0.25 mm × 2.5 µm); carrier gas He, flow rate 1 ml/min; oven-temp. gradient: 180° → 220° (4°/min), 220° for 2 min, 220° → 270° (1°/min), and 270° for 1 min); derivatives of D-glucose eluted at t_R 62.89 min, *m/z* 494.24.

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[2]) CCDC-671978 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB21EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).