Tetranortriterpenoids from *Clausena excavata*

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Five new tetranortriterpenoids, (11β)-21,23-dihydro-11,21-dihydroxy-23-oxoobacunone (=21,23-dihydro-21-hydroxy-23-oxozapoterin; **2**), (11β)-21,23-dihydro-11,23-dihydroxy-21-oxoobacunone (=21,23-dihydro-23-hydroxy-21-oxozapoterin; **3**), (1α,11β)-1,2,21,23-tetrahydro-1,11,23-trihydroxy-21-oxoobacunone (=21,23-dihydro-23-hydroxy-21-oxoclausenarin; **4**), (1α,11β)-23-ethoxy-1,2,21,23-tetrahydro-1,11-dihydroxy-21-oxoobacunone (=23-ethoxy-21,23-dihydro-21-oxoclausenarin; **5**); (11β)-1,2,21,23-tetrahydro-11,23-dihydroxy-21-oxoobacunoic acid; **6**), were isolated from the aerial part of *Clausena excavata* BURM. F. (Rutaceae). All compounds possessed 3,4-seco skeletons. Their structures were established by spectroscopic studies. Tetranortriterpenoids with a 4-hydroxybut-2-eno-4-lactone moiety are rarely found in the genus *Clausena*.

1. Introduction. – *Clausena excavata* BURM. F. (Rutaceae) is a bush growing in Xishuangbanna, Yunnan Province, P.R. China. Leaves and barks of this plant have been used in folk medicines for the treatment of dysentery, enteritis, and urethra infection [1]. Previous research revealed that this plant mainly contains alkaloids [2–4] and O-terpenoidal coumarins [5–10]. This paper describes the isolation and structure elucidation of the five new tetranortriterpenoids **2**–**6** together with a known one, zapoterin[1]) (=(11β)-11-hydroxyobacunone[2]); **1**). Their structures were determined by spectroscopic analysis, especially 2D NMR experiments.

In general, an equilibrium between the α- and β-hydroxy isomers at C(21) or C(23) was suggested to be the cause of the abnormality observed in the ^{1}H- and ^{13}C-NMR spectra [11–15], especially in the ^{13}C-NMR spectra of tetranortriterpenoids like **2**–**4** and **6** having a 4-hydroxybut-2-eno-4-lactone residue. Our experiments indicated that it was possible to obtain normal ^{1}H- and ^{13}C-NMR spectra for such tetranortriterpenoids by acetylation or methylation of the hydroxy group at the butenolactone residue such as in **2a** or **2c**, respectively (*Fig.*).

2. Results and Discussion. – The aerial parts of *C. excavata* were extracted with 90% EtOH. The EtOH extract was successively chromatographed over silica gel and *Sephadex LH-20* to afford the six compounds **1**–**6**.

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[1]) Zapoterin = (1*S*,3a*S*,4a*R*,4b*R*,6a*R*,11a*R*,11b*R*,12*S*,13a*S*)-1-(furan-3-yl)-1,6a,7,11a,11b,12,13,13a-octahydro-12-hydroxy-4b,7,7,11a,13a-pentamethyloxirano[4,4a]-2-benzopyrano[6,5-*g*][2]benzoxepin-3,5,9(2a*H*,4b*H*,6*H*)-trione.

[2]) Obacunone = (1*S*,3a*S*,4a*R*,4b*R*,6a*R*,11a*R*,11b*R*,13a*S*)-1-(furan-3-yl)-1,6a,7,11a,11b,12,13,13a-octahydro-4b,7,7,11a,13a-pentamethyloxireno[4,4a]-2-benzopyrano[6,5-*g*][2]benzoxepin-3,5,9(3a*H*,4b*H*,6*H*)-trione.

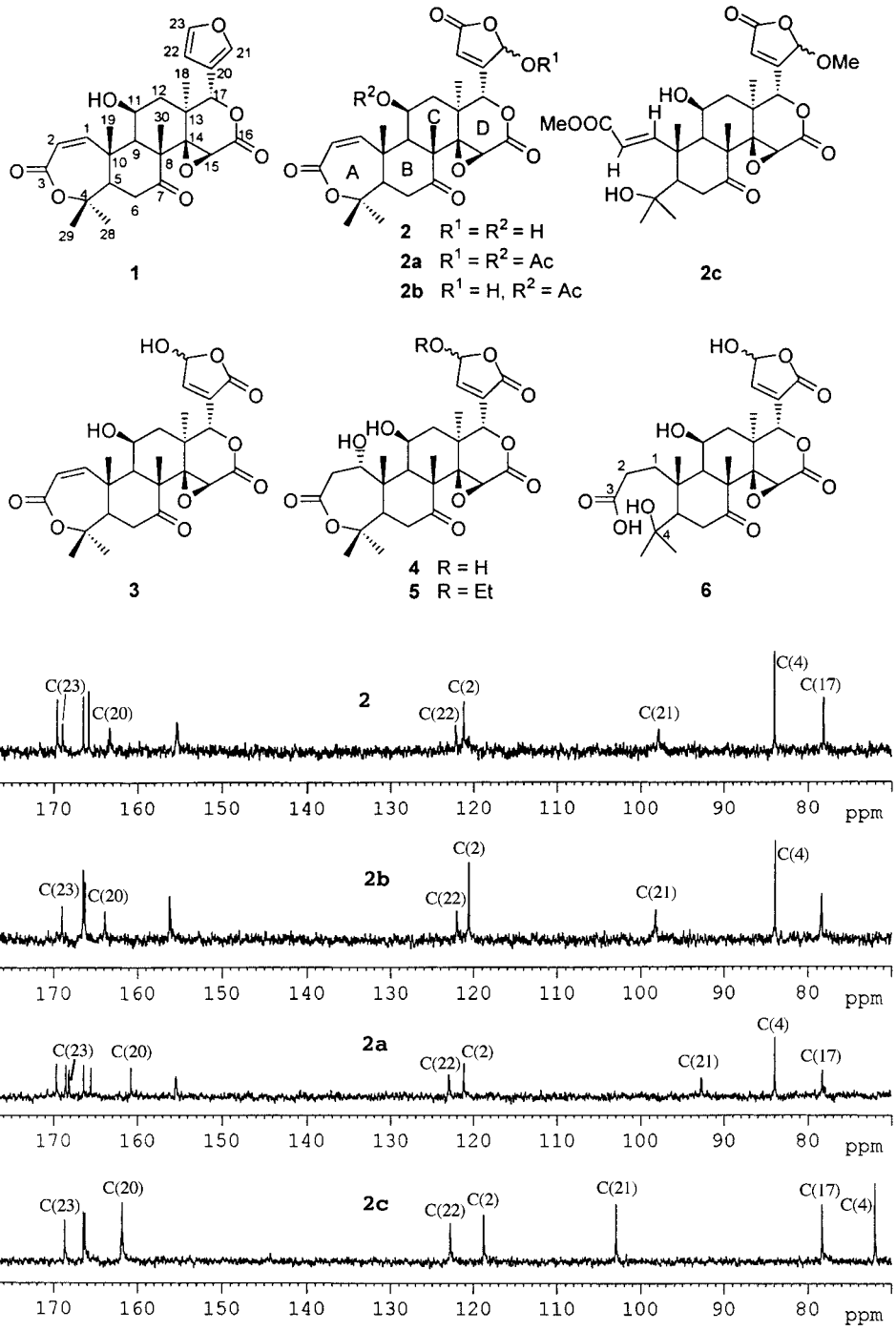

Figure. *^{13}C-NMR Spectra* (125 MHz, (D_6)DMSO) *of* **2** *and* **2a**–**c**

Compound **2**, an amorphous powder, was determined to have the molecular formula $C_{26}H_{30}O_{10}$ based on the high-resolution EI-MS peak at *m/z* 502.1875 (M^+, calc. 502.1839). The IR (KBr) data suggested the presence of carbonyl (1750, 1715 cm^{-1}) and OH (3487 cm^{-1}) groups. The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*, resp.), ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-HMBC experiments, and the comparison with the NMR data of **1** [16][17] established **2** to be 21,23-dihydro-21-hydroxy-23-oxozapoterin[1]) (=(11*β*)-21,23-dihydro-11,21-dihydroxy-23-oxoobacunone[2])).

Table 1. *^{1}H-NMR Data for Compounds* **2**–**6**

	2[a])[c])	**3**[a])[c])	**4**[b])[c])	**5**[b])[c])	**6**[b])[c])
1 or 2 H–C(1)	6.79 (*d*, *J* = 12.0)	6.61 (*d*, *J* = 12.0)	5.52 (*d*, *J* = 7.1)	5.49 (*d*, *J* = 7.0, 1 H)	1.1–1.30 (*m*, 2 H)
1 or 2 H–C(2)	5.90 (*d*, *J* = 12.0)	5.87 (*d*, *J* = 12.0)	3.50 (*dd*, *J* = 15.6, 7.1) 3.78 (*d*, *J* = 15.6)	3.49 (*dd*, *J* = 5.4, 7.0) 3.74 (*d*, *J* = 15.4)	2.45–2.85 (*m*, 2 H)
1 H–C(5)	2.72 (*dd*, *J* = 14.1, 4.8)	2.71 (*dd*, *J* = 14.1, 4.8)	3.02 (*dd*, *J* = 14.2, 4.9)	3.02 (*dd*, *J* = 14.1, 4.9)	2.66 (*dd*, *J* = 14.3, 5.6)
2 H–C(6)	2.29 (*dd*, *J* = 14.1, 4.8) 3.14 (*t*, *J* = 14.1)	2.29 (*dd*, *J* = 14.1, 4.8) 3.12 (*t*, *J* = 14.1)	2.78 (*dd*, *J* = 14.2, 4.9) 3.16 (*t*, *J* = 14.2)	2.74 (*dd*, *J* = 14.1, 4.9) 3.16 (*t*, *J* = 14.1)	2.45 *dd*, *J* = 14.3, 5.6) 2.77 (*d*, *J* = 14.3)
1 H–C(9)	1.92 (*s*)	1.91 (*s*)	2.69 (*s*)	2.67 (*s*)	2.59 (*s*)
1 H–C(11)	4.58 (br. *s*)	4.49 (br. *s*)	4.81 (br. *s*)	4.79 (*d*, *J* = 6.2)	4.33 (br. *s*)
2 H–C(12)	1.76 (*d*, *J* = 14.9) 2.05 (*dd*, *J* = 14.9, 4.2)	1.63 (*dd*, *J* = 14.7, 6.4) 1.86 (*d*, *J* = 14.7)	2.02 (*m*) 2.25 (*m*)	1.70–1.85 (*m*) 2.50–2.65 (*m*)	2.50–2.85 (*m*, 2 H)
1 H–C(15)	3.79 (*s*)	3.78 (*s*)	4.36 (*s*)	4.39 (*s*)	4.27 (*s*)
1 H–C(17)	5.22 (br. *s*)	5.26 (br. *s*)	5.95 (br. *s*)	5.91 (*s*)	5.97 (br. *s*)
Me(18)	0.93 (*s*, 3 H)	0.98 (*s*, 3 H)	1.49 (*s*, 3 H)	1.40 (*s*, 3 H)	1.45 (*s*, 3 H)
Me(19)	1.69 (*s*, 3 H)	1.66 (*s*, 3 H)	1.96 (*s*, 3 H)	1.93 (*s*, 3 H)	1.95 (*s*, 3 H)
1 H–C(21)	6.04 (br. *s*)	–	–	–	–
1 H–C(22)	6.25 (br. *s*)	7.53 (br. *s*)	7.81 (br. *s*)	7.65 (*s*)	7.82 (br. *s*)
1 H–C(23)	–	6.22 (br. *s*)	6.55 (br. *s*)	6.05 (*s*)	6.57 (br. *s*)
Me(28)	1.33 (*s*, 3 H)	1.33 (*s*, 3 H)	1.33 (*s*, 3 H)	131 (*s*, 3 H)	1.42 (*s*, 3 H)
Me(29)	1.48 (*s*, 3 H)	1.44 (*s*, 3 H)	1.58 (*s*, 3 H)	1.59 (*s*, 3 H)	1.72 (*s*, 3 H)
Me(30)	1.47 (*s*, 3 H)	1.43 (*s*, 3 H)	1.88 (*s*, 3 H)	1.84 (*s*, 3 H)	1.85 (*s*, 3 H)
Others	–	–	–	1.09 (*t*, *J* = 7.0, 3 H) 3.62 (*q*, *J* = 7.0) 3.74 (*q*, *J* = 7.0)	–

[a]) In (D_6)DMSO. [b]) In C_5D_5N. [c]) Coupling constants in Hz.

The ^{1}H-NMR spectra of **2** revealed the presence of 5 Me groups at *δ* 0.93, 1.33, 1.47, 1.48, and 1.69 (5*s*, each 3 H). In the ^{13}C-NMR (*Table 2*) of **2** 26 C-signals appeared: 5 Me, 2 CH_2, 9 CH, and 10 C. The ^{1}H- and ^{13}C-NMR, ^{1}H,^{1}H COSY, and HMBC experiments showed that it was a derivative of zapoterin[1]) (**1**), whose ^{1}H- and ^{13}C-NMR data were consistent with those in [16][17]. The differences between **2** and **1** arose from the furan ring. The structure of the furan ring in **2** was assigned by analyzing the ^{1}H- and ^{13}C-NMR data with the aid of HMQC and HMBC experiments. In the ^{1}H-NMR spectrum, a pair of protons at *δ* 6.79 and 5.90 (*d*, *J* = 12.0 Hz, 1 H each) was attributed to a *cis*-disubstituted double bond of an *α*,*β*-unsaturated lactone at C(1) and C(2), respectively. The carbonyl group at *δ*(C) 207.6 was attributed to C(7)=O by means of ^{1}H,^{13}C long-range

Table 2. *^{13}C-NMR Data for Compounds* **1**–**6**

	1[a])	**2**[a])	**2a**[a])	**2b**[a])	**2c**[a])	**3**[a])	**4**[b])	**5**[b])	**6**[b])
CH(1) or CH_2(1)	157.0	156.2	155.3	155.2	161.7	156.3	72.8	72.7	36.4
CH(2) or CH_2(2)	120.8	120.6	121.2	121.3	118.7	120.5	35.8	35.7	42.4
C(3)	166.9	166.3	165.5	165.8	166.3	166.5	170.2	169.6	174.2
C(4)	84.1	83.9	83.9	83.9	71.9	83.8	85.0	84.6	73.9
CH(5)	55.5	55.2	54.5	54.8	57.8	55.1	51.8	52.4	55.9
CH_2(6)	39.9[c])	39.4	39.0	39.2	37.2	39.5	39.7	39.5	39.7
C(7)	208.1	207.6	206.5	206.6	209.5	207.8	208.3	207.8	210.4
C(8)	51.2[c])	51.1	51.3	51.0	50.8	50.9	52.6	51.5	52.2
CH(9)	49.7	49.2	47.5	47.7	47.3	49.3	47.2	48.8	47.0
C(10)	43.6[c])	43.5	43.0	43.0	45.0	43.6	45.7	47.0	48.0
CH(11)	65.7	65.2	68.4	68.0	64.8	65.1	65.3	65.1	67.0
CH_2(12)	43.2[c])	42.2	36.4	38.5	41.9	41.4	43.4	43.5	43.5
C(13)	36.0	36.1	36.0	36.1	35.9	36.3	37.6	37.4	37.1
C(14)	64.7	64.4	64.1	64.2	64.3	64.3	65.4	65.2	63.7
CH(15)	53.2	52.5	52.3	52.4	52.3	53.0	54.5	54.4	54.0
C(16)	167.7	166.5	166.4	166.4	166.3	166.6	167.8	167.8	167.7
CH(17)	78.0	78.4[d])	78.3	78.2[d])	78.3	75.3[d])	76.6[d])	76.5	76.8[d])
Me(18)	20.0	19.6	20.0	19.4	19.5	19.2	20.1	20.0	20.1
Me(19)	18.2	18.1	17.7	17.5	16.5	18.0	17.8	16.6	18.5
C(20)	120.3	163.9[d])	160.8	163.8[d])	166.1	131.8[d])	133.1[d])	133.8	133.3[d])
C(21) or CH(21)	141.7	98.3[d])	92.7	98.0[d])	102.9	170.1[d])	169.9[d])	169.6	170.8[d])
CH(22)	110.4	122.0[d])	122.9	122.2[d])	122.8	153.5[d])	153.8[d])	151.0	153.9[d])
C(23) or CH(23)	143.6	169.0[d])	168.2	168.9[d])	168.5	98.2[d])	99.0[d])	102.3	99.6[d])
Me(28)	31.8	31.5	31.6	31.5	30.5	31.5	33.7	31.3	33.4
Me(29)	26.5	26.2	26.3	26.3	29.6	26.1	23.2	23.0	29.4
Me(30)	19.4	18.9	18.5	18.5	18.5	18.9	20.7	19.9	19.6
Others	–	–	169.7 (*s*)	169.6 (*s*)	51.1 (*q*)	–	–	66.1 (*t*)	–
			168.5 (*s*)	21.1 (*q*)				13.7 (*q*)	
			21.4 (*q*)						
			21.1 (*q*)						

[a]) In (D_6)DMSO. [b]) In C_5D_5N. [c]) Revised assignments are based on the HMQC, HMBC, and ^{1}H,^{1}H COSY experiments. [d]) Weak and broad signals.

correlations between δ(H) 1.14 (Me(30)) and δ(C) 49.2 (C(9)), 51.1 (C(10)), 64.4 (C(14)), and 207.6. In the ^{1}H,^{1}H COSY plot, δ 4.58 (*d*, J = 4.2 Hz) showed linear coupling with δ 2.07 (*dd*, J = 12.0, 4.2 Hz, H–C(12)), establishing that δ(C) 65.2 (*d*) was arising from C(11). In the ^{13}C-NMR spectrum, δ(C) 64.4 (*s*) and 52.5 (*d*) were attributed to an epoxy ring between C(14) and C(15), which was supported by the ^{1}H,^{13}C long-range correlations between δ(H) 3.79 and δ(C) 51.1 (C(8)), 64.4 (C(14)), and 166.5. Thus, the ^{13}C- and ^{1}H-chemical shifts of the rings A, B, C, and D of compounds **2** and **1** correspond to each other, so that the structures of these rings are identical, including their relative configurations. As for ring E of **2**, the ^{13}C-NMR signals at δ(C) 98.3 (*d*), 122.0 (*d*), 163.9 (*s*), and 169.0 (*s*) revealed the presence of a 4-hydroxybut-2-eno-4-lactone function. The signals at δ(C) 122.0 (*d*), and 169.0 (*s*) were assigned to C(22) and C(23), resp. In the HMBC, the long-range correlations between δ(H) 5.22 (H–C(17)) and δ(C) 163.9 (*s*) suggested that the olefinic C-atom at δ(C) 163.9 (*s*) was C(20), which was in agreement with the conjugative effect of the C(23) carboxylate moiety. Then, the hemiacetal C-atom at δ(C) 98.3 (*d*) was C(21). The signals of C(17), C(20), C(21), C(22), and C(23) appeared broad in the ^{13}C-NMR spectra (see *Fig.*)), due to the equilibrium between the α- and β-hydroxy isomers at C(21). Other limonoids with a 4-hydroxybut-2-eno-4-lactone function and an OH group either at C(21) or at C(23) also were mixtures of their α- and β-hydroxy isomers [11–15]. Another noteworthy phenomenon was that the signal of C(4) at δ(C) 83.9 (*s*) was strong, which was not indicated in previous reports.

Compounds **2a** and **2b** were the di- and monoacetates of **2**, and **2c** was the methylester of (11β)-21,23-dihydro-11-hydroxy-21-methoxy-23-oxoobacunonic acid[3]). The signals of C(17), C(20), C(21), C(22), and C(23) were broad in **2** and **2b**, but turned out normal in **2a** and **2c** (*Fig.*).

Compound **3** was obtained as an amorphous powder. Its IR spectrum showed absorptions of OH (3498 cm^{-1}). The ^1H- and ^{13}C-NMR (*Tables 1* and *2*, resp.) and HR-FAB-MS data (negative mode) were consistent with the molecular formula $C_{26}H_{30}O_{10}$. The ^1H- and ^{13}C-NMR, HMQC, HMBC, and $^1H,^1H$-COSY experiments and the comparison with the NMR data of **2** established **3** to be 21,23-dihydro-23-hydroxy-21-oxozapoterin[1]) (=(11β)-21,23-dihydro-11,23-dihydroxy-21-oxoobacunone[2])).

The ^1H- and ^{13}C-NMR spectra of **3** revealed the presence of 5 Me at δ(H) 0.98, 1.33, 1.43, 1.44, and 1.66 (5*s*, each 3 H); *cis*-positioned olefinic protons at δ(H) 6.81 and 5.87 (*d*, J = 12.0 Hz, 1 H each), 4 CH–O at δ(H) 4.49 (br. *s*, H–C(11)), 3.78 (*s*, H–C(15)), 5.23 (br. *s*, H–C(17)), 6.22 (br. *s*, H–C(23)); δ(C) 65.1 (C(11)), 53.0 (C(15)), 75.3 (C(17)), 98.2 (C(13)). The ^{13}C-NMR spectra showed 26 C-signals: 5 Me, 2 CH_2, 9 CH, and 10 C. The ^1H- and ^{13}C-NMR data were similar to those of **2**, except for the signals of the furan ring, suggesting that **3** and **2** have the same rings A–D. This was supported by the HMBC and $^1H,^1H$-COSY experiments of **3**. The ^{13}C-NMR signals at δ(C) 98.2 (*d*), 131.8 (*s*), 153.5 (*d*), and 170.1 (*s*) showed the presence of a 4-hydroxybut-2-eno-4-lactone function. The signal at δ(C) 170.1 (*s*) was assigned to the α,β-unsaturated γ-lactone carbonyl at C(21), and the hemiacetal C-atom at δ(C) 98.2 (*d*) was attributed to C(23). The remaining two C-signals at δ(C) 131.8 (*s*) and 153.5 (*d*) were ascribed to the olefinic C-atoms C(20) and C(22), resp., which was consistent with the α,β-conjugative effect of the C(21) carboxylate moiety. In compound **3**, the signal of C(11) at δ(C) 75.3 was broad, and the signals of C(20), C(21), C(22), and C(23) were split.

Compound **4** was obtained as a powder. Its IR spectrum showed absorptions of OH (3498 cm^{-1}), and its ^1H- and ^{13}C-NMR (*Tables 1* and *2*, resp.) and HR-FAB-MS (negative mode) were consistent with the molecular formula $C_{26}H_{32}O_{11}$. The ^1H- and ^{13}C-NMR, HMQC, HMBC, and $^1H,^1H$-COSY experiments and the comparison with those of **3** and clausenarin [16] established **4** to be 21,23-dihydro-23-hydroxy-21-oxoclausenarin[4]) (=(1α,11β)-1,2,21,23-tetrahydro-1,11,23-trihydroxy-21-oxoobacunone[2])).

The ^1H-NMR of **4** revealed the presence of 5 Me at δ(H) 1.33, 1.49, 1.58, 1.88, and 1.96 (5*s*, each 3 H). The ^{13}C-NMR showed 26 C-signals: 5 Me, 3 CH_2, 8 CH (including 5 CH–O at δ 54.5 (C(15)), 65.3 (C(11)), 72.8 (C(17)), 76.6 (C(1)), and 99.0 (C(23))), and 10 C. Compound **4** has the same A–D ring structure as clausenarin [16] according to its ^1H- and ^{13}C-NMR. The ^{13}C-NMR signals at δ(C) 99.0 (*d*), 131.1 (*s*), 153.8 (*d*), and 169.9 (*s*) showed the presence of the same 4-hydroxybut-2-eno-4-lactone function as in **3**.

The HR-EI-MS of **5** gave its molecular formula $C_{28}H_{36}O_{11}$. Based on the similarities of the NMR spectra of **5** and **4** (*Tables 1* and *2*), the structure of **5** was determined to be 23-ethoxy-21,23-dihydro-21-oxoclausenarin[4]) (=1α,11β)-23-ethoxy-1,2,21,23-tetrahydro-1,11-dihydroxy-21-oxoobacunone[2]).

The ^1H-NMR data of **5** revealed the presence of 6 Me at δ(H) 1.09 (*t*), 1.31 (*s*), 1.40 (*s*), 1.59 (*s*), 1.84 (*s*), and 1.93 (*s*). The ^1H- and ^{13}C-NMR spectra of **5** showed similarities with those of **4**, except for the presence of

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[3]) Obacunonic acid = (3*S*,3a*S*,5a*R*,6*R*,7*R*,9a*R*,9b*R*,10a*S*)-3-[3-(furan-3-yl)dodecahydro-7-(1-hydroxy-1-methylethyl)-3a,6,9a-trimethyl-1,9-dioxonaphth[2,1-*c*]oxireno[*d*]pyran-6-yl]prop-2-enoic acid.

[4]) Clausenarin = (1*S*,3a*S*,4a*R*,4b*R*,6a*R*,11*S*,1a*R*,11b*R*,12*S*,13a*S*)-1-(furan-3-yl)decahydro-11,12-dihydroxy-4b,7,7,11a,13a-pentamethyloxireno[4,4a]-2-benzopyrano[6,5-*g*][2]benzoxepin-3,5,9(3a*H*,4b*H*,6*H*)-trione.

an EtO group (δ(H) 3.74 (*m*, 1 H), 3.62 (*q*, *J* = 7.0 Hz, 1 H), 1.09 (*t*, *J* = 7.0 Hz, 3 H); δ(C) 66.1 (*t*), 13.7 (*q*)). The chemical shift of C(23) of **5** was shifted downfield to δ(C) 102.3 (*d*) compared with that of **4**, suggesting that the EtO group was linked at C(23). This was also confirmed by the HMBC experiment.

The HR-FAB-MS (negative mode) of **6** showed its molecular formula to be $C_{26}H_{34}O_{11}$. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.) and their comparison with the data of **3** revealed the structure of **6** to be (11β)-1,2,21,23-tetrahydro-11,23-dihydroxy-21-oxoobacunoic acid[3]).

The ^{13}C-NMR of **6** revealed the presence of 26 C-atoms: 5 Me, 4 CH_2, 7 CH, and 10 C (including 2 C–O at δ 63.7, and 73.9). On the basis of the similarities between the ^{13}C-NMR spectra of **6** and **3**, it was concluded that rings B – E of **6** were the same as those of **3**. The difference between **6** and **3** was in ring A. The signals of the *cis*-disubstitued double bond were absent in **6** and replaced by two CH_2 at δ(C) 36.4 and 42.4, and the resonances of C(4) and C(3) were shifted upfield to 73.9 and 174.2 ppm, resp., consistent with a C(1)/C(2) saturated acid.

Experimental Part

General. UV Spectra: *UV-210A* spectrophotometer; λ_{max} in nm. IR Spectra: KBr pellets; *Perkin-Elmer 577* spectrophotometer; in cm^{-1}. NMR Spectra: 1D, *Bruker AM-400* spectrometer; 2D, *Bruker DRX-500* spectrometer; δ in ppm rel. to $SiMe_4$ (= 0 ppm), *J* in Hz. MS: *VG Autospec-3000* spectrometer.

Plant Material. The aerial parts of *Clausena excavata* BURM. F. were collected in Xishuangbanna, Yunnan, China. A voucher specimen of this plant was deposited in the Kunming Institute of Botany, Kunming, China.

Extraction and Isolation. The powdered aerial part of *C. excavata* (6.0 kg) was extracted three times with 90% EtOH (12 l) under reflux for 8 h each time. The extract (620 g) was chromatographed (silica gel, $CHCl_3$, $CHCl_3$/AcOEt, AcOEt, and MeOH, successively). The $CHCl_3$/AcOEt eluate (60 g) was further subjected to column chromatography (silica gel, gradient of petroleum ether/AcOEt 7:3, 6:4, 1:1, 4:6 and 3:7). The last two fractions (petroleum ether/AcOEt 4:6 and 3:7) were combined and chromatographed over silica gel and *Sephadex LH-20* to give **1** (2.618 g), **2** (189 mg), **3** (12 mg), **4** (15 mg), **5** (9 mg), and **6** (10 mg).

(11β)-21,23-Dihydro-11,21-dihydroxy-23-oxoobacunone[2]) (**2**). Amorphous powder. $[\alpha]_D^{24} = -32.4$ (*c* = 0.55, MeOH). UV: 210. IR: 3487, 2992, 2947, 1750, 1713, 1461, 1433, 1399, 1378, 1275, 1230, 1138, 1119, 1049, 978, 905, 843. ^{1}H-NMR. *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 502 (2), 484 (3), 458 (6), 440 (11), 425 (8), 387 (10), 251 (15), 136 (74), 91 (73), 55 (100). HR-EI-MS: 502.1876 ($C_{26}H_{30}O_{10}^+$; calc. 502.1839).

Compounds **2a** *and* **2b**. Obacunone **2** (60 mg), pyridine (4 ml), and Ac_2O (2 ml) were stirred for 48 h. Usual workup and chromatography (silica gel) gave **2a** (30 mg) and **2b** (24 mg).

(11β)-11,21-Diacetoxy-21,23-dihydro-23-oxoobacunone[2]) (**2a**): ^{1}H-NMR ((D$_6$)DMSO, 400 MHz): 1.03, 1.33, 1.42, 1.43, 1.50, 2.07, 2.09 (7*s*, 7 Me); 3.93 (*s*, CH(15)); 5.58 (*d*, *J* = 6.7, CH(11)); 5.28 (br. *s*, CH(17)); 5.93 (*d*, *J* = 12.0, CH(2)); 6.51 (*s*, CH(22)); 6.83 (*d*, *J* = 12.0, CH(1)); 6.89 (*s*, CH(21)). ^{13}C-NMR: *Table 2*. EI-MS: 586 (1), 485 (5), 468 (5), 426 (9), 136 (100), 108 (56).

(11β)-11-Acetoxy-21,23-dihydro-21-hydroxy-23-oxoobacunone[2]) (**2b**): ^{1}H-NMR ((D$_6$)DMSO, 400 MHz): 0.98, 1.33, 1.41, 1.42, 1.46, 2.07 (6*s*, 6 Me); 3.89 (*s*, CH(15)); 5.67 (br. *s*, CH(11)); 5.15 (br. *s*, CH(17)); 5.93 (*d*, *J* = 12.0, CH(2)); 6.01 (br. *s*, CH(21)); 6.25 (br. *s*, CH(22)); 6.83 (*d*, *J* = 12.0, CH(1)). ^{13}C-NMR: *Table 2*. EI-MS: 544 (3), 486 (5), 469 (4), 443 (17), 425 (11), 136 (100), 108 (57).

Methyl (11β)-21,23-Dihydro-11-hydroxy-21-methoxy-23-oxoobacunonate[3]) (**2c**). Obacunone **2** (50 mg) and 3% aq. H_2SO_4 soln. (10 ml) were refluxed for 3 h. Usual workup and chromatography (silica gel) afforded **2c** (28 mg). ^{1}H-NMR ((D$_6$)DMSO, 400 MHz): 0.95, 1.08, 1.09, 1.41, 1.65 (5*s*, 5 Me); 3.50 (*s*, 1 MeO); 3.67 (*s*, 1 MeO); 4.97 (*s*, CH(17)); 5.13 (br. *s*, CH(21)); 5.90 (*d*, *J* = 16.0, CH(2)); 6.00 (*s*, CH(22)); 6.95 (*d*, *J* = 16.0, CH(1)). EI-MS: 548 (3), 530 (4), 446 (43), 431 (11), 107 (52), 59 (100).

(11β)-21,23-Dihydro-11,23-dihydroxy-21-oxoobacunone[2]) (**3**). Amorphous powder. $[\alpha]_D^{25} = -5.0$ (*c* = 0.45, MeOH). UV: 214. IR: 3498, 2999, 2960, 1767, 1728, 1692, 1434, 1399, 1382, 1284, 1251, 1117, 1075, 1021, 986, 934, 682. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 502 (1), 484 (2), 136 (86), 55 (100). FAB-MS (neg.): 501. HR-FAB-MS (neg.): 501.1708 ($C_{26}H_{29}O_{10}^+$; calc. 501.1761).

(1α,11β)-1,2,21,23-Tetrahydro-1,11,23-trihydroxy-21-oxoobacunone[2]) (**4**). Amorphous powder. $[\alpha]_D^{24} = -49.6$ (*c* = 0.63, MeOH). UV: 203.5. IR: 3472, 2992, 2947, 1749, 1715, 1630, 1431, 1399, 1378, 1279, 1231,

1118, 1028, 979, 937. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 520 (1), 502 (2, $[M-H_2O]^+$), 440 (21), 422 (49), 407 (42), 165 (59), 91 (100). HR-EI-MS: 520.1940 ($C_{26}H_{32}O_{11}^+$; calc. 520.1945).

(1α,11β)-23-Ethoxy-1,2,21,23-tetrahydro-1,11-dihydroxy-21-oxoobacunone[2]) (**5**). Amorphous powder. $[\alpha]_D^{25} = -21.9$ ($c = 0.40$, MeOH). UV: 205. IR: 3487, 2985, 2944, 1750, 1717, 1461, 1432, 1377, 1277, 1230, 1119, 1029, 979, 935. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. EI-MS: 548 (2), 530 (10, $[M-H_2O]^+$), 472 (20), 433 (19), 415 (11), 136 (100). HR-EI-MS: 548.2263 ($C_{28}H_{36}O_{11}^+$; calc. 548.2258).

(11β)-1,2,21,23-Tetrahydro-11,23-dihydroxy-21-oxoobacunoic Acid[3]) (**6**). Amorphous powder. $[\alpha]_D^{25} = -53.8$ ($c = 0.40$, MeOH). UV: 204.5. IR: 3471, 2978, 2940, 1745, 1731, 1380, 1270, 1207, 1140, 1024, 939, 689. ^{1}H-NMR: *Table 1*. ^{13}C-NMR: *Table 2*. FAB-MS (neg.): 521. HR-FAB-MS (neg.): 521.1995 ($C_{26}H_{33}O_{11}^+$; calc. 521.2013).

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