Tetranortriterpenoids from *Walsura yunnanensis*

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Five new tetranortriterpenoids—walsurin (**1**), isowalsuranolide (**2**), walsuranolide (**3**), 11β-acetoxywalsuranolide (**4**), and 20,22-dihydro-22,23-epoxywalsuranolide (**5**)—and three new natural tetranortriterpenoids—11β-hydroxydihydrocedrelone (**6**), 11β-acetoxydihydrocedrelone (**7**), and 11β-hydroxycedrelone (**8**)—together with a known tetranortriterpenoid, cedrelone (**9**), were isolated from the bark of *Walsura yunnanensis*. The structures of **1**−**8** were determined on the basis of spectral evidence.

The genus *Walsura* Roxb. (Meliaceae), comprising 30−40 species, is naturally distributed in the People's Republic of China, India, and Indonesia.[1] In previous literature, triterpenoids and tetranortriterpenoids were isolated from species in this genus.[2−4] In the course of searching the family Meliaceae for new limonoids with activity against insects, we undertook the investigation of *W. yunnanensis* C. Y. Wu as there were no chemical constituents published for this plant. Five new tetranortriterpenoids[walsurin (**1**), isowalsuranolide (**2**), walsuranolide (**3**), 11β-acetoxywalsuranolide (**4**), and 20,22-dihydro-22,23-epoxywalsuranolide (**5**)] along with three new natural tetranortriterpenoids [11β-hydroxydihydrocedrelone (**6**), 11β-acetoxydihydrocedrelone (**7**), and 11β-hydroxycedrelone (**8**)] were obtained from EtOH extracts of the bark of the plant. They were elucidated based on the spectral data. In addition, a known tetranortriterpenoid, cedrelone (**9**),[5] was also isolated.

Results and Discussion

Compound **1** was found to possess a molecular formula of $C_{26}H_{32}O_5$ as determined by negative-ion HRFABMS,

which was confirmed from the ¹³C and DEPT NMR spectra. Its IR spectrum revealed absorption bands for hydroxyl (3499 cm^{-1}) and carbonyl groups (1736, 1716, and 1674 cm^{-1}). The UV spectrum indicated the presence of an α,β-unsaturated carbonyl group (216.5 nm). The ¹H and ¹³C NMR spectra showed signals due to five tertiary methyl groups (δ_C 17.1, 18.8, 22.2, 24.7, 27.3); six olefinic carbons, four of which were attributed to a β-substituted furan ring moiety; four skeleton quaternary carbons [δ_C 42.3 (C-13), 42.9 (C-4), 45.1 (C-8), 45.3 (C-10)]; and three carbonyl groups (δ_C 220.1, 209.3, 203.2). These data suggested that **1** is a tetranortriterpenoid with three ketonic carbonyl groups.

The signals at δ_C 125.2 (d), 154.7 (d), and 203.2 (s) in the ¹³C NMR spectrum of **1** and corresponding protons at δ_H 7.05 (1H, d, $J = 10.3$ Hz, H-1) and 5.82 (1H, d, $J = 10.3$ Hz, H-2) in the ¹H NMR spectrum are typical signals for an α,β-unsaturated ketone moiety in the A ring.[7−9] In the HMBC spectrum, cross-peaks between δ_H 7.05 (H-1), δ_H 3.79 (s, H-5), and methyl protons δ_H 1.45 (s, H-28), 1.17 (s, H-29) to δ_C 203.2 (s, C-3) (Figure 1) permitted the assignment of a ketonic carbonyl group at C-3 and a double bond between C-1 and C-2. The signal at δ_H 3.74 (d, $J = 5.5$ Hz), attributed to a proton attached to a carbon adjacent to an oxygen atom, showed cross signals to δ_C 209.3 (C-6), 55.7 (C-5), and 17.1 (C-30) (Figure 1), respectively, in the HMBC spectrum, which placed a hydroxyl at C-7. The stereochemistry of this functionality was determined as α, based on a NOE correlation between H-7 and δ_H 1.00 (3H, s, H-30) in the NOESY spectrum of **1**. The presence of a large coupling constant ($J = 5.5$ Hz) between H-7 and the resonance at δ_H 3.66 (1H, OH-7) in the ¹H NMR spectrum was attributed to the formation of a hydrogen bond between the C-6 carbonyl group and the C-7 hydroxyl proton. The existence of hydrogen bonding led the −OH proton exchange to slow and allowed the coupling between H-7 and OH-7. The OH-7 proton signal and the coupling between H-7 and OH-7 disappeared when D₂O was added.

The ketonic carbonyl group present at δ_C 220.1 in the ¹³C NMR spectrum of **1**, suggested that it was present in a five-membered ring (D). The H-14 signal appeared as a singlet at δ_H 2.83 and H-17 as a triplet at δ_H 3.45 in the ¹H NMR spectrum and suggested the presence of a ketonic carbonyl at C-15. This inference was further supported by the HMBC spectrum. In the NOESY spectrum, NOE interactions of H-14 with H-9, H-14 with H-18, and H-14 with OH-7 indicated their cis relationships. Based on the above evidence, we propose structure **1** for
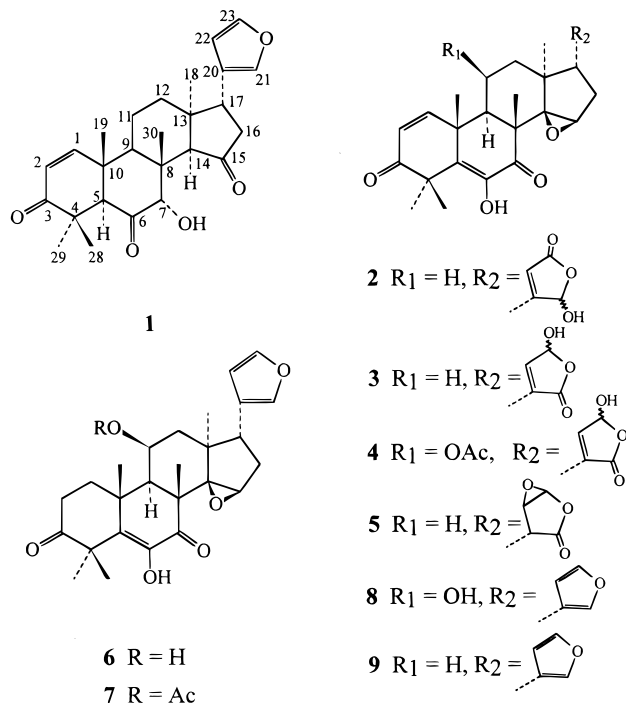
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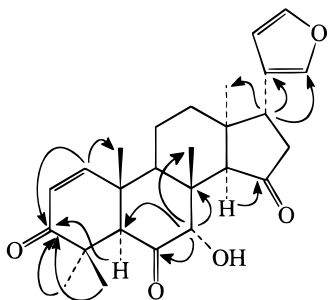
Figure 1. Selected HMBC of Compound **1** (from H to C).

this tetranortriterpenoid, which has been assigned the trivial name walsurin.

Compound **2** was assigned the molecular formula $C_{26}H_{30}O_7$ on the basis of its EIMS and ^{13}C and DEPT NMR spectra, which was also supported by its negative-ion HRFABMS. The ^1H and ^{13}C NMR spectra indicated signals for five tertiary methyl groups (δ_H 1.82, 1.80, 1.22, 1.19, and 0.96), two olefinic protons conjugated to carbonyls (δ_H 7.02 and 6.27, $J = 9.6$ Hz), four characteristic quaternary carbons (δ_C 49.1, 47.8, 42.9, 40.5), two ketonic carbonyl groups (δ_C 203.8 and 198.2), an ester carbonyl group (δ_C 171.2), and a hemiacetal carbon (δ_C 99.9). These data suggest that **2** is a tetranortriterpenoid similar to cedrelone (**9**).[5] Comparison of the molecular formulas of these two compounds revealed the presence of two more oxygen atoms in **2**. Analysis of the ^1H and ^{13}C NMR spectra indicated that the difference between two compounds was only in the furan ring. For compound **2**, instead of a furan unit as in cedrelone (**9**), there was a γ-hydroxybutyrolactone unit attached to C-17. The ^{13}C NMR signals at δ_C 171.2 (s), 170.0 (s), 119.6 (d), and 99.9 (d) were attributed to C-23, C-20, C-22, and C-21, and the corresponding ^1H NMR resonances at δ_H 6.42 (s) and 6.07 (s), were assigned to H-22 and H-21, respectively.[11–13] According to these spectral data, compound **2** was structurally elucidated as having a 21-hydroxybut-20(22)-ene-21,23-γ-lactone as the side chain and has been named isowalsuranolide.

Compound **3** also exhibited a molecular ion peak at m/z 454 in its EIMS. Together with ^1H and ^{13}C NMR spectral data, a molecular formula $C_{26}H_{30}O_7$ was established and confirmed by HRFABMS. The ^1H and ^{13}C NMR spectra of **3** showed similarities to those of isowalsuranolide (**2**) and cedrelone (**9**),[5] with the exception of the side chain. The presence of a γ-hydroxybutyrolactone unit as the side chain was revealed by the signals at δ_H 6.98 (H-22) and 6.24 (H-23) in the ^1H NMR spectrum. This was corroborated by the ^{13}C NMR spectrum, which showed a hemiacetal carbon at δ_C 98.3 (C-23) and an α,β-unsaturated-γ-lactone [δ_C 136.5 (s, C-20), 171.9 (s, C-21), and 148.6 (d, C-22)]. These signals required the presence of a 23-hydroxy-20(22)-ene-21,23-γ-lactone in walsuranolide (**3**), by comparison with reference ^{13}C and ^1H NMR spectral data in the literature.[13,14]

The molecular formula of compound **4** was determined as $C_{28}H_{32}O_9$ by EIMS, ^{13}C NMR, and DEPT NMR spectral data and confirmed by HRFABMS. The EIMS exhibited a fragment ion peak at m/z 452, which was attributed to the loss of acetic acid $[M - 60]^+$ from the molecular ion peak at m/z 512. The ^1H and ^{13}C NMR spectra of **4** were very similar to those of **3**, except for the presence of an acetate in **4**. Instead of three methylene groups in **3**, signals for two methylene groups (δ_C 31.4, 43.2), an oxymethine (δ_C 68.7), and an acetate group (δ_C 170.2, 22.3) were present in the ^{13}C NMR spectrum of **4**. The acetate was placed at

C-11 by comparing the ^{13}C and ^1H NMR spectra of the two compounds. A broad doublet signal ($J = 6.4$ Hz) for H-7 in pyridine-d_5 suggested an 11β-configuration,[10] as in compound **6**. Thus, compound **4** was elucidated as 11β-acetoxy walsuranolide. The presence of double signals for some carbons (Table 1) and protons (see Experimental Section) in compounds **2**–**4** was attributed to the equilibrium between the two epimeric forms at the hemiacetal carbon of the γ-hydroxybutenolide ring.

From its HRFABMS and ^{13}C and DEPT NMR spectra, compound **5** was established with the molecular formula $C_{26}H_{30}O_7$, which is identical with those of compounds **2** and **3**. The ^1H and ^{13}C NMR spectra of isowalsuranolide (**2**), walsuranolide (**3**), compound **5**, and cedrelone (**9**)[5] suggested that these molecules are identical in rings A–D and differ only in the nature of the side chain attached at C-17. The side chain of **5** was somewhat different from that of **2** and **3**. Signals belonging to the side chain were present at δ_C 169.8 (s), 77.9 (d), 53.6 (d), and 43.5 (d) in the ^{13}C NMR spectrum and the corresponding protons at δ_H 5.55 (d, $J = 4.4$ Hz, H-23) and 3.67 (dd, $J = 4.4$, 1.9 Hz, H-22) in the ^1H NMR spectrum of **5**. The extra degree of unsaturation required by the molecular formula of **5** indicated the presence of one more ring in the side chain, due to the absence of olefinic carbon signals for the side chain in the ^{13}C NMR spectrum of **5**. The available data suggested a 22,23-epoxy-21,23-γ-lactone unit for the side chain. This inference was further supported by a correlation between δ_H 3.67 (H-22) and a signal at δ_H 5.55 (H-23) and between δ_H 3.67 (H-22) and δ_H 2.65 (dd, $J = 6.8$, 1.9 Hz, H-20) in the ^1H–^1H COSY spectrum. Accordingly, compound **5** was deduced as 20,22-dihydro-22,23-epoxywalsuranolide.

The EIMS of compound **6** showed a molecular ion peak at m/z 440 and, together with its ^{13}C and DEPT NMR spectra, suggested a molecular formula of $C_{26}H_{32}O_6$, which was confirmed by HREIMS. The ^1H NMR spectrum exhibited signals for five tertiary methyl groups as singlets at δ_H 1.82, 1.75, 1.69, 1.56, and 0.86, as well as characteristic signals for a β-substituted furan ring moiety (δ_H 7.56, 7.34, and 6.27) and a proton attached to the carbon bearing an oxygen atom (δ_H 4.83). The above data suggest a tetranortriterpenoid skeleton for compound **6**. The ^{13}C NMR spectrum of **6** was very similar to that of 1,2-dihydroanthothecol.[5] The proton at δ_H 4.83 (H-11) in **6** appeared as a broad doublet signal when measured in pyridine-d_5 and as a double doublet peak ($J = 5.0$, 1.8 Hz) in acetone-d_6, which suggested a cis relationship between H-9 and H-11.[10] In addition, H-9 appeared as a singlet and also supported this inference. In the ROESY spectrum, a NOE correlation between H-11 and H-9 further confirmed an OH-11β substitutent. Thus, compound **6** was deduced to be 11β-hydroxydihydrocedrelone. This isolate may be identical to deacetyldihydroanthothecol (a compound obtained from dihydroanthothecol by alkaline hydrolysis) on the basis of similar physical data.[6]

Compound **7** showed in its EIMS a molecular ion peak at m/z 482 in accordance with the formula $C_{28}H_{34}O_7$, and the presence of 28 carbons was confirmed by its ^{13}C NMR spectrum and HREIMS. The ^1H and ^{13}C NMR spectra of **7** displayed similarities to those of compound **6**, except for an acetoxyl in **7**, which was consistent with its higher molecular formula. On comparison of the spectral data of these two compounds, it was evident that there was an acetyl at C-11 in **7** instead of a hydroxyl, as in **6**. The OAc-11 unit was assigned as β on the basis of the small coupling constants for H-11 (δ_H 5.57, dd, $J = 4.8$, 2.4 Hz), as in compound **6**. Thus, compound **7** was elucidated as 11β-

Table 1. ^{13}C NMR Spectral Data for Compounds **1**−**9** (100 MHz)[a]

carbon	1	2	3	4	5	6	7	8	9
1	154.7 d	153.4 d	153.4 d	152.1 d	152.1 d	35.8 t	35.6 t	151.5 d	152.2 d
2	125.2 d	127.3 d	127.2 d	127.6 d	127.5 d	33.2 t	32.4 t	127.6 d	127.2 d
3	203.2 s	203.8 s	203.7 s	203.5 s	203.8 s	214.4 s	213.6 s	203.2 s	203.3 s
4	42.9 s	49.1 s	49.1 s	49.1s	48.6 s	48.4 s	47.8 s	48.6 s	48.5 s
5	55.7 d	133.7 s	133.6 s	133.3 s	133.6 s	139.6 s	138.9 s	134.6 s	133.9 s
6	209.3 s	143.9 s	143.8 s	143.7 s	141.8 s	142.4 s	140.1 s	140.8 s	141.2 s
7	79.0 d	198.2 s	198.3 s	197.8 s	197.8 s	199.1 s	198.0 s	197.2 s	197.8 s
8	45.1 s	47.8 s	47.9 s	47.1 s	46.8 s	46.7 s	45.6 s	45.9 s	46.8 s
9	46.3 d	44.7 d	45.9 d	44.1 d	43.8 d	48.6 d	46.5 d	45.5 d	43.2 d
10	45.3 s	40.5 s	40.5 s	40.8 s	40.4 s	39.8 s	39.2 s	40.9 s	40.2 s
11	17.8 t	19.6 t	19.8 t	68.7 d	19.6 t	66.1 d	67.7 d	67.3 d	19.4 t
12	33.9 t	35.2 t	35.6 t	43.2 t	35.4 t	46.7 t	42.5 t	46.5 t	35.1 t
13	42.3 s	42.9 s	42.7 s	42.9 s	42.1 s	41.2 s	40.4 s	41.2 s	41.9 s
14	60.5 d	70.0 s	70.2 s	68.9 s	69.5 s	69.6 s	68.5 s	69.5 s	69.7 s
15	220.1 s	55.1 d	55.1 d	55.9 d	55.1 d	57.0 d	55.9 d	58.8 d	55.0 d
16	43.2 t	31.3 t	32.0 t	31.4 t	31.5 t	31.8 t	31.4 t	31.3 t	31.9 t
17	38.0 d	43.7 d	43.6 d	43.1 d	42.6 d	42.7 d	42.0 d	42.6 d	41.7 d
18	27.3 q	24.0 q	23.4 q	23.0 q	23.9 q	23.5 q	23.1 q	22.1 q	23.8 q
19	18.8 q	19.9 q	20.1 q	21.1 q	20.2 q	17.5 q	16.3 q	25.5 q	20.1 q
20	122.6 s	170.0 s	136.5 s	136.2 s	43.5 d	124.2 s	122.8 s	122.7 s	123.2 s
21	140.2 d	99.9, 100.8 d	172.1, 170.9 s	171.8, 171.6 s	169.8 s	140.0 d	139.5 d	139.5 d	139.3 d
22	110.7 d	119.6, 120.2 d	148.9, 148.6 d	149.1, 148.9 d	53.6 d	111.4 d	110.6 d	110.5 d	110.6 d
23	143.1 d	171.2 s	98.3, 98.1 d	98.3, 98.2 d	77.9 d	143.5 d	143.1 d	143.2 d	142.9 d
28	22.2 q	27.2 q	27.1 q	27.2 q	26.9 q	24.7 q	24.4 q	26.9 q	26.7 q
29	24.7 q	21.7 q	21.6 q	21.6 q	21.3 q	21.1 q	21.4 q	21.2 q	21.2 q
30	17.1 q	24.5 q	24.0 q	24.9 q	22.4 q	22.6 q	22.2 q	22.6 q	22.9 q
OAc				170.2 s			170.4 s		
				22.3 q			20.4 q		

[a] Compounds **1**, **5**, **7**, **8**, and **9** were measured in CDCl$_3$ and compounds **2**, **3**, **4**, and **6** in pyridine-d_5; chemical shifts are in parts per million, with TMS as internal standard.

acetoxydihydrocedrelone. According to similar physical properties, compound **7** is probably the same as 1,2-dihydroanthothecol,[5,6] a hydrogenated derivative of anthothecol.

Compound **8** was assigned the molecular formula C$_{26}$H$_{30}$O$_6$ on the basis of its EIMS and ^{13}C and DEPT NMR spectra. Comparison of the spectral data of compounds **6** and **8** suggested that **8** was 1,2-dehydro derivative of **6**. That OH-11 is β was supported by the ROESY spectrum of **8** and the evidence that H-9 occurs as a singlet in its ^{1}H NMR spectrum, as in **6**. Accordingly, compound **8** was deduced as 11β-hydroxycedrelone. This compound may be identical to deacetylanthothecol,[6] a derivative from anthothecol. The physical properties of compounds **6**−**8** were similar to those of corresponding derivatives from anthothecol. As 11α-substituents are rare in tetranortriterpenoids and direct evidence of an OAc-11α functionality for anthothecol was not obtained in the original paper,[6] we propose an 11β-configuration for anthothecol.

Compound **9** was identified as cedrelone by comparing its ^{13}C NMR spectral data with previously published values,[5] despite some errors in the original assignments. Due to the absence of spectral data for compounds **6**−**8** in the previous literature and some wrong assignments for cedrelone, spectral and physical data of **6**−**9** are listed in Table 1 and in the Experimental Section.

Experimental Section

General Experimental Procedures. Melting points were obtained on a Sichuan micromelting point apparatus and are uncorrected. Optical rotations were obtained with a Horiba SEAP-300 spectropolarimeter. UV spectra were measured with a Shimadzu double-beam 210A spectrophotometer in MeOH solution. IR spectra (KBr) were obtained on a Bio-Rad FTS-135 infrared spectrophotometer. ^{1}H, ^{13}C, and 2D NMR spectra were recorded on a Bruker AM-400 and a DRX-500 NMR spectrometer with TMS as internal standard. MS data were obtained on a VG Autospec-3000 spectrometer, at 70 eV for

EI. Si gel (200−300 mesh) for column chromatography and GF$_{254}$ for TLC were obtained from the Qindao Marine Chemical Factory, Qindao, People's Republic of China.

Plant Material. The bark of *W. yunnanensis* was collected from Mengna County, Yunnan Province, People's Republic of China, in December 1996. It was identified by Prof. G. D. Tao, Xishuangbangna Botanic Garden. A voucher specimen has been deposited in the herbarium of the Department of Taxonomy, Kunming Institute of Botany, no. 38001.

Extraction and Isolation. The air-dried and powdered bark (4.2 kg) of *W. yunnanensis* was extracted with EtOH three times under reflux. After removal of the solvent in vacuo, the residue was suspended in H$_2$O and extracted EtOAc. The EtOAc fraction was concentrated in vacuo to give 66 g of a residue, which was subjected to column chromatography on Si gel, eluted with gradient mixtures of CHCl$_3$−Me$_2$CO (from CHCl$_3$ to CHCl$_3$−Me$_2$CO, 2:1). According to differences in composition monitored by TLC (Si gel GF$_{254}$), 10 fractions were obtained. Then, fractions 2 (3.1 g) and 3 (1.0 g) were purified by Si gel column chromatography, using petroleum ether−Me$_2$CO (8:1) as eluent and recrystallization from acetone to afford 11β-acetoxydihydrocedrelone (**7**) (34 mg), 20,22-dihydro-22,23-epoxywalsuranolide (**5**) (3 mg), and cedrelone (**9**) (1.85 g). Fractions 4 (1.3 g) and 5 (1.9 g) were subjected to column chromatography on Si gel with petroleum ether−EtOAc (2:1), then recrystallized from acetone to afford walsurin (**1**) (28 mg) and 11β-hydroxycedrelone (**8**) (325 mg). Fraction 6 (2.3 g) was further subjected to Si gel column chromatography with petroleum ether−Me$_2$CO (5:1) and recrystallized from acetone, finally yielding 11β-hydroxydihydrocedrelone (**6**) (62 mg) and isowalsuranolide (**2**) (12 mg). Fraction 7 (2.6 g) was subjected to Si gel column chromatography with CHCl$_3$−EtOAc (2:1) to give two subfractions, which were further purified on reversed-phase C$_{18}$ Si gel, respectively, using CH$_3$OH−H$_2$O (3:1−2:1) as eluent and recrystallized from acetone, to yield walsurannolide (**3**) (20 mg) and 11β-acetoxywalsuranolide (**4**) (28 mg).

Walsurin (1): prisms (Me$_2$CO); mp 248−250 °C; [α]^{29}$_D$ −20.0° (*c* 0.21, CH$_3$OH); UV (MeOH) λ_{max} (log ε) 216.5 (4.11) nm; IR (KBr) ν_{max} 3499, 3115, 2943, 2880, 1736, 1716, 1674, 1503, 1460, 1392, 1321, 1273, 1168, 1074, 1047, 1032, 873

cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.39 (1H, t, J = 1.6 Hz, H-23), 7.27 (1H, s, H-21), 7.05 (1H, d, J = 10.3 Hz, H-1), 6.27 (1H, d, J = 1.6 Hz, H-22), 5.82 (1H, d, J = 10.3 Hz, H-2), 3.79 (1H, s, H-5), 3.74 (1H, d, J = 5.5 Hz, H-7), 3.66 (1H, d, J = 5.5 Hz, OH-7), 3.45 (1H, t, J = 10.1 Hz, H-17), 2.83 (1H, s, H-14), 2.50 (2H, dd, J = 11.4, 1.8 Hz, H-16), 2.0 (2H, m, H-12), 1.80 (2H, m, H-11), 1.77 (1H, m, H-9), 1.45 (3H, s, H-28), 1.17 (3H, s, H-29), 1.15 (3H, s, H-19), 1.00 (3H, s, H-30), 0.80 (3H, s, H-18); ^{13}C NMR (CDCl$_3$, 100 MHz) spectral data, see Table 1; EIMS m/z 424 [M]$^+$ (45), 409 (5), 396 (2), 313 (4), 233 (5), 20 (4), 173 (4), 163 (21), 149 (7), 137 (16), 119 (8), 108 (14), 94 (100), 83 (73), 65 (15); HRFABMS m/z 423.2186 [M − H]$^−$ (calcd for C$_{26}$H$_{31}$O$_5$, 423.2171).

Isowalsuranolide (2): crystalline solid (Me$_2$CO); mp 278−280 °C; [α]^{29}$_D$ −31.7° (c 0.23, C$_5$H$_5$N); UV (MeOH) λ$_{max}$ (log ε) 217 (4.13), 276.5 (4.05) nm; IR (KBr) ν$_{max}$ 3406, 3104, 2977, 2939, 1767, 1673, 1449, 1363, 1299, 1260, 1248, 1179, 1122, 1036, 946, 904, 812 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 10.60 (1H, s, OH-6), 7.02 (1H, d, J = 9.6 Hz, H-1), 6.42 (1H, br s, H-22), 6.27 (1H, d, J = 9.6 Hz, H-2), 6.07 (1H, s, H-21), 3.92 (1H, s, H-15), 1.82 (3H, s, H-28), 1.80 (3H, s, H-29), 1.22 (3H, s, H-19), 1.19 (3H, s, H-30), 0.96 (3H, s, H-18); ^{13}C NMR (pyridine-d_5, 100 MHz) spectral data, see Table 1; EIMS m/z 454 [M]$^+$ (50), 439 (5), 411 (4), 316 (30), 245 (7), 215 (8), 203 (10), 189 (13), 177 (11), 164 (100), 147 (15), 135 (30), 121 (39), 105 (36), 91 (64), 79 (31); HRFABMS m/z 454.1943 [M]$^+$ (calcd for C$_{26}$H$_{30}$O$_7$, 454.1991).

Walsuranolide (3): colorless needles (Me$_2$CO); mp 232−234 °C; [α]^{28}$_D$ −33.0° (c 0.25, CH$_3$OH); UV (MeOH) λ$_{max}$ (log ε) 215 (4.32), 276.5 (4.09) nm; IR (KBr) ν$_{max}$ 3341, 2980, 2939, 2874, 1766, 1676, 1619, 1462, 1418, 1339, 1296, 1254, 1126, 1090, 1025, 928, 875 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 10.53 (10.49) (1H, s, OH-6), 7.15 (7.18) (1H, d, J = 10.8 Hz, H-1), 6.95 (6.98) (1H, d, J = 10.0 Hz, H-22), 6.45 (6.47) (1H, d, J = 10.8 Hz, H-2), 6.24 (6.21) (1H, d, J = 10.0 Hz, H-23), 3.88 (3.85) (1H, s, H-15), 1.81 (3H, s, H-28), 1.78 (3H, s, H-29), 1.21 (3H, s, H-30), 1.18 (3H, s, H-19), 0.95 (0.88) (3H, s, H-18); ^{13}C NMR (pyridine-d_5, 100 MHz) spectral data, see Table 1; EIMS m/z 454 [M]$^+$ (50), 439 (5), 411 (3), 327 (5), 316 (83), 289 (6), 273 (8), 246 (6), 229 (8), 217 (15), 205 (7), 191 (11), 175 (15), 164 (96), 149 (35), 135 (35), 119 (26), 105 (42), 91 (91), 67 (57), 55 (100); HRFABMS m/z 453.1821 [M − H]$^−$ (calcd for C$_{26}$H$_{29}$O$_7$, 453.1761).

11β-Acetoxywalsuranolide (4): crystalline solid (Me$_2$CO); mp 181−183 °C; [α]^{28}$_D$ −17.0° (c 0.24, C$_5$H$_5$N); UV (MeOH) λ$_{max}$ (log ε) 215.5 (4.15), 277 (4.19) nm; IR (KBr) ν$_{max}$ 3353, 3096, 2988, 2939, 1763, 1742, 1690, 1631, 1449, 1384, 1347, 1285, 1237, 1118, 1091, 1033, 960, 939, 910, 798 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 10.70 (10.73) (1H, s, OH-6), 7.24 (7.17) (1H, d, J = 10.0 Hz, H-1), 7.16 (1H, d, J = 10.0 Hz, H-22), 6.44 (1H, d, J = 9.4 Hz, H-2), 6.24 (6.21) (1H, d, J = 10.0 Hz, H-23), 6.03 (6.02) (1H, br d, J = 6.4 Hz, H-11), 4.03 (4.00) (1H, s, H-15), 2.07 (3H, s, OAc), 1.81 (1.80) (3H, s, H-28), 1.78 (3H, s, H-29), 1.56 (3H, s, H-30), 1.37 (1.35) (3H, s, H-19), 0.94 (0.87) (3H, s, H-28); ^{13}C NMR (pyridine-d_5, 100 MHz) spectral data, see Table 1; EIMS m/z 512 [M]$^+$ (94), 497 (12), 481 (3), 470 (8), 452 (10), 437 (12), 419 (6), 409 (10), 382 (7), 314 (100), 299 (16), 283 (13), 271 (17), 245 (15), 227 (21), 215 (22), 187 (20), 175 (24), 164 (92), 149 (47), 137 (37), 121 (48), 107 (44), 91 (80); HRFABMS m/z 511.1982 [M − H]$^−$ (calcd for C$_{28}$H$_{31}$O$_9$, 511.1968).

20,22-Dihydro-22,23-epoxywalsuranolide (5): crystalline solid (Me$_2$CO); mp 192−194 °C; [α]^{29}$_D$ −23.6° (c 0.10, CH$_3$OH); UV (MeOH) λ$_{max}$ (log ε) 223.5 (4.11), 278 (4.09) nm; IR (KBr) ν$_{max}$ 3418, 2931, 2857, 1801, 1681, 1626, 1384, 1359, 1249, 1071, 1034, 855 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.89 (1H, d, J = 9.9 Hz, H-1), 6.43 (1H, s, OH-6), 6.10 (1H, d, J = 9.9 Hz, H-2), 5.55 (1H, d, J = 4.4 Hz, H-23), 3.71 (1H, s, H-15), 3.67 (1H, dd, J = 4.4, 1.9 Hz, H-22), 2.65 (1H, dd, J = 6.8, 1.9 Hz, H-20), 1.56 (3H, s, H-28), 1.48 (3H, s, H-29), 1.29 (3H, s, H-30), 1.10 (3H, s, H-19), 1.02 (3H, s, H-18); ^{13}C NMR (CDCl$_3$, 100 MHz) spectral data, see Table 1; EIMS m/z 454 [M]$^+$ (45), 439 (5), 411 (5), 327 (5), 316 (20), 299 (5), 263 (7), 217 (7), 191 (8), 175 (11), 164 (52), 149 (26), 135 (31), 121 (35), 105 (37), 91

(60), 79 (46), 67 (50), 55 (100); HRFABMS m/z 453.1840 [M − H]$^−$ (calcd for C$_{26}$H$_{29}$O$_7$, 453.1913).

11β-Hydroxydihydrocedrelone (6): colorless needles (Me$_2$CO); mp 201−202 °C; (lit.[6] mp 230 °C); [α]^{29}$_D$ −38.6° (c 0.45, C$_5$H$_5$N) (lit.[6] [α]^{20}$_D$ −75°); UV (MeOH) λ$_{max}$ (log ε) 209 (3.89), 278 (4.22) nm; IR (KBr) ν$_{max}$ 3563, 3392, 2974, 2944, 2934, 1702, 1685, 1616, 1505, 1455, 1384, 1279, 1255, 1168, 1148, 1034, 959, 875, 802 cm^{-1}; ^{1}H NMR (pyridine-d_5, 400 MHz) δ 10.06 (1H, s, OH-6), 7.56 (1H, t, J = 1.6 Hz, H-23), 7.34 (1H, s, H-21), 6.27 (1H, d, J = 1.6 Hz, H-22), 4.83 (1H, br d, J = 5.6 Hz, H-11), 4.06 (1H, s, H-15), 2.97 (1H, dd, J = 10.8, 6.4 Hz, H-17), 2.80, 2.67 (1H each, dd, J = 18.8, 9.6 Hz, H-2), 2.51 (1H, s, H-9), 2.31, 2.02 (1H each, dd, J = 14.8, 6.0 Hz, H-12), 2.30, 1.80 (1H each, m, H-1), 2.21, 1.94 (1H each, dd, J = 13.2, 6.4 Hz, H-16), 1.82 (3H, s, H-28), 1.75 (3H, s, H-29), 1.69 (3H, s, H-30), 1.56 (3H, s, H-19), 0.86 (3H, s, H-18); ^{13}C NMR (pyridine-d_5, 100 MHz) spectral data, see Table 1; EIMS m/z 440 [M]$^+$ (98), 425 (38), 407 (8), 381 (7), 334 (65), 283 (7), 249 (8), 235 (40), 217 (13), 205 (24), 187 (13), 177 (15), 165 (24), 151 (56), 137 (29), 121 (25), 107 (100), 94 (51), 79 (58), 67 (46); HREIMS m/z 440.2197 [M]$^+$ (calcd for C$_{26}$H$_{32}$O$_6$, 440.2199).

11β-Acetoxydihydrocedrelone (7): colorless needles (Me$_2$CO); mp 235−237 °C; (lit.[6] mp 188 °C); [α]^{28}$_D$ −54.3° (c 0.63, CH$_3$OH) (lit.[6] [α]^{20}$_D$ −86°); UV (MeOH) λ$_{max}$ (log ε) 212.5 (3.81), 276.5 (4.15) nm; IR (KBr) ν$_{max}$ 3403, 3144, 2978, 2941, 1727, 1711, 1684, 1628, 1583, 1457, 1308, 1192, 1172, 1126, 1072, 1036, 959, 873, 803 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.32 (1H, t, J = 1.5 Hz, H-23), 7.10 (1H, s, H-21), 6.34 (1H, s, OH-6), 6.12 (1H, s, H-22), 5.57 (1H, dd, J = 4.8, 2.4 Hz, H-11), 3.84 (1H, s, H-15), 2.09 (3H, s, OAc), 1.48 (3H, s, H-28), 1.42 (3H, s, H-29), 1.36 (3H, s, H-30), 1.09 (3H, s, H-19), 0.67 (3H, s, H-18); ^{13}C NMR (CDCl$_3$, 100 MHz) spectral data, see Table 1; EIMS m/z 482 [M]$^+$ (50), 467 (16), 422 (35), 407 (20), 389 (7), 360 (6), 316 (50), 257 (8), 235 (12), 188 (14), 165 (22), 149 (13), 137 (20), 121 (18), 107 (54), 94 (89), 79 (53), 67 (43), 55 (100); HREIMS m/z 482.2314 [M]$^+$ (calcd for C$_{28}$H$_{34}$O$_7$, 482.2305).

11β-Hydroxycedrelone (8): prisms (Me$_2$CO); mp 148−150 °C (lit.[6] mp 218 °C); [α]^{19}$_D$ −30.4° (c 0.83, CHCl$_3$) (lit.[6] [α]^{20}$_D$ −59°); UV (MeOH) λ$_{max}$ (log ε) 216 (4.18), 278 (4.15) nm; IR (KBr) ν$_{max}$ 3528, 3428, 2978, 2943, 1689, 1677, 1620, 1580, 1501, 1461, 1386, 1248, 1120, 1032, 958, 909, 875, 789, 735 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.35 (1H, d, J = 1.5 Hz, H-23), 7.15 (1H, s, H-21), 6.94 (1H, d, J = 9.9 Hz, H-1), 6.38 (1H, s, OH-6), 6.15 (1H, s, H-22), 6.11 (1H, d, J = 9.9 Hz, H-2), 4.62 (1H, dd, J = 9.0, 4.9 Hz, H-11), 4.00 (1H, s, H-15), 2.80 (1H, dd, J = 9.8, 7.4 Hz, H-17), 2.48 (1H, s, H-9), 1.53 (6H, s, H-28, H-19), 1.48 (3H, s, H-29), 1.35 (3H, s, H-30), 0.68 (3H, s, H-18); ^{13}C NMR (CDCl$_3$, 100 MHz) spectral data, see Table 1; EIMS m/z 438 [M]$^+$ (58), 423 (20), 405 (5), 332 (30), 255 (5), 245 (7), 233 (10), 215 (10), 205 (28), 191 (22), 176 (16), 164 (58), 149 (32), 135 (36), 121 (46), 107 (87), 94 (100), 77 (87), 67 (83).

Cedrelone (9): cubic crystals (Me$_2$CO); mp 174−176 °C (lit.[15] mp 209−214 °C); [α]^{29}$_D$ −64.2° (c 0.73, CHCl$_3$) {(lit.[15] [α]^{20}$_D$ −64.5°) (c 1, CHCl$_3$)}; UV (MeOH) λ$_{max}$ (log ε) 219.5 (4.10), 277.5 (4.03) nm; IR (KBr) ν$_{max}$ 3398, 3035, 2981, 2963, 2865, 1677, 1627, 1615, 1576, 1508, 1410, 1300, 1283, 1250, 1059, 1035, 879, 780 cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.31 (1H, t, J = 1.5 Hz, H-23), 7.09 (1H, s, H-21), 6.86 (1H, d, J = 9.8 Hz, H-1), 6.46 (1H, s, OH-6), 6.12 (1H, s, H-22), 6.05 (1H, d, J = 9.8 Hz, H-2), 3.74 (1H, s, H-15), 1.51, 1.43, 1.23, 1.06, 0.69 (3H each, s, CH$_3$ × 5); ^{13}C NMR (CDCl$_3$, 100 MHz) spectral data, see Table 1; EIMS m/z 422 [M]$^+$ (70), 407 (88), 396 (50), 389 (30), 379 (23), 360 (19), 351 (10), 337 (12), 316 (67), 257 (15), 241 (24), 231 (30), 215 (28), 203 (35), 189 (62), 177 (67), 164 (75), 149 (57), 137 (82), 119 (50), 107 (72), 91 (100), 79 (90).

References and Notes

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