Triterpenoids from *Melia toosendan*

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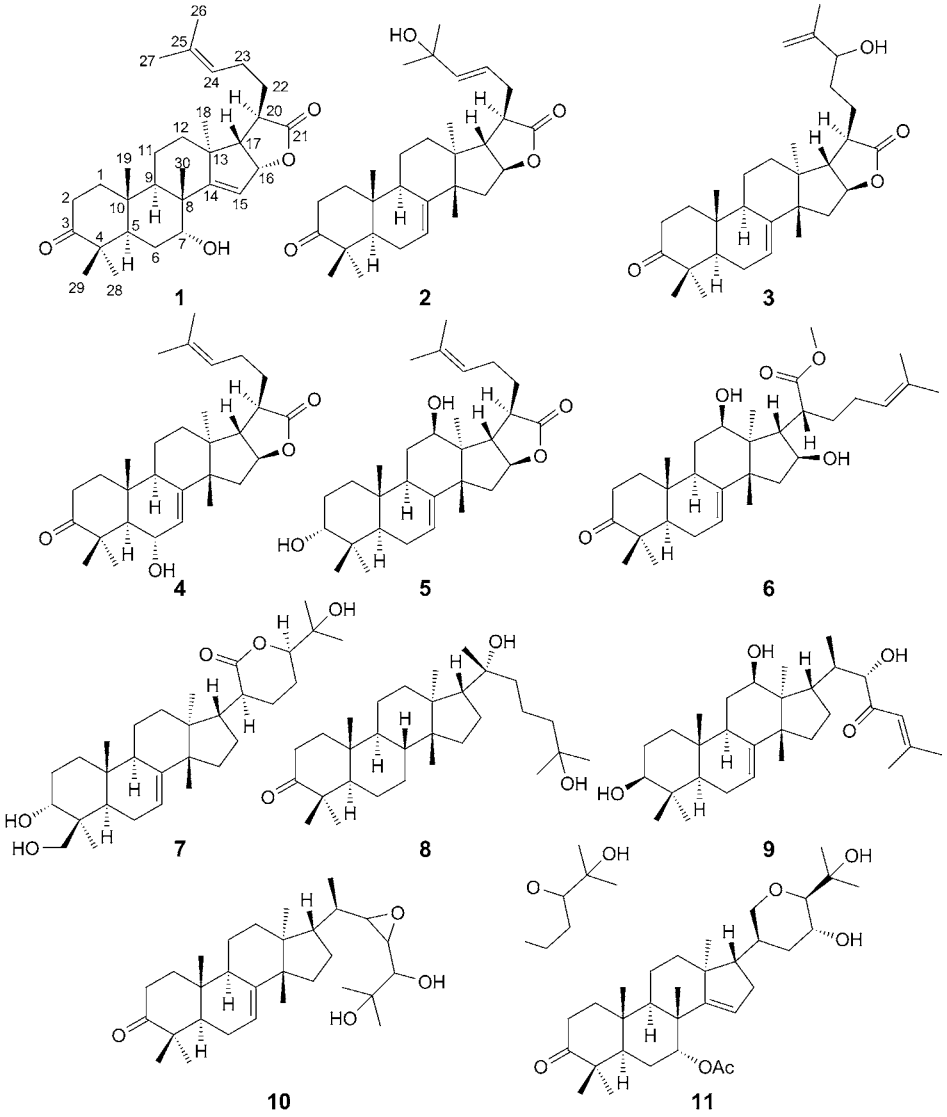
Eleven new triterpenoids, named mesendanins K–U (**1**–**11**, resp.), together with seven known analogs, were isolated from the leaves and twigs of *Melia toosendan*. Their structures were elucidated on the basis of extensive spectroscopic analysis.

Introduction. – Triterpenoids are a group of chemically and pharmacologically interesting secondary metabolites, occurring in a wide variety of species [1], and many of them are being studied from the aspects of structure determination [2] and total synthesis [3]. Interest in the biological activities of triterpenoids is still increasing [4]. In our continuing investigation on the Chinese traditional medicine, from *Melia toosendan* SIEB. et ZUCC. (Maliaceae) collected in Yunnan Province of P. R. China [5], eleven new triterpenoids, mesendanins K – U (**1**–**11**, resp.), were isolated, together with seven known analogs, 12β-hydroxykulactone [6], cinamodiol [7], 3,16-dihydroxy-eupha-7,24-dien-21-oic acid methyl ester [8], (22*S*,23*R*)-22,23-epoxytirucall-7-ene-3α,24,25-triol [9], 22,23-epoxytirucall-7-ene-3β,24,25-triol [10], and meliasenins G and H [11]. Compound **1** is the first apoeuphane-type triterpenoid featuring a five-membered γ-lactone ring between C(21) and C(16). Here, we report the isolation and structure elucidation of these compounds.

Results and Discussion. – Compound **1**, a white, amorphous powder, has the molecular formula of $C_{30}H_{44}O_4$, as determined by the sodiated molecular-ion peak at *m*/*z* 491.3133 ($[M+Na]^+$, $C_{30}H_{44}NaO_4^+$; calc. 491.3137) in the HR-ESI-MS, implying nine degrees of unsaturation. The IR spectrum of **1** revealed the presence of OH (3435 cm^{-1}) and CO (1765 and 1705 cm^{-1}) groups, and the peak at 1765 cm^{-1} strongly suggested the presence of a γ-lactone moiety [6]. The ^{13}C-NMR data (*Table 1*) with DEPT experiments revealed the presence of seven Me, seven CH_2, and eight CH (two olefinic and two O-bearing) groups, and eight quaternary C-atoms (two CO groups and two olefinic C-atoms). The two trisubstituted C=C bonds (δ(C) 117.6, 122.6, 133.2, and 173.3), and an ester CO (δ(C) 179.9) and a keto CO (δ(C) 217.1) group accounted for four of the nine degrees of unsaturation, the remaining five requiring **1** to be pentacyclic. The above analysis suggested that **1** was an apotirucallane (apoeuphane)-type triterpenoid featuring a γ-lactone subunit [12–14]. The structure of **1** was further elucidated by analysis of 2D-NMR spectra, especially the HMBC (*Fig. 1*), in which the keto CO (δ(C) 217.1) was placed at C(3) by the correlations from CH_2(1), CH_2(2),



Me(28), and Me(29) to C(3). The signal at δ(C) 72.2 was assigned to C(7) bearing an OH group by the HMBCs Me(30)/C(7) and H–C(7)/C(5) and C(9). The trisubstituted C(24)=C(25) bond (δ(H) 5.10 (*t*, $J = 5.8$, H–C(24)); δ(C) 122.6 and 133.2) was located by the HMBC networks CH_2(22), CH_2(23), Me(26), and Me(27)/C(24), and CH_2(23), Me(26), and Me(27)/C(25); the other trisubstituted C(14)=C(15) bond (δ(H) 5.74 (*d*, $J = 3.4$, H–C(15)); δ(C) 117.6 and 173.3) was assigned by the HMBCs Me(18), Me(30), H–C(15), and H–C(16)/C(14), and H–C(15)/C(16) and C(17). The presence of 21(16)-lactone was indicated by the chemical shifts of C(21) and C(16) at δ(C) 179.9

Table 1. *^{13}C-NMR Data of Compounds* **1**–**11**. δ in ppm.

Position	**1**[a])	**2**[a])	**3**[a])	**4**[a])	**5**[a])	**6**[a])	**7**[b])	**8**[a])	**9**[a])	**10**[a])	**11**[a])
1	38.4	38.3	38.3	35.9	31.1	38.3	32.8	39.8	37.1	38.5	38.8
2	33.8	34.7	34.7	34.3	25.3	34.8	27.6	34.1	27.6	34.8	34.0
3	217.1	216.4	216.4	216.4	76.0	216.5	71.6	218.2	79.2	216.8	217.0
4	46.8	47.8	47.8	47.4	37.4	47.8	44.0	47.4	38.9	47.8	46.9
5	46.3	52.5	52.6	60.1	44.5	52.2	47.1	55.3	50.5	52.3	48.2
6	25.2	24.3	24.3	68.8	23.9	24.3	25.2	19.6	24.0	24.3	24.3
7	72.2	118.5	118.5	122.7	119.3	119.2	120.0	27.5	118.9	118.2	75.3
8	44.8	143.4	143.4	146.6	143.0	143.7	147.6	42.4	144.7	145.4	42.0
9	40.6	47.8	47.8	46.8	48.1	47.3	50.4	49.9	48.1	48.4	43.0
10	37.1	35.5	35.5	40.0	35.0	34.9	36.2	36.8	34.9	35.0	36.9
11	15.8	16.7	16.8	16.8	29.9	30.4	19.4	18.4	29.8	21.6	16.8
12	32.8	29.5	29.6	29.2	72.1	73.9	32.8	34.5	74.7	33.2	34.8
13	47.5	39.5	39.5	39.4	44.3	49.8	45.1	40.2	47.9	43.8	46.4
14	173.3	55.1	55.2	54.9	54.9	49.9	52.9	50.2	51.7	50.7	159.2
15	117.6	35.6	35.6	35.5	36.1	45.6	34.9	31.2	35.1	34.2	119.2
16	86.1	82.6	82.5	82.2	82.2	77.0	26.7	24.8	28.2	27.3	34.8
17	57.3	57.0	57.9	58.1	53.2	51.7	48.2	49.8	40.7	50.4	52.2
18	24.7	21.6	21.6	21.5	19.8	21.0	23.1	15.1	19.7	22.0	19.9
19	15.2	12.4	12.4	13.2	12.8	12.7	14.8	16.0	13.1	12.7	15.2
20	42.8	45.8	45.7	45.3	45.5	47.4	41.6	75.4	39.6	38.7	35.8
21	179.9	179.8	180.5	180.4	180.6	177.4	178.0	25.6	11.6	16.3	70.0
22	31.2	31.4	25.0	29.4	29.0	31.0	24.8	40.9	78.6	60.3	36.3
23	26.0	123.2	32.4	26.0	25.9	26.1	21.3	22.0	201.0	58.9	64.4
24	122.6	141.1	75.8	123.3	123.7	123.2	87.8	44.4	119.0	74.0	86.5
25	133.2	70.6	146.9	132.8	132.6	132.6	72.6	71.0	159.9	72.8	74.2
26	25.7	29.8	111.6	25.7	25.7	17.7	25.9	29.2	28.0	25.4	24.0
27	17.9	29.8	17.5	17.9	17.9	25.7	26.1	29.4	21.4	25.4	28.5
28	26.4	24.4	24.4	29.3	27.7	21.5	22.9	26.7	27.6	21.6	21.2
29	21.0	21.4	21.4	22.1	21.6	24.4	66.1	21.0	14.7	24.5	25.8
30	27.6	32.2	32.2	31.8	33.6	28.9	28.4	16.3	28.2	27.5	26.9
AcO											170.2, 21.0
MeO						51.7					

[a]) Recorded in $CDCl_3$ at 100 MHz. [b]) Recorded in CD_3OD at 100 MHz.

and 86.1, respectively, and confirmed by the HMBCs H–C(16)/C(13), H–C(15)/C(16), and H–C(17), H–C(20), and CH_2(22)/C(21) (*Fig. 1*).

The relative configuration of **1** was deduced from the analysis of its ROESY spectrum and NMR data. The ROESY cross-peaks Me(29)/Me(19), Me(19)/Me(30), and Me(30)/H–C(17) indicated that Me(19), Me(29), Me(30), and H–C(17) were cofacial and arbitrarily assigned β-orientation. In consequence, the ROESY correlations Me(28)/H–C(5), H–C(5)/H–C(9), and H–C(9)/Me(18) suggested that they were α-oriented. The absence of an 1,2-diaxial coupling of H–C(7) (δ(H) 4.06 (br. *s*)) suggested that the OH group at C(7) was α-oriented, which was confirmed by the ROESY correlations H–C(7)/H–C(15) and H–C(7)/Me(30) (*Fig. 1*). The H-atom H–C(16) preferred β-orientation on the basis of the ROESY correlations H–C(16)/H–C(17) and H–C(16)/CH_2(22) (*Fig. 1*), which was consistent with the coupling

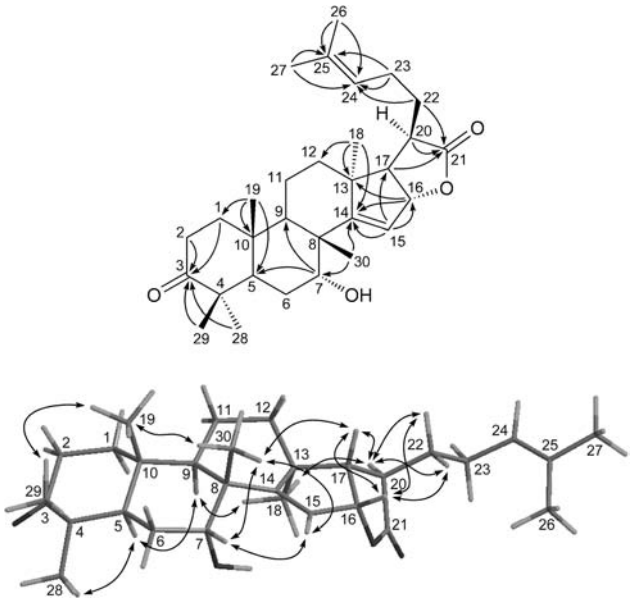


Fig. 1. *Selected HMBC* (H → C) *and ROESY* (H ↔ H) *correlations of* **1**

constant between H–C(16) and H–C(17) ($J = 6.5$). H–C(20) was assigned α-orientation on the basis of the ROESY correlations H–C(17)/H–C(20) and Me(18)/H–C(20) (*Fig. 1*), implying that compound **1** is an apoeuphane-type triterpenoid. Thus, the structure of **1** (mesendanin K) was determined as shown. To the best of our knowledge, this is the first report of an apoeuphane-type triterpenoid featuring a 21(16)-lactone moiety [6][11][12].

Compound **2** gave a sodiated molecular-ion peak in the HR-ESI-MS (*m/z* 491.3141 ($[M + Na]^+$, $C_{30}H_{44}NaO_4^+$; calc. 491.3137)), corresponding to the molecular formula $C_{30}H_{44}O_4$. The IR spectrum of **2** revealed the presence of OH (3439 cm^{-1}) and CO (1780 and 1709 cm^{-1}) groups, and the peak at 1780 cm^{-1} strongly suggested the presence of a γ-lactone moiety [6]. The 1D-NMR data of **2** (*Tables 1* and *2*) revealed the presence of seven Me groups (*singlet*s), an ester CO (δ(C) 179.8), a keto CO (δ(C) 216.4), an O-bearing CH group (δ(H) 4.18 (*ddd*, $J = 18.0$, 10.4, 7.7); δ(C) 82.6), an O-bearing quaternary C-atom (δ(C) 70.6), a trisubstituted C=C bond (δ(H) 5.33 (*dd*, $J =$ 6.0, 2.9); δ(C) 118.5 and 143.4), and a disubstituted C=C bond (δ(H) 5.59 (*dt*, $J = 15.6$, 7.5) and 5.70 (*dd*, $J = 15.6$, 1.1); δ(C) 123.2 and 141.1). The aforementioned data suggested that **2** was an euphane-type triterpenoid featuring a 21(16)-lactone moiety and shared the same pentacyclic core with kulactone [8][15], based on the analysis of its HMBC spectrum. The main differences were the substitution patterns of the side chain. In the HMBC spectrum (*Fig. 2*), the disubstituted C(23)=C(24) bond was located by the correlations of Me(26), Me(27), and CH_2(22)/C(24), and H–C(20) and CH_2(22)/C(23); the O-bearing quaternary C-atom was assigned to C(25) (δ(C) 70.6), bearing an OH group, by the HMBCs from H–C(23), H–C(24), Me(26), and Me(27)

Table 2. *^{1}H-NMR Data of Compounds* **1**–**5**[a]). δ in ppm.

Position	**1**	**2**	**3**	**4**	**5**
1α	1.53–1.57 (*m*)	1.42–1.46 (*m*)	1.47–1.50 (*m*)	1.58–1.60 (*m*)	1.36–1.40 (*m*)
1β	1.82–1.88 (*m*)	1.95 (*ddd*, *J* = 13.2, 5.3, 2.8)	1.92–1.98 (*m*)	1.87 (*ddd*, *J* = 13.4, 6.7, 3.2)	1.57–1.64 (*m*)
2α	2.48–2.53 (*m*, 2 H)	2.21–2.25 (*m*)	2.22–2.26 (*m*)	2.43–2.47 (*m*)	1.59–1.63 (*m*)
2β		2.74–2.77 (*m*)	2.74–2.78 (*m*)	2.56–2.59 (*m*)	1.91–1.94 (*m*)
3					3.47 (br. *s*)
5	2.12–1.16 (*m*)	1.71–1.76 (*m*)	1.72–1.77 (*m*)	1.81 (*d*, *J* = 9.4)	1.78 (*dd*, *J* = 11.9, 5.9)
6α	1.80–1.82 (*m*, 2 H)	2.11–2.15 (*m*, 2 H)	2.16–2.19 (*m*, 2 H)	4.40 (br. *d*, *J* = 9.4)	1.94–1.98 (*m*)
6β					2.04–2.08 (*m*)
7	4.06 (br. *s*)	5.33 (*dd*, *J* = 6.0, 2.9)	5.34 (*dd*, *J* = 6.5, 3.4)	5.37 (*t*, *J* = 3.1)	5.32 (br. *d*, *J* = 3.0)
9	2.70 (*dd*, *J* = 12.1, 7.4)	2.48–2.50 (*m*)	2.49 (*dd*, *J* = 7.8, 5.0)	2.63–2.67 (*m*)	2.40–2.43 (*m*)
11α	1.72–1.77 (*m*)	1.58–1.62 (*m*)	1.72–1.77 (*m*, 2 H)	1.75–1.79 (*m*, 2 H)	2.34–2.38 (*m*)
11β	1.59–1.63 (*m*)	1.68–1.72 (*m*)			1.44–1.48 (*m*)
12α	1.81–1.86 (*m*)	1.67–1.73 (*m*, 2 H)	1.73–1.77 (*m*, 2 H)	1.94–1.98 (*m*)	3.99–4.02 (*m*)
12β	1.42–1.44 (*m*)			1.46–1.49 (*m*)	
15α	5.74 (*d*, *J* = 3.4)	2.28–2.33 (*m*)	2.27–2.31 (*m*)	2.33 (*dd*, *J* = 13.7, 10.1)	2.25 (*dd*, *J* = 13.5, 10.5)
15β		1.71–1.74 (*m*)	1.71–1.75 (*m*)	1.74–1.77 (*m*)	1.70–1.76 (*m*)
16	5.17 (*dd*, *J* = 6.5, 3.4)	4.18 (*ddd*, *J* = 18.0, 10.4, 7.7)	4.17 (*ddd*, *J* = 18.0, 10.2, 7.6)	4.16 (*ddd*, *J* = 17.8, 10.1, 7.6)	4.17 (*ddd*, *J* = 18.1, 10.5, 7.3)
17	2.20 (br. *d*, *J* = 6.5)	2.18–2.20 (*m*)	2.11–2.14 (*m*)	2.13–2.16 (*m*)	2.49–2.51 (*m*)
18	1.14 (*s*, 3 H)	0.94 (*s*, 3 H)	0.97 (*s*, 3 H)	0.98 (*s*, 3 H)	0.83 (*s*, 3 H)
19	1.00 (*s*, 3 H)	1.01 (*s*, 3 H)	1.02 (*s*, 3 H)	0.94 (*s*, 3 H)	0.78 (*s*, 3 H)
20	2.63 (*dd*, *J* = 9.6, 5.8)	2.51–2.53 (*m*)	2.45 (*dd*, *J* = 7.7, 4.9)	2.41–2.45 (*m*)	2.37–2.42 (*m*)
22a	1.80–1.82 (*m*)	2.56–2.60 (*m*)	1.96–1.99 (*m*, 2 H)	1.75–1.78 (*m*)	1.97–2.00 (*m*)
22b	1.58–1.61 (*m*)	2.33–2.35 (*m*)			1.54–1.58 (*m*)
23	2.11–2.17 (*m*, 2 H)	5.59 (*dt*, *J* = 15.6, 7.5)	1.70–1.74 (*m*, 2 H)	2.12–2.16 (*m*, 2 H)	2.12–2.17 (*m*, 2 H)
24	5.10 (*t*, *J* = 5.8)	5.70 (*dd*, *J* = 15.6, 1.1)	4.10 (*t*, *J* = 5.0)	5.09–5.11 (*m*)	5.10 (*t*, *J* = 7.0)
26a	1.71 (*s*, 3 H)	1.31 (*s*, 3 H)	4.97 (*dd*, *J* = 1.5, 0.9)	1.69 (*s*, 3 H)	1.68 (*s*, 3 H)
26b			4.87 (*t*, *J* = 1.5)		
27	1.63 (*s*, 3 H)	1.31 (*s*, 3 H)	1.73 (*s*, 3 H)	1.62 (*s*, 3 H)	1.61 (*s*, 3 H)
28	1.11 (*s*, 3 H)	1.04 (*s*, 3 H)	1.05 (*s*, 3 H)	1.34 (*s*, 3 H)	0.93 (*s*, 3 H)
29	1.05 (*s*, 3 H)	1.11 (*s*, 3 H)	1.12 (*s*, 3 H)	1.28 (*s*, 3 H)	0.91 (*s*, 3 H)
30	1.13 (*s*, 3 H)	1.23 (*s*, 3 H)	1.25 (*s*, 3 H)	1.26 (*s*, 3 H)	1.34 (*s*, 3 H)

[a]) Recorded in $CDCl_3$ at 400 MHz.

to C(25). The (*E*)-geometry of C(23)=C(24) bond was deduced from the coupling constant between H–C(23) and H–C(24) ($J = 15.6$). Configurations at the other stereogenic centers in **2** were established to be identical with those in kulactone by the

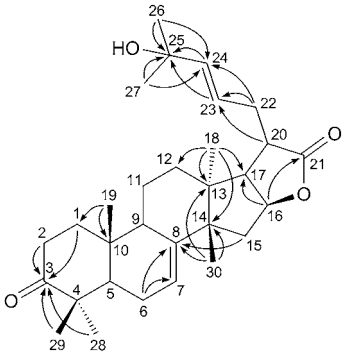


Fig. 2. *Selected HMBCs* (H → C) *of* **2**

analysis of its ROESY spectrum as well as comparing their NMR data [8][15]. Thus, the structure of **2**, mesendanin L, was determined.

Compound **3** had the molecular formula $C_{30}H_{44}O_4$, as determined by its HR-ESI-MS. The IR spectrum of **3** indicated the presence of OH (3450 cm^{-1}) and CO (1780 and 1707 cm^{-1}) groups, and further the peak at 1780 cm^{-1} strongly suggested the presence of a γ-lactone moiety [6]. The 1D-NMR data of **3** (*Tables 1* and *2*) closely resembled those of meliasenins N and O [16], a pair of *C(24)*-epimers with nearly identical NMR data, except for the presence of an OH group instead of the OOH group in meliasenins N and O. The proposed structure of **3** was confirmed by detailed analysis of its 2D-NMR (HSQC and HMBC) spectra. As a result, the resonance of C(24) in **3** shifted upfield by 13.4 ppm as compared to that in meliasenins N and O [16]. Configurations at the stereogenic centers in the pentacyclic core of **3** were determined to be identical to those of meliasenins N and O [16] by analysis of its ROESY spectrum, while the configuration of C(24) was not determined. Thus, the structure of **3**, mesendanin M, was elucidated as shown.

Compound **4** had the molecular formula $C_{30}H_{44}O_4$, as determined by the HR-ESI-MS. Features of an euphane-type triterpenoid with the 21(16)-lactone moiety for **4** were evident from its ^{1}H- and ^{13}C-NMR specta (*Tables 1* and *2*), which were very similar to those of 6β-hydroxykulactone [6], except for the presence of an upfield-shifted H–C(6) resonance at δ(H) 4.40 (br. *d*, $J = 9.4$) instead of that of 6β-hydroxykulactone at δ(H) 4.49 (br. *s*). The above analysis indicated that **4** is the *C(6)*-epimer of 6β-hydroxykulactone [6], which was supported by the ROESY correlations H–C(6)/Me(19) and H–C(6)/Me(29). Configurations at the other stereogenic centers in **4** were determined to be identical to those of 6β-hydroxykulactone by the analysis of its ROESY spectrum (*Fig. 3*, *top*). Thus, the structure of **4**, mesendanin N, was elucidated as 6α-hydroxykulactone.

Compound **5** was assigned the molecular formula $C_{30}H_{46}O_4$, as deduced from its HR-ESI-MS. The ^{1}H- and ^{13}C-NMR data (*Tables 1* and *2*) revealed that **5** was also an euphane-type triterpenoid featuring a 21(16)-lactone moiety and had the same *B*, *C*, *D*, and *E* rings and side chain with 12β-hydroxykulactone [6], based on the analysis of its HMBC spectrum. The main difference was the presence of an O-bearing CH group (δ(H) 3.47 (br. *s*); δ(C) 76.0) instead of the C(3)=O group (δ(C) 216.3) in 12β-hydroxykulactone [6], indicating that **5** was the hydrogenated derivative of 12β-

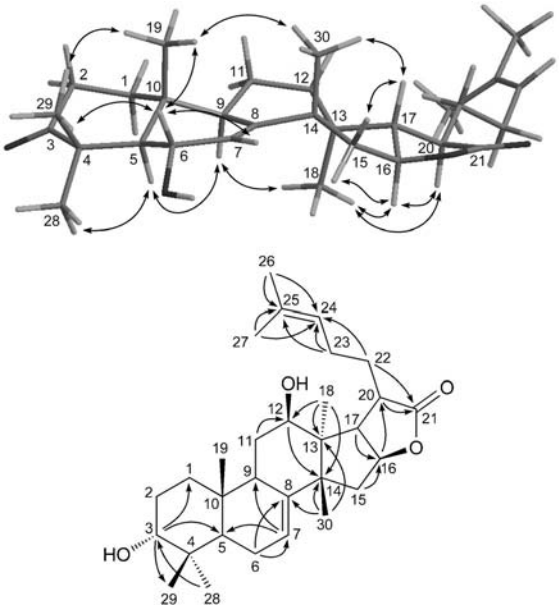


Fig. 3. *Selected ROESY* (H ↔ H) *correlations of* **4** (*top*) *and selected HMBCs* (H → C) *of* **5** (*bottom*)

hydroxykulactone [6]. This deduction was confirmed by the HMBCs Me(28)/C(3) and H–C(3)/C(1), C(5), and C(29) (*Fig. 3*, (*bottom*)). As a result, the resonances of C(1), C(2), C(4), and C(5) of **5** were shifted upfield by 7.5, 9.6, 10.7, and 8.1 ppm, respectively, as compared with those in 12β-hydroxykulactone [6]. The OH group at C(3) in **5** was determined to be α-oriented by its NMR data (δ(H) 3.47 (br. *s*); δ(C) 76.0). Configurations at the other stereogenic centers in **5** were established to be identical to those of 12β-hydroxykulactone by analysis of its ROESY spectrum. Therefore, the structure of **5**, mesendanin O, was assigned as shown.

The HR-ESI-MS of compound **6** displayed a sodiated molecular-ion peak at *m*/*z* 523.3413 ($[M+Na]^+$, $C_{31}H_{48}NaO_5^+$; calc. 523.3394), corresponding to the molecular formula $C_{31}H_{48}O_5$. The ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *3*) displayed resonances assignable to eight Me groups (*singlets*; one MeO), two trisubstituted C=C bonds, and a keto CO, an ester CO, and two O-bearing CH groups. These data revealed that **6** was also an euphane-type triterpenoid, and shared the same *A*, *B*, and *D* rings and side chain with methyl kulonate [8][17], isolated from the title plant previously. The main difference was the presence of the H- and C-atom signals for the additional O-bearing CH group (δ(H) 3.82 (*t*, *J* = 8.7); δ(C) 73.9), which was assigned to C(12) bearing an OH group by the HMBCs Me(18) and CH_2(11)/C(12), and H–C(12)/C(13) and C(14) (*Fig. 4*). A ROESY correlation between H–C(12) and Me(18) (*Fig. 4*) suggested that the OH group at C(12) in **6** was β-oriented. Configurations at the other stereogenic centers in **6** were determined to be identical to those in methyl kulonate by analysis of its ROESY spectrum (*Fig. 4*). Thus, the structure of **6**, mesendanin P, was depicted as methyl 12β-hydroxykulonate.

Table 3. *^{1}H-NMR Data of Compounds* **6**–**11**. δ in ppm.

Position	**6**[a])	**7**[b])	**8**[a])	**9**[a])	**10**[a])	**11**[a])
1α	1.42–1.47 (*m*)	1.35–1.39 (*m*)	1.43–1.48 (*m*)	1.10–1.15 (*m*)	1.44–1.49 (*m*)	1.49–1.52 (*m*)
1β	1.99–2.03 (*m*)	1.54–1.58 (*m*)	1.91 (*ddd*, *J* = 12.7, 7.5, 4.5)	1.69–1.73 (*m*)	1.97–2.02 (*m*)	1.90–1.94 (*m*)
2α	2.23–2.27 (*m*)	1.11–1.16 (*m*)	2.41–2.45 (*m*)	1.65–1.70 (*m*, 2 H)	2.23–2.26 (*m*)	2.41 (*ddd*, *J* = 15.8, 5.9, 5.5)
2β	2.76 (*ddd*, *J* = 20.2, 14.9, 5.6)	1.26–1.31 (*m*)	2.50–2.54 (*m*)		2.72–2.76 (*m*)	2.59 (*ddd*, *J* = 18.4, 11.1, 5.5)
3		3.84 (br. *s*)		3.23 (*dd*, *J* = 11.0, 4.3)		
5	1.69–1.72 (*m*)	1.90–1.92 (*m*)	1.37 (*dd*, *J* = 11.5, 2.6)	1.30 (*dd*, *J* = 12.2, 5.7)	1.71 (*dd*, *J* = 16.9, 8.0)	1.85–1.89 (*m*)
6α	2.09–2.13 (*m*, 2 H)	2.08–2.12 (*m*)	1.45–1.49 (*m*, 2 H)	2.10–2.13 (*m*)	2.07–2.12 (*m*, 2 H)	1.70–1.73 (*m*)
6β		1.90–1.93 (*m*)		2.00–2.02 (*m*)		1.86–1.90 (*m*)
7	5.32 (br. *s*)	5.26 (br. *s*)	1.85–1.87 (*m*, 2 H)	5.31 (br. *s*)	5.31 (*dd*, *J* = 6.4, 3.6)	5.20 (br. *s*)
9	2.22–2.24 (*m*)	2.39–2.41 (*m*)	1.42–1.45 (*m*)	2.19–2.23 (*m*)	2.29–2.32 (*m*)	2.00–2.03 (*m*)
11α	2.18–2.23 (*m*, 2 H)	1.56–1.60 (*m*, 2 H)	1.47–1.51 (*m*, 2 H)	1.10–1.13 (*m*)	1.57–1.62 (*m*, 2 H)	1.55–1.60 (*m*, 2 H)
11β				1.47–1.52 (*m*)		
12α	3.82 (*t*, *J* = 8.7)	1.54–1.58 (*m*)	1.32–1.36 (*m*)	3.85 (*t*, *J* = 7.8)	1.82–1.86 (*m*)	1.86–1.89 (*m*)
12β		1.77–1.80 (*m*)	1.55–1.59 (*m*)		1.64–1.67 (*m*)	1.55–1.60 (*m*)
15α	1.57–1.60 (*m*)	1.50–1.54 (*m*)	1.10–1.14 (*m*)	1.55–1.60 (*m*, 2 H)	1.51–1.55 (*m*, 2 H)	5.30 (br. *d*, *J* = 1.9)
15β	2.03–2.07 (*m*)	1.55–1.60 (*m*)	1.47–1.52 (*m*)			
16α	4.09 (*dd*, *J* = 8.5, 4.7)	1.59–1.61 (*m*)	1.50–1.54 (*m*)	1.64–1.68 (*m*, 2 H)	1.33–1.35 (*m*)	1.91–1.95 (*m*)
16β		1.88–1.92 (*m*)	1.75–1.77 (*m*)		1.92–1.96 (*m*)	2.26–2.29 (*m*)
17	2.50–2.56 (*m*)	2.31 (*dd*, *J* = 18.7, 9.3)	1.72–1.78 (*m*)	2.54 (*dd*, *J* = 18.0, 10.5)	1.66–1.71 (*m*)	1.62–1.68 (*m*)
18	0.76 (*s*, 3 H)	0.95 (*s*, 3 H)	0.99 (*s*, 3 H)	0.82 (*s*, 3 H)	0.80 (*s*, 3 H)	0.96 (*s*, 3 H)
19	1.03 (*s*, 3 H)	0.75 (*s*, 3 H)	0.94 (*s*, 3 H)	0.77 (*s*, 3 H)	1.01 (*s*, 3 H)	1.03 (*s*, 3 H)
20	2.53–2.57 (*m*)	2.55–2.60 (*m*)		1.85–1.90 (*m*)	1.30–1.34 (*m*)	1.87–1.92 (*m*)
21a			1.14 (*s*, 3 H)	0.75 (*d*, *J* = 6.8, 3 H)	1.03 (*d*, *J* = 6.6, 3 H)	3.43 (*dd*, *J* = 11.3, 2.4)
21b						3.96 (br. *d*, *J* = 11.3)
22α	1.75–1.80 (*m*)	2.00–2.04 (*m*)	1.44–1.49 (*m*, 2 H)	4.20 (br. *d*, *J* = 2.8)	2.76–2.81 (*m*)	2.01–2.06 (*m*)
22β	1.60–1.64 (*m*)	1.73–1.76 (*m*)				1.50–1.54 (*m*)
23α	1.88–1.92 (*m*)	1.83–1.88 (*m*, 2 H)	1.50–1.55 (*m*, 2 H)		3.10 (br. *s*)	3.86 (*ddd*, *J* = 13.1, 9.5, 4.5)

Table 3 (cont.)

Position	**6**[a])	**7**[b])	**8**[a])	**9**[a])	**10**[a])	**11**[a])
23β	1.97–2.00 (*m*)					
24	5.06 (*t*, *J* = 7.0)	4.18 (*dd*, 9.9, 5.8)	1.47–1.50 (*m*, 2 H)	6.09 (*s*)	3.48 (br. *s*)	2.89 (*d*, *J* = 9.5)
26	1.57 (*s*, 3 H)	1.22 (*s*, 3 H)	1.22 (*s*, 3 H)	1.98 (*s*, 3 H)	1.28 (*s*, 3 H)	1.27 (*s*, 3 H)
27	1.68 (*s*, 3 H)	1.24 (*s*, 3 H)	1.22 (*s*, 3 H)	2.23 (*s*, 3 H)	1.29 (*s*, 3 H)	1.31 (*s*, 3 H)
28	1.11 (*s*, 3 H)	1.01 (*s*, 3 H)	1.07 (*s*, 3 H)	0.97 (*s*, 3 H)	1.11 (*s*, 3 H)	1.03 (*s*, 3 H)
29a	1.03 (*s*, 3 H)	3.77 (*d*, *J* = 11.7)	1.03 (*s*, 3 H)	0.86 (*s*, 3 H)	1.04 (*s*, 3 H)	1.01 (*s*, 3 H)
29b		3.51 (d, *J* = 11.7)				
30	1.35 (*s*, 3 H)	1.01 (*s*, 3 H)	0.88 (*s*, 3 H)	1.13 (*s*, 3 H)	1.02 (*s*, 3 H)	1.16 (*s*, 3 H)
AcO						1.95 (*s*, 3 H)
MeO	3.72 (*s*, 3 H)					

[a]) Recorded in $CDCl_3$ at 400 MHz. [b]) Recorded in CD_3OD at 400 MHz.

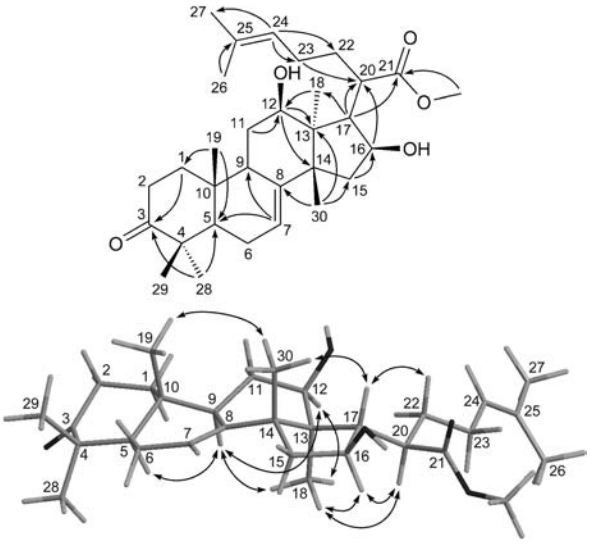


Fig. 4. *Selected HMBC* (H → C) *and ROESY* (H ↔ H) *correlations of* **6**

Compound **7** had the a molecular formula $C_{30}H_{48}O_5$, as established by the HR-ESI-MS displaying a sodiated molecular-ion peak at *m/z* 511.3412 ($[M+Na]^+$, $C_{30}H_{48}NaO_5^+$; calc. 511.3394). The ^{13}C-NMR data (*Table 1*) with DEPT experiments revealed the presence of six Me, ten CH_2 (one O-bearing), and seven CH (one olefinic and two O-bearing) groups, and seven quaternary C-atoms (one ester CO, one olefinic, and one O-bearing). These data suggested that **7** was a tirucallane-type triterpenoid, and shared the same *B*, *C*, and *D* rings as cneorin-NP_{32} [18], with the major differences being due to the different substitution patterns of their *A* ring and side chain. The structure of **7** was further elucidated by analysis of its 2D-NMR spectra, especially the HMBC (*Fig. 5*), in which the O-bearing CH group (δ(H) 3.84 (br. *s*); δ(C) 71.6) was assigned to C(3) bearing an OH group by the correlations from CH_2(1), Me(28), and CH_2(29) to C(3). The O-bearing CH_2 (δ(H) 3.51 (*d*, *J* = 11.7) and 3.77 (*d*, *J* = 11.7); δ(C) 66.1) was attributed to C(29) bearing an OH group by the HMBCs CH_2(29)/C(3) and Me(28)/C(29), and the ROESY correlation between H_a–C(29) and Me(19). The OH-bearing quaternary C-atom was C(25) (δ(C) 72.6) by the HMBCs Me(26), Me(27), and H–C(24)/C(25). The presence of a lactone between C(21) and C(24) was deduced from by their chemical shifts (δ(C) 178.0 and 87.8) and the HMBCs CH_2(22)/C(24), H–C(24)/C(26) and C(27), and H–C(17) and CH_2(22)/C(21) (*Fig. 5*). The relative configuration of **7** was determined by analysis of its ROESY spectrum (*Fig. 5*) and NMR data (*Tables 1* and *3*). The OH group at C(3) was determined as being α-oriented by the splitting pattern of H–C(3) (br. *s*). H–C(24) was assigned to be in α-orientation by the ROESY correlation between H–C(20) and H–C(24) (*Fig. 5*). Configurations at the other stereogenic centers in **7** were identical to those in cneorin-NP_{32}, based on the analysis of its ROESY spectrum and their similar NMR patterns [18]. Thus, the structure of **7**, mesendanin Q was elucidated as shown.

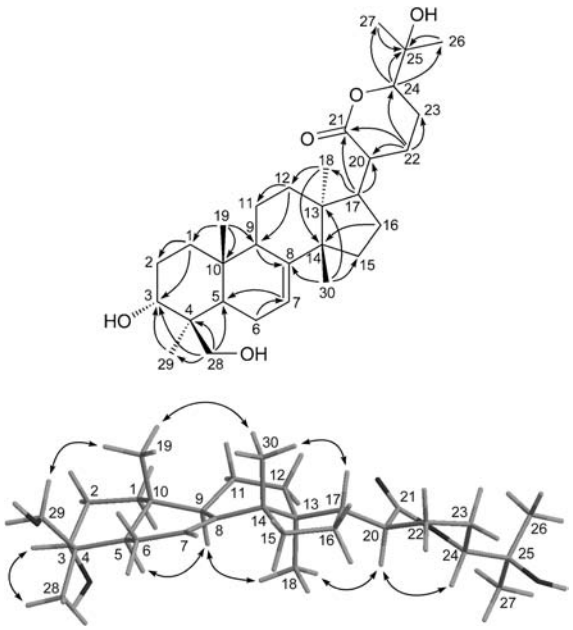


Fig. 5. *Selected HMBC* (H → C) *and ROESY* (H ↔ H) *correlations of* **7**

Compound **8** had the molecular formula $C_{30}H_{52}O_3$, as established by the HR-ESI-MS (*m*/*z* 483.3825 ($[M+Na]^+$, ($C_{30}H_{52}NaO_3^+$; calc. 483.3809)). Analysis of ^{1}H- and ^{13}C-NMR spectra of **8** (*Tables 1* and *3*) suggested a tirucallane-type triterpenoid with eight Me groups (*singlets*), a keto CO (*δ*(C) 218.2), group and two O-bearing quaternary C-atoms (*δ*(C) 71.0 and 75.4) [19]. In the HMBC spectrum of **8** (*Fig. 6*, *left*), the keto CO was established as C(3)=O by the correlations from CH_2(1), Me(28), and Me(29) to C(3). An O-bearing quaternary C-atom at signal *δ*(C) 71.0 was assigned to C(25) bearing an OH group by the HMBCs Me(26), Me(27), and CH_2(23)/C(25); the other O-bearing quaternary C-atom signal at *δ*(C) 75.4 was attributed to C(20),

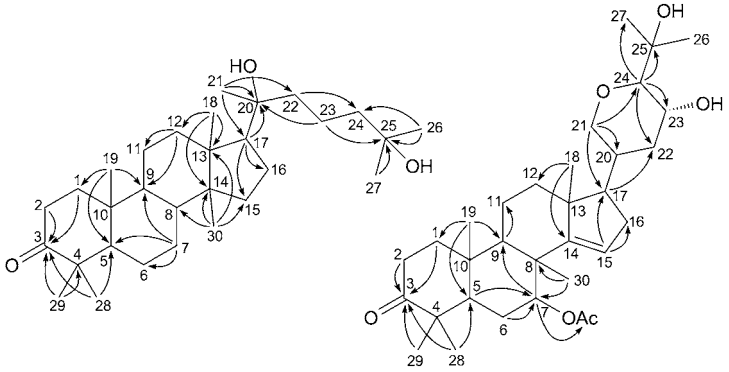


Fig. 6. *Selected HMBCs* (H → C) *of* **8** (*left*) *and* **11** (*right*)

bearing an OH group by the HMBCs from H–C(17), Me(21), and CH_2(23) to C(20) (*Fig. 6*, *left*). The relative configuration of **8** was assigned as shown by the analysis of its ROESY spectrum, in which the OH group at C(20) was assigned as being α-oriented by the correlations H–C(17)/CH_2(22), Me(21)/H–C(17), and Me(21)/Me(18). Thus, the structure of **8**, mesendanin R was elucidated.

The molecular formula of compound **9** was determined as $C_{30}H_{48}O_4$ by the HR-ESI-MS. The ^{1}H- and ^{13}C-NMR data (*Tables 1* and *3*) of **9** displayed the resonances assignable to two trisubstituted C=C bonds (δ(H) 5.31 (br. *s*) and 6.09 (*s*); δ(C) 118.9, 119.0, 144.7, and 159.9), a keto CO group (δ(C) 201.0), and three O-bearing CH groups (δ(H) 3.23 (*dd*, J = 11.0, 4.3), 3.85 (*t*, J = 7.8), and 4.20 (br. *d*, J = 2.8); δ(C) 74.7, 78.6, and 79.2). These data revealed that **9** was the *C(3)*-hydrogenated derivative of meliasenin G [11], which was confirmed by the HMBCs from Me(28), Me(29), and CH_2(1) to C(3) (δ(C) 79.2). The OH group at C(3) was determined as being β-oriented by the splitting pattern of H–C(3) at δ(H) 3.23 (*dd*, J = 11.0, 4.3). Configurations at the other stereogenic centers in **9** were identical to those in meliasenin G based on its ROESY spectrum and comparison of their NMR data. Thus, the structure of **9**, mesendanin S, was determined.

Compound **10** had the molecular formula $C_{30}H_{48}O_4$, as determined by the HR-ESI-MS. The 1D-NMR data (*Tables 1* and *3*) showed many similarities to those of 22,23-epoxytirucall-7-ene-3β,24,25-triol [10], with the major difference being due to the presence of a C(3)=O moiety (δ(C) 216.8) instead of the OH group at C(3) in the known analog [10], which was confirmed by the HMBCs from Me(28), Me(29), and CH_2(1) to C(3). Configurations of the stereogenic centers of **10** were identical to those in 22,23-epoxytirucall-7-ene-3β,24,25-triol, as revealed by analysis of its ROESY spectrum. Thus, the structure of **10**, mesendanin T, was assigned as shown.

Compound **11** had the molecular formula $C_{32}H_{50}O_6$, as determined by its HR-ESI-MS. The 1D-NMR data (*Tables 1* and *3*) displayed resonances assignable to a keto CO group (δ(C) 217.0), a trisubstituted C=C bond (δ(H) 5.30 (br. *d*, J = 1.9); δ(C) 119.2 and 159.2), an O-bearing CH_2 group (δ(H) 3.43 (*dd*, J = 11.3, 2.4) and 3.96 (br. *d*, J = 11.3); δ(C) 70.0), three O-bearing CH groups (δ(H) 2.89 (*d*, J = 9.5), 3.86 (*ddd*, J = 13.1, 9.5, 4.5), and 5.20 (br. *s*); δ(C) 64.4, 75.3, and 86.5), an O-bearing quaternary C-atom (δ(C) 74.2), and an Ac group. These data resembled those of grandifoliolenone [20], except for the absence of the C(1)=C(2) bond in **11**, indicating that **11** was the hydrogenated derivative of grandifoliolenone [20]. As a result, the resonance of C(3)=O in **11** shifted downfield by 12.3 ppm relative to that in grandifoliolenone [20]. This deduction was further confirmed by its 2D-NMR experiments, especially the HMBC spectrum (*Fig. 6*, *right*). The relative configuration of **11** was assigned as being identical to that of grandifoliolenone by analysis of its ROESY spectrum and comparing their NMR data [20]. Thus, the structure of **11**, mesendanin O, was determined as shown.

Financial support of the *National Natural Science Foundation* (Grant Nos. 30630072, 30721005, and 20932007) and *National Science & Technology Major Project 'Key New Drug Creation and Manufacturing Program'* (Grant No. 2009ZX09301-001) of the P. R. China is gratefully acknowledged. We thank Prof. *Y.-K. Xu*, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, for the identification of the plant material.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 300–400 mesh; *Qingdao Marine Chemical Plant*, Qingdao, P. R. China), *MCI* gel (*CHP20P*, 75–150 μM, *Mitsubishi Chemical Industries, Ltd.*), and C_{18} reversed-phase (RP) silica gel (250 mesh, *Merck*). TLC: pre-coated silica gel *GF 254* plates (*Qingdao Marine Chemical Plant*, Qingdao, P. R. China). Semi-prep. HPLC: *Waters 515* pump with a *Waters 2487* detector (254 nm), and an *YMC–Pack ODS–A* column (250 × 10 mm, *S-5* μm, 12 nm). Optical rotations: *Perkin-Elmer 341* polarimeter. IR Spectra: *Perkin-Elmer 577* IR spectrometer. NMR Spectra: *Bruker AM-400* NMR spectrometer with TMS as internal standard. HR-ESI-MS: *Bruker Daltonics micrOTOFQ II* mass spectrometer.

Plant Material. The twigs and leaves of *Melia toosendan* were collected from Xishuangbanna, Mengla County, Yunnan Province, P. R. China, and were authenticated by Prof. *You-Kai Xu* of Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences. A voucher specimen (2008-Meltoo-1Y) has been deposited with the Shanghai Institute of Materia Medica.

Extraction and Isolation. The air-dried powder of leaves and twigs (5 kg) of *M. toosendan* was extracted three times with 95% EtOH (each 25 l, 3 d) at r.t. to give an EtOH extract (340 g), which was partitioned between AcOEt and H_2O, to obtain the AcOEt-soluble fraction (200 g). The AcOEt-soluble fraction was subjected to CC (*MCI* gel CC; MeOH/H_2O 3:7 → 9:1) to give four fractions, *Frs. A–D. Fr. C* (22 g) was separated by CC (SiO_2; petroleum ether (PE)/acetone 20:1 → 1:1) to afford five sub-fractions, *C1–C5*). *Fr. C4* was subjected to CC (RP C_{18} silica gel; MeOH/H_2O 6:4 → 9:1) to give three major fractions, *C4a–C4c*, each of which was separated in turn by CC (SiO_2; $CHCl_3$/MeOH 200:1 → 50:1) to provide compounds **6** (10 mg), **9** (7 mg), and **11** (8 mg), resp. Using the same purification procedures, *Fr. C5* gave 3,16-dihydroxyeupha-7,24-dien-21-oic acid methyl ester (10 mg). *Fr. D* (15 g) was subjected to CC (SiO_2; PE/acetone 20:1 → 1:1), to afford four major fractions, *Fr. D1–D4*. *Fr. D1* was subjected to CC (RP C_{18} silica gel; MeOH/H_2O 6:4 → 9:1) to give sub-fractions *D1a–D1d*, each of which was purified by semi-prep. HPLC (MeCN/H_2O 85:15; 3 ml/min) to give compounds **1**, **4**, **5**, and 12β-hydroxykulactone (3, 9, 12, and 20 mg, resp.), resp. By the same procedure, *Fr. D2* was purified to yield compounds **2**, **3**, meliasenins G and H, and cinamodiol (6, 8, 12, 10, and 15 mg, resp.), while *Fr. D3* was purified to give compounds **7**, **8**, **10**, (22*S*,23*R*)-22,23-epoxytirucall-7-ene-3α,24,25-triol, and 22,23-epoxytirucall-7-ene-3β,24,25-triol (5, 11, 8, 12, and 15 mg, resp.).

Mesendanin K (= *7α-Hydroxy-21-oxo-21,16β-epoxyapoeuphol-14,24-dien-3-one* = *(5α,7α,13α,16α,17α,20*R*)-7-Hydroxy-4,4,8-trimethyl-16,21-epoxycholesta-14,24-diene-3,21-dione*; **1**). White amorphous powder. $[\alpha]_D^{20} = -8.0$ ($c = 0.25$, MeOH). IR (KBr): 3435, 2933, 2874, 1765, 1705, 1628, 1458, 1385, 1180, 1055. ^{1}H- and ^{13}C-NMR: see *Tables 2* and *1*, resp. HR-ESI-MS: 491.3133 ($[M+Na]^+$, $C_{30}H_{44}NaO_4^+$; calc. 491.3137).

Mesendanin L (=(*23*E*)-25-Hydroxy-21-oxo-21,16β-epoxyeuphol-7,23-dien-3-one* = *(13α,14β,16β,17α,20*R*,23*E*)-25-Hydroxy-16,21-epoxylanosta-7,23-diene-3,21-dione*; **2**). White amorphous powder. $[\alpha]_D^{20} = -63.0$ ($c = 0.25$, MeOH). IR (KBr): 3439, 2968, 2935, 1780, 1709, 1460, 1387, 1369, 1161. ^{1}H- and ^{13}C-NMR: see *Tables 2* and *1*, resp. HR-ESI-MS: 491.3141 ($[M+Na]^+$, $C_{30}H_{44}NaO_4^+$; calc. 491.3137).

Mesendanin M (=*24-Hydroxy-21-oxo-21,16β-epoxyeuphol-7,25-dien-3-one* = *(13α,14β,16β,17α,20*R*)-24-Hydroxy-16,21-epoxylanosta-7,25-diene-3,21-dione*; **3**). White amorphous powder. $[\alpha]_D^{20} = -45.0$ ($c = 0.20$, MeOH). IR (KBr): 3450, 2947, 2875, 1780, 1707, 1450, 1387, 1369, 1157, 1030. ^{1}H- and ^{13}C-NMR: see *Tables 2* and *1*, resp. HR-ESI-MS: 491.3147 ($[M+Na]^+$, $C_{30}H_{44}NaO_4^+$; calc. 491.3137).

Mesendanin N (=*6α-Hydroxy-21-oxo-21,16β-epoxyeuphol-7,24-dien-3-one* = *(6α,13α,14β,16β,17α,20*R*)-6-Hydroxy-16,21-epoxylanosta-7,24-diene-3,21-dione*; **4**). White amorphous powder. $[\alpha]_D^{20} = +4.0$ ($c = 0.28$, MeOH). IR (KBr): 3562, 3485, 2962, 2877, 1776, 1703, 1452, 1383, 1159, 1028, 953. ^{1}H- and ^{13}C-NMR: see *Tables 2* and *1*, resp. HR-ESI-MS: 491.3135 ($[M+Na]^+$, $C_{30}H_{44}NaO_4^+$; calc. 491.3137).

Mesendanin O (=*3α,12β-Dihydroxy-21-oxo-21,16β-epoxyeuphol-7,24-diene* = *(3α,12β,13α,14β,16β,17α,20*R*)-3,12-Dihydroxy-16,21-epoxylanosta-7,24-dien-21-one*; **5**). White amorphous powder. $[\alpha]_D^{20} = -35.0$ ($c = 0.23$, MeOH). IR (KBr): 3523, 3456, 2970, 2928, 1767, 1448, 1394, 1163, 1030, 754. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*. HR-ESI-MS: 493.3311 ($[M+Na]^+$, $C_{30}H_{46}NaO_4^+$; calc. 493.3294).

Mesendanin P (=*12β,16β-Dihydroxy-3-oxoeuphol-7,24-dien-21-oic Acid Methyl Ester* = *Methyl (12β,13α,14β,16β,17α)-12,16-Dihydroxy-3-oxolanosta-7,24-dien-21-oate*; **6**). White amorphous powder.

$[\alpha]_D^{20} = -36.5$ ($c = 0.34$, MeOH). IR (KBr): 3462, 2968, 1709, 1450, 1385, 1167, 1032. ^{1}H- and ^{13}C-NMR: see *Tables 3* and *1*, resp. HR-ESI-MS: 523.3413 ($[M+Na]^+$, $C_{31}H_{48}NaO_5^+$; cal. 523.3399).

Mesendanin Q (*= 3α,25,29-Trihydroxy-21-oxo-21,24β-epoxytirucall-7-ene = (3α,13α,14β,17α,20*S*,24*R*)-3,25,29-Trihydroxy-21,24-epoxylanost-7-en-21-one*; **7**). White amorphous powder. $[\alpha]_D^{20} = -24.0$ ($c = 0.21$, MeOH). IR (KBr): 3452, 2968, 2935, 1716, 1184, 1041. ^{1}H- and ^{13}C-NMR: see *Tables 3* and *1*. HR-ESI-MS: 511.3412 ($[M+Na]^+$, $C_{30}H_{48}NaO_5^+$; calc. 511.3394).

Mesendanin R (*= 20α,25-Dihydroxytirucall-3-one = (13α,14β,17α,20*R*)-20,25-Dihydroxylanostan-3-one*; **8**). White amorphous powder. $[\alpha]_D^{20} = +100.0$ ($c = 0.19$, MeOH). IR (KBr): 3423, 2958, 1668, 1703, 1460, 1381, 1163, 905. ^{1}H- and ^{13}C-NMR: see *Tables 3* and *1*, resp. HR-ESI-MS: 483.3825 ($[M+Na]^+$, $C_{30}H_{52}NaO_3^+$; calc. 483.3809).

Mesendanin S (*= 3β,12β,22α-Trihydroxytirucalla-7,24-dien-23-one = (3β,12β,13α,14β,17α,20*R*,22*S*)-3,12,22-Trihydroxylanosta-7,24-dien-23-one*; **9**). White amorphous powder. $[\alpha]_D^{20} = +39.0$ ($c = 0.20$, MeOH). IR (KBr): 3450, 2947, 1668, 1446, 1356, 1126, 1047, 916. ^{1}H- and ^{13}C-NMR: see *Tables 3* and *1*, resp. HR-ESI-MS: 495.3462 ($[M+Na]^+$, $C_{30}H_{48}NaO_4^+$; calc. 495.3445).

Mesendanin T (*= 24,25-Dihydroxy-22,23-epoxytirucall-7-en-3-one = (5*R*,9*R*,10*R*,13*S*,14*S*,17*S*)-17-{(1*R*)-1-[3-(1,2-Dihydroxy-2-methylpropyl)oxiran-2-yl]ethyl}-1,2,4,5,6,9,10,11,12,13,14,15,16,17-tetradecahydro-4,4,10,13,14-pentamethyl-3*H*-cyclopenta[a]phenanthren-3-one*; **10**). White amorphous powder. $[\alpha]_D^{20} = -162.0$ ($c = 0.27$, MeOH). IR (KBr): 3456, 2970, 1709, 1462, 1387, 1109, 889. ^{1}H- and ^{13}C-NMR: see *Tables 3* and *1*, resp. HR-ESI-MS: 495.3457 ($[M+Na]^+$, $C_{30}H_{48}NaO_4^+$; calc. 495.3445).

Mesendanin U (*= 23α,25-Dihydroxy-21,24β-epoxy-7α-acetoxytirucall-14-en-3-one = (5α,7α,13α,17α,20*S*,23*R*)-23,25-Dihydroxy-4,4,8-trimethyl-3-oxo-21,24-epoxycholest-14-en-7-yl Acetate*; **11**). White amorphous powder. $[\alpha]_D^{20} = -65.0$ ($c = 0.10$, MeOH). IR (KBr): 3439, 2937, 1734, 1705, 1381, 1248, 1074, 1032. ^{1}H- and ^{13}C-NMR: see *Tables 3* and *1*, resp. HR-ESI-MS: 553.3524 ($[M+Na]^+$, $C_{32}H_{50}NaO_6^+$; calc. 553.3505).

Supplementary Information. IR, HR-ESI-MS, 1D- and 2D-NMR spectra of compounds **1**–**11** are available from the corresponding author.

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Received May 16, 2011