Oleanane-Type Triterpenoids from *Glochidion assamicum*

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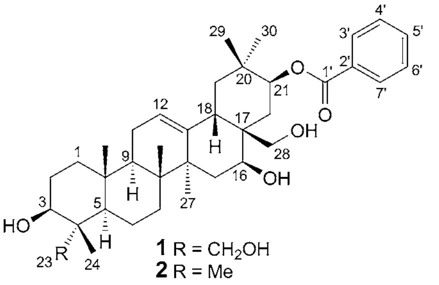
Phytochemical analysis of the extract of the leaves and twigs of *Glochidion assamicum* led to the isolation of four new oleanane-type triterpenoids, 21β-(benzoyloxy)olean-12-ene-3β,16β,23,28-tetraol (**1**), 21β-(benzoyloxy)olean-12-ene-3β,16β,28-triol (**2**), 21β-{(*E*)-cinnamoyloxy]olean-12-ene-3β,16β,23,28-tetraol (**3**), and 21β-[(*Z*)-cinnamoyloxy]olean-12-ene-3β,16β,23,28-tetraol (**4**). Their structures were elucidated on the basis of spectroscopic evidence and mass-spectral data.

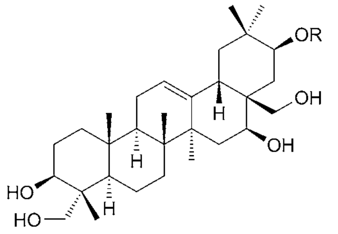
Introduction. – The genus *Glochidion*, with *ca.* 25 species distributed in China, belongs to the family Euphorbiaceae. Many *Glochidion* species have been used in traditional medicine for lowering body temperature, eliminating damp, and activating blood circulation, in addition to their antitumor-promoting and cytotoxic effects [1][2]. Previous phytochemical studies on this genus led to the identification of triterpenoids including oleanane- and ursane-type [3]. In our continuing study on the chemical constituents of this genus, we obtained an AcOEt-soluble extract of a mixture of the leaves and twigs of *Glochidion assamicum* HOOK collected from Yunnan Province of China, which furnished four new oleanane-type triterpenoid derivatives, 21β-(benzoyloxy)olean-12-ene-3β,16β,23,28-tetraol (**1**), 21β-(benzoyloxy)olean-12-ene-3β,16β,28-triol (**2**), 21β-[(*E*)-cinnamoyloxy]olean-12-ene-3β,16β,23,28-tetraol (**3**), and 21β-[(*Z*)-cinnamoyloxy]olean-12-en-3β,16β,23,28-tetraol (**4**). Here, we describe the elucidation of their structures by spectroscopic methods.

Results and Discussion. – Compound **1** was obtained as a white amorphous powder. It gave rise to a positive *Liebermann–Burchard* coloration test, indicating a triterpenoid structure. Its molecular formula was determined as $C_{37}H_{54}O_6$ from its HR-ESI-MS (*m/z* 612.4250 ($[M+NH_4]^+$)), which was confirmed by ^{13}C-NMR and DEPT analysis, corresponding to eleven degrees of unsaturation. The IR spectrum of **1** showed absorption bands for C=O (1689 cm^{-1}) and OH (3401 cm^{-1}) functions and benzene ring (1600, 1583, 1452 cm^{-1}). The ^{1}H- and ^{13}C-NMR data of **1** (*Table 1*) indicated a pentacyclic triterpenoid, assignments being confirmed with the help of 2D-NMR (HMBC, HSQC, and NOESY) experiments (*Fig. 1,a*).

The ^{1}H-NMR spectrum exhibited the characteristic signals of triterpenoids in the higher field, *i.e.*, signals for six *singlet*s of Me groups (δ(H) 1.03, 1.05, 1.06, 1.10, 1.29, and 1.31). In addition, one trisubstituted olefinic H-atom signal at δ(H) 5.39 (br. *s*, H–C(12)), together with typical ^{13}C-NMR resonances at δ(C) 124.1 and 143.1, and a



1 R = CH$_2$OH
2 R = Me



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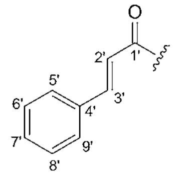
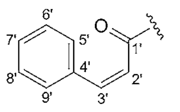


4 R =



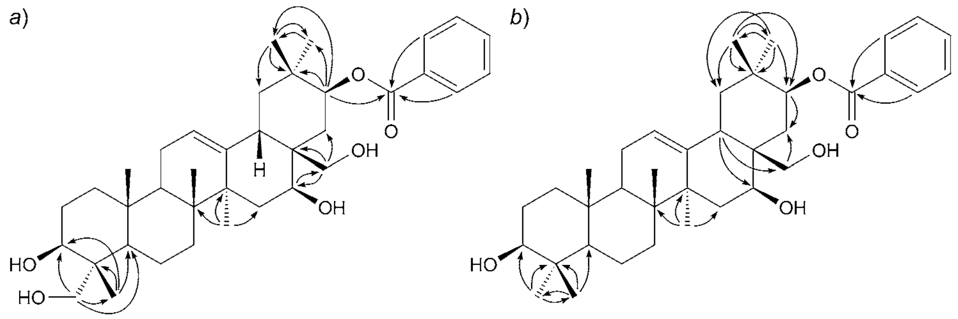


Fig. 1. *Key HMBCs of a)* **1** *and b)* **2**

characteristic signal at δ(H) 2.82 (*dd*, $J = 14.0, 4.0$, H–C(18))) indicated an olean-12-ene triterpene derivative [4]. The ^{13}C-NMR spectrum of **1** (*Table 1*) shows signals for 37 C-atoms, the substitution patterns of which were revealed by means of DEPT and HSQC experiments as six Me, ten CH$_2$, twelve CH group, and nine quaternary C-atoms, which also indicated the presence of three O-bearing CH groups (δ(C) 77.7 (CH–O), 73.6 (CH–O), 67.2 (CH–O)) and of two O-bearing CH$_2$ groups (δ(C) 68.1 (CH$_2$–O), 66.9 (CH$_2$–O)).

In the low-field section of the ^{1}H-NMR spectrum, there were three characteristic group signals of monosubstituted benzene derivative at δ(H) 8.27 (*dd*, $J = 8.0, 1.6$, 2 H), 7.49 (*t*, $J = 8.0$, 2 H), and 7.56 (*d*, $J = 8.0$, 1 H). In the ^{13}C-NMR spectrum, there were signals of nine sp^2-C-atoms including that of an ester COO group. The presence of a benzoyloxy moiety was supported by the HMBCs of the signals at δ(H) 8.27 (H–C(3')) and 8.27 (H–C(7')) with the signal at δ(C) 166.7 (C(1')). In the ^{1}H-NMR spectrum, four H-atom signals at δ(H) 6.45 (br. *s*), 6.38 (br. *s*), 6.17 (*d*, $J = 6.0$), and

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1** *and* **2**. At 400 (^{1}H) and 100 MHz (^{13}C); δ in ppm, *J* in Hz.

Position	**1**a)		**2**b)	
	δ(H)	δ(C)	δ(H)	δ(C)
1	1.60–1.62 (*m*), 1.13–1.15 (*m*)	39.4 (*t*)	1.38–1.67 (*m*), 0.95–1.01 (*m*)	38.6 (*t*)
2	2.04–1.88 (*m*)	28.2 (*t*)	1.38–1.67 (*m*)	27.1 (*t*)
3	4.21–4.28 (*m*)	73.6 (*d*)	3.23 (*dd*, *J* = 10.8, 4.4)	77.3 (*d*)
4		43.4 (*s*)		38.8 (*s*)
5	1.56–1.59 (*m*)	48.9 (*d*)	0.74 (*d*, *J* = 11.6)	55.1 (*d*)
6	1.65–1.77 (*m*), 1.42–1.49 (*m*)	19.0 (*t*)	1.38–1.67 (*m*)	18.3 (*t*)
7	1.65–1.77 (*m*), 1.32–1.40 (*m*)	33.2 (*t*)	1.38–1.67 (*m*)	32.6 (*t*)
8		40.6 (*s*)		39.8 (*s*)
9	1.65–1.77 (*m*)	47.7 (*d*)	1.38–1.67 (*m*)	46.7 (*d*)
10		37.5 (*s*)		36.8 (*s*)
11	1.88–2.04 (*m*)	24.4 (*t*)	1.87–1.94 (*m*)	23.5 (*t*)
12	5.39 (*s*)	124.1 (*d*)	5.28 (*t*, *J* = 3.2)	123.5 (*d*)
13		143.1 (*s*)		141.2 (*s*)
14		44.2 (*s*)		43.6 (*s*)
15	1.65–1.77 (*m*), 2.16–2.21 (*m*)	37.2 (*t*)	1.38–1.67 (*m*), 1.87–1.94 (*m*)	35.4 (*t*)
16	4.74 (*m*)	67.2 (*d*)	4.48 (*dd*, *J* = 11.6, 4.8)	68.4 (*d*)
17		44.7 (*s*)		42.9 (*s*)
18	2.82 (*dd*, *J* = 14.0, 4.0)	43.5 (*d*)	2.16 (*dd*, *J* = 8.4, 4.4)	44.0 (*d*)
19	2.09–2.16 (*m*), 1.32–1.44 (*m*)	47.7 (*t*)	1.94–1.87 (*m*), 1.28 (*dd*, *J* = 16.0, 4.8)	46.9 (*t*)
20		36.4 (*s*)		35.4 (*s*)
21	5.69 (*dd*, *J* = 12.0, 4.4)	77.7 (*d*)	5.05 (*dd*, *J* = 12.4, 4.4)	76.5 (*d*)
22	3.19 (*dd*, *J* = 12.8, 4.4), 2.21–2.29 (*m*)	31.0 (*t*)	2.69 (*dd*, *J* = 13.6, 4.4), 1.38–1.67 (*m*)	30.6 (*t*)
23	3.76 (*d*, *J* = 10.5), 4.21–4.28 (*m*)	68.1 (*t*)	1.01 (*s*)	28.1 (*q*)
24	1.10 (*s*)	13.7 (*q*)	0.80 (*s*)	15.5 (*q*)
25	1.03 (*s*)	16.7 (*q*)	0.95 (*s*)	15.5 (*q*)
26	1.06 (*s*)	17.5 (*q*)	1.00 (*s*)	16.7 (*q*)
27	1.29 (*s*)	27.4 (*q*)	1.25 (*s*)	27.0 (*q*)
28	4.38 (*d*, *J* = 10.0), 3.88 (*dd*, *J* = 10.0, 4.8)	66.9 (*t*)	4.10 (*d*, *J* = 11.2), 3.18 (*d*, *J* = 11.2)	70.2 (*t*)
29	1.31 (*s*)	19.3 (*q*)	1.13 (*s*)	18.5 (*q*)
30	1.05 (*s*)	29.6 (*q*)	0.98 (*s*)	29.0 (*q*)
1′		166.7 (*s*)		166.5 (*s*)
2′		132.0 (*s*)		130.6 (*s*)
3′	8.27 (*dd*, *J* = 8.0, 1.6)	130.4 (*d*)	8.03 (*d*, *J* = 7.6)	129.5 (*d*)
4′	7.49 (*t*, *J* = 8.0)	129.4 (*d*)	7.45 (*t*, *J* = 7.6)	128.4 (*d*)
5′	7.56 (*t*, *J* = 8.0)	133.7 (*d*)	7.57 (*t*, *J* = 7.6)	132.9 (*d*)
6′	7.49 (*t*, *J* = 8.0)	129.4 (*d*)	7.45 (*t*, *J* = 7.6)	128.4 (*d*)
7′	8.27 (*dd*, *J* = 8.0, 1.6)	130.4 (*d*)	8.03 (*d*, *J* = 7.6)	129.5 (*d*)
3-OH	5.90 (br. *s*)			
16-OH	6.17 (*d*, *J* = 6.0)			
23-OH	6.45 (br. *s*)			
28-OH	6.38 (br. *s*)			

a) In (D$_5$)pyridine. b) In CDCl$_3$.

5.90 (br. *s*), without correlation in the HSQC spectrum, were in agreement with the presence of a OH function in the molecule. Moreover, in the HMBC experiment, the location of additional four OH groups were supported by the cross-peaks between the signals at δ(H) 6.45 (br. *s*) and δ(C) 68.1 (C(23)); at δ(H) 6.38 (br. *s*) and δ(C) 66.9 (C(28)); at δ(H) 6.17 (*d*, $J = 6.0$) and δ(C) 67.2 (C(16)); and δ(H) 5.90 (br. *s*) and δ(C) 73.6 (C(3)). In the HMBC spectrum (*Fig. 1,a*), correlation peaks were observed from the signal at δ(H) 5.69 (H–C(21)) to those at δ(C) 166.7 (C(1′)), 19.3 (Me(29)), 29.6 (Me(30)), and 36.4 (C(20)), which indicated that the benzoyloxy unit was at C(21). Therefore, one of the five O-bearing C-atoms was in ring *E*, and the remaining ones in rings *A* and *D* [5]. In the HMBC spectrum, correlation peaks were observed from δ(H) 4.38 (*d*, $J = 10.0$, H_a–C(28)) to δ(C) 43.5 (C(18)), and 31.0 (C(22)), and from δ(H) 3.88 (*dd*, $J = 10.0, 4.8$, H_b–C(28)) to δ(C) 67.2 (C(16)), 44.7 (C(17)), and 43.5 (C(18)), which indicated that a OH group was located at C(28), and another OH group was located at C(16). The signals at δ(H) 3.76 (*dd*, $J = 10.0$) and 4.21–4.28 (*m*), respectively, which were coupled with the signal at δ(C) 68.1 (C(23)) in the HSQC spectrum, were assigned to the moiety, bearing a OH function, at C(23). One OH group was considered to be at C(23), based on the HMBCs of the signals at δ(H) 3.76 and 4.21–4.28 (CH_2(23)) with those at δ(C) 13.7 (C(24)), 73.6 (C(3)), and 48.9 (C(5)), which also suggested that a OH group in compound **1** is located at C(3). These conclusions were confirmed by ^{1}H,^{1}H-COSY, HSQC, and HMBC experiments.

The relative configuration of **1** was confirmed by a NOESY experiment. The correlations H–C(23)/H–C(5) and H–C(3)/H–C(5) suggested that OH at C(3) was β-oriented. The β-position of OH at C(16) was in accordance with the NOESY correlation δ(H) 4.74 (H–C(16))/1.29 (Me(27)). Furthermore, H–C(21) correlated with Me(30), indicating a β-benzoyloxy moiety at C(21). Hence, compound **1** was identified as 21β-(benzoyloxy)olean-12-ene-3β,16β,23,28-tetrol.

Compound **2**, a white amorphous powder, showed a positive *Liebermann–Burchard* coloration test. The molecular formula $C_{37}H_{54}O_5$ was deduced from HR-ESI-MS (*m/z* 601.3871 ($[M + Na]^+$)), indicating eleven degrees of unsaturation. The IR spectrum exhibited absorptions for C=C (1653 cm^{-1}), OH (3438 cm^{-1}), C=O (1701 cm^{-1}) groups, as well as benzene ring (1603, 1582, 1454 cm^{-1}). Careful comparison of the ^{13}C-NMR data of **2** with those of **1** indicated that the signals for C(9) to C(22) and C(24) to C(30) were basically similar to each other, indicating analogous rings *C*, *D*, and *E*. However, the signal for Me(23), observed at δ(H) 1.01 and δ(C) 28.1 in ring *A*, was not present in **1**; instead, the signals of a CH_2OH group at δ(H) 3.76 (*d*, $J = 10.5$) and 4.21–4.28 (*m*), and δ(C) 68.1 were not detected in the spectra of **2**. Compound **2** was completely characterized by HSQC and HMBCs (*Fig. 1,b*).

The relative configuration of **2** was determined from NOESY spectra incorporating the coupling constant of ^{1}H-NMR. The axial H–C(3) atom signal at δ(H) 3.23 (*dd*, $J = 10.8, 4.4$, 1 H) indicates a β-orientation of the HO–C(3) in **2** [6]. The NOESY correlations H–C(18)/Me(29) and Me(30)/H–C(21) indicated that the β-benzoyloxy unit was at C(21). An additional NOESY correlation H–C(16)/Me(27) suggested the β-orientation of OH at C(16). Thus, based on the above evidence, the structure of compound **2** was elucidated as 21β-(benzoyloxy)olean-12-ene-3β,16β,28-triol.

Compound **3**, isolated as a white amorphous powder, gave a positive *Liebermann–Burchard* coloration test. The molecular formula, $C_{39}H_{56}O_5$, was deduced from

HR-ESI-MS (*m/z* 638.4420 ($[M+NH_4]^+$)), corresponding to twelve degrees of unsaturation. The IR spectrum revealed the presence of C=C (1636 cm^{-1}), OH (3398 cm^{-1}), and C=O (1697 cm^{-1}) group, and benzene ring (1577, 1540, 1452 cm^{-1}). These data, together with a comparison of the ^{1}H- and ^{13}C-NMR data of **3** (*Table 2*)

Table 2. *^{1}H- and ^{13}C-NMR Data of* **3** *and* **4**. At 400 (^{1}H-) and 100 MHz (^{13}C-), in MeOD; δ in ppm, *J* in Hz.

Position	**3**		**4**	
	δ(H)	δ(C)	δ(H)	δ(C)
1	1.60–1.71 (*m*), 0.95–0.98 (*m*)	39.8 (*t*)	1.58–1.69 (*m*), 0.94–0.99 (*m*)	39.8 (*t*)
2	1.60–1.71*m*	27.5 (*t*)	1.58–1.69 (*m*)	27.6 (*t*)
3	3.62 (*dd*, *J* = 11.2, 4.8)	73.9 (*d*)	3.61 (*dd*, *J* = 11.2, 4.8)	73.9 (*d*)
4		43.5 (*s*)		43.5 (*s*)
5	1.20–1.45 (*m*)	47.3 (*d*)	1.23–1.16 (*m*)	48.7 (*d*)
6	1.46–1.53 (*m*)	19.2 (*t*)	1.45–1.54 (*m*)	19.2 (*t*)
7	1.60–1.71 (*m*), 1.33–1.42 (*m*)	33.5 (*t*)	1.58–1.69 (*m*), 1.29–1.35 (*m*)	33.5 (*t*)
8		41.2 (*s*)		41.2 (*s*)
9	1.60–1.71 (*m*)	48.3 (*d*)	1.58–1.69 (*m*)	48.3 (*d*)
10		37.9 (*s*)		37.9 (*s*)
11	1.89–1.98 (*m*)	24.8 (*t*)	1.85–1.95 (*m*)	24.8 (*t*)
12	5.34 (br. *s*)	125.0 (*d*)	5.30 (br. *s*)	125.0 (*d*)
13		143.1 (*s*)		143.1 (*s*)
14		44.7 (*s*)		44.7 (*s*)
15	1.78 (*t*, *J* = 12.0), 1.33–1.38 (*m*)	36.6 (*t*)	1.74–1.80 (*m*), 1.58–1.69 (*m*)	36.6 (*t*)
16	4.31 (*dd*, *J* = 11.6, 4.8)	68.0 (*d*)	4.27 (*dd*, *J* = 11.6, 4.8)	68.0 (*d*)
17		44.8 (*s*)		44.8 (*s*)
18	2.47 (*dd*, *J* = 13.6, 4.4)	43.8 (*d*)	2.38 (*dd*, *J* = 13.6, 3.2)	43.8 (*d*)
19	1.89–1.98 (*m*)	48.1 (*t*)	1.95–1.85 (*m*)	48.1 (*t*)
20		36.6 (*s*)		36.4 (*s*)
21	5.03 (*dd*, *J* = 12.4, 4.4)	77.7 (*d*)	4.92 (*dd*, *J* = 12.8, 4.8)	77.8 (*d*)
22	2.27 (*dd*, *J* = 13.2, 4.4), 1.60–1.71 (*m*)	30.4 (*t*)	2.27 (*dd*, *J* = 13.6, 4.8), 1.51–1.57 (*m*)	30.2 (*t*)
23	3.54 (*d*, *J* = 10.8), 3.29–3.31 (*m*)	67.3 (*t*)	3.53 (*d*, *J* = 10.8), 3.29–3.31 (*m*)	68.1 (*t*)
24	0.72 (*s*)	12.9 (*q*)	0.71 (*s*)	12.9 (*q*)
25	1.01 (*s*)	16.6 (*q*)	1.00 (*s*)	16.6 (*q*)
26	1.04 (*s*)	17.6 (*q*)	1.02 (*s*)	17.6 (*q*)
27	1.28 (*s*)	27.5 (*q*)	1.25 (*s*)	27.5 (*q*)
28	3.68 (*d*, *J* = 10.8), 3.39 (*d*, *J* = 10.8)	66.7 (*t*)	3.70 (*d*, *J* = 10.4), 3.31–3.35 (*m*)	66.9 (*t*)
29	1.08 (*s*)	18.9 (*q*)	0.84 (*s*)	18.7 (*q*)
30	0.92 (*s*)	29.5 (*q*)	0.84 (*s*)	29.5 (*q*)
1′		168.7 (*s*)		168.1 (*s*)
2′	7.67 (*d*, *J* = 16.0)	119.4 (*d*)	5.97 (*d*, *J* = 12.4)	121.2 (*d*)
3′	6.44 (*d*, *J* = 16.0)	146.4 (*d*)	7.04 (*d*, *J* = 12.4)	144.3 (*d*)
4′		135.9 (*s*)		136.8 (*s*)
5′	7.53 (*d*, *J* = 7.2)	129.4 (*d*)	7.54 (*d*, *J* = 6.4)	130.8 (*d*)
6′	7.39 (*t*, *J* = 2.8)	130.2 (*d*)	7.31–7.36 (*m*)	129.3 (*d*)
7′	7.39 (*t*, *J* = 2.8)	131.7 (*d*)	7.31–7.36 (*m*)	130.1 (*d*)
8′	7.39 (*t*, *J* = 2.8)	130.2 (*d*)	7.31–7.36 (*m*)	129.3 (*d*)
9′	7.53 (*d*, *J* = 7.2)	129.4 (*d*)	7.54 (*d*, *J* = 6.4)	130.8 (*d*)

with those of **1** (*Table 1*), indicated that **3** was also a triterpenoid with an olean-12-ene skeleton. Comparison of the ^{13}C-NMR data of **3** with those of **1** showed that the signals of C(1) to C(30) were basically identical in both compounds, indicating identical rings *A*–*E*. However, in the lowest field of the ^{1}H-NMR spectrum, there were three characteristic-group signals of a monosubstituted benzene at δ(H) 7.53 (*d*, *J* = 7.2, 2 H) and 7.39 (*m*, 3 H). The spectrum also exhibited a pair of (*E*)-oriented olefinic H-atom signals at δ(H) 7.67 (*d*, *J* = 16.0, 1 H) and 6.44 (*d*, *J* = 16.0, 1 H). The presence of a (*E*)-cinnamoyloxy unit could be deduced from the ^{1}H- and ^{13}C-NMR, and DEPT spectra, and the group was at C(21), as confirmed by the key HMBCs (*Fig. 2,a*) from δ(H) 5.03 (H–C(21)) to δ(C) 168.7 (C(1′)), 36.6 (C(20)), 18.9 (C(29)), and 29.5 (C(30)). The structural features described above were corroborated by 2D-NMR experiments (^{1}H,^{1}H-COSY, HSQC, and HMBC).

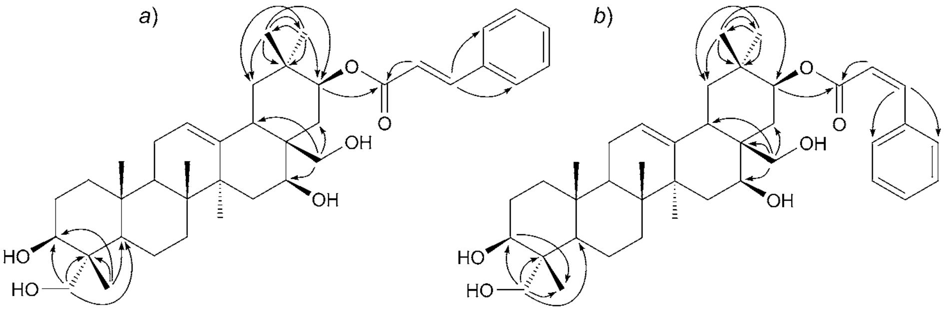


Fig. 2. *Key HMBCs of a*) **3** *and b*) **4**

The relative configuration was assigned by analysis of coupling constants and correlations in the ROESY spectrum. A typical signal of an axial H-atom at C(3) at δ(H) 3.61 (*dd*, *J* = 11.2, 4.8) was observed, indicating a β-orientation of the OH group at C(3) of **1** [6]. The NOESY correlations H–C(16)/Me(27), as well as H–C(18)/Me(29) and H–C(21)/Me(30), indicated a β-OH group at C(16) and the (*E*)-cinnamoyloxy moiety at C(21). On the basis of the above evidence, the structure of compound **3** was determined as 21β-[(*E*)-cinnamoyloxy]olean-12-ene-3β,16β,23,28-tetrol.

Compound **4**, obtained as a white amorphous powder, also gave a positive *Liebermann–Burchard* test. The HR-ESI-MS provided the molecular formula $C_{39}H_{56}O_5$ (*m/z* 638.4429 ($[M + NH_4]^+$)), suggesting twelve degrees of unsaturation. The IR spectrum of **4** showed absorption bands at 3417, 1706, and 1628 cm^{-1}, attributed to OH, C=O, and C=C moieties, respectively, and broad bands at 1575, 1490, 1455 cm^{-1}, suggestive of a benzene ring. The above data, together with a detailed comparison of the ^{1}H- and ^{13}C-NMR data (*Table 2*) with those of **3**, revealed that **3** and **4** were a pair of (*E*)- and (*Z*)-isomers based on the presence of a pair of (*Z*)-oriented olefinic H-atom signals at δ(H) 7.04 (*d*, *J* = 12.4, 1 H) and 5.97 (*d*, *J* = 12.4, 1 H). The constitutional formula of **4** was confirmed with the help of HSQC and HMBC experiments (*Table 2*).

The relative configuration of **4** was deduced from NOESY experiment. The 16β-OH and 21β-[(*Z*)-cinnamoyloxy] groups were in accordance with the NOESY correlations H–C(16)/Me(27) and H–C(16), and H–C(21)/H–C(19b), H–C(22a). Furthermore, H–C(3) correlated with H–C(5), which indicated a β-OH group at C(3). Accordingly, the structure of **4** was unambiguously established as 21β-[(*Z*)-cinnamoyloxy]olean-12-ene-3β,16β,23,28-tetrol.

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Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Marine Chemical Factory*), *RP-C18* silica gel (40–75 µm; *Merck*), and *Sephadex LH-20* gel (*Amersham Pharmacia Biotech*). TLC: silica gel GF_{254} plates (10–40 µm; *Qingdao Marine Chemical Factory*); visualization under UV light and by spraying with 5% H_2SO_4 in EtOH (*v*/*v*) or phosphomolybdic acid hydrate, followed by heating. Optical rotations: *Perkin-Elmer Model 341* polarimeter. IR Spectra: *Nicolet NEXUS 670* FT-IR spectrometer; in cm^{-1}. NMR Spectra: *Bruker NMR* spectrometer; at 400 (^1H) and 100 MHz (^{13}C); δ in ppm rel. to Me_4Si, *J* in Hz. HR-ESI-MS: *Bruker APEX II* mass spectrometer; in *m*/*z*.

Plant Material. The leaves and twigs of *Glochidion assamicum* HOOK were collected in Yunnan Province, P. R. China, in October 2009, and identified by Prof. *Guoda Tao*. A voucher specimen (No. 200910GA) was deposited with the Institute of Organic Chemistry , Lanzhou University.

Extraction and Isolation. The air-dried leaves and twigs (10.0 kg) of *Glochidion assamicum* were extracted with 95% aq. EtOH at 40° for 4 h under reflux (3 ×). The combined extract was concentrated under vacuum, and the residue (710 g) was suspended in H_2O, and extracted first with AcOEt and then with BuOH.

The AcOEt fraction, after evaporation, was further separated by CC (SiO_2 (260 g), petroleum ether (PE)/acetone 50 : 1 → 1 : 1 and 0 : 1): *Frs. 1–8* (detected by TLC). *Fr. 6* was subjected to CC (SiO_2; $CHCl_3$/MeOH 50 : 1 to 0 : 1) to afford ten subfractions, *Frs. 6.1–6.10*. *Fr. 6.2* was purified by CC (1. *Sephadex LH-20*; $CHCl_3$/MeOH 2 : 1; 2. *RP-C18* silica gel; 60% aq. MeOH; 3. SiO_2, $CHCl_3$/MeOH 50 : 1 → 0 : 1) afforded the compounds **1** (55 mg) and **2** (9 mg). Purification of *Fr. 6.4* by CC (1. *Sephadex LH-20*, $CHCl_3$/MeOH 2 : 1; 2. *RP-C18* silica gel; 50% aq. MeOH; 3. SiO_2, $CHCl_3$/MeOH 50 : 1 → 0 : 1) to afford **3** (3 mg) and **4** (4 mg).

21β-(Benzoyloxy)olean-12-ene-3β,16β,23,28-tetraol (= *(3β,16β,21β)-3,16,23,28-Tetrahydroxyolean-12-en-21-yl Benzoate*; **1**). White amorphous powder. $[\alpha]_D^{20} = -10$ (*c* = 0.1, $CHCl_3$). IR (KBr): 3401, 3066, 2948, 2924, 2980, 1689, 1600, 1583, 1452, 1280. ^1H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS: 612.4250 ($[M + NH_4]^+$, $C_{37}H_{58}NO_6^+$; calc. 612.4259).

21β-(Benzoyloxy)olean-12-ene-3β,16β,28-triol (= *(3β,16β,21β)-3,16,28-Trihydroxyolean-12-en-21-yl Benzoate*; **2**). White amorphous powder. $[\alpha]_D^{20} = +30$ (*c* = 0.1, MeOH). IR (KBr): 3517, 3438, 3062, 2931, 2872, 1701, 1653, 1603, 1582, 1454, 1385, 1288. ^1H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS: 601.3871 ($[M + Na]^+$, $C_{37}H_{54}NaO_5^+$; calc. 601.3863).

21β-[(E)-Cinnamoyloxy]olean-12-ene-3β,16β,23,28-tetraol (= *(3β,16β,21β)-3,16,23,28-Tetrahydroxyolean-12-en-21-yl (2E)-3-Phenylprop-2-enoate*; **3**). White amorphous powder. $[\alpha]_D^{20} = +10$ (*c* = 0.1, MeOH). IR (KBr): 3398, 2927, 2879, 1697, 1636, 1577, 1540, 1452, 1184, 1049, 1009. ^1H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS: 638.4420 ($[M + NH_4]^+$, $C_{39}H_{60}NO_5^+$; calc. 638.4415).

21β-[(Z)-Cinnamoyloxy]olean-12-ene-3β,16β,23,28-tetraol (= *(3β,16β,21β)-3,16,23,28-Tetrahydroxyolean-12-en-21-yl (2Z)-3-Phenylprop-2-enoate*; **4**). White amorphous powder. $[\alpha]_D^{20} = +10$ (*c* = 0.1, MeOH). IR (KBr): 3417, 2949, 2883, 1706, 1628, 1575, 1540, 1490, 1455, 1170, 1048. ^1H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS: 638.4429 ($[M + NH_4]^+$, $C_{39}H_{60}NO_5^+$; calc. 638.4415).

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