Three Triterpenes and a Triterpene Ferulate from *Rhoiptelea chiliantha*

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Three new triterpenes and a new triterpene ferulate were isolated from the bark of *Rhoiptelea chiliantha* DIELS *et* HAND.-MAZZ. (Rhoipteleaceae). Their structures were elucidated on the basis of spectral and chemical evidence.

Key words *Rhoiptelea chiliantha*; Rhoipteleaceae; triterpene; triterpene ferulate

In the course of our chemical and chemotaxonomical studies on the Rhoipteleaceae, we have reported on novel triterpene-lignan esters having dimeric structures,[1] a new rearranged ursane triterpene named rhoiptelic acid (**1**),[2] triterpene caffeates,[3] dimeric ellagitannins[4] and diarylheptanoids[5] from *Rhoiptelea chiliantha* DIELS *et* HAND.-MAZZ. Here we describe the isolation and structural elucidation of four triterpenoids (**2**, **4**, **6** and **7**) from the bark.

Compound **2**, $C_{32}H_{50}O_4$, a white amorphous powder, showed an M^+ ion peak at *m/z* 498 in electron impact mass spectrum (EI-MS). The ^{1}H- and ^{13}C-NMR data (Table 1) of **2** showed close similarities to those of 3-*O*-acetyl rhoiptelic acid methyl ester (**3**),[2] except for the downfield shift of the carboxyl signal and the absence of the methoxyl signal. These observations indicated that **2** is 3-*O*-acetyl rhoiptelic acid, and this was confirmed by acetylation of **1**.

Compound **4** was isolated as colorless needles (mp 207—209 °C). Its molecular formula, $C_{30}H_{46}O_5$, was established from the results of EI-MS ($[M]^+$, *m/z* 486) and elemental analysis. The ^{1}H-NMR spectrum of **4** showed signals due to six tertiary methyls, an oxygenated methine, a hydroxymethyl group and a trisubstituted double bond. The ^{13}C-NMR data (Table 1) are closely related to those of compound **5**[3] which was also isolated from the bark of *Rhoiptelea chiliantha*. The differences in the spectra were the appearance of a conjugated carbonyl (δ 201.8) in place of a methylene (C-11) of **5**, and the downfield shifts of the C-8, C-9, C-12 and C-13 carbon signals . The UV absorption at 253 nm also supported the presence of a conjugated carbonyl group whose position was established by the observation of its heteronuclear multiple bond correlation (HMBC) (Fig. 1) with H-9 (δ 3.68, s) and H-12 (δ 6.38, s). Taking the molecular formula into account, these findings suggested that **4** is an 11-keto derivative of **5**. The whole structure was further confirmed by the HMBC shown in Fig. 1. Thus, **4** was assigned as 3β,27-dihydroxy-11-oxo-olean-12-en-28-oic acid.

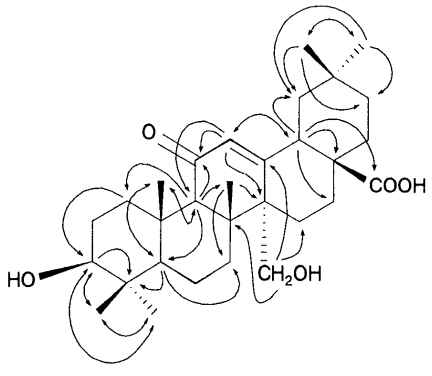

Fig. 1. The HMBC Correlations (H to C) of **4**

Compound **6**, colorless needles, showed an M^+ ion peak at *m/z* 484 in the EI-MS, *i.e.*, two mass units less than that of **4**. The ^{1}H- and ^{13}C-NMR data (Table 1) of **6** closely resembled those of **4**, except for the appearance of an unconjugated ketone signal at δ 216.2 instead of the oxygen-bearing methine (C-3) signal of **4**, and the downfield shifts ($\Delta\delta$ +4.7, +7.7, +4.3, respectively) for C-2, C-4 and C-24[6] compared with those of **4**. Thus, **6** was determined to be 27-hydroxy-3,11-dioxo-olean-12-en-28-oic acid.

Table 1. ^{13}C-NMR Spectral Data for **2**—**8**

No.	**2**[a]	**3**[b]	**4**[c]	**5**[c]	**6**[d]	**7**[e]	**8**[e]
C-1	18.9	18.8	39.9	38.9	40.3	39.9	39.9
C-2	25.5	25.4	28.2	28.1	32.9	27.9	27.8
C-3	78.6	78.5	77.9	78.1	216.2	79.6	79.6
C-4	39.2	39.1	39.7	39.4	47.4	39.8	39.8
C-5	142.2	142.2	55.5	55.8	55.2	56.7	56.7
C-6	119.9	119.9	18.0	18.9	19.2	19.5	19.5
C-7	23.8	23.7	33.8	33.7	34.4	34.5	34.4
C-8	45.0	44.9	45.9	40.5	45.6	41.3	41.2
C-9	34.7	34.6	62.4	48.8	61.7	50.0	50.0
C-10	50.1	50.0	38.1	37.6	37.4	38.4	38.3
C-11	34.1	34.1	201.8	23.8	201.3	24.0	23.9
C-12	28.9	28.8	131.8	127.7	131.6	128.2	128.1
C-13	38.7	38.6	163.1	139.9	163.6	139.1	139.0
C-14	39.3	39.3	49.5	48.0	49.6	46.8	46.7
C-15	27.7	27.7	25.0	24.4	25.0	25.1	25.1
C-16	32.4	32.2	23.5	24.1	23.5	24.7	24.7
C-17	44.2	44.2	46.2	46.6	46.2	47.5	47.3
C-18	46.1	46.1	42.4	41.8	42.4	42.6	42.5
C-19	36.8	36.6	43.5	45.6	43.5	46.3	46.2
C-20	32.5	32.3	30.7	31.0	30.7	31.6	31.5
C-21	29.3	29.39	33.9	34.1	33.9	34.8	34.7
C-22	29.5	29.42	32.3	33.2	32.3	33.8	33.7
C-23	29.2	29.2	28.7	28.7	26.8	28.7	28.7
C-24	25.1	25.0	16.5	16.5	20.8	16.4	16.3
C-25	17.2	17.1	17.1	16.0	16.4	16.2	16.1
C-26	15.2	15.1	21.2	18.8	21.3	18.9	18.9
C-27	14.6	14.5	63.6	64.5	63.7	66.8	66.8
C-28	187.4	181.2	179.8	180.2	179.8	181.8	181.6
C-29	23.3	23.2	32.9	33.2	32.9	33.5	33.5
C-30	21.3	21.2	23.6	23.9	23.6	24.1	24.1
Ac	21.4	21.3					
	171.0	170.9					
–OMe		52.1					

a) 75 MHz, $CDCl_3$. *b*) 125 MHz, $CDCl_3$. *c*) 125 MHz, pyridine-d_5. *d*) 75 MHz, pyridine-d_5. *e*) 75 MHz, CD_3OD.

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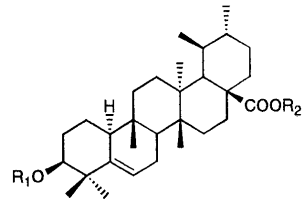
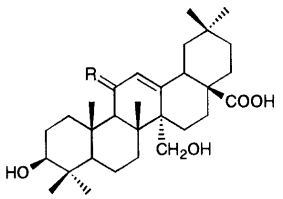
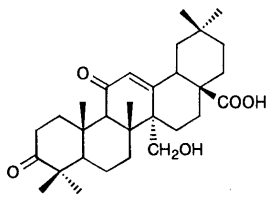


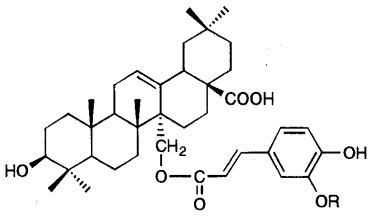
1 R_1=H, R_2=H
2 R_1=Ac, R_2=H
3 R_1=Ac, R_2=Me



4 R=O
5 R=H, H



6



7 R=Me
8 R=H

Compound **7**, $C_{40}H_{56}O_7$, was isolated as a white amorphous powder. Its EI-MS showed an M^+ ion peak at *m/z* 648, *i.e.*, 14 mass units more than that of the triterpene caffeate **8**[1] which was isolated from the bark. In the ^{1}H- and ^{13}C-NMR spectrum, the signals arising from a triterpene and an α,β-unsaturated carboxyl group were almost superimposable on those of **8**. Chemical shifts of the remaining methoxyl (δ_H 3.89, δ_C 56.5) and aromatic signals coincided with those of the feruloyl group.[7] Accordingly, compound **7** was determined to be 27-*trans*-feruloyloxy-3-hydroxyolean-12-en-28-oic acid.

Experimental

General The instruments used to measure the physical data and the experimental conditions for chromatography were the same as those described in our previous paper.[3]

Extraction and Separation The air-dried ground bark (4.5 kg) was extracted with 95% EtOH. The extract (570 g) was partitioned between Et_2O (1 l) and H_2O (1 l) twice, then the Et_2O layer was concentrated and treated with MeOH. The MeOH-soluble fraction was subjected to MCI-gel CHP 20P (80%—100% MeOH then acetone) to afford fraction 1 (129 g) and fraction 2 (125 g). A part of fraction 1 (77 g) was then chromatographed on silica gel [$CHCl_3$–MeOH–H_2O (8:2:0.2)] and MCI-gel CHP 20P (80%—90% MeOH) and MPLC (ODS, 80% CH_3CN) to afford compounds **4** (45 mg), **6** (40 mg) and **7** (11 mg). Fraction 2 was chromatographed over silica gel [*n*-hexane–EtOAc (1:0—3:1)] yielding compound **2** (147 mg).

Compound 2 A white amorphous powder, $[\alpha]_D^{20}$ +77.1° (*c*=0.3, $CHCl_3$). EI-MS *m/z* (rel. int. %): 498 (M^+, 20). *Anal.* Calcd for $C_{32}H_{50}O_4 \cdot 3/2H_2O$: C, 73.10; H, 10.16. Found: C, 73.56; H, 9.74. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.54 (1H, s, H-6), 4.70 (1H, s, H-3), 2.46 (2H, m, H-18, 21), 2.02 (3H, s, acetyl), 1.11, 1.08, 1.05, 1.03, 0.93 (each 3H, s, H_3-23, 24, 25, 26, 27), 1.00 (3H, d, *J*=7 Hz, H_3-29), 0.87 (3H, d, *J*=5 Hz, H_3-30). ^{13}C-NMR data see Table 1.

Acetylation of 1 Compound **1** (300 mg) was treated with pyridine (2 ml) and Ac_2O (2 ml) at room temperature for 12 h. The reaction solution was subjected to silica gel column chromatography with *n*-hexane–EtOAc (5:1—3:1) to give **2** (250 mg).

3β,27-Dihydroxy-11-oxoolean-12-en-28-oic Acid (4) Colorless needles (MeOH), mp 207—209°, $[\alpha]_D^{15}$ +58.9° (*c*=0.3, MeOH). EI-MS *m/z* (rel. int. %): 486 (M^+, 20), 468 ($M^+ - H_2O$, 20), 456 ($M^+ - CH_2OH$, 100). *Anal.* Calcd for $C_{30}H_{46}O_5 \cdot H_2O$: C, 71.39; H, 9.58. Found: C, 70.91; H, 9.22. UV λ_{max}^{EtOH} nm (log ε): 253 (2.6). ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 6.38 (1H, s, H-12), 4.46, 4.06 (each 1H, d, *J*=12 Hz, H_2-27), 3.68 (1H, s, H-9), 3.47 (1H, dd, *J*=4, 14 Hz, H-18), 3.36 (1H, dd, *J*=5, 11 Hz, H-3), 3.30 (1H, dt, *J*=13, 3 Hz, H-1$_{eq}$), 2.19 (1H, dt, *J*=3, 13 Hz, H-15$_{ax}$), 1.30 (3H, s, H_3-25), 1.27 (3H, s, H_3-26), 1.21 (3H, s, H_3-23), 1.05 (3H, s, H_3-24), 0.98 (1H, d, *J*=11 Hz, H-5), 0.93 (3H, s, H_3-30), 0.82 (3H, s, H_3-29). ^{13}C-NMR data see Table 1.

27-Hydroxy-3,11-dioxoolean-12-en-28-oic Acid (6) Colorless needles (MeOH), mp 237—239°, $[\alpha]_D^{15}$ +105.7° (*c*=0.3, MeOH). EI-MS *m/z* (rel. int. %): 484 (M^+, 20), 466 ($M^+ - H_2O$, 15), 454 ($M^+ - CH_2OH$, 100). *Anal.* Calcd for $C_{30}H_{44}O_5 \cdot 1/2H_2O$: C, 72.99; H, 9.19. Found: C, 72.81; H, 8.96. UV λ_{max}^{EtOH} nm (log ε): 253 (2.5). ^{1}H-NMR (300 MHz, pyridine-d_5): δ 6.39 (1H, s, H-12), 4.41, 4.04 (each 1H, d, *J*=12 Hz, H_2-27), 3.75 (1H, s, H-9), 3.48 (1H, dd, *J*=4, 14 Hz, H-18), 3.25 (1H, ddd, *J*=5, 8, 13 Hz, H-1$_{eq}$), 2.57 (1H, ddd, *J*=8, 10, 16 Hz, H-2$_{ax}$), 2.35 (1H, ddd, *J*=5, 7, 16 Hz, H-2$_{eq}$), 2.17 (1H, dt, *J*=3, 12 Hz, H-16$_{ax}$), 1.62 (1H, ddd, *J*=7, 10, 13 Hz, H-1$_{ax}$), 1.26 (3H, s, H_3-26), 1.24 (3H, s, H_3-25), 1.10 (3H, s, H_3-24), 1.04 (3H, s, H_3-23), 0.93 (3H, s, H_3-30), 0.81 (3H, s, H_3-29). ^{13}C-NMR data see Table 1.

27-*trans*-Feruloyloxy-3-hydroxyolean-12-en-28-oic Acid (7) A white amorphous powder, $[\alpha]_D^{24}$ +52.6° (*c*=0.8, MeOH). EI-MS *m/z* (rel. int. %): 648 (M^+, 1). *Anal.* Calcd for $C_{40}H_{56}O_7 \cdot 2H_2O$: C, 70.15; H, 8.83. Found: C, 70.31; H, 8.42. ^{1}H-NMR (300 MHz, CD_3OD): δ 7.57 (1H, d, *J*= 16 Hz, H-7′), 7.16 (1H, d, *J*=2 Hz, H-2′), 7.02 (1H, dd, *J*=2, 8 Hz, H-6′), 6.82 (1H, d, *J*=8 Hz, H-5′), 6.28 (1H, d, *J*=16 Hz, H-8′), 5.60 (1H, t, *J*=3 Hz, H-12), 4.41, 4.16 (each 1H, d, *J*=13 Hz, H_2-27), 3.89 (3H, s, methoxyl), 3.10 (1H, dd, *J*=4, 12 Hz, H-3), 2.95 (1H, dd, *J*=3, 14 Hz, H-18), 0.954, 0.951, 0.94, 0.85, 0.84, 0.76 (each 3H, s, methyl). ^{13}C-NMR (75 MHz, CD_3OD) δ: triterpene moiety: see Table 1; feruloyl moiety: 168.9 (C-9′), 150.8 (C-3′), 149.5 (C-4′), 146.8 (C-7′), 127.6 (C-1′), 124.2 (C-6′), 116.6 (C-5′), 115.8 (C-8′), 111.5 (C-2′), 56.5 (methoxyl).

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