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A REARRANGED URSANE TRITERPENOID FROM *RHOIPTELEA CHILIANTHA*

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Key Word Index—*Rhoiptelea chiliantha*; Rhoipteleaceae; triterpenoid; rearranged ursane; rhoiptelic acid.

Abstract—Rhoiptelic acid, the first representative of a rearranged ursane-type triterpenoid acid with a Δ^5 double bond, was isolated from the bark of *Rhoiptelea chiliantha*. Its structure has been established by means of mass and 2D-NMR spectroscopy.

INTRODUCTION

Rhoipteleaceae is a monotypic family that consists of one species, i.e., *Rhoiptelea chiliantha* Diels et Hand.-Mazz., which grows in Guangxi, Guizhou and Yunnan Province of China and northern Vietnam. We have investigated the chemical constituents of this plant for chemotaxonomic reasons and have reported on the seed fatty acids [1], the leaf volatiles [2], and the dimeric triterpene-lignan esters from the bark [3]. Further investigation of the chemical constituents from the bark resulted in the isolation of a new rearranged ursane-type triterpenoid acid, named rhoiptelic acid (**1**), possessing a migrated ursane skeleton with Δ^5 double bond in the molecule. In this paper, we describe the isolation and the structure elucidation of compound **1**.

RESULTS AND DISCUSSION

Compound **1** (yield 0.2%) gave a positive Liebermann-Burchard reaction. Its high resolution EI-MS showed $[M]^+$ at *m/z* 456.3616 (calcd. 456.3604) suggesting a molecular formula of $C_{30}H_{48}O_3$. The IR spectrum showed the presence of a hydroxyl (ν_{max}^{KBr} cm^{-1}: 3480, 1100) and a carboxyl (ν_{max}^{KBr} cm^{-1}: 1700) group. Methylation of **1** with CH_2N_2 gave a methyl ester (**1a**) which on acetylation gave a methyl ester acetate (**1b**). The low resolution EI-MS of **1** (Scheme 1) showed major fragment ions at *m/z* 152 (66% of the base peak), 134 [152-H_2O]$^+$ (100), 304 (59), 234 (27) and 189 [234-COOH]$^+$ (10). The base peak (*m/z* 134) indicated that compound **1** had a double bond at C-5 like glutinyl acetate (**2a**) [4] while the last three fragment ions indicated that the carboxyl group was situated in the right counterpart of the molecule. The base peak (*m/z* 274) of **2a** was formed by cleavage of the allylic position of the double bond and based on the right counterpart of the molecule. The ion at *m/z* 304 of **1** was 30 mass units more than the corresponding ion observed in **2a**, which indicated that one of the methyl groups in rings C, D or E of **2a** was replaced with a carboxyl group.

The ^{1}H NMR spectrum (Table 1) of **1** in pyridine-d_5 contained the signals of five tertiary methyls, two secondary methyls, an axial hydroxyl and a trisubstituted double bond proton. The chemical shifts of the olefinic proton (H-6) and two methyl protons (H_3-23, H_3-24) of **1** were very similar to those of glutinol (**2**) [4]. The splitting pattern of the H-6 signal was also very similar to that of **2**. Furthermore, the chemical shifts of H_3-23, H_3-24 and H-6 of **1a** in $CDCl_3$ coincided with those of simiarenol [5]. The aforementioned results indicated that compound **1** was a pentacyclic triterpenoid acid belonging to the migrated ursane or lupane series with a Δ^5 double bond in the molecule.

To elucidate the structure of **1**, all the ^{1}H and ^{13}C NMR signals of **1** and **2** in pyridine-d_5 and **1b** in $CDCl_3$ were assigned unambiguously by detailed analyses of 2D NMR, eg H-H, C-H COSY, HSQC (Heteronuclear Single Quantum Coherence Spectroscopy), HMBC and NOESY spectra (Table 1). The most informative results as to the backbone structure of **1** were obtained by HMBC (Table 2). Thus two and three bond correlation data were obtained from the signals of seven methyl group protons (H_3-23 ~ H_3-30). As the signal δ2.913 $d(J = 4.2$ Hz) appeared at lower magnetic field and no overlapping signal was observed around the peak, a lower level contour plot of the HMBC spectrum clearly showed seven cross peaks from the H-18 methine

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Table 1. ^{1}H (500 MHz) and ^{13}C (125.65 MHz) NMR spectral data for compounds **1**, **2**, **1a** and **1b**

	1*		**2†**		**1a†**		**1b†**	
H&C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	1.61	18.92	1.55	19.03		18.02	1.49	18.77
	2.15		2.10				1.49	
2	1.94	29.22	1.98	29.28		27.20	1.78	25.38
	2.02		2.02				1.78	
3	3.760	75.53	3.757	75.53	3.479	76.25	4.700	78.54
	(*bs*)		(*bs*)		(*dd* 2.4, 2.4)		(*dd* 2.7, 2.7)	
4	—	41.10	—	41.11		40.75		39.10
5	—	144.26	—	144.04		141.86	—	142.16
6	5.849	119.86	5.805	119.88	5.612	121.74	5.539	119.87
	(*d* 5.8)‡		(*ddd* 1.8, 1.8, 5.8)		(*ddd* 1.8, 1.8, 6.0)		(*ddd* 2.1, 2.1, 5.8)	
7	1.92§	24.18	1.92	23.96		23.75	1.81	23.67
	2.05		2.07				1.94	
8	1.71	45.52	1.56	47.83		44.93	1.52	44.91
9	—	35.12	—	35.23		34.64	—	34.64
10	2.30	50.86	2.22	50.68		49.82	2.07	44.99
11	1.65	34.55	1.30	35.27		34.01	1.55	34.07
	1.72		1.40				1.55	
12	1.36	29.30	1.33	30.67		28.68	1.28	28.77
	1.72		1.33				1.55	
13	—	39.06	—	38.09		38.54	—	38.64
14	—	39.68	—	39.53		39.24	—	39.29
15	1.28	28.08	1.24	32.14		27.65	1.27	27.65
	1.28		1.41				1.80	
16	1.59	33.08	0.89	39.09		32.21	1.27	32.15
	2.13		1.55				1.34	

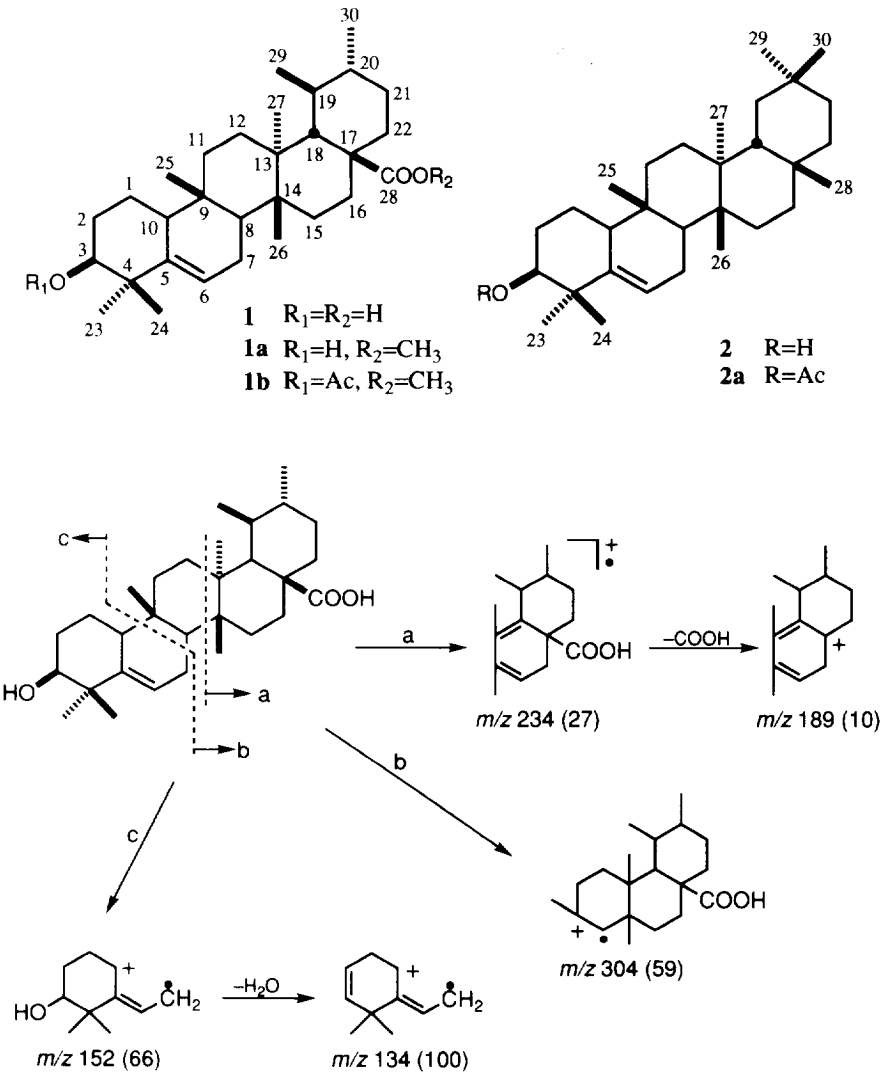
17	—	44.34	—	30.26		44.14	—	44.21
18	2.913 (*d* 4.2)	46.69	1.58	43.41		46.05	2.470 (*d* 3.1)	46.14
19	1.13	37.28	1.27 1.44	33.45		36.58	0.90	36.63
20	1.52	32.52	—	28.40		32.10	0.97	32.27
21	1.17 1.70	30.28	1.48 1.58	34.97		29.37	1.72 2.42	29.39
22	1.82 2.88	30.02	1.36 1.48	36.31		29.37	1.05 1.56	29.42
23	1.175	29.65	1.176	29.60	1.050	28.98	1.076	29.15
24	1.441	26.36	1.445	26.38	1.144	25.39	1.046	25.02
25	1.093	17.64	1.012	16.58	0.919	17.20	0.915	17.09
26	1.279	15.41	1.071	19.66	1.087	15.13	1.095	15.10
27	1.139	14.86	1.025	18.66	1.018	14.50	1.020	14.54
28		183.37	1.152	32.16	—	181.16	—	181.23
29	1.267 (*d* 6.7)	23.73	1.038	34.56	0.953 (*d* 5.8)	23.18	0.955 (*d* 6.2)	23.24
30	0.882 (*d* 6.4)	21.53	1.003	32.63	0.836 (*d* 5.8)	21.22	0.848 (*d* 6.8)	21.24
COOMe					3.693	52.09	3.612	52.13
OCOMe							2.017	21.26
OCOMe								170.88

*In C_5D_5N.

†In $CDCl_3$.

‡Coupling constants are shown in parentheses.

§Proton chemical shifts shown to two decimals were specified by H–H COSY and C–H COSY or HSQC spectra but their splitting patterns and coupling constants were not elucidated due to severely overlapping signals.



Scheme 1. Mass fragmentation pattern of **1**.

proton. In addition, some cross peaks were also observed from H-3α and H-6 (Table 2). Thus, the partial structure (shown by heavy lines in Fig. 1) in **1** was solved by the HMBC spectrum. Connectivities of unsolved C–C bond shown by broken lines in Fig. 1 were elucidated by analysis of the H–H COSY and C–H COSY or HSQC spectra. The relative configurations of C-18, C-19, C-20 and the carboxyl group at C-17 were established by the NOESY spectrum (Fig. 2). NOE interactions between methyl groups and methine groups situated on the α-side (H_3-23–H-10–H-8–H_3-27) and on the β-side (H_3-25–H_3-26–H-18–H_3-29–H-20), respectively, were observed. Since the NOE interaction between the methyl protons of the carbomethoxy group (δ3.612) and H-18β (δ2.470 *d*, 3.1 Hz) was observed in **1b**, the carboxyl group of **1** is determined to be on the β-side. The NOE interactions in **1** and **1b** are summarized in Fig. 2. By detailed analysis of the 2D-NMR spectrum, the structure of **1** was established as the first example of a migrated ursane-type triterpenoid acid representing a D:B-friedoursane skeleton [6].

EXPERIMENTAL

General. Mps: uncorr.; ^{1}H (500 MHz) and ^{13}C NMR (125.65 MHz): TMS as int. standard; 2D NMR; condi-

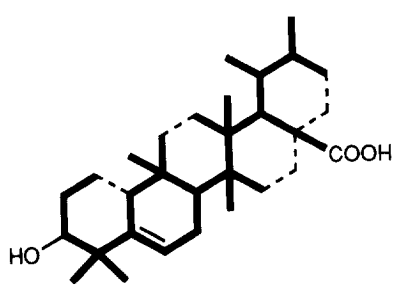


Fig. 1. Partial structure of **1** solved by HMBC spectrum.

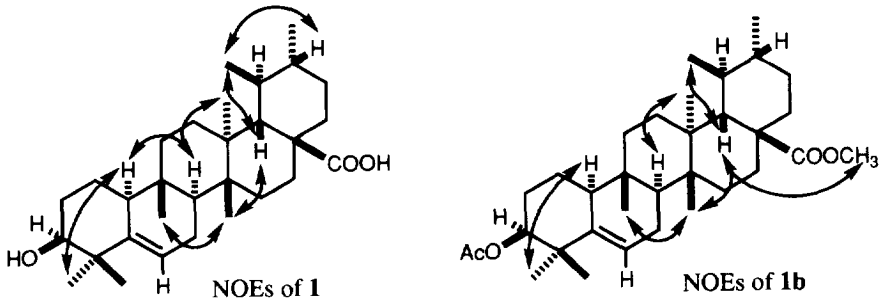


Fig. 2. NOE interactions observed in the NOESY spectra of **1** and **1b**.

Table 2. One bond (H–C COSY) and multiple bond (HMBC) H–C correlation data of **1**

δ_H (ppm)	*One bond correlation* δ_C (ppm)		*Multiple bond correlation* δ_C (ppm)		
1.175 (H_3-23)	29.65 (C-23)	26.36 (C-24)	41.10 (C-4)	144.26 (C-5)	75.53 (C-3)
1.441 (H_3-24)	26.36 (C-24)	29.65 (C-23)	41.10 (C-4)	144.26 (C-5)	75.53 (C-3)
1.093 (H_3-25)	17.64 (C-25)	34.55 (C-11)	35.12 (C-9)	45.52 (C-8)	50.86 (C-10)
1.279 (H_3-26)	15.41 (C-26)	28.08 (C-15)	39.06 (C-13)	39.68 (C-14)	45.52 (C-8)
1.139 (H_3-27)	14.86 (C-27)	29.30 (C-12)	39.06 (C-13)	39.68 (C-14)	46.69 (C-18)
1.267 (H_3-29) (*dd* 6.7 Hz)	23.73 (C-29)	32.52 (C-20)	37.28 (C-19)	46.69 (C-18)	
0.882 (H_3-30) (*d* 6.4 Hz)	21.53 (C-30)	30.28 (C-21)	32.52 (C-20)	37.28 (C-19)	
2.913 (H-18) (*d* 4.2)	46.96 (C-18)	14.86 (C-27)	23.73 (C-29)	30.02 (C-22)	37.28 (C-19)
		39.68 (C-14)	44.34 (C-17)	183.37 (C-28)	
3.760 (H-3α)	75.53 (C-3)	18.92 (C-1)	144.26 (C-5)		
5.849 (H-6) (*d* 5.8 Hz)	119.86 (C-6)	24.18 (C-7)	41.10 (C-4)	45.52 (C-8)	50.86 (C-10)

tions as given in ref. [5]; TLC: precoated Kieselgel 60 F_{254} plate (0.2 mm) using *n*-hexane–EtOAc (2:1) as the developing phase. Detection was carried out by spraying with conc. H_2SO_4 followed by heating.

Plant material. The bark of *Rhoiptelea chiliantha* was collected in Huaping, Guangxi, China in Oct., 1988. The voucher specimen was deposited in the laboratory of Plant Chemotaxonomy, China Pharmaceutical University, Nanjing, China.

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 resulting insoluble precipitate (29.5 g) was subsequently chromatographed on silica gel with *n*-hexane–EtOAc (2:1) to afford needles of **1**.

Rhoiptelic acid (**1**). Needles, mp > 300° ($CHCl_3$–MeOH), $[\alpha]_D^{23}$ + 101° (pyridine; *c* 0.8). IR ν_{max}^{KBr} cm^{-1}: 3480, 1750, 1100: EI-MS 30 eV *m/z* (rel. int.): 456.3616 $[M]^+$ (3), 441 $[M-CH_3]^+$ (2), 438 $[M-H_2O]^+$ (4), 423 $[M-CH_3-H_2O]^+$ (2), 304 (59), 289 (19), 259 (8), 234 (27), 152 (66), 134 (100); ^1H and ^{13}C NMR: Table 1.

Methylation of **1**. Treatment of **1** (40 mg) in MeOH with CH_2N_2 gave white crystals. The crude product was purified by Bond Elut Si CC using *n*-hexane–benzene (1:1) as an eluant to give the methyl ester **1a** (38 mg).

Compound **1a**. Needles, mp 190–191°, EI-MS 30 eV, *m/z* (rel. int.): 470 $[M]^+$ (3), 452 $[M-H_2O]^+$ (2), 437 $[M-CH_3]^+$ (3), 411 $[M-H_2O-CH_3]^+$ (3), 318 (83), 303 (17), 259 (28), 258 (26), 248 (43), 243 (19), 189 (48), 152 (33), 134 (100); ^1H and ^{13}C NMR: Table 1.

Acetylation of **1a**. **1a** (24 mg) was acetylated with Ac_2O–pyridine. The crude product was dissolved in *n*-hexane–benzene (1:1) and the soln was passed through Bond ELUT SI to give the acetate **1b** (20 mg).

Compound **1b**. Needles, mp 184–185°, EI-MS 30 eV, *m/z* (rel. int.): 512 $[M]^+$ (3), 452 $[M-AcOH]^+$ (11), 437 $[M-AcOH-CH_3]^+$ (5), 318 (100), 303 (18), 259 (18), 258 (19), 248 (40), 194 (9), 189 (20), 134 (68); ^1H and ^{13}C NMR: Table 1.

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