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Three new triterpenes from the roots of *Rhus javanica* L. var. *roxburghiana*

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Three new triterpenes, lantabetulal (**1**), lantanolal (**2**), and lantanolol (**3**) along with lantabetulic acid (**4**) and lantanolic acid (**5**) were isolated from the roots of *Rhus javanica* L. var. *roxburghiana*. The structural assignments of all these compounds were carried out by their spectroscopic analysis.

Keywords: *Rhus javanica* L. var. *roxburghiana*; Anacardiaceae; lantabetulal; lantanolal; lantanolol

1. Introduction

Rhus javanica L. var. *roxburghiana*, a small-sized deciduous tree, is widely distributed in thickets and secondary forests at low altitudes throughout East Asia including India, China, Taiwan, Korea, and Japan [1]. Its roots have been used in folk medicines as refrigerant and anti-parasitic agents, and for the treatments of malaria and respiratory organ-related diseases [2]. Previous chemical examinations on *R. javanica* afforded flavonoids [3,4], triterpenoids [5–7], phenolics [3,8], one tannin [9], and one aromatic alkane [5] from its stem, bark, leaves, gall, and adventitious root cultures. However, there has been no report on the constituents of the roots of *R. javanica* L. var. *roxburghiana*. In the course of investigations into the chemical constituents of *R. javanica* L. var. *roxburghiana* root, two lupane triterpenes **1** and **4** accompanied with three oleanane triterpenes **2**, **3**, and **5** were isolated and identified from the roots of this

plant. We now report the structural assignments of these compounds.

2. Results and discussion

Chemical investigations on the roots of *R. javanica* L. var. *roxburghiana* afforded three new triterpenes **1–3** and two known analogues, lantabetulic acid (**4**) [10] and lantanolic acid (**5**) [11]. The structures of **1–3** (Figure 1) were established mainly by ¹H, ¹³C NMR and DEPT spectra and 2D-NMR experiments including HMQC, HMBC, and NOESY, and the results of NMR assignments were further confirmed by the data of mass spectrometry and FT-IR spectroscopy.

Compound **1** was assigned a molecular formula of C₃₀H₄₆O₃, as deduced from the HR-EI-MS, ¹H, and ¹³C NMR spectral data. Its IR spectrum indicated the presence of a hydroxyl group (3395 cm⁻¹) and a carbonyl

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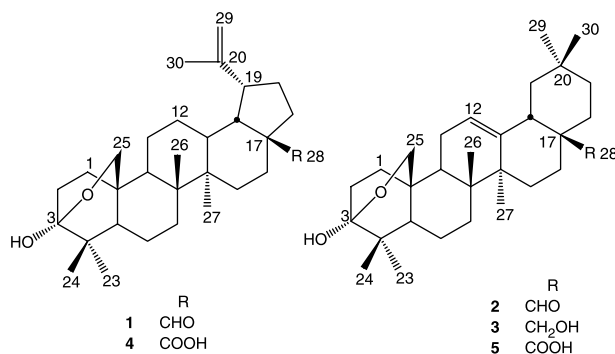


Figure 1. Structures of compounds **1–5**.

group (1724 cm^{-1}). The ^1H NMR spectrum (Table 1) of **1** showed signals due to four tertiary methyl groups at δ_{H} 0.80, 0.94, 0.95, and 1.00 two olefinic protons at δ_{H} 4.62 (1H, br s) and 4.74 (1H, br s), two oxygen-bearing methylene protons at δ_{H} 3.70 (1H, dd, $J = 1.6, 8.4\text{ Hz}$) and 4.21 (1H, dd, $J = 2.4, 8.4\text{ Hz}$), and an aldehyde functionality at δ_{H} 9.63 (1H, br s). The carbon signals observed in the ^{13}C NMR and DEPT spectra of **1** suggested the presence of one aldehyde carbonyl group at δ_{C} 206.4, one 1,1-disubstituted double bond at δ_{C} 110.2 and 149.6, one oxygen-bearing methylene carbon at δ_{C} 68.0, and one hemiacetal carbon at δ_{C} 98.0. On account of the molecular formula $\text{C}_{30}\text{H}_{46}\text{O}_3$, the degree of unsaturation of **1** was eight including one aldehyde carbonyl and one olefinic functionality. Thus, the number of rings of **1** should be six. The COSY spectrum of **1** showed that the two oxygen-bearing methylene protons at δ_{H} 3.70 and 4.21 had W-shaped $^1\text{H}-^1\text{H}$ correlations with those of $\text{H}_{\alpha}\text{-1}$ and H-5, respectively. The HMQC and HMBC spectra of **1** showed that two oxymethylene protons at δ_{H} 3.70 and 4.21 had long-range correlations with C-3 (δ_{C} 98.0) and C-5 (δ_{C} 49.8). All above spectroscopic data suggested that **1** was closely comparable to a lupane-type triterpene aldehyde skeleton except for that $\text{H}_3\text{-25}$ singlet was converted to an oxymethylene functionality that bridged between C-3 and C-25, the same as in **4**. The NOESY spectrum of

1 exhibited mutual correlations between $\text{H}_{\text{a}}\text{-25}$, $\text{H}_{\text{b}}\text{-25}$, and $\text{H}_3\text{-26}$ (Figure 2), confirming $\text{H}_2\text{-25}$ to be axial oriented. Further analysis of all the 2D-NMR spectral data allowed the complete assignments of ^1H and ^{13}C NMR spectra of **1**, as illustrated in Table 1. Accordingly, compound **1** was concluded to be 3 β ,25-epoxy-3-hydroxylupan-28-al, and named lantabetulal.

Compound **2** was obtained as colorless needles. Its molecular formula $\text{C}_{30}\text{H}_{46}\text{O}_3$ was deduced from the $[\text{M}]^+$ ion at m/z 454.3440 in the HR-EI-MS. Analysis of the IR spectrum of **2** suggested that it contained a hydroxyl group (3540 cm^{-1}) and a carbonyl group (1724 cm^{-1}). The ^1H NMR signals of **2** included six singlet methyl groups at δ_{H} 0.64, 0.88, 0.89, 0.94, 1.00, and 1.12, one trisubstituted olefinic proton at δ_{H} 5.35 (dd, $J = 3.6, 3.6\text{ Hz}$, H-12), and an aldehyde functionality at δ_{H} 9.35 (1H, s) at low-field region (Table 1). The ^{13}C NMR and DEPT spectral data showed an oxygenated and dioxygenated carbons (δ_{C} 67.7 and 98.0), a trisubstituted double bond (δ_{C} 123.2 and 142.7), and a carbonyl functional group (δ_{C} 207.1). Based on the above data together with a base peak of EI-MS at m/z 203, compound **2** was deduced to be an oleanene-type triterpene aldehyde skeleton with one aldehyde group at C-17, and one double bond at C-12. Its COSY, NOESY, and HMBC correlations also indicated a β -oriented oxygen-bearing methylene spin system located at C-25, the same as

Table 1. ^1H and ^{13}C NMR spectral data for compounds **1**, **2**, and **3** (CDCl_3 , 500 MHz).

No.	1		2		3	
	δ_{C}	δ_{H} mult. (J/Hz) ^a	δ_{C}	δ_{H} mult. (J/Hz) ^a	δ_{C}	δ_{H} mult. (J/Hz) ^a
1	29.9	1.65	29.5	1.68	29.6	1.14
		2.16		2.10		1.69
2	35.2	1.08	34.9	1.16	35.0	1.12
		2.14		2.09		1.18
3	98.0		98.0		98.0	
4	35.6		34.9		35.0	
5	49.8	1.18	50.4	1.18	50.4	1.18
6	19.7	1.42	19.5	1.39	19.7	1.18
		1.48		1.48		1.50
7	32.1	1.30	31.2	1.35	31.0	1.29
		1.42		1.42		1.39
8	39.8		38.5		38.8	
9	45.1	1.40	41.8	1.59	41.9	1.64
10	40.4		40.1		40.2	
11	22.0	1.28	23.7	1.90	23.8	1.90
		1.54		1.98		1.94
12	25.8	1.72	123.2	5.35 dd (3.6, 3.6)	122.3	5.21 t (2.8)
		1.78				
13	38.9	2.04	142.7		144.1	
14	42.3		41.8		41.8	
15	29.0	1.38	26.7	1.56	25.5	1.06
		2.08		1.60		1.30
16	28.9	1.20	22.1	1.54	22.1	1.18
		1.39		1.94		1.85
17	59.3		49.2		37.1	
18	47.8	1.74	40.9	2.61 dd (4.4, 14.0)	42.8	1.98
19	47.3	2.85 dt (5.6, 10.8)	45.3	1.18	46.2	1.06
				1.67		1.72
20	149.6		30.6		30.9	
21	29.6	1.36	27.6	1.20	34.1	1.16
		1.40		1.37		1.28
22	33.1	1.62	33.1	1.02	30.9	1.24
		1.74		1.24		1.52
23	26.9	1.00 s	27.2	1.00 s	27.2	1.03 s
24	18.3	0.95 s	18.2	0.94 s	18.2	0.97 s
25	68.0	3.70 dd (1.6, 8.4)	67.7	3.72 dd (1.6, 8.8)	67.9	3.88 dd (1.6, 8.8)
		4.21 dd (2.4, 8.4)		4.21 dd (2.8, 8.8)		4.26 dd (2.8, 8.8)
26	16.2	0.80 s	17.5	0.64 s	17.2	0.88 s
27	13.9	0.94 s	24.9	1.12 s	25.3	1.15 s
28	206.4	9.63 br s	207.1	9.35 s	69.9	3.19 d (10.8)
						3.51 d (10.8)
29	110.2	4.62 br s	33.0	0.89 s	33.1	0.88 s
		4.74 br s				
30	19.1	1.68 s	23.3	0.88 s	23.5	0.86 s

^a Signals without multiplicity were picked up from COSY or HMQC spectra.

in **1**. When comparing the spectral data of **2** with those of **5**, the difference is only an aldehyde functionality in **2** instead of a carboxylic acid group at C-17 in **5**. Thus, compound **2** was established as 3 β ,25-epoxy-

3-hydroxyolean-12-en-28-al, and we called it lantanolal.

Compound **3** possessed spectroscopic data closely comparable to those of **2** except that its aldehyde functionality in **2** was

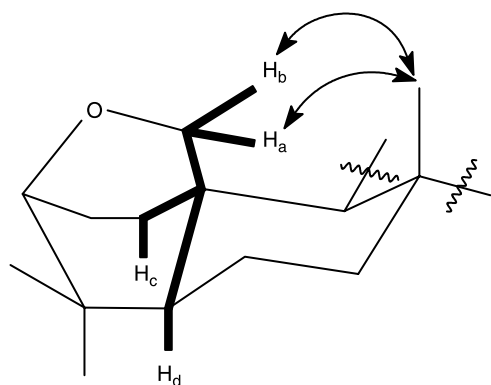


Figure 2. Key NOESY correlations (\leftrightarrow) of **1**.

replaced with a hydroxymethylene group in **3**. Its ^1H NMR (Table 1) spectrum exhibited signals for additional two oxygen-bearing methylene protons at δ_{H} 3.19 and 3.51 (d, $J = 10.8$ Hz), not the aldehyde protons (δ_{H} 9.35, s) observed in **2**. Hence, **3** contained a hydroxymethylene moiety instead of an aldehyde, which was also supported by the evidence that both H_a-28 and H_b-28 correlated with one quaternary carbon (C-17, δ_{C} 37.1) and one secondary carbon (C-22, δ_{C} 30.9) in the HMBC spectrum of **3**. The peaks of EI-MS in **3** at m/z 234 (16%) and 203 (100%) also indicated a 12-oleanene with a hydroxymethylene at C-17 [12]. Therefore, **3** was assigned as 3 β ,25-epoxy-3-hydroxyolean-12-en-28-ol, and named lantanolol.

3. Experimental

3.1 General experimental procedures

Melting points were collected using a Yanaco MP-53 apparatus and are uncorrected. Optical rotations were measured with JASCO DIP-180 digital polarimeter at room temperature. IR spectra were recorded on a Perkin-Elmer 983G spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 and DMX-500 instruments using tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ values (ppm) and coupling constants (J) are given in hertz (Hz). EI-MS was obtained on JMS-HX 110 mass spectrometer. For thin-layer chromatography

analysis, silica gel 60 F₂₅₄ plates (Merck, Germany) were used. HPLC was performed on GBC LC-1440 and LDC Analytical-III liquid chromatographs with Lichrosorb Si-60 column (7 μm , 250 \times 10 mm, Merck, Germany).

3.2 Plant material

The roots of *R. javanica* L. var. *roxburghiana* were collected at Kaohsiung, Taiwan, in June 2000. The plant material was identified by Mr Muh-Tsuen Gun, a former technician in the Department of Botany, National Taiwan University. A voucher specimen (YHK071020) has been deposited at the Herbarium of the Department of Botany, National Taiwan University, Taipei, Taiwan.

3.3 Extraction and isolation

The air-dried roots of *R. javanica* L. var. *roxburghiana* (18.0 kg) were extracted with 120 l MeOH thrice (7 days each time) at room temperature. The combined extracts were evaporated under vacuum to give a residue (1050 g) that was suspended in 8 l water and then partitioned with EtOAc and *n*-BuOH successively. The ethyl acetate layer was then chromatographed by Si-column and HPLC repeatedly. The eluent systems are combinations of *n*-hexane, EtOAc, and MeOH in a stepwise elution mode. Fractions eluted by EtOAc/hexane (3:7) were further purified by repetitive HPLC with EtOAc/hexane (3:7) as eluent to afford **1** (5 mg), **2** (20 mg), **4** (6 mg), and **5** (9 mg). Fractions eluted by EtOAc/hexane (1:1) were further purified by HPLC using the same column with EtOAc/hexane (1:1) as eluent to afford **3** (6 mg).

3.3.1 Lantabetulal (**1**)

Colorless needles; mp 153–155°C; $[\alpha]_{\text{D}}^{24} + 49.4$ (c 0.14, CHCl_3); IR ν_{max} (neat) 3395, 2926, 1724, 1457, 1378 cm^{-1} ; ^1H and ^{13}C NMR spectral data, see Table 1; EI-MS m/z (rel. int. %) 454 (M^+ , 100), 425 (26), 407 (36),

219 (17), 189 (25); HR-EI-MS m/z 454.3440 $[M]^+$ (calcd for $C_{30}H_{46}O_3$, 454.3449).

3.3.2 *Lantanolol* (2)

Colorless needles; mp 145–147°C; $[\alpha]_D^{24} + 95.0$ (c 2.79, $CHCl_3$); IR ν_{max} (neat) 3450, 1724, 1466, 1383 cm^{-1} ; 1H and ^{13}C NMR spectral data, see Table 1; EI-MS m/z (rel. int. %) 454 (M^+ , 98), 425 (48), 407 (42), 232 (27), 203 (100), 189 (44), 145 (72); HR-EI-MS m/z 454.3440 $[M]^+$ (calcd for $C_{30}H_{46}O_3$, 454.3449).

3.3.3 *Lantanolol* (3)

Colorless plates; mp 128–129°C; $[\alpha]_D^{24} + 128.0$ (c 0.52, $CHCl_3$); IR ν_{max} (neat) 3404, 1648, 1465, 1365 cm^{-1} ; 1H and ^{13}C NMR spectral data, see Table 1; EI-MS m/z (rel. int. %) 456 (M^+ , 22), 425 (21), 407 (8), 255 (42), 234 (10), 203 (100), 189 (22), 145 (42); HR-EI-MS m/z 456.3576 $[M]^+$ (calcd for $C_{30}H_{48}O_3$, 456.3605).

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