

ABIETANE QUINONES FROM *RABDOSIA LOPHANTHOIDES*

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Key Word Index—*Rabdosia lophanthoides*, Labiatae, abietane quinones

Abstract—Two new abietane quinones have been isolated, together with royleanone, 6,7-dehydroroyleanone, horminone, 16-acetoxy-7 α -methoxyroyleanone, β -sitosterol and stigmasterol, from the leaves of *Rabdosia lophanthoides* var. *gerardiana*. The new quinones were elucidated as 16-acetoxy-7-*O*-acetylhorminone and 16-acetoxy-12-*O*-acetylhorminone, respectively by spectroscopic analysis.

INTRODUCTION

Decoctions of *Rabdosia lophanthoides* (Buch.-Ham. ex D Don) Hara var. *gerardiana* (Benth.) Hara are used in Chinese traditional medicine for the treatment of infectious hepatitis, acute cholecystitis and ascariasis [1]. As a continuation of our phytochemical investigations on *Rabdosia* plants, the constitutions of two new abietane quinones, 16-acetoxy-7-*O*-acetylhorminone (**1**) and 16-acetoxy-12-*O*-acetylhorminone (**2**) were elucidated. In addition four known quinones, royleanone (**3**), 6,7-dehydroroyleanone (**4**), horminone (**5**) and 16-acetoxy-7 α -methoxyroyleanone (**6**) together with β -sitosterol and stigmasterol were identified.

RESULTS AND DISCUSSION

Compounds **3–6** were identified by comparison of their spectral data (UV, IR, ^1H NMR, ^{13}C NMR and MS) with those of published compounds [2–4].

Compound **1**, $\text{C}_{24}\text{H}_{32}\text{O}_7$ (M^+ at m/z 432), was obtained as yellow needles. Its UV, IR, ^1H NMR, ^{13}C NMR and MS were very similar to those of **6**, and this suggested that **1** and **6** had almost the same constitution [4]. The only differences in the ^1H NMR spectra of **1** and **6** are that that of **1** shows the presence of an extra acetoxy signal at δ 2.03, the absence of a methoxy group and a downfield shift of the signal for H-7 β from δ 4.30 ppm to δ 5.93. Thus, the chemical constitution of **1** is deduced to be 16-acetoxy-7-*O*-acetylhorminone (**1**).

Compound **2**, $\text{C}_{24}\text{H}_{32}\text{O}_7$, was obtained as yellow needles. The only differences between the ^1H NMR spectra of **1** and **2** are that that of **2** lacks a 12-OH signal and the signal for H-7 β is shifted upfield from δ 5.93 to 4.72. This fact suggests **2** is 16-acetoxy-12-*O*-acetylhorminone (**2**). The ^{13}C and ^1H NMR spectra of **1**, **2** and **6** are shown in Tables 1 and 2.

EXPERIMENTAL

Mps: uncorr. UV EtOH IR KBr, ^1H and ^{13}C NMR 90 and 22.63 MHz respectively, CDCl_3 with TMS as int. standard; MS: direct inlet 70 eV.

Plant material *Rabdosia lophanthoides* var. *gerardiana* leaves were collected in Mianning, Sichuan of China in Sept. 1986 and identified by Prof. H. W. Li, botanist at our institute where a voucher specimen has been deposited.

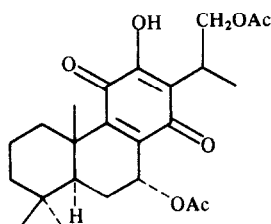
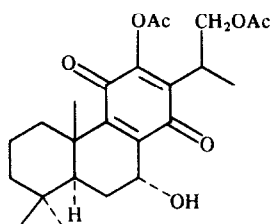
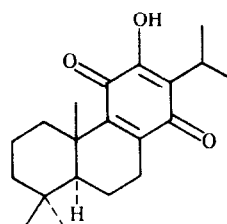
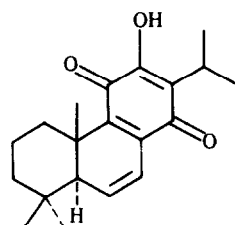
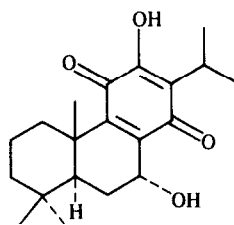
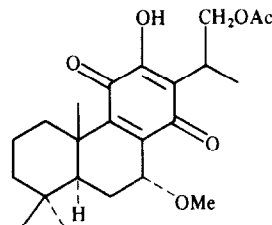
Extraction and isolation of constituents. Dried and powdered leaves (2.5 kg) were extracted with Et_2O and the solvent evapd. The residue (168 g) was dissolved in MeOH (10 l) and decolourized by treatment with active charcoal (150 g) when the soln was warm. The filtrate was concd to about 500 ml and the deposit

Table 1 ^{13}C NMR of compounds **1**, **2** and **6** (22.63 MHz, CDCl_3 , TMS)

C	1	2	6
1	35.8 t	35.8 t	35.7 t
2	18.8 t	18.9 t	18.9 t
3	41.0 t	41.1 t	41.0 t
4	33.0 s	33.0 s	33.1 s
5	46.1 d	45.8 d	45.5 d
6	24.6 t	25.9 t	22.2 t
7	64.5 d	63.1 d	70.8 d
8	139.5 s	143.3 s	141.7 s
9	150.3 s	148.2 s	148.1 s
10	39.1 s	39.2 s	39.3 s
11	183.3 s	183.5 s	183.8 s
12	152.1 s	152.3 s	151.5 s
13	120.2 s	119.8 s	120.1 s
14	185.2 s	188.6 s	186.0 s
15	29.4 d	29.3 d	29.4 d
16	66.2 t	66.3 t	66.2 t
17	14.9 q	15.0 q	15.0 q
18	33.0 q	33.0 q	33.1 q
19	21.6 q	21.7 q	21.9 q
20	18.5 q	18.5 q	18.5 q
OAc	171.0 s	171.0 s	170.9 s
	169.4 s	169.5 s	20.9 q
	20.9 q	20.9 q	
	20.9 q	20.9 q	
OMe			57.3 q

Table 2 ^1H NMR data of compounds **1**, **2** and **6** (90 MHz, CDCl_3 , TMS)

H	1	2	6
1 β	2.73 m ($W_{1/2} = 20$ J ² = 13)	2.73 m ($W_{1/2} = 20$ J ² = 13)	2.68 m ($W_{1/2} = 12$ J ² = 12)
7 β	5.93 t(3)	4.72 t(3)	4.30 t(3)
12-OH	7.31 s		7.27 s
15	3.36 sextet(7)	3.36 sextet(7)	3.38 sextet(7)
16	4.29 } $dd(7,11)$ 4.21 }	4.29 } $dd(7,11)$ 4.21 }	4.30 } $dd(7,11)$ 4.19 }
17-Me	1.24 d(7)	1.23 d(7)	1.22 d(7)
18-Me	0.89 s	0.91 s	0.91 s
19-Me	0.89 s	0.98 s	0.95 s
20-Me	1.25 s	1.23 s	1.22 s
	2.01 s	2.01 s	2.01 s
OAc			
	2.03 s	2.03 s	
OMe			3.44 s

**1****2****3****4****5****6**

formed on standing removed. The MeOH soln. was evapd and the residue (73.5 g) was submitted to CC (silica gel) eluting with increasing proportions of $\text{Me}_2\text{CO}-\text{CHCl}_3$. Fractions were monitored by TLC. All fractions were purified by prep. TLC (silica gel), yielding in order of increasing polarity **4** (25 mg), **3** (20 mg), **5** (3.5 g), **1** (1.0 g), **2** (0.5 g), **6** (40 mg), β -sitosterol (100 mg) and stigmasterol (100 mg).

Compound 1. $\text{C}_{24}\text{H}_{32}\text{O}_7$, yellow needles, mp. 135° ; UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ) 225 (3.94), 274.5 (4.37), IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} 3400–3200, 1740, 1720, 1670, 1658, 1632, 1602, 1270–1220; MS m/z (70 eV) 432 $[\text{M}]^+$, 390, 372, 330, 312, 297, 43 (base peak); ^1H and ^{13}C NMR. Tables 1 and 2

Compound 2. $\text{C}_{24}\text{H}_{32}\text{O}_7$, yellow needles, mp 158° , UV, IR and MS spectra similar to those of **1**, ^1H and ^{13}C NMR. Tables 1 and 2

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