Phytochemistry, Vol. 28, No. 1, pp. 189–191, 1989.
Printed in Great Britain.

0031-9422/89 $3.00 + 0.00

ABIETANE QUINONES FROM *RABDOSIA LOPHANTHOIDES*

XU YUNLONG, WANG DAN, LI XIAOJIE and FU JIAN

Kunming Institute of Botany, Academia Sinica, Kunming, China

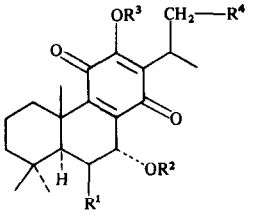
(*Received in revised form* 21 *April* 1988)

Key Word Index—*Rabdosia lophanthoides*; Labiatae; abietane quinones.

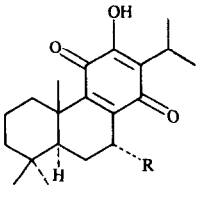
Abstract—The dried leaves of *Rabdosia lophanthoides* were found to contain six new diterpenoids having a royleanone-skeleton, lophanthoidins A–F, and the known compounds, enmein, β-sitosterol and stigmasterol. The structures of the new compounds were elucidated by spectroscopic methods.

INTRODUCTION

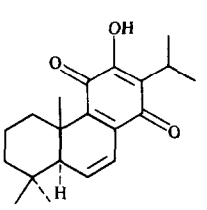
Rabdosia lophanthoides (Buch.-Ham. ex D. Don) Hara decoctions are used in Chinese traditional medicine for the treatment of enteritis, jaundice, hepatitis, laryngo-pharyngitis, lepromatous leprosy and ascariasis [1]. The dried leaves of *R. lophanthoides* var. *gerardiana* are, however, quite rich in abietane quinones and the isolation and constitutional determination of several new abietane quinones (**1**–**6**) from this source was reported previously [2]. The present communication describes the isolation of six novel abietane quinones, lophanthoidin A (**7**), B (**8**), C (**9**), D (**10**), E (**11**) and F (**12**) from the dried leaves of *R. lophanthoides*. Three known constituents, enmein, β-sitosterol and stigmasterol, were also identified.



	R^1	R^2	R^3	R^4
1	H	Ac	H	OAc
2	H	H	Ac	OAc
6	H	Me	H	OAc
7	OH	Me	H	OAc
8	OH	Ac	H	OAc
9	OH	Ac	H	OH
10	OH	Et	H	OH
11	OH	H	H	OAc
12	OH	Et	H	OAc



3 R = H
5 R = OH



4

RESULTS AND DISCUSSION

The spectral data indicated that compounds **7**–**11** had a similar constitution. Furthermore, these components are analogous to 16-acetoxy-7-*O*-acetylhorminone (**1**), 16-acetoxy-12-*O*-acetylhorminone (**2**), royleanone (**3**), 6,7-dehydroroyleanone (**4**), horminone (**5**) and 16-acetoxy-7α-methoxyroyleanone (**6**) isolated from *R. lophanthoides* var. gerardiana (2).

Lophanthoidin A (**7**), $C_{23}H_{32}O_7$ (M^+ at *m/z* 420), yellow needles, gave IR absorption bands for hydroxy groups (3500, 3250 cm^{-1}) and an ester group (1718, 1270, 1240 and 1230 cm^{-1}). Also there were characteristic peaks due to the quinonoid structure (1665, 1658, 1650, 1635 and 1605 cm^{-1}). The presence of which was further confirmed by the typical UV absorption maxima at 223 (log ε 4.20) and 273.5 nm (log ε 4.00) [3]. Compound **7** differed from **6** by an extra hydroxy absorption at 3500 cm^{-1} and an additional proton signal at δ 4.47 for a proton attached to a hydroxy-bearing carbon. Other differences noted between **7** and **6** were that the three signals for tertiary methyl groups were shifted from δ 1.22, 0.91 and 0.95 in **6** to δ 1.60, 1.25 and 1.04 in **7**. This indicated the hydroxy was located at a position sterically (6β or 2β) near to the tertiary methyls [4, 5]. The ^{13}C NMR of **7** suggested that there was no oxygen-containing substituents on ring A [6]. Thus, the unassigned hydroxy was assigned to the 6β position, and the chemical constitution of **7** was determined as 16-acetoxy-6β-hydroxy-7α-methoxyroyleanone. This constitution was supported by its ^{13}C NMR spectrum. The chemical shift values of C-19 and C-20 were shifted from δ 21.9 and 18.5 in **6** to δ 24.3 and 22.0 in **7** due to the deshielding effect of the 6β-OH (Table 1).

Lophanthoidin B (**8**), $C_{24}H_{32}O_8$ (M^+ at *m/z* 448), yellow needles, differed from 16-acetoxy-7-*O*-acetylhorminone (**1**) by the presence of an additional hydroxy absorption at 3475 cm^{-1} and an extra proton signal at δ 4.32 due to a hydroxy-bearing carbon. Other signal differences between **8** and **1** were that the three tertiary methyls were shifted from δ 1.25, 0.89 and 0.89 in **1** to δ 1.63, 1.23 and 0.95 in **8**. On the basis of the above evidence and the ^{13}C NMR data, we assigned **8** as 7α,16-diacetoxy-6β-hydroxyroyleanone, namely 6β-hydroxy-16-acetoxy-7-*O*-acetylhorminone.

Lophanthoidin C (**9**), $C_{22}H_{30}O_7$ (M^+ at *m/z* 406), yellow needles. Comparison of the ^1H NMR spectra of **9** and **8** showed the presence of only an acetoxy group and the AB parts of an $ABMX_3$ system in **9** [4, 5] instead of a simple signal for 16-H_2 as in **8**. The above information indicated that **9** was the 16-deacetylated product of **8**, the

Table 1. ^{13}CNMR of compounds **7**, **8**, **11** and **12** (22.63 MHz, TMS)

C	7	8	11	12
1	38.5 *t*	38.8 *t*	37.8 *t*	37.7 *t*
2	19.6 *t*	19.0 *t*	18.8 *t*	18.8 *t*
3	42.8 *t*	42.3 *t*	42.2 *t*	42.1 *t*
4	34.0 *s*	33.6 *s*	33.4 *s*	33.4 *s*
5	49.7 *d*	49.8 *d*	47.7 *d*	48.5 *d*
6	67.0 *d*	66.7 *d*	65.8 *d*	64.7 *d*
7	77.2 *d*	68.8 *d*	68.3 *d*	74.0 *d*
8	139.9 *s*	137.4 *s*	140.9 *s*	139.0 *s*
9	148.8 *s*	150.3 *s*	146.9 *s*	147.5 *s*
10	39.5 *s*	38.4 *s*	38.3 *s*	38.2 *s*
11	184.8 *s*	182.9 *s*	183.4 *s*	183.2 *s*
12	156.6 *s*	152.0 *s*	153.7 *s*	153.9 *s*
13	120.6 *s*	120.0 *s*	119.4 *s*	119.5 *s*
14	187.8 *s*	185.6 *s*	186.9 *s*	186.6 *s*
15	30.0 *d*	29.3 *d*	28.8 *d*	28.7 *d*
16	65.2 *t*	66.3 *t*	65.8 *t*	65.7 *t*
17	15.5 *q*	14.9 *q*	15.0 *q*	15.0 *q*
18	34.2 *q*	33.6 *q*	33.4 *q*	33.4 *q*
19	24.3 *q*	23.7 *q*	23.7 *q*	23.6 *q*
20	22.0 *q*	21.5 *q*	21.4 *q*	21.3 *q*
OAc	170.9 *s*	171.2 *s*	170.2 *s*	170.2 *s*
	20.8 *q*	169.8 *s*	20.6 *q*	20.7 *q*
		20.9 *q*		
		20.9 *q*		
OMe	58.4 *q*			
OEt				65.6 *t*
				15.7 *q*

7 in C_5D_5N; **8** in $CDCl_3$; **11** and **12** in DMSO-d_6.

stronger anisotropic property of the hydroxy group accounting for the signal differences. Thus **9** was determined as 16-deacetyl-lophanthoidin B or 7α-acetoxy-6β,16-dihydroxyroyleanone.

Lophanthoidin D (**10**), $C_{22}H_{32}O_6$ (M^+ at *m/z* 392), yellow needles. The significant differences between **10** and **9** were the absence of an ester group absorption in the IR and the disappearance of an acetoxy group signal in the ^{1}H NMR of the former. The presence of an ABX_3 system [7] in the ^{1}H NMR due to the ethoxy group of **10** caused the upfield shift of the signal for H-7β to δ 4.22. Thus, **10** was 7α-ethoxy-6β,16-dihydroxyroyleanone.

Lophanthoidin E (**11**), $C_{22}H_{30}O_7$ (M^+ at *m/z* 406), yellow needles. Comparison of the ^{1}H NMR spectra of **11** with that of **8** showed the lack of an acetoxy signal and the upfield shift of the H-7β signal from δ 5.66 in the latter to δ 4.54 in the former. Therefore, the chemical constitution of lophanthoidin E was established as 6β,7α-dihydroxy-16-acetoxyroyleanone.

Lophanthoidin F (**12**), $C_{24}H_{34}O_7$ (M^+ at *m/z* 434), yellow needles, differed from **10** by an extra acetoxy group at δ 2.02 and the downfield shift of the 16-H_2 signals from about δ 3.80 in **10** to 4.27 in **12**. Therefore, lophanthoidin F was 16-acetyllophanthoidin D, i.e. 6β-hydroxy-7α-ethoxy-16-acetoxyroyleanone.

The UV, IR and MS data of lophanthoidins A–F is given in Table 2.

EXPERIMENTAL

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

Plant material. Rabdosia lophanthoides leaves samples were collected in the Maer Mountain, Heqing, Yunnan of China in Sept. 1985 and identified by Prof. H. W. Li, botanist of our institute where a voucher specimen has been deposited.

Extraction and isolation of constituents. Dried and powdered leaves (2.0 kg) were extracted with Et_2O. The solvent was evapd and the residue (123 g) dissolved in warm EtOH (10 l) and decolourized with active charcoal. The transparent orange filtrate was concd to about 500 ml and the solid which was deposited on standing removed. The EtOH soln was evapd and the residue (58.5 g) was submitted to CC (silica gel) eluting with increasing proportions of Me_2CO–$CDCl_3$. Fractions were monitored by TLC. All compounds were further purified by recrystallization and prep. TLC (silica gel), yielding in order of increasing polarity **12** (3.1 g), **7**(250 mg), **8** (270 mg), **11** (150 mg), **9** (24 mg), **10** (32 mg), β-sitosterol (150 mg), stigmasterol (85 mg) and enmein (37 mg).

Lophanthoidin A (**7**), $C_{23}H_{32}O_7$, mp. 198–202°; UV, IR and MS: Table 2; ^{13}C NMR: Table 1. ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.32 (*br s*, 12-OH), 4.47 (*br s*, $W_{1/2}$ = 4, 6α-H), 4.32 and 4.23 (each 1 H, *dd*, 11,7.6, 16-H_2), 4.13 (*d*, 2.3, 7β-H), 3.53 (3 H, *s*, OMe), 3.40 (*sextet*, 7.6, 15-H), 2.58 (*m*, $W_{1/2}$ = 20, J^2 = 12, 1β-H), 2.01 (3 H, *s*, OAc), 1.60 (3 H, *s*, 20-Me), 1.25 (3 H, *s*, 19-Me), 1.24 (3 H, *d*, 7.6, 17-Me), 1.04 (3 H, *s*, 18-Me).

Lophanthoidin B (**8**), $C_{24}H_{32}O_8$, mp 138–139°; ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.34 (*br s*, 12-OH), 5.66 (*d*, 1.8, 7β-H), 4.32 (*br s*, $W_{1/2}$ = 3, 6α-H), 4.30 and 4.22 (ea. 1 H, *dd*, 11, 7.6, 16-H_2), 3.36 (*sextet*, 7.6, 15-H), 2.58 (*m*, $W_{1/2}$ = 20, J^2 = 11, 1β-H), 2.18 (*s*,

Table 2. UV, IR, and MS of lophanthoidin A (**7**), B (**8**), C (**9**), D (**10**), E (**11**) and F (**12**)

Compound	UV λ_{max}^{EtOH} nm (log ε)	IR ν_{max}^{KBr} cm^{-1}	MS(*m/z*)
7	223 (4.20), 273.5 (4.00)	3500, 3250, 1718, 1665, 1658, 1650, 1635, 1605, 1270, 1240.	420 [M]$^+$, 388, 374, 360, 346, 328, 313, 300, 285.
8	225 (4.30), 274 (3.91)	3475, 3325, 1726, 1673, 1660, 1633, 1610, 1320, 1265, 1235.	448 [M]$^+$, 415, 406, 388, 373, 360, 346, 328, 316, 300, 285.
9	224 (4.22), 275 (3.95)	3540, 3425, 1733, 1668, 1660, 1650, 1635, 1605, 1275, 1240.	406 [M]$^+$, 388, 373, 360, 346, 328, 300, 285.
10	222 (4.26), 274 (4.01)	3500, 1677, 1660, 1650, 1630, 1605, 1325.	392 [M]$^+$, 374, 359, 346, 328, 316, 303, 287.
11	223 (4.14), 274.5 (3.90)	3385, 1716, 1673, 1658, 1650, 1640, 1606, 1276, 1264, 1235.	406 [M]$^+$, 388, 373, 360, 346, 328, 306, 300, 285.
12	223.5 (4.18), 274 (3.97)	3490, 3290, 1722, 1675, 1658, 1650, 1640, 1605, 1255, 1230.	434 [M]$^+$, 416, 388, 374, 359, 346, 328, 313, 300, 285.

5α-H), 2.05 and 2.01 (each 3 H, *s*, 2 × OAc), 1.63 (3 H, *s*, 20-Me), 1.24 (3 H, *d*, 7.6, 17-Me), 1.23 (3 H, *s*, 19-Me), 0.95 (3 H, *s*, 18-Me).

Lophanthoidin C (**9**), $C_{22}H_{30}O_7$, mp 167–169.5°; ^{1}H NMR (90 MHz, C_5D_5N): δ 6.66 (3 H, *br* exchangeable with D_2O, 3 × OH), 5.43 (*d*, 1.4, 7β-H), 4.93 (*br s*, $W_{1/2} = 5$, 6α-H), 4.73 and 4.60 (ea. 1 H, *dd*, 11, 7, 16-H_2), 3.89 (*sextet*, 7, 15-H), 2.95 (*m*, $W_{1/2} = 20$, $J^2 = 12$, 1β-H), 2.09 (4 H, *s*, OAc and 5α-H), 1.92 (3 H, *s*, 20-Me), 1.53 (3 H, *s*, 19-Me), 1.38 (3 H, *d*, 7, 17-Me), 1.22 (3 H, *s*, 18-Me).

Lophanthoidin D (**10**), $C_{22}H_{32}O_6$, mp 205–210°; ^{1}H NMR (90 MHz, $CDCl_3$): δ 4.45 (*br s*, $W_{1/2} = 5$, 6α-H), 4.22 (*d*, 1.8, 7β-H), 3.87 and 3.74 (each 1 H, *dd*, 10.5, 7, 16-H_2), 3.84 and 3.72 (ea. 1 H, *dq*, 10.5, 7, –O–CH_2–Me), 3.31 (*sextet*, 7, 15-H), 2.59 (*m*, $W_{1/2} = 20$, $J^2 = 12$, 1β-H), 1.59 (3 H, *s*, 20-Me), 1.25 (3 H, *s*, 19-Me), 1.23 (3 H, *d*, 7, 17-Me), 1.19 (3 H, *t*, 7, –O–CH_2–CH_3), 1.02 (3 H, *s*, 18-Me).

Lophanthoidin E (**11**), $C_{22}H_{30}O_7$, mp 152.5–154°; ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.45 (*br s*, 12-OH), 4.54 (*d*, 2, 7β-H), 4.46 (*br s*, $W_{1/2} = 4$, 6α-H), 4.33 and 4.25 (ea. 1 H, *dd*, 11, 7.6, 16-H_2), 3.39 (*sextet*, 7.6, 15-H), 2.65 (*m*, $W_{1/2} = 20$, $J^2 = 12$, 1β-H), 2.18 (*s*, 5α-H), 2.03 (3 H, *s*, OAc), 1.62 (3 H, *s*, 20-Me), 1.26 (3 H, *s*, 19-Me), 1.23 (3 H, *d*, 7.6, 17-Me), 1.05 (3 H, *s*, 18-Me).

Lophanthoidin F (**12**), $C_{24}H_{34}O_7$, mp 184–185°; ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.28 (*br s*, 12-OH), 4.45 (*br s*, $W_{1/2} = 5$, 6α-H), 4.31 and 4.23 (ea. 1 H, *dd*, 11, 7, 16-H_2), 4.23 (*br s*, $W_{1/2} = 2$, 7β-H), 3.84 and 3.72 (ea. 1 H, *dq*, 10.5, 7,–O–CH_2–Me), 3.40 (*sextet*, 7, 15-H), 2.58 (*m*, $W_{1/2} = 20$, $J^2 = 12$, 1β-H), 2.02 (3 H, *s*, OAc), 1.60 (3 H, *s*, 20-Me), 1.25 (3 H, *s*, 19-Me), 1.24 (3 H, *d*, 7, 17-Me), 1.18 (3 H, *t*, 7, –O–CH_2–Me), 1.03 (3 H, *s*, 18-Me).

REFERENCES

1. Cheng-yih, W. and Hsi-wen, L. (1977) in *Flora Reipublicae Popularis Sinicae* Vol. 66, p. 479. Beijing Academic Press, Beijing.
2. Yunlong, X., Yunbao, M., Lin, Z. and Handong, S. (1988) *Phytochemistry* **27** (in press).
3. Hensch, M., Ruedi, P. and Eugster, C. H. (1975) *Helv. Chim. Acta* **58**, 1921.
4. Ruedi, P. and Eugster, C. H. (1975) *Helv. Chim Acta* **58**, 1899.
5. Schmid, J. M., Uchida, M., Ruedi, P. and Eugster, C. H. (1982) *Helv. Chim. Acta* **65**, 2164.
6. Ruedi, P. (1984) *Helv. Chim. Acta* **67**, 1116.
7. Schmid, J. M., Ruedi, P. and Eugster, C. H. (1982) *Helv. Chim. Acta* **65**, 2136.