Phytochemistry, Vol. 28, No. 12, pp. 3405–3409, 1989.
Printed in Great Britain.

0031-9422/89 $3.00 + 0.00

DITERPENOIDS FROM *RABDOSIA KUNMINGENSIS*

ZHANG HONGJIE and SUN HANDONG*

Phytochemistry Laboratory, Kunming Institute of Botany, Academia Sinica, Kunming, China

(*Received* 26 *January* 1989)

Key Word Index—*Rabdosia kunmingensis*; rabdokunmin A, B, C, D, E; *ent*-kaurene diterpenoid.

Abstract—The investigation of the dried leaves of *Rabdosia kunmingensis* afforded rabdoloxin B, 4-*epi-iso*pimaric acid, callitrisic acid and five new *ent*-kaurene diterpenoids. The structures were elucidated by spectroscopic and chemical means.

INTRODUCTION

The genus *Rabdosia* (Labiatae) is known to produce *ent*-kaurene diterpenoids [1]. This paper reports our examination of the chemical constituents of *Rabdosia kunmingensis* C. Y. Wu et H. W. Li, a perennial herb of southeastern China which has not been investigated previously for its chemical constituents. From the ethereal extract of dried leaves of *R. kunmingensis*, eight diterpenoids (**1**–**8**), including five new *ent*-kaurene diterpenoids (**1**–**5**) were isolated.

RESULTS AND DISCUSSION

The leaves gave 4-*epi-iso*pimaric acid (**7**) [2], callitrisic acid (**8**) [3], rabdoloxin B (**6**) [4], as well as five new diterpenoids, named rabdokunmin A (**1**), B (**2**), C (**3**), D (**4**), and E (**5**).

Rabdokunmin A (**1**), $C_{22}H_{32}O_6$ ($[M]^+$ at *m/z* 392), was shown to be a monoacetate from the NMR spectra (Tables 1 and 2) (δ2.10, 3H, *s*; δ_C 21.9 *q*, 171.4 *s*). The very similar mass spectrum to that of rabdoloxin B (**6**) suggested that **1** was a monoacetate of rabdoloxin B (**6**). This was confirmed by treating **1** with 5% sodium carbonate to give rabdoloxin B (**6**). The appearance of the 14α-H signal of **1** at a lower field (δ7.25, 1H, *br s*) comparing with that of rabdoloxin B (δ5.94, 1H, *br s*) revealed that the acetoxyl group took the place of the secondary hydroxyl group at C-14 of **1**. Structure **1** is therefore proposed for rabdokunmin A.

Rabdokunmin C (**3**), $C_{20}H_{30}O_5$ ($[M]^+$ at *m/z* 350), has a five-membered ketone conjugated with an *exo*-methylene group [λ_{max} 231 nm (log ε 3.81); ν_{max} 1720, 1650 cm^{-1}; δ5.42, 6.29 (each 1H, *br s*); δ_C 117.0 (*t*), 147.7 (*s*), 209.0 (s)] and two tertiary methyl group (δ_H 0.87, 1.67, each 3H, *s*; δ_C 17.0 *q*, 18.0 *q*). The ^{13}C NMR spectrum (Table 2) also showed the presence of six methylenes, six methines and three quaternary carbons. Based on these facts and the consideration of the structures of diterpenoids from the genus *Rabdosia*, together with the negative Cotton effect of dihydrorabdokunmin C (**9**) [5], we presume compound **3** has an *ent*-kaurene skeleton. Rabdokunmin C (**3**) has four hydroxy groups (ν_{max} 3340 cm^{-1}; δ6.15, 6.93, 7.41, 7.88, each 1H, *br s*, disappeared after D_2O), which could be confirmed by acetylation of **3** with pyridine–acetic anhyride giving a tetraacetate (**10**) ($C_{28}H_{38}O_9$ [M − MeCOOH]$^+$ at *m/z* 518; ν_{max} 1735, 1238 cm^{-1}; δ_H 1.79, 2.11, 2.15, 2.16, each 3H, *s*; δ_C 20.8 *q*, 21.1 *q*, 21.2 *q*, 21.3 *q*, 169.6 *s*, 169.7 *s*, 170.7 *s*, 170.9 *s*). The four hydroxy groups were presumably assigned as 18-OH, 14β-OH, 12α-OH, 7α-OH of **3**, respectively, by observing the ^{1}H and ^{13}C NMR spectral signals. The ^{1}H and ^{13}C NMR spectra of **3** showed the presence of a hydroxymethyl group (δ_H 3.37, 3.69, each 1H, AB.*d*, J = 10.0 Hz; δ_C 71.6 *t*), which was assigned to C-18 according to the following observation [6]. The location of the hydroxymethyl group at C-18 resulted in a striking γ-effect on C-3 ($\Delta\delta$ −6.2) and β-effect on C-4 ($\Delta\delta$ +5.4) compared with compound **6**. The signal for C-5 showed nearly the same shielding γ-effects ($\Delta\delta$ −6.7) (Table 2). The presence of 14β-OH (δ5.82, 1H, *br s*, 14α-H) and 7α-OH (δ4.98, *dd*, J = 3.7, 10.0 Hz, 7β-H) groups was confirmed by formation of the acetonide (**11**) owing to their co-planar relationship [7] ($C_{23}H_{34}O_5$, $[M]^+$ at *m/z* 390), ν_{max} 3430, 1728, 1641, 1109 cm^{-1}; δ_H 1.43, 1.60, each 3H, *s*, 2 × Me on dimethoxypropyl group; 4.82, 1H, *dd*, J = 3.7, 10.0 Hz, 7β-H; 5.44, 1H, *br s*, 14α-H; δ_C 25.4 *q*, 31.4 *q*, 67.4 *d*, 71.2 *d*, 97.4 *s*) which proved to be the 7α, 14β-acetonide of compound **3**. The downfield shift of the ^{13}C NMR signal for C-13 (δ55.7*d*) and the downfield shifts of 20-H (1.63, 3H, *s*) and 14α-H (5.59 1H, *br s*) indicated the presence of a 12α-OH (4.35, 1H, *m*, 12β-H), which was confirmed by observing the γ-*gauche* shielding effect between 12α-OH and 14α-H (Table 2). Compound **3** was oxidized with Beckmann's reagent to give **12**, the ^{1}H and ^{13}C NMR spectral data of which were identical with the known compound macrocalyxin C (12) [8]. Thus, structure **3** was assigned to rabdokunmin C.

Rabdokunmin B (**2**), D (**4**), and E (**5**) have similar structures to rabdokunmin C (**3**). By observing the spectra of these three compounds, we noticed that their NMR spectra were similar to those of **3**, which suggested that **2**, **4** and **5** had the same skeleton as **3**. The ^{1}H and ^{13}C NMR spectra showed the presence of 18-CH_2OH and 14β-OH in **2**, **4** and **5** (Tables 1 and 2).

Rabdokunmin B (**2**), $C_{20}H_{30}O_4$ ($[M]^+$ at *m/z* 334), λ_{max} 231 nm (log ε 3.82), was shown to contain three hydroxy groups including 18-CH_2OH and 14β-OH (δ5.13, 6.62, 7.07, each 1H, *br s*, disappeared after D_2O).

* Author to whom correspondence should be addressed.

Table 1. ^{1}H NMR spectra of compounds **1–6** (ppm from int. TMS)

	1	**2**	**3**	**4**	**5**	**6**
7β-H	4.89 *dd* (4.2, 12.0)		4.98 *dd* (3.7, 10.0)	5.02 *dd* (3.6, 11.7)	5.12 *dd* (3.3, 11.8)	4.99 *dd* (4.5, 11.8)
11α-H	4.52 *br s*			4.25 *d* (3.3)	4.45 *br s*	4.43 *br s*
12β-H	4.81 *d* (3.1)	4.46 *m*	4.35 *m*		4.73 *m*	4.73 *m*
13α-H	3.69 *m*	3.68 *m*	3.58 *m*	3.32 *m*	3.74 *m*	3.75 *m*
14α-H	7.23 *br s*	5.59 *br s*	5.82 *br s*	5.41 *br s*	.5.97 *br s*	5.94 *br s*
17-H_a	5.55 *br s*	5.38 *br s*	5.42 *br s*	5.26 *br s*	5.48 *br s*	5.52 *br s*
17-H_b	6.35 *br s*	6.28 *br s*	6.29 *br s*	6.27 *br s*	6.35 *br s*	6.39 *br s*
18-H_a		3.37 *d* (10.6)	3.32 *d* (10.6)	3.30 *d* (10.6)	3.34 *d* (10.5)	
18-H_b		3.69 *d* (10.6)	3.65 *d* (10.6)	3.65 *d* (10.6)	3.66 *d* (10.5)	
18-Me	0.85 *s*					0.83 *s*
19-Me	0.80 *s*	0.84 *s*	0.87 *s*	0.88 *s*	0.91 *s*	0.82 *s*
20-Me	1.94 *s*	1.63 *s*	1.67 *s*	1.12 *s*	1.68 *s*	1.58 *s*
OAc	2.10					
OH*	6.29, 6.43 7.62	6.10, 6.82 7.07	6.15, 6.93 7.88	5.80, 6.05 7.47, 8.12	6.04, 7.15 7.45, 7.88	6.24, 7.35 7.48, 8.06

*These signals disappeared on addition of D_2O.

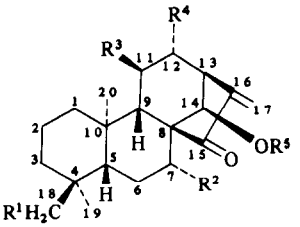
Table 2. ^{13}C NMR spectra of compounds **1–6** (ppm from int. TMS)

C	**1**	**2**	**3**	**4**	**5**	**6**
1	39.4	39.7	39.5	39.2	39.1	39.4
2	18.8	18.4	18.3	18.3	18.5	18.7
3	41.9	35.9	35.6	35.4	35.8	41.8
4	33.4	39.0	38.7	40.4	39.1	33.3
5	52.5	48.7	46.5	46.9	46.9	53.2
6	29.0	18.6	29.7	29.3	29.9	30.5
7	73.3	27.1	74.5	76.0	75.0	74.8
8	61.4	59.4	61.7	60.0	60.3	60.1
9	68.9	57.4	57.2	64.3	68.0	67.6
10	39.2	38.2	38.0	38.6	38.2	39.0
11	70.8	26.0	26.5	66.3	71.2	71.0
12	79.8	73.6	72.5	37.8	79.4	79.2
13	53.9	55.7	55.6	45.9	54.8	54.7
14	72.9	68.6	71.3	74.5	71.9	71.7
15	206.7	210.9	209.0	207.6	208.1	208.0
16	146.3	147.5	147.7	150.3	147.8	147.7
17	115.4	115.9	117.0	114.7	116.0	115.9
18	33.6	71.6	71.3	71.1	71.6	33.5
19	21.9	17.9	18.0	18.5	18.2	21.8
20	17.2	16.9	17.0	17.9	18.1	17.4
Ac_2O	171.4 21.9					

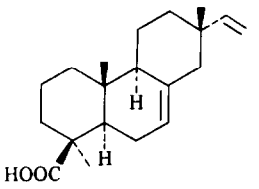
This compound was identified, as the 7-dehydroxy derivative (**2**) of rabdokunmin C (**3**) (Table 1 and 2).

Rabdokunmin D (**4**), $C_{20}H_{30}O_5$ ([M]$^+$ at *m/z* 350), λ_{max} 237 nm (log ε 3.83), was shown to have two hydroxy groups in addition to those at 18-CH_2OH and 14β-OH. The signal at δ5.02 (*dd*, *J* = 3.6, 11.7 Hz) was attributed to 7β-H compared with that of **3**. The signal at δ4.25 due to the 11α-proton appeared as a doublet (*J* = 3.3 Hz). Rabdokunmin D was therefore elucidated to have structure **4**.

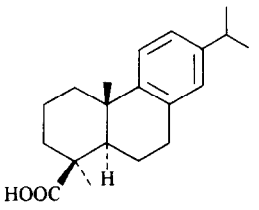
Rabdokunmin E (**5**), $C_{20}H_{30}O_6$ ([M]$^+$ at *m/z* 366), λ_{max} 237 nm (log ε3.75), was shown to have three hydroxy groups in addition to 18-CH_2OH and 14β-OH. The comparison of the ^{1}H and ^{13}C NMR spectra of **5** with those of



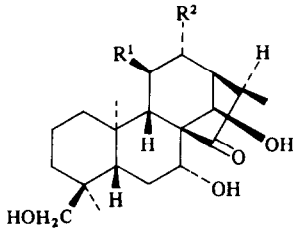
1 R^1 = H, R^2 = R^3 = R^4 = OH, R^5 = Ac
2 R^1 = R^4 = OH, R^2 = R^3 = R^5 = H
3 R^1 = R^2 = R^4 = OH, R^3 = R^5 = H
4 R^1 = R^2 = R^3 = OH, R^4 = R^5 = H
5 R^1 = R^2 = R^3 = R^4 = OH, R^5 = H
6 R^1 = R^5 = H, R^2 = R^3 = R^4 = OH
10 R^1 = R^2 = R^4 = OAc, R^3 = H, R^5 = Ac



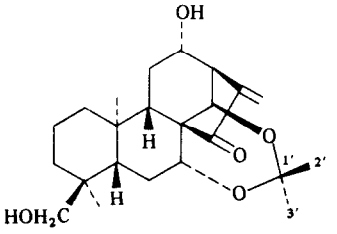
7



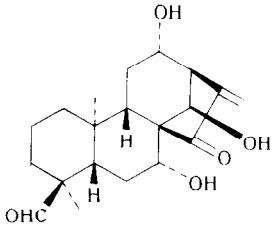
8



9 R^1 = H, R^2 = OH
13 R^1 = OH, R^2 = H



11



12

rabdoloxin B (**6**) led to the assignment of these three hydroxy groups (Table 1 and 2). Thus, structure **5** was assigned to the fifth new diterpenoid.

EXPERIMENTAL

General. Mps: uncorr. CD: MeOH. IR: KBr. UV: EtOH. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.61 MHz, broad band and DEPT): pyridine-d_5, TMS as int. standard; EIMS: 70 eV.

The dried leaves (4.5 kg) of *R. kunmingensis*, which were collected in Kunming, Yunnan, China in Nov. 1987, were extracted with Et_2O to give a green residue after evapn of the Et_2O. The residue was refluxed in MeOH with charcoal (50 g) for 1 hr then filtered (× 3) to give a yellow soln. The yellow soln was evapd to 1/3 volume of the mother liquid and filtered to give 50 g yellow powder. Evaporation of the MeOH left 100 g residue, which was chromatographed on a silica gel (1 kg) column. Elution with Me_2CO–$CHCl_3$ gave rabdokunmin A (**1**) (70 mg), B (**2**) (30 mg), C (**3**) (1.5 g), D (**4**) (500 mg), E (**5**) (80 mg), rabdoloxin B (**6**) (1.3 g) and crystals (11 g). The crystalline material was chromatographed on a RP-8 silica gel column to give 4-*epi*-*iso*pimaric acid and callitrisic acid.

Rabdokunmin A (**1**). Colourless rods (from MeOH), mp 212.0–214.0°, $[\alpha]_D^{21}$ −51.0°(Me_2CO; *c* 0.51); UV λ_{max} nm (log ε): 242 (3.77); IR ν_{max} cm^{-1}: 3410, 1722, 1706, 1645, 1260; EIMS *m/z*: 392 $[M]^+$, 350 $[M-CH_2=C=O]^+$, 332 $[350-H_2O]^+$, 314 $[350-2H_2O]^+$. (Found: C, 64.00; H, 8.33. $C_{22}H_{32}O_6 \cdot H_2O$ requires: C, 64.40; H, 8.35%).

Rabdokunmin B (**2**). Colourless needles (from MeOH), mp 259.5–261.5°, $[\alpha]_D^{21}$ −46.2° (MeOH; *c* 0.52); UV λ_{max} nm (log ε): 231 (3.83); IR ν_{max} cm^{-1}: 3340, 1701, 1641, 1078; EIMS *m/z*: 334 $[M]^+$, 316 $[M-H_2O]^+$, 298 $[M-2H_2O]^+$. (Found: C, 71.60; H, 9.01. $C_{20}H_{30}O_4$ requires: C, 71.80; H, 9.04%).

Rabdokunmin C (**3**). Colourless needles (from MeOH), mp 145.0–146.0°, $[\alpha]_D^{21}$ −85.7° (MeOH; *c* 0.54); UV λ_{max} nm (log ε): 231(3.81); IR ν_{max} cm^{-1}: 3340, 1720, 1650, 1091; EIMS *m/z*: 350 $[M]^+$, 332 $[M-H_2O]^+$, 314 $[M-2H_2O]^+$, 296 $[M-3H_2O]^+$. (Found: C, 65.30; H, 8.70. $C_{20}H_{30}O_5 \cdot H_2O$ requires: C, 65.30; H, 8.75%).

Rabdokunmin D (**4**). Colourless needles (from Me_2CO), mp 254.0–257.0°, $[\alpha]_D^{21}$ −113.3 (MeOH; *c* 0.57); UV λ_{max} nm (log ε): 237 (3.83); IR ν_{max} cm^{-1}: 3370, 3270, 1719, 1647; EIMS *m/z*: 332 $[M-H_2O]^+$, 314 $[M-2H_2O]^+$. (Found: C, 65.50; H, 8.75. $C_{20}H_{30}O_5 \cdot H_2O$ requires: C, 65.20; H, 8.75%).

Rabdokunmin E (**5**). Colourless needles (from Me_2CO), mp 286.0–288.0°, $[\alpha]_D^{21}$ −110.5° (MeOH; *c* 0.51); UV λ_{max} nm (log ε): 237 (3.75); IR ν_{max} cm^{-1}: 3320, 1715, 1645; EIMS *m/z*: 348 $[M-H_2O)]^+$, 330 $[M-2H_2O]^+$, 312 $[M-3H_2O]^+$. (Found: C, 62.20; H, 7.90. $C_{20}H_{30}O_6 \cdot H_2O$ requires: C, 62.50; H, 7.87%).

Hydrogenation of **3**. A mixture of Pd/C (8 mg), MeOH, and **3** (70 mg) was stirred under H_2 at room temp. for 4 hr. After removal of the catalyst the soln was evapd affording a residue which was crystallized from MeOH to give **9** (68 mg), mp 284.5–286.0° (decomp.); CD: $[\theta]_{306}$ −48.9; IR ν_{max} cm^{-1}: 3390, 1716, 1050, 1030; ^{1}H NMR: δ0.87 (3H, *s*, 19-Me), 1.18 (3H, *d*, *J* = 7.3 Hz, 17-Me), 1.67 (3H, *s*, 20-Me), 3.26 (1H, *d*, *J* = 7.2 Hz, 13α-H), 3.31, 3.64 (each 1H, AB *d*, *J* = 10.5 Hz, 18-H_2), 4.38 (1H, *m*, 12β-H), 4.81 (1H, *br d*, *J* = 11.2 Hz, 7β—H), 5.88 (1H, *br s*, 14α-H); ^{13}C NMR: δ9.6 (C-17), 17.0 (C-20), 17.9 (C-19), 18.2 (C-2), 26.5 (C-11), 29.6 (C-6), 35.6 (C-3), 37.9 (C-10), 38.4 (C-4), 39.2 (C-1), 43.3 (C-16), 46.7 (C-5), 50.9 (C-13), 57.0 (C-9), 60.6 (C-8), 66.6 (C-12), 71.3 (C-18), 71.5 (C-14), 75.0 (C-7), 221.7 (C-15); EIMS *m/z*: 334 $[M-H_2O]^+$, 316 $[M-2H_2O]^+$, 298 $[M-3H_2O]^+$.

Acetylation of **3**. Acetylation of **3** (50 mg) with 10 ml Ac_2O–pyridine (1:1) at room temp. overnight gave **10** (55 mg) after work-up in the usual manner. Mp 121.0–122.5°, IR ν_{max} cm^{-1}: 1735, 1367, 1235, 1030; ^{1}H NMR: δ0.82 (3H, *s*, 19-Me), 1.52 (3H, *s*, 20-Me), 1.86, 2.11, 2.15, 2.16 (each 3H, *s*, 4 × COMe), 3.48 (1H, *d*, *J* = 3.5 Hz, 13α-H), 3.65, 4.02 (each 1H, AB *d*, *J* = 11.1 Hz, 18-H_2), 5.22 (1H, *t*, *J* = 3.9, 12.0 Hz, 7β-H), 6.54 (1H, *br s*, 14α-H); ^{13}C NMR: δ16.3 (C-20), 17.7 (C-19), 17.9 (C-2), 20.8, 21.1, 21.2, 21.3 (4 × COMe), 23.0 (C-11), 24.6 (C-6), 35.8 (C-3), 36.5 (C-4), 38.6 (C-1), 39.2 (C-10), 47.3 (C-5), 49.0 (C-13), 56.5 (C-9), 61.2 (C-8), 71.5 (C-14), 72.4 (C-18), 74.7 (C-7), 74.7 (C-12), 120.1 (C-17), 143.2 (C-16), 169.6, 169.9, 170.7, 170.9 (4 × COMe), 204.1 (C-15); EIMS *m/z*: 458 $[M-MeCOOH]^+$, 430 $[458-CO]^+$, 416 $[458-H_2C=C=O]^+$, 398 $[458-MeCOOH]^+$, 356 $[416-MeCOOH]^+$, 328 $[356-CO]^+$.

7α,14β-Acetonide of **3**. Compound **3** (50 mg) was refluxed in Me_2CO in the presence of dry $CuSO_4$ for 24 hr. The reaction product was treated in the usual manner to yield **11** (49 mg), mp 127.0–128.0°, IR ν_{max} cm^{-1}: 3430, 1730, 1640, 1109; ^{1}H NMR: δ0.91 (3H, *s*, 19-Me), 1.40, 1.60 (each 3H, *s*, 2 × Me on dimethoxypropyl group), 1.66 (3H, *s*, 20-Me), 3.35, 3.68 (each 1H, AB *d*, *J* = 10.6 Hz, 18-H_2), 3.52 (1H, *d*, *J* = 3.3 Hz, 13α-H), 4.41 (1H, *m*, 12β-H), 4.82 (1H, *dd*, *J* = 3.7, 12.0 Hz, 7β-H), 5.38, 6.29 (each 1H, *br s*, 17-H_2), 5.44 (1H, *br s*, 14α-H), 6.30, 7.15 (each 1H, *br s*, disappeared after D_2O, 2 × OH); ^{13}C NMR: δ16.8 (C-20), 17.9 (C-19), 18.2 (C-2), 25.4 (C-2'), 31.4 (C-3'). 26.6 (C-11), 27.9 (C-6), 35.8 (C-3), 38.0 (C-4), 38.0 (C-10), 39.4 (C-1), 45.1 (C-5), 52.1 (C-13), 54.6 (C-9), 55.0 (C-8), 67.4 (C-14), 71.2 (C-18), 71.2 (C-12), 71.8 (C-7), 97.2 (C-1'), 116.7 (C-17), 146.5 (C-16), 207.2 (C-15); EIMS *m/z*: 375 $[M-Me]^+$.

Oxidation of **3**. To a soln of **3** (30 mg) in Me_2CO (5 ml), Beckmann's reagent (10 drops) was added at 0°, and the mixture was stirred for 5 min then MeOH (1 ml) was added. After neutralization with aq. Na_2CO_3, the solvent was distilled off. The mixture after extraction with Me_2CO was chromatographed over silica gel. The prep. TLC yielded a white powder (15 mg) which proved to be **12**, IR ν_{max} cm^{-1}: 3450, 3300, 2790, 1726, 1705, 1640, 1225, 940; ^{1}H NMR: δ1.12 (3H, *s*, 19-Me), 1.61 (3H, *s*, 20-Me), 3.63 (1H, *d*, *J* = 3.2 Hz, 13α-H), 4.38 (1H, *t*, *J* = 3.8 Hz, 12β-H), 5.01 (1H, *dd*, *J* = 3.6, 12.0 Hz, 7β-H), 5.41, 6.32 (each 1H, *br s*, 17-H_2), 5.79 (1H, *br s*, 14α-H), 6.12, 7.20, 7.95 (each 1H, disappeared after D_2O, *br s*, 3 × OH), 9.29 (1H, *s*, 18-CHO); ^{13}C NMR: δ14.2 (C-19), 16.6 (C-20), 17.1 (C-2), 26.3 (C-11), 32.3 (C-6), 32.2 (C-3), 37.6 (C-10), 38.6 (C-1), 45.3 (C-5), 49.7 (C-4), 55.6 (C-13), 56.6 (C-9), 61. (C-8), 71.1 (C-14), 72.2 (C-12), 73.7 (C-7), 117.2 (C-17), 147.5 (C-16), 205.9 (C-18), 208.4 (C-15); EIMS *m/z*: 348 $[M]^+$, 330 $[M-H_2O]^+$, 319 $[M-CHO]^+$, 315 $[M-H_2O-Me]^+$, 304 $[M-CHO-Me]^+$.

Saponification of **1**. To a soln of **1** (10 mg) in Me_2CO, 5% NaOH aq. soln (10 drops) was added, and the mixture was refluxed for 1 hr. Treatment of the reaction product as usual gave a white powder, which proved to be rabdoloxin B (**6**) by TLC.

Hydrogenation of **4**. Compound **4** (70 mg) was hydrogenated in MeOH with Pd/C (10 mg) at room temp for 5 hr, and then the reaction product was treated in the usual manner to afford **13** (70 mg), mp 253.0–255.0°; CD: $[\theta]_{305}$ −50.0; IR ν_{max} cm^{-1}: 3395, 3280, 1722, 1028; ^{1}H NMR: δ0.85 (3H, *s*, 19-Me), 1.10 (3H, *s*, 20-Me), 1.67 (3H, *d*, *J* = 7.1 Hz, 17-Me), 3.29, 3.64 (each 1H, AB *d*, *J* = 10.3 Hz, 18-H_2), 3.42 (1H, *t*, *J* = 7.0 Hz, 13α-H), 4.14 (1H, *d*, *J* = 5.3 Hz, 11α-H), 4.91 (1H, *dd*, J = 3.7, 11.2 Hz, 7β-H), 5.32 (1H, *brs*, 14α-H), 5.95, 6.22, 7.44, 8.00 (each 1H, *br s*, disappeared after D_2O, 4 × OH); ^{13}C NMR: δ11.2 (C-17), 18.1 (C-20), 18.4 (C-2), 18.6 (C-19), 29.5 (C-6), 34.5 (C-12), 35.6 (C-3), 38.0 (C-10), 38.4 (C-4), 39.2 (C-1), 43.2 (C-16), 44.8 (C-13), 47.1 (C-5), 59.4 (C-8), 63.6 (C-9), 65.5 (C-11), 71.2 (C-18), 75.2 (C-14), 76.0 (C-7), 218.9 (C-15); EIMS *m/z*: 334 $[M-H_2O]^+$, 316 $[M-2H_2O]^+$, 298 $[M-3H_2O]^+$.

Rabdoloxin B (**6**). $C_{20}H_{30}O_5$, colourless needles, mp 256.0–258.0°, $[\alpha]_D^{21}$ −92.5° (Me_2CO; *c* 0.51); UV λ_{max} nm (log ε): 231 (3.82); IR ν_{max} cm^{-1}: 3380, 1720, 1642.

*4-epi-iso*Pimaric acid (**7**). Colourless needles, mp 145.5–146.0°, $[\alpha]_D^{21}$ 0° (Me_2CO; *c* 0.50); UV λ_{max} nm (log ε): 265.5 (3.63); IR ν_{max} cm^{-1}: 3300–2500, 1690, 1632, 1268, 1259; ^{1}H NMR ($CDCl_3$): δ0.79 (3H, *s*, 17-Me), 0.86 (3H, *s*, 18-Me), 1.25 (3H, *s*. 20-Me), 4.87 (1H, *dd*, *J* = 1.0, 17.5 Hz, 16-H_a), 4.93 (1H, *dd*, *J* = 1.0, 17.5 Hz, 16-H_b), 5.38 (1H, *d*, *J* = 4.1 Hz, 14-H), 5.81 (1H, *dd*, *J* = 10.6, 17.5 Hz, 15-H); ^{13}C NMR ($CDCl_3$): δ14.3 (C-20), 19.6 (C-2), 21.0 (C-11), 21.6 (C-17), 24.4 (C-6), 29.2 (C-18), 36.0 (C-10), 36.5 (C-12), 36.9 (C-13), 38.1 (C-3), 39.9 (C-1), 43.9 (C-4), 46.3 (C-14), 51.4 (C-5), 51.8 (C-9), 109.2 (C-16), 121.5 (C-7), 134.8 (C-8), 150.4 (C-15), 183.9 (C-19); EIMS *m/z*: 302 $[M]^+$, 285 $[M-OH]^+$, 273 $[M-CHO]^+$, 256 $[M-CH_2=C=O]^+$, 242 $[M-MeCOOH]^+$.

Callitrisic acid. $C_{20}H_{28}O_2$, colourless crystals, mp 97.0–100°, $[\alpha]_D^{21}$ +127.6° (MeOH; *c* 0.52); UV λ_{max} nm (log ε): 216 (4.00); IR ν_{max} cm^{-1}: 3500–2500, 1690, 1495, 1265, 820; ^{1}H NMR ($CDCl_3$): δ1.20 (6H, *d*, *J* = 6.9 Hz, 16,17-Me), 1.40 (6H, *s*, 18, 20-Me), 7.00 (1H, *br s*, 14-H), 7.10, 7.33 (each 1H, AB *d*, *J* = 8.2 Hz, 11, 12-H_2); ^{13}C NMR ($CDCl_3$): δ21.1 (C-2), 22.0 (C-6), 24.2 (C-16), 24.2 (C-17), 29.8 (C-18), 32.7 (C-7), 33.8 (C-15), 38.8 (C-10), 39.0 (C-3), 40.4 (C-1), 44.6 (C-4), 53.4 (C-5), 123.5 (C-8), 124.2 (C-12), 125.9 (C-11), 127.2 (C-14), 145.6 (C-18), 147.1 (C-9), 181.0 (C-18); EIMS *m/z*: 300 $[M]^+$, 285 $[M-Me]^+$, 267 $[285-H_2O]^+$, 257 $[285-CO]^+$, 249 $[285-2H_2O]^+$, 240 $[M-MeCOOH]^+$.

Acknowledgements—We thank the members of analytical group in the Phytochemistry Laboratory of this institute for their measuring the spectral data. We also wish to thank Professor Li Xiwen for identification of plant material.

REFERENCES

1. Fujita, E. and Node, M. (1984) *Progr. Chem. Org. Nat. Prod.* **46**, 138.
2. Kitajima, J., Komori, T. and Kawasaki, T. (1982) *Chem. Pharm. Bull.* **30**, 3912.

3. Welch, S. C., Hagan, C. P., Kim, J. H. and Chu, D. S. (1977) *J. Org. Chem.* **42**, 2879.
4. Sun Handong, Lin Zhongwen, Takada, Y. and Fujita, T. (1985) International Symposium on Organic Chemistry of Medicinal Natural Products, Abstracts B-172. Shanghai, China
5. MacMillan, J. and Walker, E. R. H. (1972) *J. Chem. Soc. Perkin I*, 986.
6. Gonzalez, Antonio G., Fraga, Braulio M., Hernandez, Melcheor C. and Hanson, J. R. (1981) *Phytochemistry*. **20**, 846.
7. Hirotsu, K., Kamikawa, T., Kubota, T. and Shimada, A. (1973) *Chem. Letters (Japan)* 255.
8. Wang Xianyong, Wan Zhaoquan, Dong Jinguang and Xue Zhaowen. (1984) *Acta Bot. Sinica* **26**, 425.