(each 3H, *s*, 2 × Me on dimethoxypropyl group), 2.03 (3H, *s*, OAc), 3.29 (1H, *m*, 13α-H), 4.43, 5.03 (each 1H, AB *d*, $J = 12$ Hz, 20-H_2), 4.63 (1H, *br s*, 11α-H), 4.79 (1H, *br s*, 14α-H), 4.80 (1H, *br d*, $J = 10$ Hz, 7β-H), 5.43, 6.30 (each 1H, *br s*, 17-H_2), 5.89 (1H, *br s*, disappeared after D_2O, 11β-OH); ^{13}C NMR: δ18.4 (*t*, C-2), 20.9 (*q*, MeCO), 22.3 (*q*, C-19), 25.6 (*q*, C-2'), 27.8 (*t*, C-6), 31.2 (*q*, C-3'), 33.0 (*s*, C-4), 33.4 (*q*, C-18), 34.1 (*t*, C-1), 38.7 (*t*, C-12), 41.0 (*s*, C-10), 41.4 (*t*, C-3), 43.1 (*d*, C-13), 52.3 (*d*, C-5), 53.1 (*s*, C-8), 63.5 (*t*, C-20), 64.3 (*d*, C-9), 64.5 (*d*, C-11), 71.4 (*d*, C-7), 72.4 (*d*, C-14), 97.3 (*s*, C-1'), 113.7 (*t*, C-17), 149.4 (*s*, C-16), 170.7 (*s*, MeCO), 205.2 (*s*, C-15); EIMS *m/z*: 432 $[M]^+$, 417 $[M-Me]^+$.

Henryin A (**5**). $C_{22}H_{32}O_6$, mp 202–205°, $[\alpha]_D^{21}$ −70.64° (*c* 0.54, Me_2CO); UV λ_{max} nm (log ε): 232 (3.93); IR ν_{max} cm^{-1}: 3503, 3452, 3375, 1712, 1635, 1245; ^{1}H NMR: δ0.87, 0.95 (each 3H, *s*, 2 × Me), 2.15 (3H, *s*, OAc), 3.30 (1H, *m*, 13α-H), 3.55 (1H, *m*, which became *dd* on addition of D_2O, $J = 5$, 10 Hz, 1β-H), 4.81 (1H, *dd*, $J = 6$, 12 Hz, 7β-H), 4.99, 5.06 (each 1H, AB *d*, $J = 10$ Hz, 20-H_2), 5.39 (1H, *br s* 14α-H), 5.39, 6.34 (each 1H, *br s*, 17-H_2), 6.36 (1H, *d*, $J = 4$ Hz, 1α-OH), 7.46 (1H, *br s*, 14β-OH), 8.12 (1H, *d*, $J = 5$ Hz, 7α-OH); EIMS *m/z*: 392 $[M-H_2O]^+$, 374 $[M-H_2O]^+$, 356 $[M-2H_2O]^+$.

Rabdoloxin B (**6**). $C_{20}H_{30}O_5$, mp 257–259°, $[\alpha]_D^{21}$ −92.52° (Me_2CO; *c* 0.51); UV λ_{max} nm (log ε): 231 (3.82); IR ν_{max} cm^{-1}: 3390, 3310, 1711, 1645; ^{1}H NMR: δ0.83 (6H, *s*, 2 × Me), 1.62 (3H, *s*, 20-Me), 3.79 (1H, *m*, 13α-H), 4.45 (1H, *br s*, 11α-H), 4.75 (1H, *m*, which became *d* on addition of D_2O, $J = 4$ Hz, 12β-H), 5.06 (1H, *dd*, $J = 6$, 12 Hz, 7β-H), 5.52, 6.41 (each 1H, *br s*, 17-H_2), 6.00 (1H, *br s*, 14α-H), 6.26, 7.21, 7.47, 8.10 (each 1H, *br s*, 4 × OH); EIMS *m/z*: 332 $[M-H_2O]^+$, 314 $[M-H_2O]^+$.

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4-*EPI*-HENRYINE A, A DITERPENE FROM *RABDOSIA HENRYI*

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Key Word Index—*Rabdosia henryi*; Labiatae, 4-*epi*-henryine A; diterpene.

Abstract—The structure of a novel diterpene, 4-*epi*-henryine A, isolated from *Rabdosia henryi* has been established through interpretation of its spectroscopic data.

INTRODUCTION

Plants of the genus *Rabdosia* (Labiatae) have been used medicinally for gastrointestinal disorders in Japan, and in China as antitumour and antiphlogistic agents [1]. Several reviews of the chemistry and biological activity of the *Rabdosia* diterpenoids have appeared [1–3]. In this paper we report on the isolation and structure elucidation of a new diterpene from *Rabdosia henryi* (Hemsl) Hara (Labiatae), collected in October 1986 from Yun-xi County, Wu-bei Province, People's Republic of China.

RESULTS AND DISCUSSION

4-*epi*-Henryine (**1**) was obtained as needles, mp 246–248°, $[\alpha]_D$ +30.4° (pyridine; *c* 0.434), from the whole plant and its UV spectrum [λ_{max}^{MeOH} nm (log ε) 229 (3.90)] and IR spectrum (ν_{max}^{KBr} cm^{-1} 1731, 1706 and 1645) indicated the presence of saturated and α,β-unsaturated ketonic groups. The mass spectrum of 4-*epi*-henryine (**1**) displayed a molecular ion at *m/z* 348 and two major fragment ions at *m/z* 194 and 123. Accurate mass measurements of these ions established the molecular formulae of $C_{20}H_{28}O_5$, $C_{10}H_{10}O_4$ and C_9H_{15}, respectively, suggesting that they might be derived through *retro*-Diels–Alder fragmentation of ring B, followed in the latter case by loss of a hydroxyl radical.

The ^{13}C NMR spectrum (Table 1) substantiated these implications showing resonances at δ 206.24 and 208.43 for the carbonyl groups and 149.46 and 121.24 for an exomethylene group. Two olefinic protons were observed

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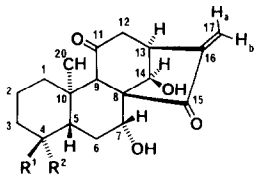
Table 1. ^1H and ^{13}C NMR spectral assignments of 4-*epi*-henryine A (**1**)

C	^1H	C	^{13}C
1α	1.48 (*m*)	1	40.68
1β	1.85 (*m*)	2	19.34
2α	1.63 (*m*)	3	36.32
2β	1.34 (*m*)	4	39.25
3α	1.19 (*m*)	5	47.43
3β	1.74 (*m*)	6	30.43
4		7	75.67
5	1.89 (*dd*, 4.5, 12.3)	8	61.92
6α	2.12 (*dd*, 12.2, 12.7)	9	69.99
6β	2.50 (*dd*, 4.5, 12.7)	10	41.10
7	4.94 (*ddd*, 3, 3, 12)	11	208.43
8	—	12	51.33
9	2.16 (*s*)	13	46.55
10		14	74.01
11		15	206.24
12α	3.01 (*dd*, 3.3, 18)	16	149.46
12β	2.73 (*dd*, 3.4, 18)	17	121.24
13	3.45 (*ddd*, 1, 1, 1)	18	72.15
14	5.69 (*d*, 1)	19	20.69
15	—	20	19.24
16			
17a	5.51 (*d*, 1)		
17b	6.32 (*d*, 1)		
18a	3.29 (*d*, 10.8)		
18b	3.66 (*d*, 10.8)		
19	0.88 (*s*)		
20	1.23 (*s*)		
7-OH	8.62 (*br* s)		
14-OH	6.29 (*br* s)		

Data were recorded using pyridine-d_5 as solvent. Chemical shift values are reported as δ values (ppm) from internal TMS. Signal multiplicity and coupling constants (Hz) are shown in parentheses. ^1H NMR data were obtained at 300 MHz, ^{13}C NMR data were recorded at 90.8 MHz.

at δ 5.52 and 6.32 in the ^1H NMR spectrum (Table 1) and the homonuclear COSY spectrum (Fig. 1) indicated that they were geminally coupled and long-range coupled to a methine proton at δ 3.45. This signal was weakly coupled ($J = 1.0$ Hz) to the signal at δ 5.69 and two doublets of doublets at 3.01 and 2.73 with J values of about 3 Hz corresponding to their ae and ee character. On the basis of the coupling pattern and the corresponding chemical shifts, the signal at δ 5.69 could be assigned as 14-H, the *ddd* at δ 3.45 to 13-H and the *dd* pair at 3.01 and 2.73 could be 12-H_a and 12-H_e, respectively, in an *ent*-kaur-16 (17)-en-11,15-dione system. From the molecular formula ($C_{20}H_{28}O_5$) three other oxygen functionalities had to be placed in the system, and from the pronton spectrum, two of these appeared to be secondary hydroxy groups at δ5.69 and 4.94, while the third was an isolated hydroxymethylene group at δ3.66 and 3.29, which could be at C-18, C-19 or C-20. Corresponding resonances were observed in the ^{13}C NMR spectrum at δ74.0, 75.7 and 72.1. The *ddd* at δ4.94 showed couplings with the *dd* at δ2.12 ($J = 12$ Hz) and 2.50 ($J = 4.5$ Hz) and should therefore be 7-H rather than 6-H. The magnitude of the coupling constants suggested an axial orientation for this



	R^1	R^2
1	CH_2OH	Me
2	Me	CH_2OH

proton. The *dd* signals at δ2.12 and 2.50 could be assigned as 6-H_a and 6-H_e, respectively, and each of them was coupled to a *dd* at 1.89 which could be assigned as 5-H_a. A singlet at δ2.16 could be attributed to 9-H, which, together with the chemical shifts and multiplicities of the protons at C-12 allowed a carbonyl group to be placed at C-11. Six methylene protons were observed in the region δ1.0–1.6 and were assigned on the basis of the ^1H–^1H COSY spectrum (Fig. 1). Two methyl groups were observed at δ0.88 and 1.23 and their assignment was established based on NOE experiments. When the signal at δ 1.23 was irradiated, substantial enhancement of the signals at 5.69 (14-H) and 2.12 (6-H_a), and weaker enhancement of the signals at 3.01 (12-H_a) and 0.88, was observed. The latter signal must therefore be C-19, and the irradiated signal could be attributed to C-20. On this basis, the hydroxy-methylene group should be C-18. Irradiation of the 18-H_2 resonance at δ3.66 did not enhance the methyl group attached to C-10. All of the other features of the ^1H NMR spectrum indicated a very close similarity to henryine A (**2**) [4], which has a primary hydroxy group at C-19.

The ^{13}C NMR spectrum of 4-*epi*-henryine (**1**) was assigned on the basis of an APT experiment and the spectral data reported previously for henryine A (**2**) [4]. Carbonyl carbon absorptions were observed at δ208.43 and 206.24 which could be attributed to C-11 and C-15, respectively, and the quaternary olefinic carbon (C-16) was observed at 149.46 with the geminal carbon at 121.24. The most downfield aliphatic quaternary carbon (C-8) was observed at δ61.92, with the two remaining quaternary aliphatic carbons being observed at δ39.25 and 41.10 for C-4 and C-10, respectively. Four other downfield alphatic carbons were observed at δ69.99, 72.15, 74.01 and 75.67. One of these, at δ72.15, was the methylene carbon (C-18) from the APT spectrum, and the others were assigned as C-9, C-14 and C-7 methine carbons, respectively. Five methylene carbons were observed and their assignment was achieved through comparison with the corresponding data for henryine A (**2**) [4]. Finally, the methyl groups at δ19.24 and 20.69 were established for C-20 and C-19, respectively. The isolate therefore has the structure **1** and is the 4-*epi* isomer of henryine A (**2**).

EXPERIMENTAL

Mp: uncorr. ^1H NMR spectra were determined using TMS as int. standard. The homonuclear COSY spectrum was obtained on a Varian XL-300 spectrometer with standard Varian pulse program. ^{13}C NMR spectra were measured at 90.8 MHz.

Plant material. Rabdosia henryi (Hemsl.) Hara was collected in October 1986 from Yun-xi County, Wu-bei Province, People's Republic of China and identified by Dr Chong-yun Wang. A

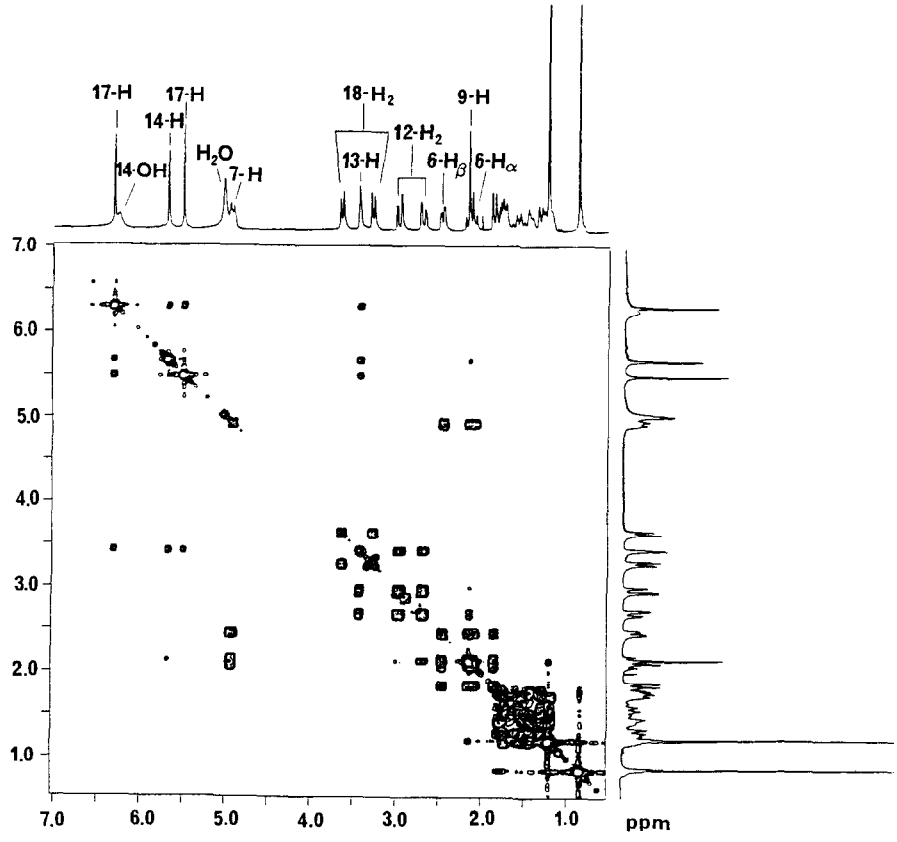


Fig. 1. ^1H–^1H COSY spectrum of 4-*epi*-henryine A (**1**).

herbarium specimen of the plant was deposited in the Wu-bei Institute of Traditional Medical Sciences.

Isolation of compound **1**. The ground whole plant material (1 kg) was refluxed with 95% EtOH and the EtOH extract after concn was trituated with EtOAc. The EtOAc layer was shaken with 5% Na_2CO_3 to remove organic acids, dried, evapd. and the residue chromatographed over silica gel. From the CH_2Cl_2–Me_2CO (10:1) eluate, 4-*epi*-henryine A (**1**) was obtained (100 mg, 0.01%), mp 246–248°; $[\alpha]_D$ +30.4° (pyridine; *c* 0.434); UV λ_{max}^{MeOH} nm (log ε): 228.5 (3.90); IR ν_{max}^{KBr} cm^{-1}: 1731, 1706 and 1645; ^1H NMR: see Table 1; ^{13}C NMR: see Table 1; MS *m/z* (rel. int.): 348 $[M]^+$ (11), 330 (5), 299 (13), 194 (35), 180 (11), 151 (18), 137 (29), 123 (100), 109 (46) and 95 (23); (calc. for $C_{20}H_{28}O_5$ 348.1937, obs. 348.1938; calc. for $C_{10}H_{10}O_4$ 194.0579, obs. 194.0579; calc. for C_9H_{15} 123.1173, obs. 123.1173).

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