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STRUCTURAL REVISION OF RABDOSIN B FROM *RABDOSIA JAPONICA*

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Key Word Index—*Rabdosia japonica*; Labiatae; diterpenoids; rabdosin B; structural revision.

Abstract—The structural revision of rabdosin B has been made by chemical correlation with rabdophyllin G. The structure of isodonal from *Isodon japonicus* may also be incorrect.

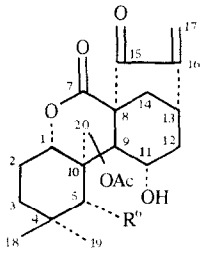
INTRODUCTION

Rabdosia japonica (Burm. f) Hara, a plant of the Labiatae family, has long been used as a home remedy for gastroenteric troubles in Henan, China. For this reason we have carried out a chemical investigation on this plant.

In a previous paper, we reported the structures of two new *ent*-kaurenoids, rabdosin A and B, isolated from the leaves of *Rabdosia japonica*. The structure of randosin B (**1**) was determined by spectroscopic analysis and chemical conversion into isodonal (**2**) [1]. Further investigation shows that the structure of **1** is incorrect and it does not belong to B-*seco*-*ent*-kaurene type of compound, but to the spiro-*seco*-kaurene type. We now wish to report the structural revision of compound **1**.

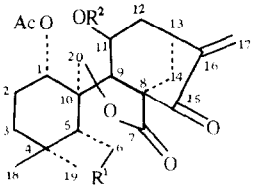
RESULTS AND DISCUSSION

Mild acidic hydrolysis of **1** afforded **3**, identical by mp, ^{1}H and ^{13}C NMR comparison with rabdophyllin G (**4**), which was isolated from plants of the same family. The structure of **4** was solved by X-ray crystallography [2]. Compounds **1** and **4** were acetylated with acetic anhydride–pyridine at room temperature to give the same triacetate (**5**). Reduction of **4** with sodium borohy-



1 R = CH_2OAc

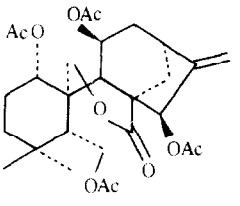
2 R = CHO



4 R^1 = OH, R^2 = H

5 R^1 = OAc, R^2 = Ac

7 R^1 = OAc, R^2 = H



6

dride followed by acetylation gave a rabdosinate (**6**) [3]. The structure of **6** was also demonstrated by means of X-ray analysis [Dr X. J. Meng, personal communication]. Based on the above facts, the molecular structure of compound **1** must be revised as formula **7**. It is thus clear that the structure of isodonal isolated from *Isodon* (Rabdosia) *japonicus* [4] is also questionable.

The assignment of ^{13}C NMR signals of **5** and **7** are given in the Experimental.

EXPERIMENTAL

Mps: uncorr. ^{1}H and ^{13}C NMR spectra were determined at 400 and 60 MHz, respectively, in $CDCl_3$ soln with TMS as int. standard. IR spectra were obtained for KBr discs. Mass spectra were taken by use of a direct inlet system.

Rabdosin B (**7**). Prisms, mp 182–184°; $[\alpha]_D^{13}$ + 130.6° (pyridine; *c* 2.2); EIMS (probe) 70 eV, *m/z* (rel. int.): 448.2118 (51) ($C_{24}H_{32}O_8$), 406.1997 (64) ($C_{22}H_{30}O_7$), 388.1990 (54) ($C_{22}H_{28}O_6$), 346.1796 (83) ($C_{20}H_{26}O_5$), 328.1283 (68) ($C_{20}H_{24}O_4$); UV λ_{max}^{MeOH} nm (log ε): 230 (3.89); IR ν_{max}^{KBr} cm^{-1}: 3450, 1740, 1720, 1640; ^{1}H NMR (400 MHz): δ 1.01 and 1.03 (3H each, *s*, H_3-18 and H_3-19), 2.03 and 2.04 (3H each, *s*, 2 × OAc), 3.11 (1H, *dd*, *J* = 9.5, 4.5 Hz, H-13), 3.92 (1H, *m*, $W_{1/2}$ = 28 Hz, H-11α), 4.11 (1H, *dd*, $J_{6A,6B}$ = 12.7 Hz, $J_{6A,5\beta}$ = 5.6 Hz, H-6A), 4.26 (1H, *d*, *J* = 12 Hz, H-20A), 4.35 (1H, *dd*, $J_{6A,6B}$ = 12.7 Hz, $J_{6B,5\beta}$ = 3.8 Hz, H-6B), 4.87 (1H, *d*, *J* = 12 Hz, H-20B), 5.13 (1H, *dd*, $J_{1a,2a}$ = 9.6 Hz, $J_{1a,2e}$ = 5.5 Hz, H-1β), 5.62, 6.12 (1H each, *s*, H-17A and H-17B); ^{13}C NMR (15.08 MHz): δ 76.22 (*d*, C-1), 23.97 (*t*, C-2), 39.53 (*t*, C-3), 34.08 (*s*, C-4), 48.61 (*d*, C-5), 62.30 (*t*, C-6), 169.70 (*s*, C-7), 57.59 (*s*, C-8), 45.26 (*d*, C-9), 44.36 (*s*, C-10), 65.94 (*d*, C-11), 41.52 (*t*, C-12), 33.91 (*d*, C-13), 29.13 (*t*, C-14), 199.00 (*s*, C-15), 149.13 (*s*, C-16), 119.66 (*t*, C-17), 23.97 (*q*, C-18), 33.91 (*q*, C-19), 66.50 (*t*, C-20), 170.66 (*s*), 168.95 (*s*), 21.35 (*q*) and 21.13 (*q*, 2 × OAc).

Acetylation of rabdosin B (**1**) and rabdophyllin G (**4**). Compounds **1** and **4** (20 mg each) were treated with Ac_2O–pyridine at room temp. for 12 hr. The products were crystallized from EtOH to afford the same triacetate (**5**). Mp 164–165.5°; UV λ_{max}^{MeOH} nm (log ε): 231 (3.85); IR ν_{max}^{KBr} cm^{-1}: 1746, 1725, 1645, 1235, 1055; EIMS, *m/z*: 448 [M − CH_2=C=O]$^+$, 406 [M − 2 × CH_2=C=O]$^+$, 388 [M−HOAc−CH_2=C=O]$^+$, 346 [M−HOAc−2 × CH_2=C=O]$^+$, 328 [M − 2 × HOAc − CH_2=C=O]$^+$. ^{1}H NMR (60 MHz): δ 1.02, 1.08 (3H each, *s*, H_3-18 and H_3-19), 2.02, 2.09 (9H, *s*, 3 × OAc), 4.0–5.20 (6H, *m*), 5.60, 6.15 (1H each, *s*, H-17A and H-17B); ^{13}C NMR (15.08 MHz): δ 76.27 (*d*, C-1), 23.74 (*t*, C-2), 39.88 (*t*, C-3), 34.08 (*s*, C-4), 48.84 (*d*, C-5), 61.28 (*t*, C-6), 169.41 (*s*, C-7), 57.19 (*s*, C-8), 43.16 (*d*, C-9), 43.84 (*s*, C-10), 67.98 (*d*, C-11), 37.03 (*t*, C-12), 34.07 (*d*, C-13), 29.53 (*t*, C-14), 198.66 (*s*, C-15), 148.63 (*s*, C-16), 119.94 (*t*, C-17), 23.74 (*q*, C-18), 33.51 (*q*, C-19), 66.56 (*t*, C-20), 168.04 (*s*), 168.56 (*s*), 168.89 (*s*), 21.96 (*q*), and 21.18 (*q*, 3 × OAc).

Hydrolysis of rabdosin B (**1**). Compound **1** (10 mg) was heated in refluxing dry EtOH (2 ml) containing 1 M HCl (2 ml) for 4.5 hr. The product was crystallized from MeOH to give prisms (**3**), mp 266 268°, identical with an authentic sample of **4** by mp, TLC, IR and ^{1}H NMR.

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