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DITERPENOID CONSTITUENTS FROM *RABDOSIA WEISIENSIS*

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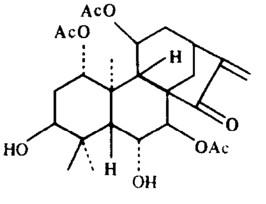
Key Word Index—*Rabdosia weisiensis*; Labiatae; trichorabdal A; *ent*-1β,7α,11α-triacetoxy-3α,6β-dihydroxy-kaur-16-en-15-one.

Abstract—A new diterpenoid was isolated from the ethereal extract of the dried leaves of *Rabdosia weisiensis* and its chemical structure shown to be *ent*-1β,7α,11α-triacetoxy-3α,6β-dihydroxykaur-16-en-15-one on the basis of detailed spectroscopic analysis and comparison with related compounds. Trichorabdal A, a known component, was also isolated from this plant and its ^{13}C NMR data assigned.

Rabdosia weisiensis C. Y. Wu is distributed over the northwestern district of Yunnan, China [1]. An ethereal extract of its dried leaves was fractionated by column chromatography (CC) on silica gel. Components were further purified by numerous silica gel CC and/or silica gel preparative TLC and crystallization.

Weisiensin A(**1**), $C_{26}H_{36}O_9$, mp 298–300°, showed the presence of three methyl groups, three methylene groups, eight methine groups, three quaternary carbons, two olefinic carbons, one ketonic carbon and three acetoxy groups in the ^{13}C NMR (DEPT) spectrum (Table 1). It had a five-membered ketone conjugated with an *exo*-methylene group, judging from the following spectral data: λ_{max}^{EtOH} 236.5 nm (log ε 3.86); ν_{max}^{KBr} 1740–1708, 1645 cm^{-1}; ^{1}H NMR: δ5.91 and 5.13 (each 1H, *br s*), ^{13}C NMR: δ 111.72 (*t*), 151.21 (*s*) (*exo*-methylene) and 205.51 (ketone) [2]. The above-mentioned data together with three tertiary methyl signals at δ1.74, 1.57 and 1.30 in the ^{1}H NMR spectrum suggested that this compound had the typical *ent*-kaur-16-en-15-one nucleus as a basic skeleton [3]. Weisiensin A was found to have two hydroxy groups and three acetoxy groups: ν_{max}^{KBr} 3570, 3520, 1740–1708, 1252 cm^{-1}; ^{1}H NMR: δ6.08 (1H, *d*, J = 3.96 Hz), 5.83 (1H, *dd*, J = 10.08, 5.76 Hz), 5.58 (1H, *d*, J = 3.60 Hz), 4.47 (1H, *br s*, $W_{1/2}$ = 5.0 Hz), 3.71 (1H, *t*, J = 3.0 Hz), 2.21, 2.14 and 1.967 (each 3H, *s*), ^{13}C NMR: δ81.01, 76.26, 75.81, 70.40, and 69.38 (each *d*).

The locations of five oxygen functional groups were deduced as follows. The chemical shift values of C-10 and C-20 were δ43.62 and 16.06, respectively, which suggested that there was an oxygen substituent on the 1α-position [4]. In the ^{13}C NMR spectrum C-4 was at δ38.84, C-18 at 29.53 and C-5 at 41.66 which suggested that there were oxygen substituents on the 3β- and 7β-positions [5, 6]. The chemical shift value of C-5 was δ41.66 and C-19 was 24.68 which indicated that there was an oxygen substitute on the 6α-position [5, 6]. The C-13 signal was at δ37.10 which indicated there were no oxygen substituents on C-12 or C-14 [7]. The C-9 signal was at δ55.62 and C-8 was at 49.14 which suggested that there was an oxygen substitute on the 11β-position [6]. The functional group at C-3β was a hydroxyl judged by ^{1}H NMR data (δ3.71, *t*,



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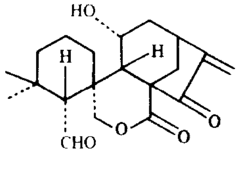

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Table 1. ^{13}C NMR chemical shifts of weisiensin A (**1**) and trichorabdal A (**2**)

C	**1**	**2**
1	81.01 *d*	31.60 *t*
2	33.37 *t*	18.64 *t*
3	75.81 *d*	40.16 *t*
4	38.84 *s*	34.31 *s*
5	41.66 *d*	56.91 *d*
6	69.38 *d*	205.41 *d*
7	76.26 *d*	171.26 *s*
8	49.14 *s*	60.70 *s*
9	55.62 *d*	47.70 *d*
10	43.62 *s*	42.06 *s*
11	70.40 *d*	64.98 *d*
12	38.64 *t*	42.65 *t*
13	37.10 *d*	35.23 *d*
14	36.84 *t*	28.51 *t*
15	205.51 *s*	201.62 *s*
16	151.21 *s*	150.24 *s*
17	111.72 *t*	117.66 *t*
18	29.53 *q*	32.30 *q*
19	24.68 *q*	26.12 *q*
20	16.06 *q*	70.94 *t*
OAc	170.29 *s*	
	170.22 *s*	
	169.26 *s*	
	21.89 *q*	
	21.37 *q*	
	21.10 *q*	

$J = 3.0$ Hz) [8]. The location of the other hydroxyl group at C-6α was supported by the following decoupling experiments. On irradiation at δ4.47 (*br s*, 6β-H), the doublet at 5.58 (7α-H) changed into a singlet and the broad singlet at 2.66 (5β-H) changed into a sharp singlet. On the other hand, on irradiation at δ5.58, the broad singlet at 4.47 sharpened. Further, on irradiation at 6.08 (11α-H), the broad singlet at 2.76 (9β-H) collapsed to a sharp singlet and the sextet at 2.36 (12β-H, $J = 2.0$, 2.0, 14.0 Hz) changed into a double doublet ($J = 2, 0$, 14.0 Hz). Therefore, the chemical structure of weisiensin A (**1**) could be represented as *ent*-1β,7α,11α-triacetoxy-3α,6β-dihydroxykaur-16-en-15-one (**1**). Trichorabdal A (**2**), a known component [9], was also isolated from this plant and its ^{13}C NMR data are assigned in Table 1.

EXPERIMENTAL

The experimental conditions were the same as those described in the previous paper [10].

Plant material. Rabdosia weisiensis C. Y. Wu leaves were collected by Prof. Liu Lunhui in Weixi, Yunnan, China in Sept. 1983 and the voucher specimen been deposited in our Institute.

Extraction and isolation of constituents. Dried and powdered leaves (0.75 kg) were worked-up in the same manner as the previous paper [10] yielding **1** (350 mg) and **2** (105 mg).

Weisiensin A (**1**). $C_{26}H_{36}O_9$ (M^+ at *m/z* 492), colourless needles, mp 298–300°; UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 236.5 (log ε 3.86); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3570, 3520, 1740–1708, 1645, 1252, 1025, 935; MS *m/z*: 492 $[M]^+$, 432, 390, 372, 330, 312, 294, 279, 43 (base peak). ^{1}H NMR: δ6.08 (*d*, $J = 3.96$ Hz, 11α-H), 5.91 and 5.13 (each 1H, *br s*, 17-H_2), 5.83 (*dd*, $J = 10.08$, 5.76 Hz, 1β-H), 5.58 (*d*, $J = 3.60$ Hz, 7α-H), 4.47 (*br s*, $W_{1/2} = 5.0$ Hz, 6β-H), 3.71 (*t*, $J = 3.0$ Hz, 3α-H), 3.20 (*d*, $J = 12.80$ Hz, 14α-H), 2.94 (*m*, $W_{1/2} = 7.0$ Hz, 13α-H), 2.76 (*br s*, 9β-H), 2.66 (*br s*, 5β-H), 2.36 (*sextet*, $J = 14.0$, 2.0, 2.0 Hz, 12β-H), 2.21, 2.14 and 1.97 (each 3H, *s*, 3 × OAc), 1.74 (3H, s, 20-Me), 1.57 (3H, s, 19-Me), 1.30 (3H, *s*, 18-Me).

Trichorabdal A (**2**). $C_{20}H_{26}O_5$; colourless needles, mp 202–204°; UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 231.5 (log ε 3.93); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3435, 2800, 2720, 1745, 1722, 1688, 1643, 1275, 1178, 1020, 955, 926; ^{1}H NMR: δ10.07 (*d*, $J = 4.70$ Hz, CHO), 6.02 and 5.38 (each 1H, *br s*, 17-H_2), 5.29 and 5.06 (each 1H, *d*, $J = 12.0$ Hz, 20-H_2), 4.63 (*m*, $W_{1/2} = 10.0$ Hz, 11β-H), 3.50 (*d*, $J = 11.74$ Hz, 14α-H), 2.91 (*d*, $J = 4.70$ Hz, 5β-H), 1.00 and 0.97 (each 3H, *s*, 2 × Me).

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