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Taxayuntin I from *Taxus Yunnanensis*

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Abstract: Taxayuntin I, a new 11 (15→1)abeotaxane, was isolated from the leaves and stems of *Taxus yunnanensis*. Its structure was elucidated on the basis of spectroscopic data.

Keywords: *Taxus yunnanensis*; taxoids; abeotaxane; taxayuntin I.

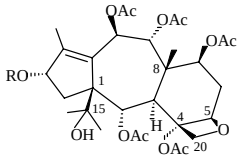
Since excellent antitumor activity and unique mechanism of action of paclitaxel (taxol®) were discovered, chemical studies on *Taxus* species have been extensively carried out[1, 2]. About 300 taxoids have been isolated from Genera *Taxus* and *Austrotaxus* plants[3]. In search for bioactive taxoids and precursors for semisynthesis of taxol we previously obtainted two taxoids from the leaves and stems of *Taxus yunnanensis*[4]. Further investigation on the extract of this plant led to the isolation of a new 11 (15→1) abeotaxane, named taxayuntin I. In this paper the structure elucidation of taxayuntin I (1) is described.

Taxayuntin I (1)**,** mp. 259-260 °C (MeOH), $[\alpha]_D^{29}$+25.5 (c, 0.048, $CHCl_3$), was obtained as colourless needles. The FAB-MS spectrum showed a $[MH]^+$ ion peak at m/z 653. Its molecular formula, $C_{32}H_{44}O_{14}$, was established by FAB-MS, ^1H and ^{13}C NMR spectroscopy. IR absorption at 3480, 1740 and 1725 cm^{-1} indicated the presence of hydroxy and ester groups respectively. The ^1H NMR spectrum of **1** (**Table 1**) showed the signals of four methyl groups of taxane skeleton (δ1.14, 1.15, 1.66 and 1.82). The presence of an oxetane ring was suggested by the signals of C-20 methylene group at 4.37 and 4.47 (ABq, J=7.4Hz) and δ_C 74.61 in the NMR spectra. The 5/7/6 membered ring skeleton was deduced from the upfield resonance of Me-16 at δ 1.14, and the absence of a carbonyl group signal at C-9[5]. This was supported by the unusual upfield resonance of C-1 (δ 67.88) and the downfield resonance of C-15 (δ 75.32)[4]. Six acetyl groups appeared at δ_H 1.96, 1.99. 2.02, 2.08, 2.09 and 2.20. The presence of five oxymethine groups was concluded by the observation of the ^1H NMR signals between δ 5.48~6.25. A pair of doublets at δ 6.02 and 6.25 (J=9.6 Hz) were assigned to H-9βand H-10α. A doublet at δ 6.09 coupled with H-3α at δ 2.92 (J=7.9 Hz) was attributed to H-2β. Two triplets at δ 5.48 (J=7.6 Hz) and 5.61 (J=7.6 Hz) were due to H-7α and H-13β respectively. Thus it was deduced that acetoxy groups located at 2α, 7β, 9α, 10β and 13α. The remaining acetoxy group was connected to C-4α. On acetylation with acetic anhydride-pyridine at room temperature, taxayuntin H (2)[6] gave a monoacetate, the ^1H NMR data for which was completely identical with those described

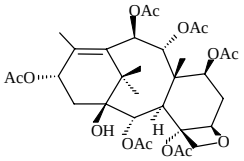
for **1**. Thus the structure of taxayuntin I was assigned to be **1**. By comparison of the NMR spectra of **1** with those of baccatin IV (3)[7, 8], both compounds possess the same substituents and differ only in skeleton, but compound **1** showed the remarkable downfield shift of H-2 ($\Delta\delta$0.47) and C-13 ($\Delta\delta$ 8.3) and the upfield shift of H-13 ($\Delta\delta$ 0.59) besides H-16, C-1 and C-15, which is completely consistent with the 5/7/6 membered ring skeleton[3, 5.9].

Table 1. ^{1}H (500 MHz) and ^{13}CNMR (125 MHz) spectral data of compound 1 (δ, $CDCl_3$)

Position	H	C	DEPT	Position	H	C	DEPT
1		67.88	s	15		75.32	s
2	6.09 d (7.9)	68.15	d	16	1.14 s	25.13	q
3	2.92 d (7.9)	43.59	d	17	1.15 s	27.60	q
4		79.41	s	18	1.82 brs	11.71	q
5	4.97 d (7.8)	84.72	d	19	1.66 s	12.49	q
6a	2.52 dt (15.5, 7.6)	34.73	t	20a	4.37 d (7.4)	74.61	t
6b	1.87 m			20b	4.46 d (7.4)		
7	5.48 t (7.6)	70.55	d	$COCH_3$	2.10 s	20.65	q
8		44.61	s		2.09 s	20.71	q
9	6.02 d (9.6)	76.50	d		2.08 s	21.02	q
10	6.25 d (9.6)	68.15	d		2.02 s	21.34	q
11		135.95	s		1.99 s	21.58	q
12		147.15	s		1.96 s	21.89	q
13	5.61 t (7.6)	78.72	d	$\underline{CO}CH_3$		167.63, 169.05	s
14a	2.27 m	36.79	t			169.64, 169.68	s
14b	1.68 dd (14.6, 7.9)					170.23, 170.61	s



1 R=OAc **2** R=OH



3

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