

Chemical Constituents of New Diterpenes From *Taxus yunnanensis*

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Recently, the intensive investigations of chemical constituents of Taxaceae, especially the antitumor diterpenes related to taxane, have already been stimulated by the significant discovery of antitumor activity of taxol^[1]. Such studies will eventually result in the development of a new type of chemotherapeutic antitumor agents.

Taxus yunnanensis Cheng et L. K. Tu, is distributed in China, especially in Yunnan Province as an especial species. Two new diterpenoid esters taxayunnansin A(1) and B(2) were isolated from EtOH extract existing between water and chloroform from the branch of *T. yunnanensis*. The chromatography of the chloroform fraction on silica gel afforded the two compounds by elution with CHCl₃-MeOH. Taxayunnansins A mp. 338—340°C and taxayunnansin B mp. 318—319°C were crystallized in diluted EtOH as white tabular crystals. Their structures are related to the isotaxane skeleton, which was previously derived by the rearrangement of taxol with the electrophilic reagent^[2]. Structurally, this carbon skeleton arises from the cleavage of C₁₁—C₁₂ bond in taxane, so that carbon C₁ is attached to C₁₁ to deduce an isopropyl C₁₅, C₁₆ and C₁₇^[3]. The group is oxidated as a hydroxyl isopropyl in taxayunnansins A and B, its signals appear at 1.07 (3H, s, CH₃), 1.691(3H, s, CH₃) ppm and 74.82(C), 12.48(CH₃), 25.19(CH₃) ppm in the ¹HNMR and ¹³CNMR spectra respectively.

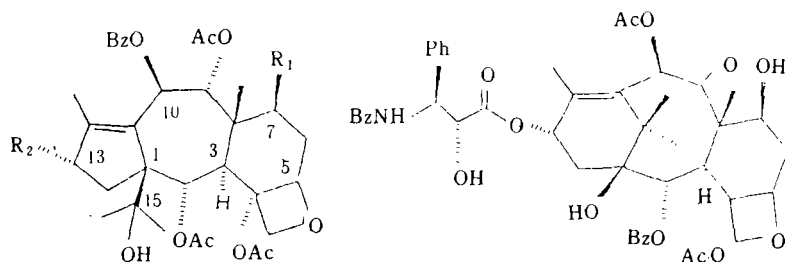


Fig. 1. Molecular structure. 1; R₁=OAc, R₂=OH. 2; R₁=OH, R₂=OAc.

The structures of compounds taxayunnansins A and B were elucidated by UV, IR, MS, FAB-MS, ¹HNMR and ¹³CNMR spectra, including ¹H-¹HCOASY, ¹H-¹³CCOSY, DEPT and COLOG spectroscopic experiments. Their spectroscopic data are

summarized in the Tables 1 and 2. X-ray diffraction analysis was undertaken to confirm the structure proposed for taxayunnansin A and to reveal the relative configuration of the diterpenes in taxayunnansins A and B (Fig. 2).

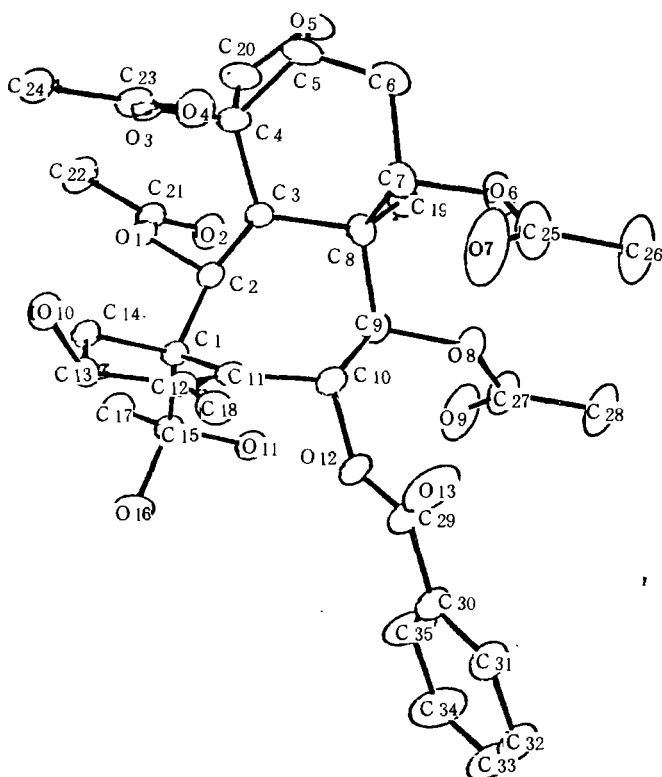


Fig. 2. X-ray diffraction of taxayunnansin A.

Table 1 UV, IR, MS and Mp. Data of Taxayunnansins A and B

Compound	Taxayunnansin A	Taxayunnansin B
Formula	$C_{35}H_{44}O_{13}$	$C_{35}H_{44}O_{13}$
Mp. ($^{\circ}C$)	338-340	318-319
UV (nm)	206, 229, 271	205, 229, 271
IR (KBr, cm^{-1})	3525, 2979, 2930, 2880, 1735, 1721, 1650, 1591, 1575, 1441, 1430, 1362, 1330, 1260, 1230, 1180, 1130, 1085, 1065, 1021, 710.	3525, 2979, 2960, 2930, 2880, 1735, 1721, 1655, 1595, 1579, 1445, 1431, 1370, 1330, 1260, 1240, 1180, 1130, 1085, 1065, 1021, 710.
MS(m/z)	695[M+Na] ⁺ , 673[M+1] ⁺ , 635, 611, 573, 551, 491, 431, 373, 313, 293, 253, 223, 195, 106, 91, 77, 59. (FAB-MS. glycerol)	594[M-18-60], 494, 490, 447, 372, 312, 252, 122, 105, 77, 60, 43 (MS. 20 eV).

Table 2 ^1H and ^{13}C NMR, DEPT Data of Taxayunnansins A and B^{a)}

Carbon	Taxayunnansin A			Taxayunnansin B		
	σ_c	σ_H	$J(\text{Hz})$	σ_c	σ_H	$J(\text{Hz})$
1. C	67.6			67.7		
2. CH	69.1	6.06d	7.8	69.3	6.07d	7.8
3. CH	44.0	3.08d	7.7	44.1	3.10d	7.8
4. C	79.7			79.9		
5. CH	84.7	4.90d	7.6	85.0	4.91d	7.8
6. CH ₂	34.7	2.20dd	16.8, 7.0	34.8	2.20m	
		1.57dd	16.8, 7.2		1.58m	
7. CH	67.9	5.50t		68.1	4.46d	7.8
8. C	43.6			43.8		
9. CH	76.4	6.10d	10.8	76.8	6.11d	11.8
10. CH	77.3	6.49d	10.8	77.1	6.50d	11.8
11. C	133.8			133.9		
12. C	151.5			151.6		
13. CH	67.6	4.45d	7.0	70.4	5.50t	8.2
			15.6, 7.6			
			8.2			
14. CH ₂	39.5	2.49ddd	15.6, 7.6	39.6	2.48m	
			8.2			
		1.84ddd	15.6, 8.6		1.86m	
			6.0			
15. C	74.8			75.0		
16. CH ₃	12.5	1.07s		12.6	1.07s	
17. CH ₃	25.2	1.69s		25.3	1.64s	
18. CH ₃	27.4	1.74s		27.5	1.70s	
19. CH ₃	11.8	1.02s		11.7	1.16s	
20. CH ₂	75.4	4.45d	7.6	75.5	4.44d	7.6
		4.36d	7.6		4.36d	
OAc CH ₃	20.5	1.97s		20.6	1.98s	
	21.3	1.94s		21.4	1.98s	
	21.5	2.02s		21.6	2.03s	
	21.2	2.11s		22.3	2.12s	
	169.7			169.8		
	169.7			169.8		
	170.3			170.4		
170.9			171.1			
O-Bz C	164.0			164.1		
C	129.0			129.2		
CH	129.4	7.79d	7.8	129.5	7.80d	7.6
			7.6, 7.4			
			7.2, 7.5			
	128.7	7.37dd		128.8	7.37t	7.7
	133.3	7.50dd		133.4	7.50t	7.4
OH		2.18d	7.2		2.07d	6.8
		2.73s			2.71s	

a) NMR was obtained using Bruker AM-400 spectrometer, the reagent was CDCl_3 , chemical shift in ppm relative to internal TMS.

In addition, a known compound taxol (3) was isolated from the plant simultaneously. Its spectroscopic data are corresponding to that of taxol in literature^[1, 2].

The diterpene skeleton of taxayunnansins A and B is related to taxane, but due to their distinction, it should be named isotaxane, which was previously obtained from the products of the rearrangement of taxol^[3]. In fact, the skeleton isotaxane naturally occurs in the plant. These naturally occurring examples provide a definite stimulus for considering the biosynthetic link between various groups of taxane types.

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