Six New Taxane Diterpenoids from the Seeds of *Taxus chinensis* var. *mairei* and *Taxus yunnanensis*

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Six new taxane diterpenoids and three known 2(3→20)*abeo*taxoids were isolated from the seeds of *Taxus chinensis* var. *mairei* and of *Taxus yunnanensis*. Their structures were established as 2α,20-dihydroxy-9α-acetoxytaxa-4(20),11-dien-13-one (**1**), 5α-cinnamoyloxy-7*β*,10*β*,13α-triacetoxy-2(3→20)*abeo*taxa-2α-ol-4(20),11-dien-9-one (**2**), 5α-cinnamoyloxy-10*β*,13α-diacetoxy-2(3→20)*abeo*taxa-2α,7*β*-diol-4(20),11-dien-9-one (**3**), 5α-cinnamoyloxy-2α,7*β*,10*β*,13α-tetraacetoxy-2(3→20)*abeo*taxa-4(20),11-dien-9-one (**4**), 7-*O*-acetyltaxine A (**5**), 2α,7*β*,10*β*,13α-tetraacetoxy-5α-phenylisoserinatoxy-2(3→20)*abeo*taxa-4(20),11-dien-9-one (**6**), 5-*O*-acetyltaxinine M (**7**), 5α-hydroxy-2α,7*β*,10*β*,13α-tetraacetoxy-2(3→20)*abeo*taxa-4(20),11-dien-9-one (**8**), and 2α,5α-dihydroxy-7*β*,10*β*,13α-triacetoxy-2(3→20)*abeo*taxa-4(20),11-dien-9-one (**9**), on the basis of 1D and 2D NMR spectroscopic analysis. Compound **1**, as a new compound isolated from *T. chinensis* var. *mairei*, is a rare example of a taxane with a 4,11-diene unit, which is considered to be an important intermediate in the biogenesis of taxoids. Compounds **2**−**4**, **6**, and **7** are new compounds, isolated from *T. yunnanensis*, which also afforded the known compounds **5**, **8**, and **9**.

The clinical activity of Taxol® (paclitaxel) against breast, ovarian, and other carcinomas has spurred a worldwide search for better sources and improved analogues of this drug. Although more than 300 taxoids have been identified to date,[1−4] new taxoids continue to be isolated from the needles, bark, stem, and roots of *Taxus* species.[5−9] In a continuing study on the phytochemistry of the taxoids, we have previously isolated several bicyclic taxoids with the verticillene skeleton, along with some related taxoids based on various skeletons, from the needles and bark of the Chinese yew, *Taxus chinensis* var. *mairei*.[10−13] Further investigation on the extracts of the seeds of this plant has resulted in the isolation of a new taxoid (**1**). Phytochemical investigation on the seeds of *T. yunnanensis* has led to the isolation of five new taxoids (**2**−**4**, **6**, and **7**), along with three known compounds (**5**, **8**, and **9**) (Chart 1). Herein we describe the isolation and the structure elucidation of these new compounds.

Compound **1** was obtained as a colorless gummy substance in 0.0003% yield. The molecular formula of **1** was established as $C_{22}H_{32}O_5$ by combined analyses of the HRFABMS and the ^{13}C NMR spectrum. Strong absorptions at 3450, 1735, and 1660 cm^{-1} in the IR spectrum implied that **1** possessed hydroxyl, ester, and α,*β*-unsaturated ketone groups, respectively. Analysis of the ^1H and ^{13}C NMR data and the HMQC spectrum of **1** indicated the presence of one acetyl, one tetrasubstituted olefin, one trisubstituted olefin, one ketone carbon, two oxymethines, two methines, one oxymethylene, four methylenes, two quaternary carbons, and four methyl groups. Four of the seven unsaturations were thus characterized, and compound **1** was therefore inferred to contain three rings. The connectivities from C-1 to C-2, C-5 to C-7, C-9 to C-10, and C-14 to C-1 were deduced from the $^1H-^1H$ COSY spectrum. In the HMBC spectrum of **1** (Figure 1), cross-peaks of CH_3-16 and CH_3-17 to C-1, C-11, and C-15 revealed that both CH_3-16 and CH_3-17 were attached at C-15, while cross-peaks of CH_3-18 to C-11, C-12, and C-13 suggested that CH_3-18 was connected to C-12. These HMBC correlations along with the $^1H-^{13}C$ long-range cross-peaks between H-14 and C-12 and C-15, and between H-10 and C-12 and C-15, implied the presence of a cyclohexene moiety (ring A). The cross-peaks of H-2 to C-1, C-8, C-14, and C-15; H-3 to C-1, C-8, C-9, and C-19; H-9 to C-3, C-11; and H-10 to C-8 and C-15 in the HMBC spectrum indicated the presence of an eight-membered ring (ring B). The $^1H-^{13}C$ long-range correlations of H-3 to C-4, C-5, and C-7, H-5 to C-4 and C-7, and H-7 to C-3 and C-5 were suggestive of the presence of a cyclohexane ring (ring C). The signal at 116.3 ppm was correlated only with the single-proton singlet at 5.44 ppm in the HMQC spectrum, so the C-4 double bond was endocyclic instead of exocyclic, as is usual in most natural taxoids. The H_2-20 signal correlated with C-3, C-4, and C-5 and indicated that the endocyclic bond was at C-4(5), with the C-20 oxymethylene group attached at C-4. The carbonyl carbon at *δ* 171.0 ppm showed a correlation with the signal at *δ* 5.29 ppm in the HMBC spectrum, and this signal showed cross-peaks with C-11, C-7, and C-19; analysis of all of this evidence was used to locate the acetoxy group at C-9. Meanwhile, the signals at *δ* 2.90 and 2.72 ppm, both of which correlated with the signal at *δ* 31.95 ppm in the HMQC spectrum and showed cross-peaks with C-11, C-12, and C-15 in the HMBC spectrum, were assigned to H-10*β* and 10α, respectively. The signal at *δ* 200.2 ppm, which correlated with H-1, H-14, and CH_3-18 in the HMBC spectrum, indicated a ketone group at C-13. Thus, the structure of **1** was concluded to be 2α,20-dihydroxy-9α-acetoxy-taxa-4(20),11-dien-13-one. The relative stereochemistry of **1** was elucidated from the NOESY spectral data as shown in Figure 2.

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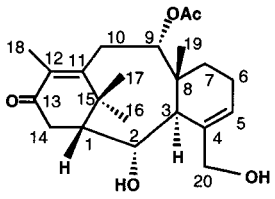
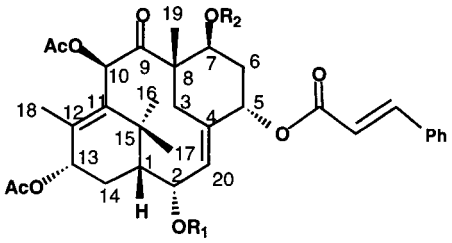
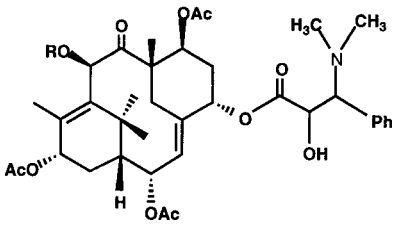
Chart 1



1



2 R_1=H R_2=Ac
3 R_1=H R_2=H
4 R_1=Ac R_2=Ac



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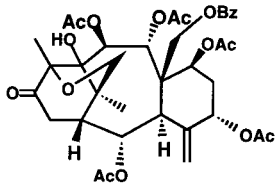
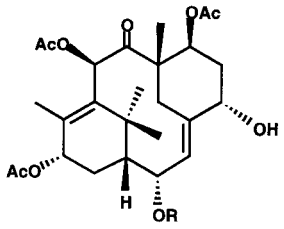
6 R=Ac



7



8 R=Ac
9 R=H

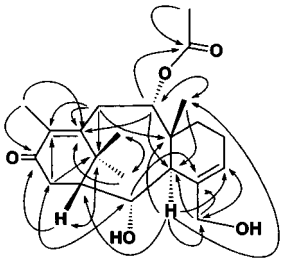


Figure 1. Major HMBC correlations of **1** (500 MHz).

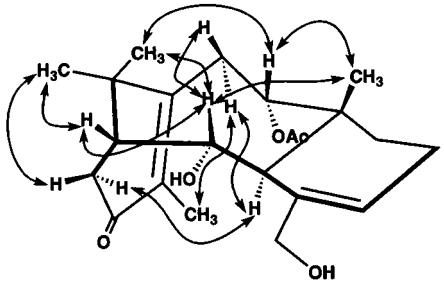


Figure 2. Relative stereochemistry of **1**, proposed through a NOESY experiment (500 MHz).

Compound **2** was obtained as a white powder and showed a molecular ion at *m*/*z* 621 $[M - H]^-$ in the negative FABMS; HRFABMS analysis revealed the molecular formula of **2** as $C_{35}H_{42}O_{10}$. Strong absorptions at 3460, 1735, and 1710 cm^{-1} in the IR spectrum implied that **2** possessed hydroxyl, ester, and ketone groups, respectively. The ^1H NMR spectrum (Table 2) showed characteristic signals due to the taxoid skeleton, including four methyl groups (δ 1.30, 1.21, 2.03, and 1.13 ppm) and three acetyl methyl groups (δ 1.89, 2.08, and 2.15 ppm). Protons due to a cinnamoyl group appeared at δ 7.52 (2H, m), 7.40 (3H, m), 6.55 (1H, d, J = 16.2 Hz), and 7.85 (1H, d, J = 16.2 Hz, trans-oriented). The UV absorption at 279 nm also supported the presence of a cinnamoyl group. A prominent fragment peak at *m*/*z* 147 was characteristic for the loss of a cinnamoyl group from **2**. Detailed analysis of the $^1H-^1H$ COSY spectrum revealed connectivities of C-14 to C-1, C-1 to C-20, C-5 to C-7, C-2′ to C-3′, and C-5′ to C-7′. The spin system derived from CH_3-18, H-13β, H-14α, and H-14β was readily interpreted. A 3H doublet at δ 2.03 ppm was assigned to CH_3-18 based on its long-range coupling with H-13β. In addition, the broad doublet at δ 5.40 ppm was assigned to H-13β; the multiplets at δ 2.68 and 1.93 ppm were assigned to the C-14 methylene protons, H-14β and H-14α, respectively, based on their geminal coupling and coupling to H-13β. The doublet of doublets at δ 1.70 ppm, which correlated with H-14β in the $^1H-^1H$ COSY spectrum, was assigned to H-1β. The signal at δ 4.64, which correlated with H-1β in the $^1H-^1H$ COSY spectrum, was attributed to H-2β. This signal was coupled with the signal at δ 5.46

Table 1. ^1H and ^{13}C NMR Spectral Data of **1** in $CDCl_3$ (500 MHz, δ in ppm, J in Hz)

position	δ ^1H	J	$^1H-^1H$ COSY	^{13}C
1	2.52 dd	7.4, 4.1	H-2β, 14β	45.4
2	4.13 dd	4.1, 9.1	H-1β, 3α	80.6
3	2.73 br d	9.1	H-2β, 5, 20	44.3
4				140.3
5	5.44 br s		H-3α, 6, 20	116.4
6	2.10 m		H-5, 7	22.7
7	1.55 m		H-6	31.6
8				40.6
9	5.29 dd	5.0, 8.5	H-10α, 10β	78.6
10α	2.72 dd	5.0, 14.3	H-9β, 10β	31.6
10β	2.90 dd	8.5, 14.3	H-9β, 10α	
11				158.2
12				136.0
13				200.2
14α	2.45 d	19.8	H-14β	35.8
14β	2.75 dd	7.4, 19.8	H-1β, 14α	39.0
15				37.4
16	1.19 s			25.8
17	1.50 s			37.8
18	1.83 s			15.4
19	0.92 s			17.4
20a	4.18 br d	2.0, 12.4	H-3, 5, 20b	
20b	4.32 br d	1.6, 12.4	H-3, 5, 20a	70.2
OAc-9	2.10 s			21.6
				171.0

Table 2. ^{1}H and ^{13}C NMR Spectral Data of **2** and **3** ($CDCl_3$, ppm, 300 MHz for ^{1}H and 125 MHz for ^{13}C)

	2				**3**			
position	^{13}C	^{1}H	*J* (Hz)	^{1}H−^{1}H COSY	^{13}C	^{1}H	*J* (Hz)	^{1}H−^{1}H COSY
1	49.9	1.70 dd	8.2, 2.2	H-2, 14*β*	49.0	1.70 dd	8.4, 2.2	H-2, 14*β*
2	68.8	4.64 br d	9.6	H-1, 20	67.8	4.62 br d	11.3	H-1, 20
3a	36.2	2.67 d	15.4	H-3b, 20	35.9	2.63 d	14.8	H-3b, 20
3b		1.92 d	15.4	H-3a		1.87 d	14.8	H-3a
4	131.9				132.0			
5	70.8	5.73 br d	6.3	H-6α, 6*β*	69.2	5.60 br d	6.6	H-6α, 6*β*
6α	33.1	2.01 m		H-5, 6*β*, 7	32.3	1.87 m		H-5, 6*β*, 7
6*β*		2.24 m		H-5, 6α, 7		2.36 m		H-5, 6α, 7
7	70.1	5.38 dd	11.8, 4.1	H-6α, 6*β*	68.0	4.32 br d	10.7	H-6α, 6*β*
8	53.9				53.9			
9	206.7				206.9			
10	78.7	6.35 br s		18-CH_3	78.4	6.44 br s		18-CH_3
11	129.5				129.4			
12	139.6				137.6			
13	71.2	5.40 br d	10.3	H-14*β*, 18-CH_3	70.7	5.43 br d	11.8	H-14*β*, 18-CH_3
14α	27.1	1.93 m		H-14*β*	26.3	1.92 m		H-14*β*
14*β*		2.68 m		H-1, 13, 14α		2.64 m		H-1, 13, 14α
15	38.4				37.7			
16	21.2	1.30 s			18.4	1.25 s		
17	25.9	1.21 s			25.0	1.24 s		
18	17.9	2.03 d	1.2	H-10, 13	16.8	1.93 d	1.1	H-10, 13
19	33.3	1.13 s			35.5	1.13 s		
20	128.8	5.46 br d	9.6	H-2, 3a	126.3	5.40 br d	11.3	H-2, 3a
1′	167.3				166.3			
2′	118.4	6.55 d	16.2	H-3′	117.5	6.50 d	15.9	H-3′
3′	147.1	7.85 d	16.2	H-2′	146.3	7.82 d	15.9	H-2′
4′	134.7				132.0			
5′	129.8	7.52 m		H-6′, 7′	129.1	7.50 m		H-6′, 7′
6′	128.9	7.40 m		H-5′, 7′	128.1	7.42 m		H-5′, 7′
7′	131.5	7.40 m		H-5′, 6′	130.8	7.42 m		H-5′, 6′
OAc-7	21.7	1.89 s						
	171.2							
OAc-10	21.9	2.08 s			21.3	1.96 s		
	170.3				170.4			
OAc-13	21.6	2.15 s			21.0	2.18 s		
	171.3				170.0			

ppm (1H, br d J = 9.6 Hz) instead of signals at δ 2.8−4.0 ppm characteristic of H-3α in most taxoids.[2,14] In the ^{1}H NMR spectrum, moreover, a pair of singlets was lacking, corresponding to the AX system (chemical shift difference about 0.30 ppm) of the exocyclic methylene protons seen in many taxoids. Additionally, no AB quartet (at about δ 4.20 ppm with a coupling constant of about 9 Hz) corresponding to an oxetane ring, was observed.[2,14] An isolated spin system of doublets at δ 2.67 and 1.92 ppm with a coupling constant J = 15.4 Hz occurred instead and was assigned to H-3a,b.

In the ^{13}C NMR spectrum of **2**, besides signals due to the cinnamoyl group, four other peaks in the alkene region (δ 129.5, 139.6, 131.9, and 128.8 ppm) revealed the existence of two double bonds, of which the one at δ 128.8 ppm carried a proton, though others were quaternary, as shown by the HMQC spectrum. The signals at δ 129.5 and 139.6 ppm were assigned to C-11 and C-12, respectively, based on the HMBC spectrum. Because the signal at δ 128.8 ppm correlated only with the single-proton broad doublet at δ 5.46 ppm in the HMQC spectrum, the C-4/C-20 double bond must be endocyclic instead of having the more common exocyclic location. Keeping the above observations in mind, the skeleton of compound **2** was elucidated as consisting of a 6/10/6-membered ring with a C-4/C-20 endocyclic double bond, representing a 2(3→20)*abeo*taxane derivative, as in taxine A,[15,16] but without the *N*,*N*-dimethylphenylisoserine side chain at C-5. The ^{1}H and ^{13}C NMR data of compound **2** were fully assigned on the basis of ^{1}H−^{1}H COSY, HMBC (Figure 3), and HMQC spectral data interpretation as shown in Figure 1. Based on the coupling constants and NOESY spectra, the protons at positions 2, 5, 7, 10, and 13 were assigned to *β*, *β*, α, α, and *β*, respectively, having the same configurations as found in taxine A and in most natural taxoids. The relative stereochemistry of compound **2** was elucidated as shown in Figure 4 from the results of the NOESY experiments. The NOESY spectrum showed NOE correlations between H-2 and H-3a and CH_3-17 and between H-20 and H-14α, which indicated an *E*-configuration of the C-4 double bond. In addition, correlations between H-13*β* and CH_3-16, H-7α and CH_3-18, and H-3b and H-6*β* implied that both rings A and B were in boat conformations, as in the case with taxine A. Therefore, compound **2** was characterized unambiguously as 5α-cinnamoyloxy-7*β*,10*β*,13α-triacetoxy-2(3→20)-*abeo*taxa-2α-hydroxy-4(20),11-dien-9-one (2-deacetyl-10-*O*-acetyltaxuspine B).[17]

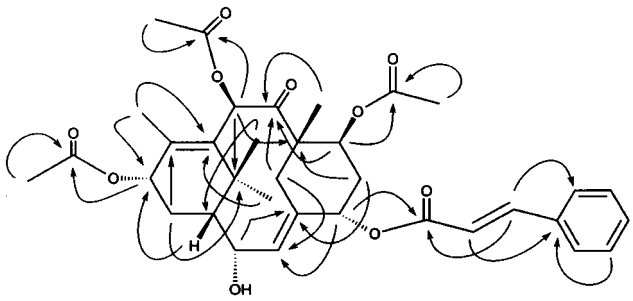


Figure 3. HMBC correlations observed for **2** (500 MHz) (most protons are omitted for clarity).

Compound **3** was obtained as a colorless gum. In the negative-mode FABMS analysis of **3**, a quasimolecular ion peak was observed at *m*/*z* 579 [M − H]$^-$, which revealed that its molecular weight was 580. From a combined

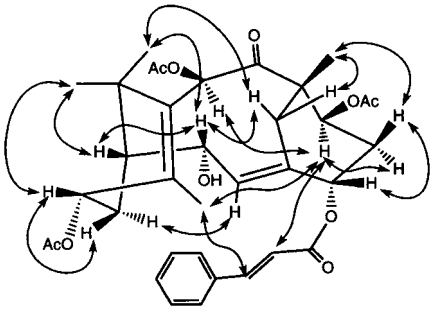


Figure 4. Relative stereochemistry of **2**, deduced from a NOESY experiment (500 MHz).

analysis of the FABMS and ^{13}C NMR data, the empirical formula was determined to be $C_{33}H_{40}O_9$, which was confirmed by HRFABMS. Absorptions at 3450, 1730, and 1700 cm^{-1} in its IR spectrum implied that **3** also possessed hydroxyl, ester, and α,β-unsaturated ketone groups, respectively. The ^1H and ^{13}C NMR spectra closely resembled those of **2**, with the exception that H-7 was shifted upfield to δ 4.32 ppm in the ^1H NMR spectrum. The ^{13}C NMR spectrum showed signals for two acetyl groups (δ 170.4 and 170.0 ppm) at relatively low field. The structure of **3** was therefore determined as 7-deacetyl **3**; that is, 5α-cinnamoyloxy-10β,13α-diacetoxy-2(3→20)*abeo*taxa-2α,7β-dihydroxy-4(20),11-dien-9-one.

Compound **4** was isolated as a colorless gum, and its ^1H NMR spectrum closely resembled that of compound **2**, with the exception that H-2 was shifted downfield to δ 5.75 ppm, and signals for four acetyl groups were observed in both the ^1H (δ 2.16, 2.08, 2.00, and 1.94 ppm) and the ^{13}C NMR (δ 170.7, 170.5, 169.9, 169.6, 21.2, 20.9, 20.8, and 20.4 ppm) spectra. Its EIMS (M^+, 664) was consistent with an acetylated structure of **2**. So the structure of **4** was thus assigned as 5α-cinnamoyloxy-2α,7β,10β,13α-tetraacetoxy-2(3→20)*abeo*taxa-4(20),11-dien-9-one.

Compound **5** was identified as 2α,7β,13α-triacetoxy-5α-phenylisoserinatoxy-2(3→20)*abeo*taxa-10β-ol-4(20),11-dien-9-one (7-*O*-acetyltaxine A)[18] on the basis of spectral analysis, including HMBC and HMQC spectra.

Compound **6** was obtained as a white gum. Its positive-ion FABMS yielded an ion peak at *m/z* 726 $[M + H]^+$, which revealed that its molecular weight was 725, 42 mass units greater than that of **5**. The ^1H NMR spectrum of **6** closely resembled that of **5**, with the exception that H-10 was shifted downfield to δ 6.41 ppm. Thus, the structure of **5** was assigned as 2α,7β,10β,13α-tetraacetoxy-5α-phenylisoserinatoxy-2(3→20)-*abeo*taxa-4(20),11-dien-9-one (7,10-*O*-diacetyltaxine A).

Compound **7** was obtained as a white gum. Its molecular formula $C_{38}H_{51}O_{10}N$ was deduced from combined analysis of the HREIMS at *m/z* 728.2677 and the ^{13}C NMR spectrum. The ^1H NMR spectrum of **7** closely resembled that of taxinine M, with the exception that H-5 was shifted upfield to δ 5.31 ppm. Thus, the structure of **7** was assigned as 5-*O*-acetyltaxinine M on the basis of spectral analysis and by comparison with taxinine M.[19−21]

Compounds **8** and **9**, both of them obtained as colorless gums, were determined to be 5α-hydroxy-2α,7β,10β,13α-tetraacetoxy-2(3→20)*abeo*taxa-4(20),11-dien-9-one and 2α,5α-dihydroxy-7β,10β,13α-triacetoxy-2(3→20)*abeo*taxa-4(20),-11-dien-9-one on the basis of 1D and 2D NMR spectral analysis and by comparison with spectral data described in the literature.[22] In the Experimental Section we report the assignment of the ^{13}C NMR spectrum of taxin B, which differs in some respects from the assignments reported in the literature.[22]

Compounds **2**−**4** and **6**−**9**, as lipophilic compounds, came into the acidic phase, suggesting that these compounds may be originally present as Winterstein esters and degraded to cinnamates or hydrolyzed during the extensive chromatographic steps employed.

Experimental Section

General Experimental Procedures. The melting point was measured on a MRK micro-melting point apparatus and is uncorrected. Optical rotations were recorded on a Horiba SEPA-300 digital polarimeter. The UV spectrum was run on a Shimadzu UV-1600 spectrophotometer. IR spectra were obtained on a JASCO IR-810 instrument. MS were measured on a JEOL JMS-700 spectrometer using the EI and FAB modes. ^1H and ^{13}C NMR spectra were obtained on Varian Unity INOVA 500 and Varian GEMINI 2000/300 spectrometers operating at 500 and 300 MHz for ^1H and 150 and 125 and 75 MHz for ^{13}C, in $CDCl_3$ at ambient temperature. Chemical shifts are reported in parts per million relative to tetramethylsilane (TMS, $\delta = 0$) as an internal standard, and coupling constants are given in Hertz. Open column chromatography was performed using Merck Si gel 60 (100−200 mesh). Analytical TLC was carried out with precoated Merck Si gel 60 F_{254} plates. TLC separations and purifications were performed on glass plates coated with Merck Si gel 60 F_{254} (20 × 20 cm, 0.85 mm thickness) and visualized by UV (254 nm) and/or by spraying with 10% H_2SO_4 and then heating on a hot plate.

Plant Material. The seeds of *Taxus chinensis* var. *mairei* were collected in Jinggangshan, in the southeast region of the People's Republic of China, in October 1995. The botanical identification was made by Prof. R. L. Liu, Ganzhou Forestry School, People's Republic of China. A voucher specimen (# 95−12−02) has been deposited at the Graduate School of Agricultural Science, Tohoku University, Japan. The seeds of *Taxus yunnanensis* were collected in Congteng County, Yunnan Province, in the southwest of the People's Republic of China, in October 1995. The botanical identification was made by Prof. J. H. Wang, School of Pharmaceutical Science, Hebei Medical University, Shijiazhuang, the People's Republic of China. A voucher specimen (# 95−12−01) has been deposited at the Graduate School of Agricultural Science, Tohoku University, Japan.

Extraction and Isolation. Air-dried and crushed seeds (1.1 kg) of *T. chinensis* var. *mairei* were extracted with hexane three times at room temperature to remove most of the undesired neutral components. The residue was extracted twice with MeOH. The MeOH extract was dried under reduced pressure. This residue was diluted with H_2O and extracted five times with EtOAc. The combined EtOAc layer was further extracted with 5% HCl. The organic layer after extraction with 5% HCl was condensed (9.5 g) and submitted to Si gel column chromatography by elution with hexane−Me_2CO (4:1, 3:1, 2:1, 1:1, and 1:2). Five fractions were obtained. Fractions 1 and 2 were repeatedly separated and purified by means of preparative TLC on Si gel with hexane−Me_2CO (2:1), hexane−EtOAc (3:2), and $CHCl_3$−MeOH (100:3) as solvent systems, and finally afforded compound **1** (4 mg).

Air-dried seeds (2.2 kg) of *T. yunnanensis* were crushed and extracted with hexane three times at room temperature to remove the majority of the undesired neutral component. The residue was extracted three times with MeOH, and the MeOH extracts were evaporated to a residue (135 g) under reduced pressure. Subsequently, this residue was diluted with H_2O and extracted five times with EtOAc (85 g). The combined EtOAc layer was further extracted with 5% HCl. After neutralization, the aqueous layer was extracted three times with EtOAc. The combined EtOAc extract, upon evaporation, yielded 8.8 g of a yellowish syrup, which was subjected to column chromatography, eluted with hexane−EtOAc (2:1, 1:1, 1:2, 1:4). Altogether 12 fractions were obtained, and fractions 3 (900 mg) and 4 (450 mg) were further separated by repeated preparative TLC with different developing solvents [$CHCl_3$−MeOH (100:

2.5−100:4); hexane−EtOAc (3:2−2:3); hexane−Me_2CO (5:2−3:2)], and finally compounds **2** (4 mg), **3** (3 mg), **4** (3 mg), **5** (8 mg), **6** (1 mg), **7** (2 mg), **8** (4 mg), and **9** (2 mg) were separated in pure form.

2α,20-Dihydroxy-9α-acetoxy-taxa-4(20),11-dien-13-one (1): a colorless gum, $[\alpha]^{24}_D$ +44° (*c* 0.01, $CHCl_3$); IR ν_{max} ($CHCl_3$, film) 3450, 1735, 1660, 1370, 1240 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; FABMS *m/z* 369 $[M + H - H_2O]^+$, 331 $[M + H - H_2O - CO]^+$, 299 $[M + H - H_2O - AcOH]^+$; HRFABMS *m/z* 359.2223 (calcd for $C_{22}H_{31}O_4$, 359.2221).

5α-Cinnamyloxy-7*β*,10*β*,13α-triacetoxy-2(3→20)*abeo*taxa-2α-hydroxy-4(20),11-dien-9-one (2): a white powder, mp 114−115 °C $[\alpha]_D^{24}$ −60° (*c* 0.01, $CHCl_3$); UV(MeOH) λ_{max} (log ϵ) 279 (4.22) nm; IR ν_{max} ($CHCl_3$, film) 3460, 1735, 1710, 1670, 1630, 1230 cm^{-1}; ^1H and ^{13}C NMR data, see Table 2; FABMS *m/z* 621 $[M - H]^-$, 579 $[M - H - CH_3CO]^-$, 561, 519, 491, 459, 305, 199, 151, 91; HRFABMS *m/z* 621.2700 (calcd for $C_{35}H_{41}O_{10}$, 621.2697).

5α-Cinnamyloxy-10*β*,13α-diacetoxy-2(3→20)*abeo*taxa-2α,7*β*-dihydroxy-4(20),11-dien-9-one (3): a colorless gum, $[\alpha]^{24}_D$ −45° (*c* 0.01, $CHCl_3$); IR ν_{max} ($CHCl_3$, film) 3450, 1730, 1710, 1670, 1630, 1240 cm^{-1}; ^1H and ^{13}C NMR data, see Table 2; FABMS *m/z* 579 $[M - H]^-$, 561, 536, 535, 519, 501, 459, 305, 199, 151, 91; HRFABMS *m/z* 579.2579 (calcd for $C_{33}H_{39}O_9$, 579.2592).

5α-Cinnamyloxy-2α,7*β*,10*β*,13α-tetraacetoxy-2(3→20)-*abeo*taxa-4-(20),11-dien-9-one (4): a colorless gum, $[\alpha]^{24}_D$ −15 ° (*c* 0.01, $CHCl_3$); IR (film, $CHCl_3$) ν_{max} 1735, 1710, 1630 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.70 (1H, dd, *J* = 8.7, 2.2 Hz, H-1), 5.75 (1H, dd, *J* = 9.8, 2.2 Hz, H-2), 2.79 (1H, d, *J* = 15.5 Hz, H-3a), 2.00 (1H, d, *J* = 15.5 Hz, H-3b), 5.73 (1H, br d, *J* = 6.5 Hz, H-5), 2.03 (1H, m, H-6a), 2.27 (1H, m, H-6b), 5.39 (1H, dd, *J* = 12.5, 3.1 Hz, H-7), 6.36 (1H, s, H-10), 5.40 (1H, br d, *J* = 10.8 Hz, H-13), 2.72 (1H, m, H-14*β*), 1.83 (1H, dd, *J* = 16.4, 2.7 Hz, H-14α), 1.12 (3H, s, 19-CH_3), 1.28 (3H, s, 16-CH_3), 1.32 (3H, s, 17-CH_3), 2.06 (3H, br s, 18-CH_3), 6.56 (1H, d, *J* = 15.9 Hz, H-2′), 7.87 (1H, d, *J* = 15.9 Hz, H-3′), 7.54 (2H, m, H-5′), 7.43 (3H, m, H-6′, -7′), 2.16 (3H, s, CH_3-CO−), 2.08 (3H, s, CH_3CO−), 1.94 (3H, s, CH_3CO−), 2.00 (3H, s, CH_3CO−); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 46.8 (C-1), 70.8 (C-2), 35.5 (C-3), 130.8 (C-4), 69.3 (C-5), 32.7 (C-6), 70.0 (C-7), 53.2 (C-8), 205.3 (C-9), 77.9 (C-10), 133.2 (C-11), 138.6 (C-12), 70.4 (C-13), 27.4 (C-14), 37.9 (C-15), 29.7 (C-16), 32.1 (C-17), 17.1 (C-18), 20.4 (C-19), 124.2 (C-20), 170.7 (CH_3CO−), (CH_3CO−), 170.5 (CH_3CO−), 169.9 (CH_3CO−), 169.6 (CH_3CO−), 21.4 (CH_3CO−), 21.2 (CH_3CO−), 20.9 (CH_3CO−), 20.8 (CH_3-CO−), 166.6 (C-1′), 117.7 (C-2′), 146.3 (C-3′), 134.0 (C-4′), 129.0 (C-5′), 128.9 (C-6′), 129.0 (C-7′); EIMS *m/z* 664 $[M]^+$, 604 [M − HOAc]$^+$, 131, 103, 43; HREIMS *m/z* 644.2878 (calcd for $C_{35}H_{44}O_{11}$, 644.2881).

2α,7*β*,10*β*,13α-Tetraacetoxy-5α-phenylisoserinatoxy-2(3→20)-*abeo*taxa-4(20),11-dien-9-one (6): a colorless gum, $[\alpha]^{24}_D$ −75° (*c* 0.01, $CHCl_3$); IR ν_{max} ($CHCl_3$, film) 3450, 1740, 1720, 1230 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.63 (1H, m, H-1), 5.66 (1H, br d, *J* = 10.2 Hz, H-2), 2.65 (1H, d, *J* = 14.8 Hz, H-3a), 1.80 (1H, d, *J* = 14.8 Hz, H-3b), 5.50 (1H, br d, *J* = 6.4 Hz, H-5), 1.80 (1H, m, H-6a), 0.70 (1H, m, H-6b), 5.17 (1H, dd, *J* = 12.5, 3.30 Hz, H-7), 6.40 (1H, s, H-10), 5.36 (1H, br d, *J* = 10.6 Hz, H-13), 2.81 (1H, m, H-14α), 2.70 (1H, m, H-14*β*), 1.23 (3H, s, 16-CH_3), 1.16 (3H, s, 17-CH_3), 2.01 (3H, s, 18-CH_3), 1.08 (3H, s, 19-CH_3), 1.99 (3H, s, CH_3CO−), 2.07 (3H, s, CH_3-CO−), 2.14 (3H, s, CH_3CO−), 2.16 (3H, s, CH_3CO−), 4.63 (1H, d, *J* = 8.5 Hz, H-2′), 3.83 (1H, d, *J* = 8.5 Hz, H-3′), 7.32 (5H, m, H−Ph), 2.17 [6H, s, N Me_2]; FABMS *m/z* 726 $[M + H]^+$, 766 [M + H − HOAc]$^+$, 154 109; HRFABMS *m/z* 726.3492 (calcd for $C_{39}H_{52}NO_{12}$, 726.3486).

5-*O*-Acetyltaxinine M (7): a white gum, $[\alpha]^{24}_D$ −7° (*c* 0.01, $CHCl_3$); IR ν_{max} ($CHCl_3$, film) 3430, 1740, 1710, 1660, 1630, 1600, 1370, 1250 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.43 (1H, br d, *J* = 12.0 Hz, H-1), 6.11 (1H, dd, *J* = 2.7, 9.6 Hz, H-2), 3.43 (1H, d, *J* = 9.6 Hz, H-3), 5.31 (1H, s, H-5), 2.26 (1H, m, H-6a), 1.67 (1H, m, H-6b), 5.45 (1H, dd, *J* = 10.7, 6.3 Hz, H-7), 5.31 (1H, s, H-9), 5.31 (1H, s, H-10), 2.55 (1H, d, *J* = 18.7 Hz, H-14α), 3.02 (1H, dd, *J* = 12.0, 18.7 Hz, H-14*β*), 4.09 (1H, d, *J* = 8.0 Hz, H-16a), 3.62 (1H, d, *J* = 8.0 Hz, H-16b), 1.27 (3H, s, 17-CH_3), 1.17 (3H, s, 18-CH_3), 5.20 (1H, d, *J* = 12.6 Hz, H-19a), 4.43 (1H, d, *J* = 12.6 Hz, H-19b), 4.67 (1H, s, H-20a), 5.42 (1H, s, H-20b), 2.17 (3H, s, CH_3CO−), 2.13 (3H, s, CH_3-CO−), 2.12 (3H, s, CH_3CO−), 2.01 (3H, s, CH_3CO−), 8.15 (2H, d, *J* = 7.1 Hz, H−Ph), 7.60 (1H, t, *J* = 7.1 Hz, H−Ph), 7.50 (2H, t, *J* = 7.1 Hz, H−Ph); EIMS *m/z* 728 $[M]^+$ (32), 668 [M − HOAc]$^+$ (75), 626 $[M - HOAc - COCH_2]^+$ (15), 368 (20), 131 (10), 105 (100); HREIMS *m/z* 728.2680 (calcd for $C_{37}H_{44}O_{15}$, 728.2677).

5α-Hydroxy-2α,7*β*,10*β*,13α-tetraacetoxy-2(3→20)*abeo*taxa-4(20),11-dien-9-one) (8): colorless gum, $[\alpha]^{24}_D$ −36° (*c* 0.01, $CHCl_3$); IR (film, $CHCl_3$) ν_{max} 3540, 3010, 2970, 2950, 2820, 1740, 1720, 1700, 1440, 1430, 1360, 1230, 1020, 960, 750 cm^{-1}; ^{13}C NMR ($CDCl_3$, 125 MHz) δ 47.1 (C-1), 70.0 (C-2), 35.7 (C-3), 139.5 (C-4), 69.3 (C-5), 38.1 (C-6), 70.8 (C07), 53.5 (C-8), 206.4 (C-9), 78.6 (C-10), 132.3 (C-11), 137.6 (C-12), 70.0 (C-13), 27.1 (C-14), 36.4 (C-15), 35.7 (C-16), 24.1 (C-17), 18.4 (C-18), 22.1 (C-19), 124.6 (C-20), 170.1, 21.6 (OAc-2), 170.7, 21.3 (OAc-7), 171.0, 21.5 (OAc-10), 169.7, 21.5 (OAc-13); FABMS *m/z* 535 ($[M + H]^+$) (0.6), 521 ($[M + H - CH_2]^+$) (0.4), 475 ([M + H − HOAc]$^+$) (1.5), 461 ($[M + H - AcOG - CH_2]^+$) (1.2), 415 ([M + H − 2HOAc]$^+$) (2), 355 ([M + H − 3HOAc]$^+$) (1.2), 295 ([M + H − 4HOAc]$^+$) (1.1), and 277 ([M + H − 4HOAc − H_2O]$^+$) (1.5); EIMS *m/z* 520 ($[M - CH_2]^+$) (12), 474 ([M − HOAc]$^+$) (10), 414 ([M − 2HOAc]$^+$) (12), 354 ([M − 3HOAc]$^+$) (10), 326 ([M − 3HOAc − CO]$^+$) (100), 312 (100), 284 (100), 266 ([M − 4HOAc − CO]$^+$) (100); HREIMS *m/z* 474.2252 (calcd for $C_{26}H_{34}O_8$, 474.2253).

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