New Regio- and Stereoselective *O*-Deacetylated and Epoxy Products of Taxanes Isolated from *Taxus mairei*

Ya-Ching Shen,*,† Chin-Lien Ko,† Yuan-bin Cheng,† Michael Y. Chiang,‡ and Ashraf Taha Khalil†

Institute of Marine Resources, National Sun Yat-sen University, 70 Lien-Hai Road, Kaohsiung, Taiwan 80424, Republic of China, and Department of Chemistry, National Sun Yat-en University, Taiwan, Republic of China

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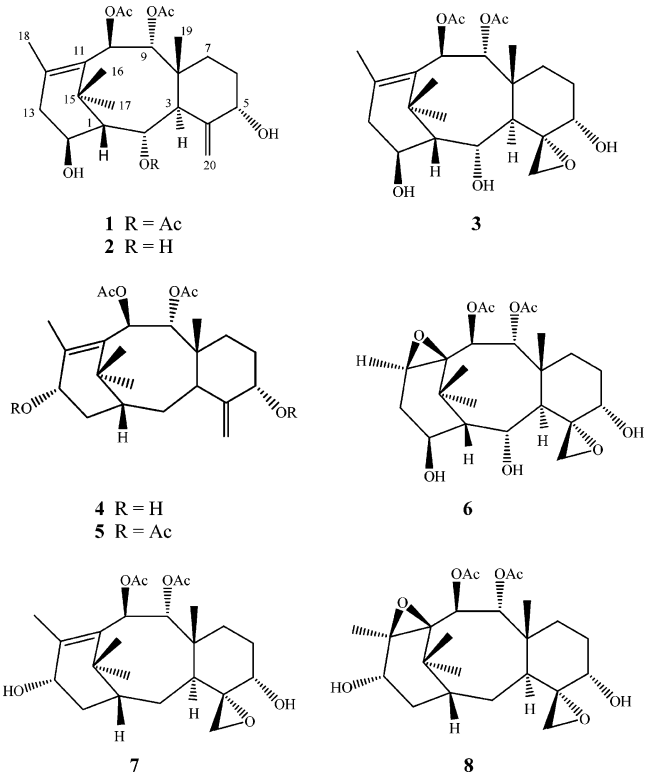
Deacylation of a taxoid mixture isolated from the roots of *Taxus mairei* followed by chromatographic fractionation resulted in the isolation of three new taxoid derivatives, 2α,9α,10β-triacetoxy-5α,14β-dihydroxy-4(20),11(12)-taxadiene (**1**), 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-4(20),11(12)-taxadiene (**2**), and 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-4,20-epoxy,11(12)-taxene (**3**). Epoxidation of **2** afforded 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-4,20:11,12-diepoxytaxane (**6**), while epoxidation of **4** yielded 9α,10β-diacetoxy-5α,13α-dihydroxy-4,20-epoxy,11(12)-taxene (**7**) and 9α,10β-diacetoxy-5α,13α-dihydroxy-4,20:11,12-diepoxytaxane (**8**). The structures were elucidated by detailed analysis of their NMR spectra. The structure and relative stereochemistry of **7** was confirmed by X-ray crystallography.

Taxol, first isolated from *Taxus brevifolia* over three decades ago,[1] has shown clinical efficacy as an anticancer drug for the treatment of a variety of human malignancies and has stimulated a tremendous interest in the chemistry and biological activities of taxoid compounds.[2,3] Research has been conducted to overcome the scarcity of this highly active compound through tissue culture, chemical transformation, and the investigation of new natural sources of taxoids. Efforts are still needed in the quest for drugs capable of treating multidrug-resistant cancers.[4] As part of our work to discover new taxoid derivatives,[5−10] we have carried out a phytochemical investigation of the roots of *Taxus mairei* (Lemee & Levl.) S. Y. Hu (Taxaceae) collected in Taiwan. Deacylation[11] of a taxoid mixture isolated from the roots of *T. mairei* followed by chromatographic separation has resulted in the isolation of three new taxoid derivatives, 2α,9α,10β-triacetoxy-5α,14β-dihydroxy-4(20),11(12)-taxadiene (**1**), 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-4(20),11(12)-taxadiene (**2**), and 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-4,20-epoxy,11(12)-taxene (**3**). The known compound 9α,10β-diacetoxy-5α,13α-dihydroxy-4(20),11(12)-taxadiene (**4**)[12] was also isolated during the course of this fractionation. Epoxidation of **2** with *m*-CPBA[13,14] afforded 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-4,20:11,12-diepoxytaxane (**6**), while epoxidation of **4** yielded a mixture of 9α,10β-diacetoxy-5α,13α-dihydroxy-4,20-epoxy,11(12)-taxene (**7**) and 9α,10β-diacetoxy-5α,13α-dihydroxy-4,20:11,12-diepoxytaxane (**8**). The structures were defined on the basis of spectral studies, especially from their 1D and 2D NMR data. X-ray crystallographic analysis of **7** provided unambiguous characterization for the structures and relative stereochemistry of the other α-epoxide taxane derivatives.



The HREIMS of **1** revealed its molecular weight as 478, consistent with the molecular formula $C_{26}H_{38}O_8$ and eight degrees of unsaturation. The IR spectrum displayed absorption bands diagnostic of hydroxyl groups, olefinic bond(s), and ester moieties. Both the ^{1}H and ^{13}C NMR spectral data (Tables 1 and 2) indicated the presence of three *O*-acetyl units at δ_H 2.08, 2.03, 2.01 (each 3H, s) and δ_C 21.6, 21.2, 20.8 and δ_C 169.6, 170.2 (double intensity). The MS data as well as the proton singlets at δ 1.17, 1.71, 2.15, and 0.82 (each 3H) along with carbons at δ_C 31.5, 26.3, 21.2, and 17.2 were characteristic of the four methyl groups on the common 6/8/6 taxoid skeleton.[15,16] A tetrasubstituted double bond was indicated by two quaternary signals at δ_C 132.0 and 139.2, assigned to C-11 and C-12, respectively. An exomethylene moiety was verified by the observation of two olefinic singlets at δ_H 4.79 and 5.17 together with signals for a methylene carbon at δ_C 114.5 and a quaternary carbon at δ_C 147.1. The proton at δ 4.79 had HMBC correlations to δ_C 42.1 (C-3) and 76.5 (C-5), thus locating the exomethylene at C-4. The ^{1}H NMR spectrum revealed five oxygenated protons at δ 4.21 (br s, H-5), 4.08 (dd, J = 9.0, 5.2 Hz, H-14), 5.47 (br s, H-2), 5.77 (d, J = 10.4 Hz, H-9), and 6.07 (d, J = 10.4 Hz, H-10). The latter three protons showed long-range correlations to three acetate carbonyls at δ_C 169.6, 170.2, and 170.2, while other

* To whom correspondence should be addressed. Tel: 886-7-525-2000, ext. 5058. Fax: 886-7-525-5020. E-mail: ycshen@mail.nsysu.edu.tw.
† Institute of Marine Resources.
‡ Department of Chemistry.

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Table 1. ^{1}H NMR Data ($CDCl_3$, 300 MHz) of Compounds **1**−**3** and **6**−**8**[a,b]

position	1	2	3	6	7	8
1	1.79 br s	1.92 br s	1.90 br s	1.64 br s	1.44 br s	1.62 br s
2	5.47 br s	4.17 brd (4.9)	4.08 br s	4.18 br s	0.98 br s	0.93 br s
					1.36 br s	1.47 br s
3	3.22 d (6.6)	3.02 d (5.5)	2.88 d (4.5)	2.60 br s	3.09 d (4.7)	2.68 br s
5	3.42 br s	3.10 br s	3.11 br s	3.22 br s	3.41 br s	3.48 br s
6	1.73 m	1.80 m	1.74 m	1.95 m	1.76 m	1.84 m
		1.65 m			1.87 m	1.93 m
7	1.65 m	1.92 m	1.68 m	1.71 m	1.59 m	1.66 m
		1.70 m				
9	5.77 d (10.4)	5.63 d (10.3)	5.65 d (10.5)	5.78 d (10.7)	5.69 d (10.3)	5.84 d (10.8)
10	6.07 d (10.4)	6.03 d (10.3)	6.05 d (10.5)	5.33 d (10.7)	6.06 d (10.3)	5.44 d (10.8)
13	2.44 dd (14.4, 4.5)	2.62 dd (14.5, 6.3)	2.50 dd (13.5, 3.0)	2.44 m	4.38 brd (7.5)	4.14 brt (9.2)
	2.68 dd (14.4, 8.0)	2.35 dd (14.5, 3.5)	2.75 m			
14	4.08 dd (9.0, 5.2)	4.05 dd (10)	4.21 dd (8.4, 5.1)	4.33 dd (8.7, 6.9)	1.65 m	1.32 m
14					2.79 m	2.49 m
20	4.79 s	5.18 s	2.66 d (4.2)	2.70 d (3.6)	2.60 br s	2.66 br s
	5.17 s	5.26 s	3.67 d (4.2)	3.80 d (3.6)		
CH_3-16	1.17 s	1.14 s	1.17 s	1.00 s	0.90 s	1.59 s
CH_3-17	1.71 s	1.59 s	1.59 s	1.65 s	1.48 s	0.85 s
CH_3-18	2.15 s	2.10 s	2.15 s	1.93 s	2.22 s	1.93 s
CH_3-19	0.82 s	0.81 s	0.96 s	1.03 s	0.79 s	0.87 s
OAc-2	2.08 s					
OAc-9	2.03 s	2.00 s	1.99s	2.03 s	2.05 s	2.04 s
OAc-10	2.01 s	1.97 s	2.05 s	2.03 s	2.00 s	2.04 s

[a] Chemical shifts in ppm, *J* values in Hz are in parentheses. [b] Assignments were made using HMQC and HMBC techniques.

Table 2. ^{13}C NMR Data ($CDCl_3$, 75 MHz) of Compounds **1**−**3** and **6**−**8**[a]

carbon	1	2	3	6	7	8
1	63.0 d	65.9 d	65.6 d	36.8 d	38.7 d	41.5 d
2	70.9 d	71.5 d	69.3 d	71.7 d	28.0 t	21.7 t
3	42.1 d	36.5 d	43.7 d	36.8 d	32.1 d	32.3 d
4	147.1 s	148.1 s	67.3 s	66.7 s	61.2 s	61.0 s
5	76.5 d	75.4 d	76.0 d	75.6 d	72.8 d	72.7 d
6	30.8 t	32.0 t	31.0 t	37.5 t	32.5 t	27.3 t
7	26.5 t	25.6 t	26.8 t	26.3 t	25.9 t	25.4 t
8	44.8 s	44.7 s	44.9 s	44.0 s	43.6 s	42.8 s
9	77.2 d	76.5 d	77.5 d	76.8 d	77.2 d	77.8 d
10	72.8 d	72.4 d	72.8 d	72.7 d	73.3 d	73.3 d
11	132.0 s	132.3 s	131.7 s	64.0 s	134.3 s	65.7 s
12	139.2 s	139.6 s	138.7 s	63.0 s	142.3 s	66.7 s
13	42.2 t	42.0 t	41.8 t	37.1 t	68.4 d	67.0 d
14	67.8 d	67.6 d	67.1 d	66.6 d	35.0 t	33.8 t
15	37.6 s	37.8 s	37.4 s	37.5 s	39.3 s	39.0 s
CH_3-16	31.5 q	31.5 q	31.7 q	25.3 q	25.9 q	26.4 q
CH_3-17	26.3 q	26.5 q	26.6 q	31.2 q	21.9 q	30.5 q
CH_3-18	21.2 q	21.1 q	21.3 q	23.0 q	16.3 q	16.1 q
CH_3-19	17.2 q	17.1 q	17.3 q	17.3 q	17.3 q	17.7 q
20	114.5 t	115.6 t	54.1 t	53.7 t	48.5 t	48.4 q
OAc-2	21.6 q					
	169.6 s					
OAc-9	21.2 q	20.8 q	20.9 q	20.8 q	21.1 q	20.9 q
	170.2 s	170.4 s	170.6 s	170.2 s	170.6 s	169.8 s
OAc-10	20.8 q	21.1 q	21.2 q	20.5 q	20.8 q	20.7 q
	170.2 s	170.0 s	170.2 s	169.7 s	170.0 s	170.4 s

[a] Assignments were made using HMQC and DEPT techniques.

correlations were observed between H-14/C-15, C-2 and between H-5/C-3, C-6. The COSY experiment displayed connectivities between H-13/H-14/H-1/H-2/H-3, H-5/H-6/H-7, and H-9/H-10. A proposed structure of a triacetoxy taxane was further confirmed through HMBC correlations between H-1/C-11, C-13, C-16; H-2/C-8, C-14, C-15; H-9/C-7, C-19; H-10/C-12, C-15; and H-18/C-11, C-13. The relative stereochemistry of **1** was determined through comparing ^{1}H NMR data as well as the optical rotation with those of related taxane diterpenes and from its NOESY spectrum (Figure 1). Naturally occurring taxanes of this type have H-1 and H-19 in the β-orientation, while H-3 is

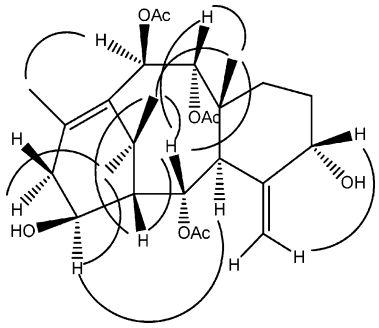

Figure 1. Key NOESY correlations of **1**.

in the α-orientation.[16] The correlations between H-1/H-16β, H-2 and H-19/H-9 implied the β-orientation of H-2 and H-9. In addition, the correlation between H-14/ H-17α, H-3 indicated the α-orientation of H-14. On the basis of this evidence, the structure of **1** was determined as 2α,9α,10β-triacetoxy-5α,14β-dihydroxy-4(20),11(12)-taxadiene.

Comparative inspection of the ^{1}H and ^{13}C NMR spectral data of **2** and **1** (Tables 1 and 2) indicated the presence of the key structural features of a taxane skeleton in **2** with two acetate substituents at δ_H 2.00 and 1.97 (each 3 H, s), δ_C 20.9 and 20.2, and two carbonyls at δ_C 170.6 and 170.2. The signal attributable to H-2 (δ 4.17) was shifted to higher field when compared to the corresponding value of **1** (δ 5.47), implying that the acetoxy group in **1** was replaced by a hydroxy group in **2**. A COSY experiment revealed connectivities between H-2/H-1 and H-3, confirming the presence of a hydroxy at C-2. In addition, the HMBC spectrum determined the attachment of the two acetoxy groups to C-9 and C-10 through revealing correlations of the carbonyl with the corresponding methine protons. Furthermore, long-range correlations were detected between H-10/C-15, C-12 and H-9/C-19, C-3. On the basis of these results, **2** was identified as 9α,10β-diacetoxy-2α,5α,-14β-trihydroxy-4(20),11(12)-taxadiene.

The HREIMS of **3** revealed a molecular formula of $C_{24}H_{36}O_8$, indicating the presence of one oxygen atom more

than that of **2**. The spectral data of **3** (Tables 1 and 2) were similar to those of **2** except for the values of C-4, C-20, and H-20. The oxygenated CH_2 at δ_C 54.1 was assigned to C-20, while the two proton signals at δ 2.66 (d, J = 4.2 Hz) and 3.67 (d, J = 4.2 Hz) were attributable to H-20. These data were in good agreement with the presence of an exo-epoxide at C-4,[16−18] which was confirmed by the quaternary carbon at δ 67.3 (C-4) and the long-range correlations between H-20/C-5, C-4. The HMBC spectral data supported the proposed structure by showing correlations between H-9/C-19; H-10/C-12, C-15; and H-14/C-15, C-12. The NOESY correlations between H-16β/H-1, H-2, H-9 and H-20/H-5, H-19 implied the β-orientation of H-2, H-9, and H-20, while the correlation between H-17α/H-14 was in agreement with the α-orientation of H-14. It was concluded that **3** possesses the structure 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-4,20-epoxy,11(12)-taxene.

Compound **5** was reported from *Taxus* spp.[19] and later isolated in a pure form and identified from the same taxane mixture used as a starting material for the deacylation reaction in the present study.[20] Obviously, obtaining **4** as a major deacylation product of the same taxane mixture was a proof of the presence of **5** as the major natural taxane in this fraction. Likewise, the deacylation products **1** (or **2**) and **3** implied the presence of 2α,5α,9α,10β,14β-pentaacetoxy-4(20),11-taxadiene and 2α,5α,9α,10β,14β-pentaacetoxy-4,20-epoxy,11-taxene, respectively, as their natural precursors. It is worth mentioning that taxoids with a C-4(20) double bond and that are oxygenated at C-14 are rare in nature, and most of them have been found in the Chinese yew: *T. yunnanesis* or *T. chinensis* var. *mairei.* In this type of compound, the C-14 hydroxyl group is invariably in the β-orientation, and C-13 is not oxygenated. On the other hand, taxoids with a C-4(20) unsaturation are related to baccatin I, one of the first taxoids to have been discovered. The newer members of this group differ primarily in the number and position of acetyl groups on the hydroxy groups around the periphery of the ring system.[16]

Reaction of **2** with *m*-CPBA afforded **6**.[13,14] The FABMS of **6** revealed a molecular ion peak at *m/z* 491 $[M + Na]^+$ consistent with the molecular formula, $C_{24}H_{36}O_9$. The ^{13}C NMR (Table 2) of **6** revealed that the diacetoxytaxane skeleton was still intact with the apparent absence of four olefinic carbons attributable to C-4, C-11, C-12, and C-20. In addition, the ^1H NMR spectrum (Table 1) did not show the characteristic two olefinic signals of an exomethylene at C-20. The presence of a 4,20-epoxy ring was proved from the two proton signals at δ 3.80 and 2.70 (each d, J = 3.6 Hz, H-20), the CH_2 signal at δ_C 53.7 (C-20), and the quaternary carbon resonance at δ_C 66.7 (C-4). Another epoxy ring was verified by the two quaternary signals at δ_C 64.0 and 63.0 (C-11 and C-12, respectively). Analysis of the HMBC and COSY spectra confirmed that **6** is a 4,20- and 11,12-diepoxy derivative of **2**. The NOESY spectrum exhibited correlations between H-20/H-5β and H-19β, indicating the α-orientation of the 4,20-epoxy ring. On the basis of the spectral data of **6**, its structure was established as 9α,10β-diacetoxy-2α,5α,14β-trihydroxy-α-4,20:11,12-diepoxytaxane.

Epoxidation of **4** using *m*-CPBA followed by chromatographic fractionation afforded **7** and **8**. The molecular formula of **7** was assigned as $C_{24}H_{36}O_7$ as deduced from its FABMS. The ^{13}C NMR spectrum of **7** (Table 2) showed the same taxane structure as **4**, particularly for the quaternary carbons at C-11 and C-12 (δ_C 134.3 and 142.3), with the absence of signals for a quaternary carbon assignable to C-4 and an exomethylene carbon (C-20). Instead, the ^{13}C NMR spectrum revealed a CH_2 signal at δ_C 48.5 (C-20) and a broad singlet at δ_H 2.60 (2H, H-20) together with a quaternary signal at δ_C 61.2 (C-4). The signal assigned to H-20 (δ 2.60) showed HMBC correlations to C-3 (δ_C 32.1) and C-5 (δ_C 72.8) as well as NOESY correlations to H-5 and H-19. It was concluded that *m*-CPBA introduced an α-4(20)-epoxy ring into compound **4**.

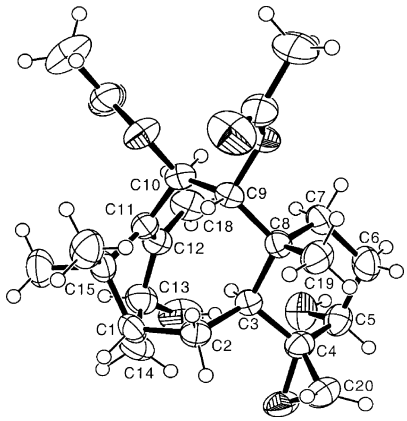

Figure 2. ORTEP diagram showing the solid state conformation of **7**.

X-ray crystallographic analysis established the complete structure and stereochemistry of **7**, and an ORTEP stereodrawing is shown in Figure 2. It is worth noting that the relative configuration of the epoxide at C-4 is different from that of 1β-hydroxybaccatin.[14,18]

Compound **8** was assigned the molecular formula $C_{24}H_{36}O_8$, with one oxygen atom more than the corresponding value of **7**, as judged from the FABMS. The 4,20-epoxy ring was evident from ^{13}C NMR signals at δ_C 48.4 (CH_2-20) and 61.0 (C-4) as well as a broad singlet at δ_H 2.66 (2H, H-20) in the ^1H NMR spectrum, which are very close to the corresponding values obtained for **7**. In addition, the ^{13}C NMR data lacked signals for any olefinic carbon and revealed two quaternary carbon signals at δ_C 65.7 and 66.7, which were assigned to C-11 and C-12, respectively. Hence, compound **8** was found to possess epoxy rings at C-4, C-20 and C-11, C-12. This was confirmed by HMBC correlations between H-5/C-20; H-20/C-3; H-10/C-11; and H-14/C-12. The structure of **8** was deduced as 9α,10β-diacetoxy-5α,-13α-dihydroxy-α-4,20:11,12-diepoxytaxane.

It is concluded therefore that selective reductive deacylation with Red-Al as well as the stereoselective epoxidation of taxanes with *m*-CPBA yields hydroxy and epoxy derivatives that can be used in preparation of other potentially useful taxane derivatives.

Experimental Section

General Experimental Procedures. Optical rotations were recorded on a JASCO DIP-1000 polarimeter. IR and UV spectra were measured on a Hitachi T-2001 and a Hitachi U-3210 spectrophotometer, respectively. The ^1H, ^{13}C NMR, COSY, HMQC, HMBC, and NOESY spectra were recorded on a Bruker FT-300 spectrometer or on a Varian Unity INOVA 500 FT-NMR at 500 MHz for ^1H and 125 MHz for ^{13}C, respectively, using TMS as internal standard. The chemical shifts are given in δ (ppm) and coupling constants in Hz. Low-resolution EIMS and FABMS were recorded on a VG Quattro 5022 mass spectrometer, and high-resolution mass spectra were measured on a JEOL HX 110 mass spectrometer. Silica gel 60 (Merck) was used for column chromatography, and precoated silica gel plates (Merck, Kieselgel 60 F-254, 1 mm)

were used for preparative TLC. Sephadex LH-20 (Amersham Pharmacia Biotech AB, Sweden) was used for either purification or separation. Red-Al [65% solution of sodium bis(2-methoxyethoxy)aluminum hydride in toluene] was obtained from Aldrich Chemical Co., Inc., Milwaukee, WI, and *m*-chloroperbenzoic acid (*m*-CPBA) from Tokyo Chemical Industries, TCI, Tokyo, Japan.

Plant Material. The roots of *Taxus mairei* (Lemee & Levl.) S. Y. Hu were purchased in Kaohsiung, in October 1995. A voucher specimen (TPG8-1) was kept in the Institute of Marine Resources, National Sun Yat-sen University, Kaohsiung, Taiwan.

Extraction and Isolation. Dried roots (90 kg) were ground and extracted with EtOH (300 L) three times at room temperature. The combined extracts were concentrated in vacuo to a brown paste (9.5 kg), which was extracted with a gradient solvent mixture of *n*-hexane/EtOAc (2:1, 1:1, 1:2, 0:1) to yield portions A (900 g), B (1080 g), C (1500 g), and D (2500 g), respectively. Part of A (260 g) was chromatographed on a silica gel column using CH_2Cl_2/acetone (10:1) to afford a taxane mixture (3.1 g). NMR analysis revealed that the mixture contained 5α,9α,10β,13α-tetraacetoxy-4(20),11-taxadiene (taxusin, **5**) as a major compound.[19] Part of the latter mixture (2 g) was dissolved in THF (10 mL); to this solution was added Red-Al (2.78 mL, 65% solution in toluene, 0.014 mmol) at −20 °C, and the solution was stirred for 20 min.[12] The solution was then quenched with a saturated solution of potassium tartarate (10 mL of saturated aqueous solution), and the reaction mixture was extracted with EtOAc (20 mL). The organic layer was washed with H_2O and brine solution, then dried over Na_2SO_4. Concentration under reduced pressure furnished a residue (1.7 g), which was chromatographed on a silica gel column using a gradient of *n*-hexane/CH_2Cl_2/MeOH (100:100:1 to 10:10:1) to yield **4** (501 mg, 9α,10β-diacetoxy-5α,13α-dihydroxy-4(20),11-taxadiene), **1** (7 mg), **2** (114 mg), and **3** (22.5 mg). Part (42 mg) of compound **2** was dissolved in 3 mL of CH_2Cl_2 and treated with 34 mg of *m*-chloroperbenzoic acid (*m*-CPBA) at room temperature for 1 h. The reaction product was purified on a column of Sephadex LH-20 eluting with MeOH/CH_2Cl_2 (2:1) to afford **6** (20 mg, 46% yield). Compound **4** (107 mg) was dissolved in 8 mL of CH_2Cl_2 and treated with 87.6 mg of *m*-CPBA at room temperature for 1 h. The reaction product was purified on a column of Sephadex LH-20 eluting with MeOH/CH_2Cl_2 (2:1) followed by separation by NP-HPLC using *n*-hexane/CH_2Cl_2/MeOH (25:20:1) to give **7** (39 mg, 36% yield) and **8** (7.5 mg, 7% yield).

2α,9α,10β-Triacetoxy-5α,14β-dihydroxy-4(20),11-taxadiene (1): colorless powder; $[\alpha]_D$ +35.8° (*c* 2.66, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectral data, see Tables 1 and 2; EIMS *m/z* 419 $[M - AcO]^+$ (1), 358 (1), 315 (3), 298 (6), 283 (6), 269 (5), 227 (7), 185 (14), 151 (27), 135 (37), 121 (43), 107 (44), 91 (43); FABMS *m/z* 479 $[M + H]^+$; HREIMS *m/z* 419.2432 (calcd for $C_{24}H_{35}O_6$ [$C_{26}H_{38}O_8 - C_2H_3O_2$], 419.2428).

9α,10β-Diacetoxy-2α,5α,14β-trihydroxy-4(20),11-taxadiene (2): colorless powder; $[\alpha]_D$ +69.3° (*c* 1.28, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectral data, see Tables 1 and 2; EIMS *m/z* 358 (0.1), 347 (0.2), 316 (1), 298 (2), 269 (3), 227 (4), 185 (6), 151 (19), 135 (7), 121 (33), 107 (43); FABMS *m/z* 437 $[M + H]^+$, 459 $[M + Na]^+$; HRESIMS *m/z* 459.2357 (calcd for $C_{24}H_{36}O_7$, 459.2360).

9α,10β-Diacetoxy-2α,5α,14β-trihydroxy-4,20-epoxy,11(12)-taxene (3): colorless powder; $[\alpha]_D$ +72.3° (*c* 0.8, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectral data, see Tables 1 and 2; EIMS *m/z* 452 $[M]^+$ (0.1), 389 (4), 151 (27), 135 (29), 121 (38), 107 (39), 91 (43); FABMS *m/z* 453 $[M + H]^+$; HREIMS *m/z* 452.2414 (calcd for $C_{24}H_{36}O_8$, 452.2405).

9α,10β-Diacetoxy-2α,5α,14β-trihydroxy-4,20:11,12-diepoxytaxane (6): $[\alpha]_D$ +19.8° (*c* 3.76, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectral data, see Tables 1 and 2; EIMS *m/z* 468 $[M]^+$ (0.1), 450 $[M - H_2O]^+$ (0.1), 408 $[M - AcOH]^+$ (0.9), 391 $[M - AcOH - H_2O + 1]^+$ (0.8), 348 [M − 2AcOH] (0.9), 330 [M − 2AcOH − H_2O] (0.5), 213 (3), 197 (4), 151 (15), 133 (22), 107 (33), 95 (47); FABMS *m/z* 491 $[M + Na]^+$, 473 $[M + Na - H_2O]^+$; HRESIMS *m/z* 491.2259 (calcd for $C_{24}H_{36}O_9Na$, 491.2257).

9α,10β-Diacetoxy-5α,13α-dihydroxy-4,20-epoxy,11(12)-taxene (7): $[\alpha]_D$ +199.4° (*c* 0.58, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectral data, see Tables 1 and 2; FABMS *m/z* 459 $[M + Na]^+$, 437 $[M + H]^+$, 419 $[M - OH]^+$; EIMS *m/z* 436 $[M]^+$ (0.2), 419 $[M - H_2O + H]^+$ (2), 377 $[M - AcOH + H]^+$ (0.7), 316 $[M - 2AcOH]^+$ (0.8), 299 $[M - 2AcOH - OH]^+$ (4), 281 $[M - 2AcOH - H_2O - OH]^+$ (2), 234 (10), 192 (5), 161 (11), 133 (13), 121 (16), 107 (19), 105 (21), 91 (20), 81 (15); HRESIMS *m/z* 459.2354 (calcd for $C_{24}H_{36}O_7Na$, 459.2359.

9α,10β-Diacetoxy-5α,13α-dihydroxy-4,20:11,12-diepoxytaxane (8): $[\alpha]_D$ +66.6° (*c* 1.44, CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectral data, see Tables 1 and 2; FABMS *m/z* 475 $[M + Na]^+$, 452 $[M]^+$, 435 $[M - OH]^+$; EIMS *m/z* 435 $[M - H_2O + H]^+$, 393 $[M - AcOH + H]^+$ (1.3), 375 $[M - AcOH - H_2O + H]^+$ (2), 357 $[M - AcOH - 2H_2O + H]^+$ (1), 333 $[M - 2AcOH + H]^+$ (5), 315 (9), 289 (12), 271 (15), 243 (13), 227 (14), 215 (14), 173 (17), 119 (45), 107 (64), 95 (67); HRESIMS *m/z* 475.2312 (calcd for $C_{24}H_{36}O_8Na$, 475.2308).

Crystallographic Data and X-ray Structure Analysis of 7. A suitable colorless crystal prism, 0.40 × 0.60 × 0.90 mm^3, of **7** was obtained by the slow evaporation of a *n*-hexane/CH_2Cl_2 solution. Crystal data: $C_{24}H_{36}O_7$, orthorhombic; space group $P2_12_12_1$; $Z = 4$, unit cell parameter $a = 17.367(5)$ Å, $b = 17.553(3)$ Å, $c = 7.6384(7)$ Å, $V = 2328.5(8)$ $Å^3$, $d_{calcd} = 1.245$ Mg m^{-3}, $T = 293(2)$ K, $F(000) = 944$, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.09 mm^{-1}. Final refinement with 1868 reflections ($I > 2\sigma$) led to $R(F)$ of 0.0449 and GOF of 1.05. The final X-ray model is shown in Figure 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (deposit No. CCDC 251676). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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