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Novel taxoids from the Chinese yew *Taxus yunnanensis*

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Abstract—Six new taxoids, taxuyunnanines W (**1**), X (**2**), Y (**3**), Z (**5**), 10-deacetyl-10-(β-glucopyranosyl)-yunnanxane (**8**), and 7-(β-xylosyl)-*N*-methyl-taxol C (**10**), as well as taxuchin B (**4**) and yunnanxane (**7**), have been isolated from the bark of *Taxus yunnanensis*. Compounds **1** and **2** were characterized as 11(15→1)-*abeo* taxoids containing an orthoester group, which have not been reported from any Taxus plants to date; isolates **3** and **5** are the examples of taxanes having a tetrahydronfuran ring, being reported only for the second time; and **8** is the first natural 6/8/6 skeletal type taxane glucosidic form. This is also the first report of a co-occurrence of xylosidation and *N*-methylation in a taxane (**10**). Compound **4** is the only known chlorine-containing taxane found in nature thus far, and is being reported from this plant for the first time. The structures were determined by spectroscopic and chemical means including 1D and 2D NMR spectra.

1. Introduction

The naturally occurring diterpene, paclitaxel, originally isolated from *Taxus brevifolia* by Wani et al.,[1] has been considered the most promising natural anticancer agent. Our search for novel and bioactive taxanes have resulted in the isolation of many types of new and known compounds of this class from the roots and barks of *Taxus yunnanensis* Cheng et L. K. Fu, a species endemic to Southwestern China and Burma.[2–11] In our continuing work on this plant, we have discovered two new orthoester containing taxoids, taxuyunnanines W (**1**) and X (**2**), two new tetrahydronfuran ring containing taxoids, taxuyunnanines Y (**3**) and Z (**5**), a new 6/8/6 skeletal type taxane glucoside, 10-deacetyl-10-(β-glucopyranosyl)yunnanxane (**8**), and a new *N*-methylated taxane xyloside, 7-(β-xylosyl)-*N*-methyltaxol C (**10**), as well as the known chlorine-containing taxoid, taxuchin B (**4**)[12] and the known yunnanxane (**7**).[13] The structures were determined by spectroscopic and chemical means including 1D and 2D NMR spectra. The current paper reports the isolation and structure elucidation of these novel natural products.

2. Results and discussion

Taxuyunnanine W (**1**), white amorphous solid, showed $[M+gly-H]^+$ at *m/z* 721 and $[M-H]^+$ at *m/z* 629 in the negative FABMS, which corresponds to a molecular weight of 630. A molecular formula of $C_{33}H_{42}O_{12}$ was determined for **1** through high resolution FABMS measurement of the ion at *m/z* 629 [(*m/z* 629.2546, calcd: 629.2598, $[M-H]^+$). In the ^1H and ^{13}C NMR spectra (Tables 1 and 2) of **1**, the presence of four characteristic taxane-type methyl signals [δ_H 1.81 (3H, s), 1.76 (3H, s), 1.75 (3H, s), 1.33 (3H, s); δ_C 28.1 (q), 28.0 (q), 15.4 (q), 13.2 (q)], a doublet signal at δ_H 3.29 (J=10.6 Hz) ascribable to H-3, two quaternary carbon signals at δ_C 76.2 and 66.8 and two olefinic quaternary carbons at δ_C 148.7 and 134.4 indicated that **1** is a 11(15→1)-*abeo*taxoid.[14,15] In addition, three ester groups were identified to consist of a benzoxy and two acetoxy groups in the ^1H and ^{13}C NMR spectra. However, unlike normal *abeo*taxoids, some unusual signals [δ_C 119.8 ppm (s, CD_3OD was employed as solvent unless otherwise specified), δ_H 1.50 (3H, s) and δ_C 22.1 (q)] were observed, which suggested the presence of an orthoacetoxy group in **1**. This orthoacetoxy group was thought to be connected to the taxane skeleton either through three oxygen bridges or two oxygen rings according to the number of double bond equivalents in its molecular formula.

Keywords: *Taxus yunnanensis*; taxaceae; barks; abeotaxoids; taxane glycosides; orthoester; C-2(20) epoxide; taxuyunnanines W-Z; 7-(β-xylosyl)-*N*-methyl-taxol C; 10-deacetyl-10-(β-glucopyranosyl)-yunnanxane.

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Table 1. ^{1}H NMR data of **1**, **1a** and **2** (500 MHz, *J* in Hz, δ in ppm)

Proton	**1**[a]	**1**[b]	**1a**[b]	**2**[b]
H-2	5.75 (1H, d, 10.6)	5.16 (1H, d, 10.6)	5.15 (1H, d, 10.6)	5.16 (1H, d, 10.8)
H-3	3.29 (1H, d, 10.6)	2.72 (1H, d, 10.6)	2.72 (1H, d, 10.5)	2.78 (1H, d, 10.8)
H-5	5.39 (1H, br s)	4.97 (1H, br d, 2.4)	4.99 (1H, br d, 2.4)	3.80 (1H, br d, 2.2)
H-6a	2.31 (1H, m)	1.98 (1H, dt, 4.0, 13.1)	2.01 (1H, m)	1.91 (1H, dt, 4.3, 13.5)
H-6b	1.77 (1H, m)	1.67 (1H, dt, 1.4, 13.8)	1.71 (1H, t, 13.8)	1.59 (1H, t, 12.9)
H-7	5.70 (1H, overlap)	5.26 (1H, dd, 4.3, 12.4)	5.26 (1H, dd, 4.3, 12.5)	5.59 (1H, dd, 4.5, 12.3)
H-9	5.69 (1H, overlap)	5.15 (1H, d, 5.0)	5.14 (1H, d, 5.2)	5.07 (1H, d, 5.0)
H-10	5.56 (1H, d, 4.9)	4.90 (1H, d, 5.2)	5.87 (1H, d, 5.4)	4.92 (1H, d, 5.0)
H-13	4.80 (1H, t, 7.0)	4.37 (1H, t, 7.2)	5.49 (1H, t, 7.2)	4.32 (1H, t, 7.3)
H-14a	2.66 (1H, m)	2.22 (1H, dd, 6.9, 14.7)	2.34 (1H, dd, 6.7, 14.5)	2.19 (1H, dd, 6.9, 14.7)
H-14b	2.56 (1H, m)	2.05 (1H, dd, 7.8, 14.7)	1.93 (1H, dd, 7.4, 14.7)	2.04 (1H, dd, 7.8, 14.7)
CH_3-16	1.76 (3H, s)	1.40 (3H, s)	1.43 (3H, s)	1.40 (3H, s)
CH_3-17	1.33 (3H, s)	1.02 (3H, s)	0.97 (3H, s)	1.00 (3H, s)
CH_3-18	1.75 (3H, s)	1.40 (3H, s)	1.36 (3H, s)	1.37 (3H, s)
CH_3-19	1.81 (3H, s)	1.49 (3H, s)	1.50 (3H, s)	1.45 (3H, s)
H-20a	4.83 (1H, d, 8.3)	4.62 (1H, d, 7.9)	4.65 (1H, d, 8.0)	4.56 (1H, d, 7.8)
H-20b	3.75 (1H, d, 7.8)	3.54 (1H, d, 7.4)	3.57 (1H, d, 7.8)	3.41 (1H, d, 7.8)
OBz-H-3′	8.44 (2H, d, 7.9)	8.06 (2H, dd, 1.4, 8.0)	8.08 (2H, d, 7.6)	8.05 (2H, d, 7.4)
OBz-H-4′	7.40 (2H, t, 7.4)	7.49 (2H, dt, 1.5, 8.0)	7.54 (2H, t, 7.7)	7.45 (2H, t, 7.7)
OBz-H-5′	7.48 (1H, t, 7.5)	7.61 (1H, dt, 1.3, 8.7)	7.67 (1H, t, 7.7)	7.58 (1H, t, 7.4)
CH_3-2″	1.73 (3H, s)	1.50 (3H, s)	1.50 (3H, s)	1.53 (3H, s)
5-OAc	1.66 (3H, s)	1.89 (3H, s)	1.91 (3H, s)	
7-OAc	1.93 (3H, s)	1.97 (3H, s)	1.97 (3H, s)	1.95 (3H, s)
10, 13-OAc			2.03 (3H, s)	
			2.06 (3H, s)	

[a] Data were measured in pyridine-d_5 with reference to the most downfield signal of pyridine-d_5 (δ 8.71 ppm).
[b] Data were measured in CD_3OD with reference to the center peak of CD_3OD (δ 3.30 ppm).

Compound **1** is a polyoxygenated taxoid based on the NMR data (Fig. 1). By analysis of the 2D NMR (^{1}H–^{1}H COSY, HMQC, HMBC and ROESY, see Table 3) data, the oxygenated carbons in **1** were elucidated to be C-2, C-4, C-5, C-7, C-9, C-10, C-13, C-15 and C-20, consistent with normal *abeo*taxoids. The three ester, one benzoxyl and two acetoxyl groups, were assigned to C-9, C-5 and C-7, respectively, due to the presence of the HMBC correlations of H-9 [δ_H 5.15 (1H, d, *J*=5.0 Hz)] to a benzoyl carbonyl carbon at δ_C 166.8 (s), H-5 [δ_H 4.97 (1H, br d, *J*=2.4 Hz)] to an acetyl carbonyl carbon at δ_C 171.3 (s), and H-7 [δ_H 5.26 (1H, dd, *J*=4.3, 12.4 Hz)] to an acetyl carbonyl carbon at δ_C 172.0 (s). Moreover, both H_2-20 [δ_H 4.62 (1H, d, *J*=7.9 Hz) and 3.54 (1H, d, *J*=7.4 Hz)] and the methyl signal at δ_H 1.50 (3H, s, CH_3-2″) showed long-range correlations to a quaternary carbon at δ_C 119.8 (s, C-1″), which strongly

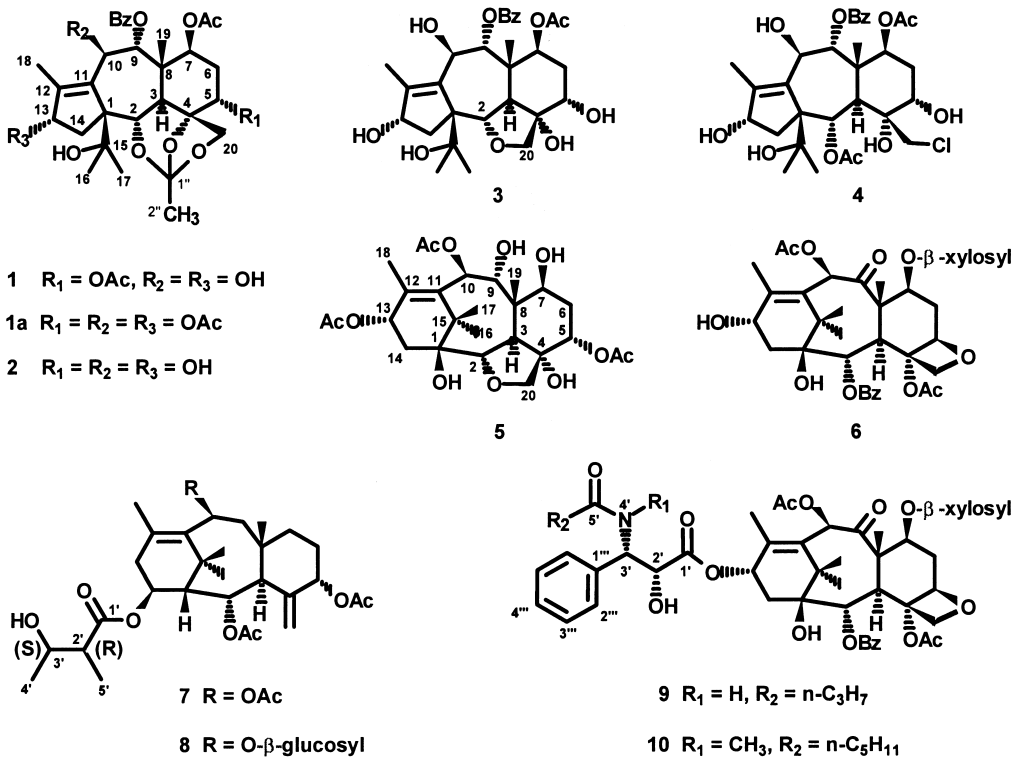

Figure 1. Structures of compounds from *T. yunnanensis*.

Table 2. ^{13}C NMR data of **1** and **2** (125 MHz, δ in ppm)

Carbon	**1**[a]	**1**[b]	**1**[c]	**1** ($\Delta\delta$)[d]	**2**[b]
C-1	66.8 s	67.055 s	67.104 s	0.049	67.1 s
C-2	72.7 d	72.935 d	72.949 d	0.014	72.9 d
C-3	37.3 d	37.775 d	37.788 d	0.013	36.6 d
C-4	81.9 s	82.453 s	82.462 s	0.009	84.3 s
C-5	73.2 d	73.869 d	73.875 d	0.006	71.8 d
C-6	28.1 t	28.336 t	28.353 t	0.017	30.9 t
C-7	70.1 d	71.165 d	71.176 d	0.011	71.5 d
C-8	44.3 s	44.838 s	44.852 s	0.014	45.0 s
C-9	77.1 d	77.427 d	77.453 d	0.026	78.1 d
C-10	67.8 d	68.161 d	68.271 d	0.110	68.2 d
C-11	134.4 s	134.912 s	134.966 s	0.054	135.1 s
C-12	148.7 s	148.948 s	148.946 s	−0.002	148.6 s
C-13	76.2 d	77.105 d	77.235 d	0.130	77.4 d
C-14	42.7 t	42.226 t	42.309 t	0.083	42.2 t
C-15	76.2 s	77.105 s	77.235 s	0.130	77.1 s
C-16	28.0 q	27.520 q	27.621 q	0.101	27.6 q
C-17	28.1 q	27.581 q	27.621 q	0.040	27.7 q
C-18	13.2 q	12.828 q	12.851 q	0.023	12.9 q
C-19	15.4 q	15.357 q	15.397 q	0.040	15.7 q
C-20	70.7 t	71.396 t	71.410 t	0.014	71.3 t
OBz-C-1′	165.9 s	166.840 s	166.829 s	−0.011	167.4 s
OBz-C-2′	130.8 s	131.059 s	131.086 s	0.027	131.3 s
OBz-C-3′	130.3 d	130.960 d	130.974 d	0.014	131.1 d
OBz-C-4′	128.9 d	129.697d	129.705 d	0.008	129.5 d
OBz-C-5′	133.5 d	134.496 d	134.496 d	–	134.2 d
C-1″	119.2 s	119.847 s	119.856 s	0.009	119.6 s
C-2″	22.3 q	22.123 q	22.147 q	0.024	22.3 q
5-OAc	169.7 s	171.336 s	171.307 s	−0.029	
	20.7 q	20.917 q	20.931 q	0.014	
7-OAc	170.1 s	171.967 s	171.942 s	−0.025	172.0 s
	20.9 q	21.958 q	21.976 q	0.018	21.0 q

[a] Signals were measured in pyridine-d_5 with reference to the center peak of the most downfield signals of pyridine-d_5 (δ 149.9 ppm).
[b] Signals were measured in CD_3OD with reference to the center peak of CD_3OD (δ 49.0 ppm).
[c] Signals were measured in CD_3OH with reference to the furthermost carbon (C-5′) signal of the benzoyl group obtained in CD_3OD (δ 134.496 ppm).
[d] $\Delta\delta=\delta$ (CD_3OH)$-\delta$ (CD_3OD).

suggested the connection of the orthoacetoxyl group to C-20 through an oxygen bridge. However, spectral evidence for the presence of the two other oxygen bridges between the orthoacetoxy group and the taxane skeleton were not observed in the HMBC spectrum, even when solvents and NMR parameters were changed. The lack of a suitable crystal for X-ray diffraction compounded the difficulty in determining the structure of this compound.

Nevertheless, the possible formation of the other two oxygen bridges could only occur between the orthoacetoxy group and any two carbons from among C-2, C-4, C-10, C-13 and C-15. Acetylation of **1** with pyridine–Ac_2O (1:1) at room temperature for 24 h yielded a 10,13-diacetate of **1**, which excluded the possibility of the formation of two oxygen bridges at C-10 and C-13. Although acetylation on C-2 was not observed, the possibility of C-2 being substituted with a hydroxy group could not be excluded due to the inherent difficulty in acetylating the hindered C-2 hydroxy group of rearranged taxoids.[10,16] In a comparison with the ^{13}C NMR data of taxuyunnanine K,[9] where the C-2, C-4 and C-15 carbons were hydroxylated, **1** showed downfield chemical shifts at C-2 and C-4 and minimal change at C-15, which suggested that two oxygen atoms are being bridged through the orthoacetoxy group to C-2 and to C-4, respectively. This conclusion was consistent with the Dreiding model of **1**. Theoretically, direct evidence for C-2 being connected to the orthoacetoxy group could be obtained from the observation of $^1H-^{13}C$ long-range correlation between H-2 and C-1″. Unfortunately, such observation was not observed from repeated HMBC experiments under different parameters.

In order to confirm that an orthoacetoxy group is connected to C-2, the ^{13}C NMR spectra of an equal molar of compound **1** were measured in CD_3OH and CD_3OD, respectively. Theoretically, a protonated hydroxy being exchanged to a deuterated hydroxy will cause a β-isotope shift of the ^{13}C NMR signal of the carbon to which the hydroxy group is

Table 3. 2D NMR data of **1** and **2** (CD_3OD, 500 MHz)

Proton	**1**		**2**	
	ROESY	HMBC	ROESY	HMBC
H-2	H-16, 19, 20a	C-1, 3, 4, 8, 14, 15	H-3, 16, 19, 20a	C-1, 14, 15
H-3	H-7	C-1, 2, 4, 7, 8, 9, 19	H-2, 7	C-1, 2, 4, 5, 7, 8, 19, 20
H-5	H-6a, 6b, 20b	C-3, 4, 6, 20, Oac	H-6a, 6b, 20b	C-3, 4, 5
H-6a	H-5, 7	C-4, 5, 7, 8	H-5, 7, 6b	C-4, 5, 7
H-6b	H-5, 20a, 20b	C-7, 8	H-5, 6a	C-5, 7
H-7	H-3, 6a, 10	C-6, 8, 9, 19, Oac	H-3, 6a, 10	C-6, 8, 9, 19, Oac
H-9	H-19	C-3, 7, 8, 10, 11, 19, 1′	H-16, 18, 19	C-3, 8, 10, 11, 1′
H-10	H-7, 18	C-1, 8, 9, 11, 12	H-7, 18	C-1, 8, 9, 11, 12
H-13	H-14a, 17	C-11, 12	H-14a, 14b, 17, 18	C- 11, 12
H-14a	H-13, 14b	C-1, 11, 12, 13, 15	H-13, 14b, 16	C-1, 11, 12, 13, 15
H-14b	H-14a	C-1, 2, 13, 15	H-13, 14a	C-1, 2, 13, 15
CH_3-16	H-2	C-1, 15, 17	H-2, 9, 14a	C-1, 15, 17
CH_3-17	H-13	C-1, 15, 16	H-13	C-1, 15, 16
CH_3-18	H-10	C-11, 12, 13	H-9, 10	C-11, 12, 13
CH_3-19	H-2, 9, 20a	C-3, 7, 8, 9	H-2, 9, 20a	C-3, 7, 8, 9
H-20a	H-6b, 19, 20b	C-3, 5, 1″	H-2, 6b, 19, 20b	C-3, 1″
H-20b	H-6b, 20a	C-3, 4, 5, 1″	H-5, 6b, 20a	C-3, 4, 5, 1″
OBz-H-3′	H-4′	C-1′, 2′, 4′, 5′	H-4′	C-1′, 2′, 4′, 5′
OBz-H-4′	H-3′, 5′	C-2′, 3′, 5′	H-3′, 5′	C-2′, 3′, 5′
OBz-H-5′	H-4′	C-3′, 4′	H-4′	C-3′, 4′
CH_3-2″		C-1″		C-1″

attached.[17] In compound **1**, the δ_C data (Table 2) compared between solvents CD_3OH and CD_3OD showed small β-isotope shifts ($\Delta\delta_{CD3OH-D3OD}$=0.026, 0.011 and 0.006 ppm, respectively) for the esterified C-9, C-7 and C-5, while the hydroxylated C-10 and C-13 gave obvious β-isotope shifts ($\Delta\delta_{CD3OH-CD3OD}$=0.11 and 0.13 ppm, respectively). In addition, the small β-isotope shifts of C-2 and C-4 (0.014 and 0.009 ppm, respectively) indicated that both carbons were not oxygenated by free hydroxyl groups. On the other hand, an apparent β-isotope shift was observed on C-15 (Fig. 2), which strongly supported the presence of a hydroxyl group on this carbon. Thus, the C-1 and C-4 oxygen atoms were determined to be bridged through the orthoacetoxy group.

The stereochemistry of **1** was established by 2D ROESY data (Table 3). ROEs between H-2/Me-16 and -19, H-20a/Me-19, H-7/H-3, H-9/Me-19, H-10/H-7 and Me-18, H-13/Me-17 fixed the oxy-groups at C-2, C-4, C-7, C-9, C-10 and C-13 to be α-, α-, β-, α-, β- and α-oriented, respectively. The ROEs between H-5/H-20b, as well as the small coupling constant of H-5 (J=2.4 Hz), established an α-orientation for the acetoxy group at C-5. Accordingly, **1** was deduced to be 5α, 7β-diacetoxy-9α-benzoxy-2α, 4α, 20-orthoacetoxy-10β, 13α, 15-trihydroxy-11(15→1)-*abeo*-taxa-11-ene, and was given the trivial name of taxuyunnanine W.

Taxuyunnanine X (**2**) was obtained as a white amorphous solid (Fig. 1). The FABMS exhibited $[M+gly]^+$ at m/z 680 and $[M]^+$ at m/z 588, corresponding to a molecular formula of $C_{31}H_{40}O_{11}$, which was confirmed by HRFABMS (m/z $[M-H]^+$ 587.2430, calcd: 587.2492). The close resemblance of the NMR spectra (Tables 1 and 2) to those of **1** suggested **2** to be a related *abeo*taxoid. Compound **2** also contains a benzoxy and an orthoacetoxy group, but differing from **1**, it has only one acetoxy group. The H-5 signal shifted dramatically upfield from δ_H 4.97 (1H, br d, J=2.4 Hz) in **1** to δ_H 3.80 (1H, br d, J=2.2 Hz) in **2**, suggesting **2** to be deacetylated at C-5. Like **1**, the acetyl and benzoyl groups were determined to be at C-7 and C-9, respectively, due to the presence of the HMBC correlations (Table 3) of H-7 to an acetyl carbonyl carbon, and H-9 to a benzoyl carbonyl carbon in **2**. Although only the HMBC correlations of H_2-20 to the quaternary carbon at δ_C 119.8 (s) were observed, the orthoacetoxy group was assigned to C-2, C-4 and C-20 due to the closely similar NMR data to those of **1**. Additionally, **2** showed very similar 2D NMR ($^1H-^1H$ COSY, HMQC, HMBC and ROESY, Table 3) data to those of **1**. Compound **2** was therefore elucidated to be 7β-acetoxy-9α-benzoxy-2α, 4α, 20-orthoacetoxy-5α, 10β, 13α, 15-tetrahydroxy-11(15→1)-*abeo*-taxa-11-ene, and assigned the trivial name of taxuyunnanine X.

An orthoesterified taxane, 4-deacetyl-5-epi-20, *O*-secotaxol-4, 5, 20-orthoacetate had been previously proposed as an intermediate of taxol in its reaction with Meerwein's reagent, which led to a product (20-acetoxy-4-deacetyl-5-epi-20,O-secotaxol) with an opened oxetane ring.[18] In the present study, however, the orthoesterified taxoids, taxuyunnanines W and X, were obtained. We speculate that these compounds might be the biosynthetic precursors of the opened D-ring 11(15→1)-*abeo*taxoids. Although orthoesters have been reported to occur in daphnane and tigliane diterpenoids, the current paper is the first report of the existence of orthoesters in taxane diterpenoids.

Taxuyunnanine Y (**3**) was isolated as white powders (Fig. 1). It has a molecular formula of $C_{29}H_{38}O_{10}$ based on the negative ion HRFABMS peak at m/z 545.2329 ($[M-H]^-$, calcd 545.2387) and the NMR data (see Tables 4 and 5). In addition the signals for a benzoate and an acetate, its ^1H NMR spectrum contained four methyl singlets (δ 1.40, 1.76, 1.84, 2.31) and a methine doublet (δ 3.37, J=11.3 Hz). The ^{13}C NMR (DEPT) spectra showed 20 carbons, with a quaternary carbon at δ 66.7 and two olefinic quaternary carbons at δ 136.3 and 146.7, respectively. These data, in conjunction with the highly oxygenated nature of the molecule established **3** to be an 11(15→1)-*abeo*taxoid substituted by a benzoxy group, an acetoxy and several hydroxy groups. However, complete assignments using 2D NMR (see Table 6) experiments indicated that, unlike normal rearranged taxanes, the large coupling constant between H-9 and H-10 (J=5.1 Hz) was greatly reduced in **3**. Moreover, ^3J long-range correlations between H-20b [δ 4.08 (1H, d, J=7.9 Hz)] and C-2 [δ 77.5 (d)], and between H-2 [δ 5.99 (1H, d, J=11.3 Hz)] and C-20 [δ 75.4 (t)] were observed in the HMBC spectrum, suggesting the presence of an oxygen bridge between C-2 and C-20, forming a C-2(20) tetrahedrofuran ring moiety in **3**. The reason for the small coupling constant between H-9 and H-10 in **3** could be explained by the conformational transformation of the B-ring, which is very common in 5/7/6-skeletal type taxanes. The conformational change of the B-ring caused by the formation of the C-2(20) tetrahedrofuran ring in **3** resulted in a change of the dihedral angle between H-9 and H-10, which in turn led to a change of the coupling constant between H-9 and H-10.

The benzoxy and the acetoxy group were assigned to C-7 and C-9, respectively, based on the presence of HMBC correlations of H-7 [δ 6.29 (1H, dd, J=4.5, 11.9 Hz)] to the

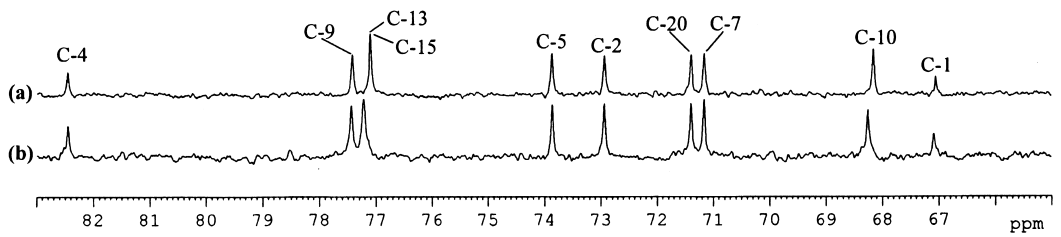

Figure 2. Expansion of the ^{13}C NMR spectra of compound **1** recorded in different solvents: (a) signals were measured in CD_3OD; (b) signals were measured in CD_3OH.

Table 4. ^{1}H NMR data of compounds **3**–**5** (J in Hz, δ in ppm)

Proton	**3**[a,b]	**4**[c,d,e]	**5**[a,d]	**5**[b,c]
H-2	5.99 (d, 11.3)	6.23 (broadened signal)	4.23 (d, 9.3)	4.89 (d, 9.8)
H-3	3.37 (d, 11.3)	2.46 (d, 6.4)	2.39 (d, 9.8)	2.87 (d, 9.8)
H-5	4.58 (br s)	3.95 (br t, 3.6)	4.83 (covered by H_2O)	5.43 (t, 2.8)
H-6a	2.88 (t, 11.9)	2.09 (m)	2.19 (m)	2.88 (m)
H-6b	2.33 (m)	1.70 (m)	1.82 (m)	2.49 (br dd, 4.4, 14.5)
H-7	6.29 (dd, 4.5, 11.9)	5.55 (dd, 4.4, 11.6)	4.14 (dd, 4.6, 11.4)	4.75 (dd, 4.6, 11.3)
H-9	5.91 (d, 5.1)	5.80 (broadened signal)	4.48 (d, 10.4)	5.02 (covered by H_2O)
H-10	5.63 (d, 5.1)	4.72 (d, 8.3)	6.04 (d, 10.4)	6.67 (d, 10.3)
H-13	4.96 (t, 6.9)	4.55 (t, 6.7)	5.73 (dt, 3.2, 8.9)	6.14 (dd, 3.5, 9.4)
H-14a	2.76 (dd, 6.6, 14.0)	2.30 (m)	2.38 (m)	2.93 (10.5, 15.9)
H-14b	2.55 (dd, 7.6, 14.0)	1.74 (m)	1.99 (m)	2.53 (dd, 4.7, 15.6)
CH_3-16	1.40 (s)	1.26 (s)	1.07 (s)	1.32 (s)
CH_3-17	1.84 (s)	1.02 (s)	1.40 (s)	1.71 (s)
CH_3-18	1.76 (s)	1.61 (br s)	2.02 (s)	2.28 (s)
CH_3-19	2.31 (s)	1.59 (s)	1.44 (s)	2.06 (s)
H-20a	4.60 (d, 7.9)	4.54 (d, 9.6)	3.43 (s, H_2-20)	3.91 (d, 8.5)
H-20b	4.08 (d, 7.9)	4.05 (d, 10.4)		3.85 (d, 8.5)
OBz-H-3′	8.57 (d, 8.2)	7.98 (d, 7.5)		
OBz-H-4′	7.23 (t, 7.7)	7.57 (t, 7.4)		
OBz-H-5′	7.34 (t, 7.8)	7.44 (d, 7.6)		
1-OH				6.57 (s)
4-OH				7.27 (s)
7-OH				7.07 (s)
9-OH				8.64 (d, 6.1)
OAc	1.99 (s)	2.04 (3H, s), 1.71 (3H, s)	2.11 (3H, s), 2.06 (3H, s), 2.05 (3H, s)	2.23 (s), 2.07 (s), 2.04 (s)

[a] Measured at 400 MHz.
[b] The data were obtained in pyridine-d_5.
[c] Measured at 500 MHz.
[d] The data were obtained in CD_3OD.
[e] Recorded at 50°C.

Table 5. ^{13}C NMR data of compounds **3**–**5** (δ in ppm)

Carbon	**3**[a,b]	**4**[c,d]	**5**[a,d]
C-1	66.7 s	67.0 s	80.4 s
C-2	77.5 d	71.9 d	84.0 d
C-3	44.0 d	44.3 d	48.6 d
C-4	81.6 s	76.9 s	82.2 s
C-5	68.9 d	70.4 d	71.4 d
C-6	31.4 t	29.5 t	33.5 t
C-7	72.8 d	71.7 d	73.3 d
C-8	44.5 s	46.5 s	46.2 s
C-9	78.7 d	82.0 d	80.0 d
C-10	69.1 d	68.7 d	76.7 d
C-11	136.3 s	139.0 s	137.4 s
C-12	146.7 s	145.8 s	137.6 s
C-13	77.5 d	79.0 d	72.0 d
C-14	41.7 t	41.0 t	37.6 t
C-15	76.2 s	76.5 s	43.3 s
C-16	28.1 q	27.0 q	27.9 q
C-17	28.0 q	28.0 q	23.1 q
C-18	13.5 q	11.9 q	15.2 q
C-19	16.4 q	16.2 q	16.0 q
C-20	75.4 t	52.4 t	74.9 t
OBz-C-1′	166.3 s	168.0 s	
OBz-C-2′	131.4 s	129.8 s	
OBz-C-3′	130.6 d	130.5 d	
OBz-C-4′	128.7 d	129.4 d	
OBz-C-5′	132.9 d	134.0 d	
OAc–C=O	170.3 s	172.4 s	172.1 s
	7-Oac	171.7 s	171.6 s
			172.1 s
OAc–CH_3	21.2 q	22.3 q	21.8 q
		21.8 q	21.5 q
			21.1 q

[a] Measured at 100 MHz.
[b] The data were obtained in pyridine-d_5.
[c] Measured at 125 MHz.
[d] The data were obtained in CD_3OD.

acetyl carbonyl carbon at δ 170.3, and H-9 [δ 5.91 (1H, d, J=5.1 Hz)] to the benzoyl carbonyl carbon at δ 166.3.

The stereochemistry of **3** was determined by application of 2D ROESY experiment (Table 6). The ROESY cross-peaks of H-2/CH_3-19, H-7/H-3, H-9/CH_3-19, H-10/CH_3-18 and H-13/CH_3/16 established H-2, H-7, H-9, H-10 and H-13 as in the β-, α-, β-, α- and β-configuration, respectively. The β-oriented 4-CH_2O- was deduced from the ROESY correlation of H-20a/CH_3-19, whereas, the 5-OH was assigned as α-oriented due to the small coupling constant of H-5 [δ 4.58 (1H, br s)].

Taxuyunnanine Y is the second naturally occuring rearranged taxane with a C-2(20) tetrahedrofuran ring moiety. Taxuyunnanine E, the first of this type of taxanes was isolated previously by us from the same species.[5]

Taxuyunnanine Z (**5**) was obtained as a white amorphous solid (Fig. 1) with a molecular formula of $C_{26}H_{38}O_{11}$ based on negative FAB mass spectrometry and ^{1}H and ^{13}C NMR spectra (Tables 4 and 5), which was confirmed by HRFABMS (Found: m/z 525.2272 $[M-H]^-$, calcd 525.2336). Its ^{1}H NMR spectrum showed a typical one-proton doublet due to H-3 [δ_H 2.39 (1H, d, J=9.8 Hz), CD_3OD as solvent] and four methyl singlets owing to CH_3-16, 17, 18 and 19 [δ_H 1.07, 1.40, 2.02 and 1.44, each in 3H], along with three acetyl methyl groups at δ_H 2.05 (3H, s), 2.06 (3H, s) and 2.11 (3H, s). These data, along with the ^{13}C NMR (including DEPT) spectra suggested that **5** was a baccatin IV derivative. However, in the HMBC spectrum of **5** (Table 6), the notable ^{3}J correlations of H-2 to C-20 and H_2-20 to C-2 showed that it contained a C-2(20)

Table 6. 2D ROESY and HMBC data of compounds **3** and **5**

Proton	**3**[a]		**5**[b]	
	ROESY	HMBC	ROESY	HMBC
H-2	H-19	C-8, 14, 20	H-19	C-1, 3, 8, 14, 20
H-3	H-7, 14b	C-1, 2, 3, 4, 7, 8, 19	H-7	C-2, 8, 19
H-5	H-6	C-7	H-6a, 6b, 20	C-4, 6, OAc[c]
H-6a	H-5, 6b	C-7	H-6b,	
H-6b	H-5, 6a	C-7	H-6a	C-4, 5, 7, 8
H-7	H-3, 6b	C-3, 6, 8, 9, 19, OAc[c]	H-3	C-7, 19
H-9	H-10, 19	C-3, 8, 10, 11, 19, 1′	H-19	C-7, 8, 10, 19
H-10	H-9, 18	C-1, 8, 9, 11, 12	H-7, 18	C-9, 11, 12, 15, OAc[c]
H-13	H-16, 14a	C- 11, 12	H-14a, 16	C-11, 12, OAc*
H-14a	H-13, 14b, 17	C-1, 11, 12, 15	H-13, 14b	C-1, 2, 12, 13
H-14b	H-3, 14a	C-1, 15	H-14a	C-1, 2, 13, 15
CH_3-16	H-13	C-1, 15, 17	H-13	C-1, 11, 15, 17
CH_3-17	H-14a	C-1, 15, 16	H-2, 9	C-1, 11, 15, 16
CH_3-18	H-10	C-11, 12, 13	H-10	C-11, 12, 13
CH_3-19	H-2, 9	C-3, 7, 8, 9	H-2, 9	C-3, 7, 8, 9
H-20a	H-3, 19, 20b	C-3, 4	H-3, 19	C-2, 3, 4
H-20b	H-20a	C-2, 3, 4		
OBz-H-3′	H-4′	C- 1′, 2′, 3′, 5′		
OBz-H-4′	H-3′, 5′	C-2′, 3′, 4′		
OBz-H-5′	H-4′	C-3′		

[a] Recorded in pyridine-d_5.
[b] Recorded in CD_3OD.
[c] The carbonyl carbon of acetoxy group.

tetrahedrofuran ring moiety as was the case in **3**, instead of a normal C-5(20) oxetane ring as existed in baccatin IV and its derivatives. Despite the intense water peak that prevented the H-5 signal from being seen the ^{1}H NMR spectrum of **5** conducted in CD_3OD, the HMBC cross peak between the concealed H-5 signal and one of the acetyl carbonyl carbons was still observed. Using pyridine-d_5 as the NMR solvent, the expected correlation for the H-5 signal was clearly evident. The other two acetoxy groups were assigned to C-10 and C-13, respectively, based on the presence of the HMBC correlations of H-10 [δ_H 6.04 (1H, d, J=10.4 Hz)] and H-13 [δ_H 5.73 (1H, dt, J=3.2, 8.9 Hz)] to two other acetyl carbonyl carbons. Since all these acetyl groups and the hydroxyls at C-1, -7, and -9 have been unequivocally assigned, the remaining hydroxyl must be at C-4 in **5**. This was confirmed by the significant upfield chemical shift at δ_C 82.2 (s).[5]

Although the relative stereochemistry of **5** could be deduced from analysis of the proton spin system, the more definitive assignments were obtained by a 2D ROESY experiment (Table 6). The presence of the NOEs of H-2/H-19, H-7/H-3, H-9/H-19, H-10/H-7, H-13/H-16, and H-20/H-19 established the orientation of H-2, H-7, H-9, H-10, H-13 and 4-CH_2O- as β-, α-, β-, α-, β- and β-, respectively. The acetoxy group of C-5 in **5** was α-oriented according to the ROE correlations between H-5 and H_2-20, in accordance with the small coupling constant of H-5.

10-Deacetyl-10-(β-glucopyranosyl)-yunnanxane (**8**) was a white amorphous solid (Fig. 1). Its molecular formula was determined as $C_{35}H_{54}O_{13}$ by HRFABMS (Found: m/z 681.3466 $[M-H]^-$, calcd 681.3486). In the ^{1}H NMR spectra, the presence of four characteristic taxane-type methyls at δ_H 1.22 (3H, s), 1.71 (3H, s), 2.02 (3H, br d, J=1.6 Hz) and 0.86 (3H, s) at CH_3-16, 17, 18 and 19, and a pair of broad singlets at δ_H 5.27 and 4.85 attributed to H_2-20, suggested the compound to be a taxane diterpenoid with a C-4(20) double bond. The ^{1}H and ^{13}C NMR spectra also revealed that **8** had two acetoxy groups, a glucose moiety and an α-methyl-β-hydroxyl-butanoyl residue. The α-methyl-β-hydroxyl-butanoyl residue was observed as a base peak at m/z 117 $[CH_3CH(OH)CH(CH_3)COO]^-$ in the FABMS. Further study of the NMR spectra revealed **8** as a taiwanxan-type taxoid. For comparison purpose, a very similar structure compound, yunnanxane (**7**),[19] was used to aid in the structural elucidation of **8**. The NMR spectra of the two compounds were shown to be very similar, with the aglycone moiety of **8** differing from **7** only by the absence of an acetoxy group. The HMBC correlations between H-10 and the anomeric C-1″, and between the glucose H-1″ and C-10 revealed that the 10-acetyl group in **7** was replaced by a glucosyl moiety in **8**. The stereochemistry of **8** was confirmed by analysis of the ROESY spectral data and the coupling pattern of its ^{1}H NMR spectrum. Hence, **8** was deduced as 10-deacetyl-10-(β-glucopyranosyl)-yunnanxane.

This majority of natural taxoid glycosides have been found as xylosides, with glycosylation exclusively at C-7. To date, only one taxoid glucoside, a 5/7/6-skeletal taxane containing a glucosyl moiety at C-5, had been reported in the literature.[20] Compound **8** is the second natural taxane glucoside, but the first in a 6/8/6 taxane skeleton.

7-(β-Xylosyl)-*N*-methyl-taxol C (**10**) was obtained as white needles (Fig. 1). Negative FABMS showed $[M-H]^-$ ion peak at m/z 994, in accordance with a molecular formula of $C_{52}H_{69}NO_{18}$, which was verified by HRFABMS (Found: m/z 995.4576 $[M-H]^-$, calcd 995.4515). Analysis of the NMR spectra indicated that **10** is a derivative of **9**, a paclitaxel-type taxane xyloside previously reported from the same plant,[10] with their difference occurring on the C-13 side chain. In the highfield region of the NMR spectra, the

presence of the signals for a methyl [δ_H 3.13 (3H, s), δ_C 33.8 (q)] and two methylene [δ_C 22.8 (t) and 31.7 (t)] groups in **10** in comparison to **9**, suggested that **10** was substituted by an *N*-methyl-*N*-hexanoylphenylisoserine side chain as found in *N*-methyltaxol C[21] instead of an *N*-butanoylphenylisoserine side chain in **9**. The FABMS base peak at *m/z* 292, which correspond to a fragment ion of $[C_5H_{11}CON(CH_3)CH(C_6H_5)CH(OH)COO]^-$ strongly supported this deduction.

The pentyl group at C-5′ was established by $^1H-^1H$ COSY experiment, and the N-methylation was confirmed by HMBC correlations of H-3′ to C–(N–CH_3) and H–(N–CH_3) to C-3′ and C-5′. In addition, HMBC correlations of H-10 to a carbonyl carbon at δ_C 170.0 (s), and H-7 to the anomeric C-1‴′ and the xylosyl H-1‴′ to C-7, confirmed the respective assignment of an acetoxyl and a xylosyl group to C-10 and C-7. Compound **10** was thus elucidated as 7-(β-xylosyl)-*N*-methyl-taxol C. Although the paclitaxel derivatives with a C-7 xylosyl group are very common in nature, the *N*-methylated paclitaxel-equivalent compounds are rare, with only two examples being reported to date,[21,22] and the co-occurrence of xylosidation and *N*-methylation in the same molecule has not been reported previously.

The known compounds taxuchin B (**4**) (Fig. 1) and yunnanxane (**7**) (Fig. 1) were identified by comparison of their spectroscopic data (^1H, ^{13}C NMR, MS) with those reported in literatures.[12,13] Taxuchin B, originally isolated from *Taxus chinensis* by Wei-Shuo Fang et al.,[12] is the only natural chlorine-containing taxane reported to date, and its existence in *T. yunnanensis* is being recorded for the first time.

3. Experimental

3.1. General

1D and 2D NMR experiments were performed either on a Bruker AM-400 or DRX-500 spectrometer. Unless otherwise specified, chemical shifts (δ) were expressed in ppm with reference to the solvent signals. FABMS and HRFABMS were taken on a VG Auto Spec-3000 or a Finnigan MAT 90 instrument. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectral data were obtained on a UV 210A spectrometer. Optical rotations were carried out on a HORIBA SEPA-300 High Sensitive Polarimeter or Perkin–Elmer model 241 Polarimeter. Column chromatogrphy was performed either on silica gel (200–300 mesh, Qingdao Marine Chemical Inc., China), silica gel H (10–40 μm, Qingdao Marine Chemical Inc., China), Lichroprep RP_{18} gel (40–63 μm, Merck, Darmstadt, Germany), or on MCI gel (70–150 μm, Mitsubishi Chemical Corporation, Tokyo, Japan). Fractions were monitored by TLC on silica gel and spots were visualized by heating plates sprayed with 10% H_2SO_4 in EtOH. All solvents were distilled prior to use.

3.2. Plant material

The bark of *T. yunnanensis*, Cheng et L. K. Fu (Taxaceae) was collected in Lijiang Prefecture of Yunnan Province of People's Republic of China. A voucher specimen (No. YAF-97-18) has been deposited at the Yunnan Academy of Forestry, Kunming, Yunnan, People's Republic of China.

3.3. Extraction and isolation

The barks of *T. yunnanensis*, Cheng et L. K. Fu (Taxaceae, collected in Lijiang Prefecture of Yunnan Province of People's Republic of China) were dried, milled, extracted (EtOH) and fractionated on Si gel column chromatography (2.0 kg, 200–300 mesh)) by gradient elution with $CHCl_3$ by increasing concentration of Me_2CO [$CHCl_3$–Me_2CO/100:0 (eluate F1, 25 l), 90:10 (eluates F2–F62, 600 ml), 80:20 (eluates F63–F110, 600 ml), 70:30 (eluates F111–F144, 600 ml), 0:100 (eluates F145–F172, 600 ml), respectively] to afford 172 fractions. Fraction 2 (7.5 g) was subjected to four Si gel (200–300 mesh) chromatographic columns (200 g Si gel each), eluting with $CHCl_3$–Me_2CO (7:1), petroleum ether–EtOAc (5:2), petroleum ether–Me_2CO (4:1) and cyclohexane–EtOAc (2:1), respectively, to yield compound **7** (207 mg). The pooled fractions F111–F118 (7.2 g) were rechromatographed on silica gel (150 g, 200–300 mesh), eluting with $CHCl_3$–*i*-PrOH (9:1) to afford 12 fractions (200 ml each). Of the 12 fractions, the 5th was subjected to column chromatography over RP_{18} silica gel (80 g, 40–63 μm), eluting with acetonitrile–H_2O (3:7), followed by preparative TLC using $CHCl_3$–*i*-PrOH (9:1) as the developing system to yield compound **1** (25 mg); and the 9th was chromatographed over RP_{18} silica gel (80 g, 40–63 μm) eluting with acetonitrile–H_2O (2:8), then over Si gel (100 g, 200–300 mesh) eluting with $CHCl_3$–*i*-PrOH (7:1) to afford **2** (3 mg). The pooled fractions F119–F143 (27.5 g) were chromatographed on Si gel (500 g, 200–300 mesh) eluting with $CHCl_3$–CH_3OH (9:1), on RP_{18} gel (80 g, 40–63 μm) eluting with aqueous CH_3OH (65%) and on Si gel (200 g, 200–300 mesh) with $CHCl_3$–*i*-PrOH (6:1) to afford compounds **6** (4 mg) and **10** (11 mg). The Me_2CO fractions (F145–F172) were combined, filtered and evaporated to dryness to afford 38 g of a residue, which was subjected to further Si gel (500 g, 200–300 mesh) column chromatography separation using $CHCl_3$–MeOH as the eluents (gradient ratios:19:1, 15:1, 9:1, 7:1, 4:1, 1:1) in ascending order of polarity to provide 70 fractions (500 ml each). The 41st to 58th fractions of the 70 fractions were pooled (16.5 g) and further separated using CC sequentially on Si gel (300 g, 200–300 mesh) with $CHCl_3$–CH_3OH (7:1), on MCI gel (100 g) with a gradient of 50% aqueous CH_3OH to 100% CH_3OH, on RP_{18} gel (80 g, 40–63 μm) with aqueous acetonitrile (30% CH_3CN→70% CH_3CN), on Si gel (100 g, 200–300 mesh) with $CHCl_3$–*i*-PrOH (4:1) to provide compounds **3** (11 mg), **4** (3 mg), **5** (8 mg) and a compound **8** containing fraction (110 mg). The last fraction was subjected to preparative TLC separation using $CHCl_3$–*i*-PrOH (3:1) as developing solvents to afford compound **8** (18 mg).

3.3.1. Taxuyunnanine W (1). White amorphous powder, $[\alpha]_D^{14.9}=-10.71°$ (*c* 0.35, MeOH); UV (MeOH) λ_{max} (log ε)=273 (3.5), 253 (3.6), 231 (4.4), 202 (4.6) nm; IR (KBr) ν_{max}=3432, 2927, 2862, 1743, 1723, 1448, 1404, 1372, 1328, 1274, 1174, 1147, 1116, 1049, 1002, 976, 945, 923, 888, 851, 810, 765, 715 cm^{-1}; ^1H NMR data, see Table 1; ^{13}C NMR data, see Table 2; negative FABMS (glycerol)

m/z (%)=[M+gly-H]$^-$ 721 (3), [M−H]$^-$ 629 (12), 505 (3), 339 (5), 175 (2), 121 (100), 60 (21); HRFABMS *m/z* [M−H]$^-$ 629.2546 (calcd for $C_{33}H_{41}O_{12}$ 629.2598).

Acetylation of **1**: The sample of **1** (5 mg) was acetylated in 1.0 ml pyridine–Ac_2O (1:1) at room temperature for 24 h to afford **1a** (5 mg). Further acetylation of **1a** in 1.0 ml pyridine–Ac_2O (1:1) at room temperature for 20 days to provide the unchanged product. **1a**: IR (KBr) ν_{max}=3541, 2922, 2857, 1740, 1466, 1404, 1372, 1269, 1239, 1175, 1098, 1069, 10 47, 925, 890, 851, 805, 713, 604, 558 cm^{-1}; ^{1}H NMR data, see Table 1; negative FABMS (glycerol) *m/z* (%)=[M+gly]$^-$ 806 (2), [M]$^-$ 714 (3), 671 (6), 629 (1), 490 (1), 431 (2), 339 (3), 311 (13), 277 (9), 244 (6), 184 (72), 152 (17), 121 (100), 92 (44), 59 (90).

3.3.2. Taxuyunnanine X (2). White amorphous powder, $[\alpha]_D^{15.8}$=−8.33° (*c* 0.15, MeOH); UV (MeOH) λ_{max} (log ε)=203 5 (4.6), 229 (4.3) nm; IR (KBr) ν_{max}=3632, 3614, 3446, 3415, 3120, 3108, 3064, 2981, 2930, 2860, 1717, 1609, 1447, 1398, 1373, 1278, 1174, 1148, 1115, 1070, 1047, 997, 979, 938, 923, 849, 763, 715, 687 cm^{-1}; ^{1}H NMR data, see Table 1; ^{13}C NMR data, see Table 2; negative FABMS (glycerol) *m/z* (%)=[M+gly]$^-$ 680 (15), [M]$^-$ 588 (31), 462 (6), 369 (10), 339 (10), 325 (12), 311 (8), 277 (32), 184 (100), 152 (11), 121 (98), 92 (48); HRFABMS *m/z* [M−H]$^-$ 587.2430 (calcd for $C_{31}H_{39}O_{11}$ 587.2492).

3.3.3. Taxuyunnanine Y (3). White powders, $[\alpha]_D^{14.3}$=+20.00° (*c* 0.60, CH_3OH); UV (MeOH) λ_{max} (log ε)=274.5 (3.4), 231 (4.3), 202 (4.4) nm; IR ν_{max} (KBr)=3444, 2982, 2949, 1730, 1652, 1447, 1371, 1328, 1278, 1177, 1118, 1070, 1026, 1007, 983, 948, 883, 843, 810, 759, 716, 692, 634 cm^{-1}; ^{1}H NMR data, see Table 4, ^{13}C NMR data, see Table 5; negative FABMS *m/z* (%)=545 [M−H]$^-$ (13), 529 (6), 509 (3), 479 (3), 431 (5), 381 (5), 353 (6), 339 (82), 325 (100), 311 (82), 297 (32), 283 (12), 255 (26), 235 (10), 197 (5), 173 (6), 147 (8), 121 (64), 97 (11), 80 (22); HRFABMS *m/z* 545.2329 [M−H]$^-$, calcd 545.2387.

3.3.4. Taxuchin B (4). White needles, ^{1}H NMR data, see Table 4, ^{13}C NMR data, see Table 5; negative FABMS *m/z* (%)=623 [M−H]$^-$ (78), 581 (12), 502 (8), 384 (6), 339 (7), 325 (10), 219 (3), 121 (100), 77 (8); HRFABMS *m/z* 623.2178 [M−H]$^-$, calcd for $C_{31}H_{40}O_{11}Cl$ 623.2259.

3.3.5. Taxuyunnanine Z (5). White powders; $[\alpha]_D^{14.8}$=+89.37° (*c* 0.40, CH_3OH); UV (MeOH) λ_{max} (log ε): nm; IR ν_{max} (KBr)=3460, 2944, 1734, 1656, 1432, 1374, 1244, 1041, 1019, 954, 881, 739, 709, 688, 612, 525 cm^{-1}; ^{1}H NMR data, see Table 4, ^{13}C NMR data, see Table 5; negative FABMS *m/z* (%)=525 [M−H]$^-$ (21), 483 (8), 465 (6), 423 (7), 406 (3), 339 (11), 311 (20), 207 (10), 152 (10), 99 (19), 59 (100); HRFABMS *m/z* 525.2272 [M−H]$^-$, calcd 525.2336.

3.3.6. 7-(β-Xylosyl)-baccatin III (6). White powders. UV (MeOH) λ_{max} (log ε)=202 (4.3), 230.5 (4.2), 274 (3.0) nm; IR ν_{max} (KBr)=3486, 2940, 1719, 1453, 1374, 1316, 1247, 1178, 1097, 1071, 1048, 1025, 979, 909, 778, 710 cm^{-1}; positive FABMS *m/z* (%)=719 [M+H]$^+$ (15), 659 (6), 587 (15), 527 (10), 509 (3), 449 (2), 387 (2), 327 (6), 299 (4), 237 (6), 193 (8), 133 (9), 105 (100), 77 (15); HRFABMS *m/z* 719.2870 [M+H]$^+$, calcd 719.2915.

3.3.7. Yunnanxane (7). Amorphous solid, IR ν_{max} (KBr)=3458, 2975, 2934, 2360, 2255, 1732, 1645, 1453, 1373, 1318, 1237, 1183, 1107, 1068, 1019, 959, 913, 878, 836, 733, 606, 562 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.77 (3H, s, CH_3-19), 1.05 (3H, s, CH_3-17), 1.08 (3H, d, *J*=7.2 Hz, H-5′), 1.13 (3H, d, *J*=6.3 Hz, H-4′), 1.17 (1H, br s, 3′-OH), 1.22 (1H, m, H-7a), 1.55 (1H, br d, *J*=4.1 Hz, H-9a), 1.59 (3H, s, CH_3-16), 1.74 (2H, m, H_2-6), 1.83 (1H, d, *J*=1.4 Hz, H-1), 1.88 (1H, m, H-7b), 1.95 (3H, s, OAc), 1.99 (3H, s, OAc), 2.02 (3H, s, CH_3-18), 2.11 (3H, s, OAc), 2.30 (1H, m, H-13a), 2.31 (1H, m, H-9b), 2.35 (1H, m, H-2′), 2.78 (1H, dd, *J*=9.2, 19.0 Hz, H-13b), 2.85 (1H, d, *J*=6.6 Hz, H-3), 3.80 (1H, f, H-3′), 4.74 (1H, s, H-20a), 4.95 (1H, dd, *J*=4.7, 9.1 Hz, H-14), 5.20 (1H, s, H-20b), 5.21 (1H, br d, *J*=6.5 Hz, H-5), 5.28 (1H, dd, *J*=1.9, 6.6 Hz, H-2), 5.98 (1H, dd, *J*=5.6, 12.0 Hz, H-10); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 13.7 (q, C-5′), 20.6 (q, C-4′), 20.8 (q, C-18), 21.2 (2C, q, 2×OAc–CH_3), 21.7 (q, OAc–CH_3), 22.4 (q, C-19), 25.3 (q, C-16), 28.8 (t, C-6), 31.6 (q, C-17), 33.7 (t, C-7), 37.2 (s, C-15), 39.4 (t, C-13), 39.6 (s, C-8), 42.1 (d, C-3), 43.8 (t, C-9), 46.9 (d, C-2′), 59.1 (d, C-1), 69.3 (d, C-3′), 70.0 (d, C-10), 70.4 (d, C-2), 70.6 (d, C-14), 78.1 (d, C-5), 116.8 (t, C-20), 135.4 (s, C-11), 134.5 (s, C-12), 142.2 (s, C-4), 169.7 (s, OAc–C=O), 169.8 (s, OAc–C=O), 170.1 (s, OAc–C=O), 174.5 (s, C-1′); positive FABMS *m/z* (%)=563 [M+H]$^+$ (17), 503 (30), 445 (4), 385 (14), 343 (19), 315 (10), 265 (17), 249 (14), 157 (62), 133 (100).

3.3.8. 10-Deacetyl-10-(β-glucosyl)-yunnanxane (8). Colorless amorphous solid, $[\alpha]_D^{14.4}$=−4.17° (*c* 0.90, CH_3OH); UV (MeOH) λ_{max} (log ε)=206.5 (4.0) nm; IR ν_{max} (KBr)=3462, 2922, 1730, 1638, 1430, 1375, 1243, 1197, 1105, 1074, 1019, 976, 941, 908, 876, 835, 609 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD) δ_H 0.86 (3H, s, CH_3-19), 1.09 (3H, d, *J*=7.1 Hz, H-5′), 1.16 (3H, d, *J*=6.4 Hz, H-4′), 1.22 (3H, s, CH_3-16), 1.23 (1H, m, H-7a), 1.67 (1H, dd, *J*=4.6, 14.7 Hz, H-9a), 1.71 (3H, s, CH_3-17), 1.81 (2H, m, H_2-6), 1.87 (1H, br d, *J*=2.2 Hz, H-1), 2.00 (3H, s, OAc), 2.01 (1H, m, H-7b), 2.02 (3H, br d, *J*=1.6 Hz, CH_3-18), 2.18 (3H, s, OAc), 2.42 (1H, m, H-9b), 2.43 (1H, m, H-2′), 2.48 (1H, dd, *J*=4.8, 19.0 Hz, H-13a), 2.86 (1H, dd, *J*=9.2, 19.0 Hz, H-13b), 2.97 (1H, d, *J*=6.5 Hz, H-3), 3.17 (1H, m, glc-H-5″), 3.26 (1H, t, *J*=7.9 Hz, glc-H-2″), 3.31 (1H, m, glc-H-4″), 3.32 (1H, m, glc-H-3″), 3.68 (1H, dd, *J*=5.8, 12.0 Hz, glc-H-6″a), 3.86 (1H, m, glc-H-6″b), 3.87 (1H, m, H-3′), 4.29 (1H, d, *J*=7.6 Hz, glc-H-1″), 4.85 (1H, s, H-20a), 5.01 (1H, dd, *J*=5.0, 9.2 Hz, H-14), 5.26 (1H, br t, *J*=2.8 Hz, H-5), 5.27 (1H, s, H-20b), 5.38 (1H, dd, *J*=6.7, 12.2 Hz, H-10), 5.41 (1H, dd, *J*=2.3, 6.6 Hz, H-2); ^{13}C NMR (100 MHz, CD_3OD) δ_C13.4 (q, C-5′), 20.5 (q, C-4′), 21.4 (q, C-18), 21.5 (q, OAc–CH_3), 21.9 (q, OAc–CH_3), 23.0 (q, C-19), 25.4 (q, C-17), 30.0 (t, C-6), 32.0 (q, C-16), 35.1 (t, C-7), 38.5 (s, C-15), 40.7 (s, C-8), 40.7 (t, C-13), 43.7 (d, C-3), 45.9 (t, C-9), 48.5 (d, C-2′), 60.9 (d, C-1), 62.7 (t, glc-C-6″), 70.2 (d, C-3′), 71.8 (d, C-14), 71.8 (d, glc-C-4″), 72.1 (d, C-2), 72.8 (d, C-10), 75.0 (d, glc-C-2″), 77.9 (d, glc-C-5″), 78.4 (d, glc-C-3″), 79.9 (d, C-5), 100.1 (d, glc-C-1″), 117.4 (t, C-20), 137.2 (s, C-11), 138.2 (s, C-12), 144.2 (s, C-4),

171.7 (2C, s, 2×OAc−C═O), 175.9 (s, C-1′); negative FABMS *m/z* (%)=681 $[M-H]^-$ (14), 325 (23), 179 (24), 117 (100), 59 (42); HRFABMS *m/z* 681.3466 $[M-H]^-$, calcd 681.3486.

3.3.9. 7-(β-Xylosyl)-*N*-methyl-taxol C (10). White needles, mp 220°C; $[\alpha]_D^{20}$=active (CH_3OH); UV (MeOH) λ_{max} (log ε)=213.5 (4.33), 202 (4.41) nm; IR ν_{max} (KBr)=3450, 2937, 1722, 1603, 1448, 1399, 1371, 1313, 1247, 1177, 1106, 1069, 1047, 1025, 981, 854, 778, 710, 609 cm^{-1}; ^1H NMR (500 MHz, Pyridine-d_5) δ_H 0.74 (3H, t, *J*=7.0 Hz, CH_3-10′), 1.12 (2H, m, H-9′), 1.18 (2H, m, H-8′), 1.42 (3H, s, CH_3-17), 1.61 (2H, m, H-7′), 1.67 (3H, s, CH_3-16), 2.06 (3H, s, 10-OAc), 2.19 (3H, s, CH_3-19), 2.32 (2H, t, *J*=7.5 Hz, H-6′), 2.37 (3H, br s, CH_3-18), 2.42 (1H, m, H-6a), 2.51 (3H, s, 4-OAc), 2.99 (1H, dd, *J*=6.1, 15.4 Hz, H-14a), 3.11 (H, m, H-6b), 3.11 (H, m, H-14b), 3.13 (3H, s, N-CH_3), 3.61 (1H, t, *J*=11.0 Hz, xyl-H-5′′′′a), 3.82 (1H, t, *J*=8.0 Hz, xyl-H-2′′′′), 4.06 (1H, t, *J*=8.6 Hz, xyl-H-3′′′′), 4.10 (1H, m, xyl-H-4′′′′), 4.25 (1H, dd, *J*=5.1, 11.3 Hz, xyl-H-5′′′′b), 4.35 (1H, d, *J*=6.7 Hz, H-3), 4.44 (1H, AB d, *J*=8.3 Hz, H-20a), 4.53 (1H, AB d, *J*=8.3 Hz, H-20b), 4.80 (1H, d, *J*=7.4 Hz, xyl-H-1′′′′), 4.87 (1H, dd, *J*=7.1, 10.1 Hz, H-7), 5.24 (1H, d, *J*=9.0 Hz, H-5), 5.65 (1H, br d, *J*=3.7 Hz, H-2′), 6.29 (1H, d, *J*=6.7 Hz, H-2), 6.72 (1H, t, *J*=9.4 Hz, H-13), 6.78 (1H, br d, *J*=3.5 Hz, H-3′), 7.13 (1H, s, H-10), 7.33 (2H, t, *J*=7.5 Hz, Bz-H-4′′), 7.33 (2H, t, *J*=8.0 Hz, H-4′′′), 7.41 (2H, t, *J*=7.3 Hz, Bz-H-5′′), 7.41 (2H, t, *J*=7.6 Hz, H-3′′′), 7.75 (2H, d, *J*=7.7 Hz, H-2′′′), 8.30 (2H, d, *J*=7.4 Hz, Bz-H-3′′); ^{13}C NMR (125 MHz, Pyridine-d_5) δ_C 11.6 (q, C-19), 14.1 (q, C-10′), 14.7 (q, C-18), 21.0 (q, 10-OAc−CH_3), 22.0 (q, C-16), 22.7 (q, 4-OAc−CH_3), 22.8 (t, C-9′), 25.3 (t, C-7′), 26.9 (q, C-17), 31.7 (t, C-8′), 33.8 (t, C-6′), 33.8 (q, N−CH_3), 36.5 (t, C-6), 36.5 (t, C-14), 44.3 (s, C-15), 47.8 (d, C-3), 57.9 (d, C-3′), 58.4 (s, C-8), 67.1 (t, xyl-C-5′′′′), 70.7 (d, xyl-C-4′′′′), 71.7 (d, C-13), 72.7 (d, C-2′), 74.6 (d, xyl-C-2′′′′), 75.7 (d, C-2), 76.6 (t, C-20), 77.1 (d, C-10), 77.9 (s, C-1), 77.9 (d, xyl-C-3′′′′), 80.4 (d, C-7), 81.5 (s, C-4), 84.4 (d, C-5), 105.4 (d, xyl-C-1′′′′), 127.9 (d, C-4′′′), 128.9 (d, Bz-C-4′′), 128.9 (d, C-3′′′), 129.1 (d, C-2′′′), 130.4 (d, Bz-C-3′′), 131.1 (d, Bz-C-2′′), 133.3 (d, Bz-C-5′′), 134.2 (s, C-11), 138.7 (s, C-1′′′), 141.1 (s, C-12), 166.4 (s, Bz-C-1′′), 170.0 (s, 10-OAc−C═O), 170.8 (s, 4-OAc−C═O), 174.4 (s, C-1′), 174.4 (s, C-5′), 203.1 (s, C-9); negative FABMS *m/z* (%)=994 $[M-H]^-$ (2), 933 (1), 855 (1), 774 (1), 701 (2), 477 (2), 384 (2), 292 (100), 219 (2), 121 (17), 77 (3); HRFABMS *m/z* 995.4576 $[M-H]^-$, calcd 995.4515.

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