Journal of Natural Products
Vol. 58, No. 8, pp. 1153-1159, August 1995

FOUR NEW TAXANES FROM THE ROOTS OF *TAXUS YUNNANENSIS*

HONGJIE ZHANG, HANDONG SUN,*

Phytochemistry Laboratory, Kunming Institute of Botany, Academia Sinica, Kunming 650204, Yunnan, People's Republic of China

and YOSHIO TAKEDA

Faculty of Integrated Arts and Sciences, University of Tokushima, Tokushima 770, Japan

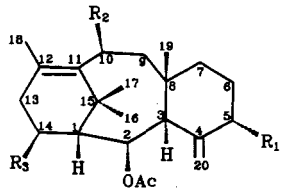
ABSTRACT.—Four new taxoids [**1**–**4**] were isolated from the roots of *Taxus yunnanensis*. Three of the new compounds were analogues of taxuyunnanine C and the fourth was a 2-deacetoxytaxuyunnanine C derivative. The structures were elucidated by spectroscopic methods.

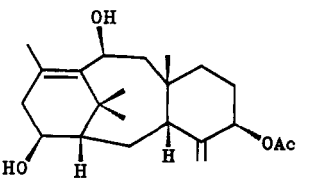
Since the discovery of the natural product paclitaxel (=Taxol®) (1) and its clinically useful anticancer activity, investigations on *Taxus* spp. have brought more than one hundred new compounds into the taxane diterpenoid family (2). However, much of this work has concentrated on the needles because they can be collected without destruction of the trees and on the bark because of its high paclitaxel content. Work on the roots has been largely ignored, but our study on the roots of *T. yunnanensis* C.Y. Cheng, W.C. Cheng & L.K. Fu (Taxaceae) showed that they were rich in taxane diterpenoids, including paclitaxel (3–5). In continuation of this research, we report herein four additional new taxoids, named taxuyunnanines G [**1**], H [**2**], I [**3**], and J [**4**], respectively, from an extract reported previously. All four compounds lack oxygenated substituents at C-13 but possess β-oxygenated substituents at C-14, and compound **4** is the second example of a natural taxoid having only three oxygenated sites in its skeleton. In addition, compounds **2** and **3** contain an uncommon isobutyrate group and a propionyloxy group, respectively, which have been reported to exist in compounds produced from cultures of *T. chinensis* var. *mairei* (6).

RESULTS AND DISCUSSION

The Et_2O extract of the roots of *T. yunnanensis* was chromatographed on Si gel eluting with $CHCl_3$ containing increasing amounts of Me_2CO. The $CHCl_3$-Me_2CO (5:1) and (4:1) fractions were separated by prep. hplc to afford taxuyunnanines G [**1**], H [**2**], I [**3**], and J [**4**], respectively.

Taxuyunnanine G [**1**] showed a molecular ion peak at *m/z* 420.24807 in its hreims, corresponding to a molecular formula of $C_{24}H_{36}O_6$ (calcd 420.25119). Analysis of its ^1H- and ^{13}C-nmr spectra (Tables 1 and 2) showed that **1** was the analogue of taxuyunnanine C [**5**], which was isolated from the same plant extract (5). Compound **1** differed from **5**





4

	R_1	R_2	R_3
1	OAc	OH	OH
2	OH	OH	$OCO\overset{1'}{C}H\overset{2'}{(}CH_2\overset{3'}{)}CH_3$
3	OH	OH	$OCO\overset{1'}{C}H\overset{2'}{(}\overset{3',4'}{(}CH_3)_2$
5	OAc	OAc	OAc

TABLE 1. ^{1}H-Nmr Data of **1–4** in $CDCl_3$ (400 MHz, δ in ppm).

Proton	δ_H (Multiplicity, J in Hz)			
	1	**2**	**3**	**4**
H-1	1.69 (br d, 1.9)	1.78 (d,2.1)	1.77 (d,2.2)	1.65 (m)
H-2/H_2-2	5.36 (dd,6.2,2.0)	5.32 (dd,6.3,2.2)	5.33 (dd,6.3,2.2)	1.73 (m)/1.66 (m)
H-3	2.82 (d,6.1)	3.19 (d,6.2)	3.19 (d,6.3)	2.57 (d,5.1)
H-5	5.19 (t,2.7)	4.14 (t,2.8)	4.14 (t,2.9)	5.27 (d,2.8)
H-6a	1.72 (m)	1.66 (m)	1.65 (m)	1.73 (m)
H-6b	1.72 (m)	1.66 (m)	1.65 (m)	1.73 (m)
H-7α	1.15 (m)	1.05 (m)	1.06 (m)	1.16 (m)
H-7β	1.86 (m)	2.04 (m)	2.03 (m)	1.88 (m)
H-9α	1.61 (dd,14.9,5.6)	1.61 (dd,14.8,5.6)	1.61 (dd,14.8,5.6)	1.58 (dd,14.5,5.5)
H-9β	2.29 (dd,14.8,11.8)	2.26 (dd,14.7,11.7)	2.27 (dd,14.8,11.7)	2.24 (dd,14.4,11.9)
H-10	5.05 (dd,11.8,5.6)	5.12 (dd,11.7,5.6)	5.12 (dd,11.7,5.6)	5.11 (dd,11.8,5.6)
H-13α	2.56 (dd,18.5,8.8)	2.74 (dd,18.8,9.3)	2.75 (dd,18.9,9.3)	2.47 (d,7.1)
H-13β	2.46 (dd,18.6,5.3)	2.29 (dd,18.4,4.3)	2.27 (dd,18.3,4.2)	2.47 (t,7.1)
H-14	4.04 (dd,8.5,5.5)	4.99 (dd,9.3,4.7)	4.98 (dd,9.3,4.7)	3.71 (t,7.1)
Me-16	1.18 (s)	1.13 (s)	1.14 (s)	1.18 (s)
Me-17	1.66 (s)	1.68 (s)	1.69 (s)	1.54 (s)
Me-18	1.94 (s)	1.95 (s)	1.95 (s)	1.92 (s)
Me-19	0.78 (s)	0.78 (s)	0.78 (s)	0.66 (s)
H-20a	5.21 (br s)	5.06 (br s)	5.07 (br s)	5.10 (br s)
H-20b	4.84 (br s)	4.73 (t,1.4)	4.72 (t,1.5)	4.77 (br d,1.2)
H_2-2′/H-2′		2.26 (q,7.6)	2.47 (heptet,7.0)	
H-3′a				
H-3′b				
Me-3′		1.08 (t,7.6)	1.11 (d,7.0)	
Me-4′			1.09 (d,7.0)	
2-OAc-CH_3	2.03 (s)	2.00 (s)	2.00 (s)	
5-OAc-CH_3	2.09 (s)			2.05 (s)

only by the lack of two acetyl groups at C-10 and C-14, as indicated by upfield shifts of the H-10α and H-14α signals [δ_H 5.05 (1H, dd, J=11.8 and 5.6 Hz, H-10α) in **1** compared with δ_H 6.06 (1H, dd, J=12.4 and 5.2 Hz, H-10α) in **5**, and δ_H 4.04 (1H, dd, J=8.5 and 5.4 Hz, H-14α) in **1** compared with δ_H 4.99 (1H, dd, J=9.2 and 4.4 Hz, H-14α) in **5**]. The two remaining acetates in **1** were assigned to C-2 and C-5, respectively, due to the identical ^{1}H- and ^{13}C-nmr chemical shifts of C-2 and C-5 with those of **5**. Thus, we determined the structure of **1** as 10,14-dideacetyltaxuyunnanine C. All assignments of proton and carbon signals and the location of substituents on **1** were confirmed by 2D ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HETCOR, and COLOC nmr spectra (see Tables 3–5).

Taxuyunnanine H [**2**], was established to have a molecular formula of $C_{25}H_{38}O_6$ by analysis of its fabms [ion at *m/z* 541 $(M+thioglycerol-1)^+$] and ^{13}C-nmr spectra (including the use of DEPT technique), and was confirmed by its hreims ($[M-CH_3CH_2COO]^+$, found *m/z* 361.23376, calcd 361.23788). The ^{1}H- and ^{13}C-nmr spectra of **2** (Tables 1 and 2) indicated that it had four oxygenated sites at C-2, C-5, C-10, and C-14 [δ_H 5.32 (1H, dd, J=6.3 and 2.2 Hz, H-2), 4.14 (1H, t, J=2.8 Hz, H-5), 5.12 (1H, dd, J=11.7 and 5.6 Hz, H-10), and 4.99 (1H, dd, J=9.3 and 4.7 Hz, H-14); δ_C 71.2 (d, C-2), 76.4 (d, C-5), 67.6 (d, C-10), and 70.7 (d, C-14)] in its skeleton, as for compound **1**. The H-5 and H-10 signals appeared at their usual chemical shifts, indicating the presence of hydroxy groups at C-5 and C-10. The downfield shift of the H-2 and H-14 signals, compared with those of **1**, revealed that two ester groups were attached to these two positions. One of the two ester groups was an acetate, and the other one proved to be a propionyloxy group [δ_H 2.26 (2H, q, J=7.6 Hz) and 1.08 (3H, t, J=7.6 Hz); δ_C 173.6 (s), 28.1 (t), and 9.2 (q)] from the ^{1}H- and ^{13}C-nmr spectra and

TABLE 2. ^{13}C-Nmr Data of **1–5** in $CDCl_3$ (100 MHz, δ in ppm).

Carbon	δ_C				
	1	**2**	**3**	**4**	DEPT
C-1	63.7	59.4	59.6	55.9	CH
C-2	71.4	71.2	71.2	26.6 t	CH
C-3	41.9	39.8	39.9	37.0	CH
C-4	142.9	148.0	147.9	149.7	C
C-5	78.8	76.4	76.5	76.5	CH
C-6	28.9	30.9	31.0	28.1	CH_2
C-7	33.8	33.2	33.3	34.0	CH_2
C-8	39.7	40.0	40.1	38.4	C
C-9	47.2	47.1	47.2	47.7	CH_2
C-10	67.3	67.6	67.6	67.8	CH
C-11	138.8	138.0	138.1	140.4	C
C-12	132.9	133.6	133.6	132.8	C
C-13	42.3	39.5	39.5	42.7	CH_2
C-14	67.8	70.7	70.6	71.4	CH
C-15	37.9	37.6	37.6	39.5	C
C-16	31.8	32.1	32.2	31.8	CH_3
C-17	25.7	25.4	25.5	26.2	CH_3
C-18	21.1	21.0	21.0	21.2	CH_3
C-19	22.4	22.3	22.3	21.7	CH_3
C-20	116.7	113.4	113.5	112.6	CH_2
C-1′		173.6	176.3		C
C-2′		28.1	34.1		CH/CH_2
C-3′		9.2	18.9		CH_3/CH_2
C-4′			18.9		CH_3
2-OAc-CH_3 ...	21.5	21.4	21.4		CH_3
2-OAc-C=O ..	169.6	169.9	169.8		C
5-OAc-CH_3 ...	21.9			21.7	CH_3
5-OAc-C=O ..	169.6			169.7	C

fabms and eims of **2** (see Experimental). The acetate group was assigned to C-2 by the observation of nOes in the 2D ^{1}H-^{1}H NOESY spectrum (Table 4) between the acetyl methyl and H-20b, which was confirmed by the presence of three-bond coupling of the acetyl carbonyl carbon to H-2 in a COLOC spectrum (Table 5). The propionyloxy group was thus assigned to C-14. Strong evidence for this assignment came from the observation of nOes in a 2D NOESY spectrum between the protons of the propionyloxy group and the 16-methyl protons. In addition, in the 2D NOESY spectrum of **2**, the correlation of H-1 to CH_3-16 and 17 (not observed in **1**) strongly supported the orientation of H-1 as β. The structure of taxuyunnanine H was thus established as 5,10,14-trideacetyl-14-propionyltaxuyunnanine C.

Taxuyunnanine I [**3**] had a molecular formula of $C_{26}H_{40}O_6$ from its fabms, *m/z* 557 $[M+thioglycerol+1]^+$, together with its ^{13}C-nmr and DEPT spectra. Also, its hreims showed an $[M-(CH_3)_2CHCOOH]^+$ fragment peak at *m/z* 360.23028 ($C_{22}H_{32}O_4$, calcd 360.23006). Compound **3** showed almost identical ^{1}H- and ^{13}C-nmr chemical shifts (Tables 1 and 2) to those of **2** except that the signals arising from the propionyloxy group of **2** were not found in the nmr spectra of **3**. Instead, signals arising from an isobutyrate group were apparent [δ_H 2.47 (1H, heptet, J=7.0 Hz), 1.11 (3H, d, J=7.0 Hz) and 1.09 (3H, d, J=7.0 Hz); δ_C 176.3 (s), 34.1 (d), and 18.9 (2C, q)]; the presence of this group was supported by ms observations (see Experimental). As in **2**, the isobutyrate group was assigned at C-14 based on the same ^{1}H- and ^{13}C-nmr chemical shifts in **3** as in **2**. Direct evidence was provided by the presence of cross-peaks between H-2′ of the isobutyrate

TABLE 3. 2D ^1H-^1H COSY Data for **1–4** in $CDCl_3$.

Proton	Correlated Proton(s)			
	1	**2**	**3**	**4**
H-1	H-2	H-2	H-2	
H-2α				H-2β
H-2β	H-1, -3	H-1, -3	H-1, -3	H-2α, -3
H-3	H-2, -20	H-2, -19, -20	H-2, -20	H-2, -20
H-5	H-6	H-6, -20a	H-6	H-6
H-6a	H-5, -7	H-5, -7	H-5, -7	H-5, -7
H-6b	H-5, -7	H-5, -7	H-5, -7	H-5, -7
H-7α	H-6, -7β	H-6, -7β	H-6, -7β	H-6, -7β
H-7β	H-6, -7α	H-6, -7α	H-6, -7α	H-6, -7α
H-9α	H-9β, -10	H-9β, -10	H-9β, -10	H-9β, -10
H-9β	H-9α, -10	H-9α, -10	H-9α, -10	H-9α, -10
H-10	H-9	H-9	H-9	H-9
H-13α	H-13β, -14	H-13β, -14	H-13β	H-14, -18
H-13β	H-13α, -14, -18	H-13α, -14, -18	H-13α, -18	H-14, -18
H-14	H-13	H-13	H-13	H-13
Me-16	H-17		H-17	H-17
Me-17	H-16		H-16	H-16
Me-18	H-13β	H-13β	H-13β	H-13
H-20a	H-3, -20b	H-3, -5, -20b	H-3, -5, -20b	H-3, -20b
H-20b	H-3, -20a	H-3, -20a	H-3, -20a	H-20a
H/H_2-2′		H-3′	H-3′, -4′	
Me-3′		H-2′	H-2′	
Me-4′			H-2′	

TABLE 4. 2D ^1H-^1H NOESY Data for **1–4** in $CDCl_3$.

Proton	Correlated Proton(s)			
	1	**2**	**3**	**4**
H-1	H-2	H-2, -14, -16, -17	H-2, -16, -17	H-16, -17
H-2α				H-20b
H-2β	H-1, -3, -17, -19, -20a	H-1, -3, -17, -19	H-1, -3, -17, -19	H-3, -17
H-3	H-2, -14, -18	H-2, -14	H-2, -14	H-2β
H-5	H-6	H-20a	H-20a	H-6, -20a
H_2-6	H-5			H-5
H-7α	H-18			
H-9α	H-9β			H-9β, -10
H-9β	H-9α, -17			H-9α, -10, -17
H-10	H-18	H-18	H-18	H-9, -18
H-13α	H-13β, -14	H-13β, -14	H-13β, -14	H-14, -16, -18
H-13β	H-13α, -16	H-13α	H-13α	H-14, -16, -18
H-14	H-1, -3, -13α	H-1, -3, -13α, -2′	H-13α	H-13
Me-16	H-13β, -17	H-1, -17, -2′, -3′	H-1, -17, -2′	H-13, -17
Me-17	H-2, -9β, -16	H-1, -2, -16	H-1, -2, -16	H-2β, -9β, -16
Me-18	H-3, -7α, -10	H-10	H-10	H-10, -13, -5-OAc
Me-19	H-2	H-2	H-2	
H-20a	H-20b, 2-OAc	H-5, -20b	H-5, -20b	H-2α, -5, -20b
H-20b	H-20a, 2-OAc	H-20a, 2-OAc	H-20a, 2-OAc	H-20a
H/H_2-2′		H-16, -3′	H-16, -3′, -4′	
Me-3′		H-16, -2′, -2-OAc	H-2′, 2-OAc	
Me-4′			H-2′, 2-OAc	
2-OAc-CH_3	H-20	H-20b, -3′	H-20b, -3′, -4′	
5-OAc-CH_3				H-18

TABLE 5. 2D COLOC Data for **1–4** in $CDCl_3$.

Carbon	Correlated Proton			
	1 (6/8 Hz)	**2** (6/8 Hz)	**3** (6 Hz)	**4** (8 Hz)
C-1	H-1, -16, -17	H-1	H-16, -17	H-16, -17
C-2	H-1, -16	H-1		
C-3	H-1, -7α, -19, -20a	H-19	H-7α, -9α, -19, -20a	H-20a
C-4	H-6, -20	H-3	H-3	
C-5	H-5, -20b	H-20		
C-6	H-7	H-7	H-7α	H-6, -7
C-7	H-19	H-9β, -19	H-5, -9β, -19	H-9β, -19
C-8	H-6, -7α, -9β, -19	H-9β	H-3, -19	H-9β, -19
C-9	H-9β, -19	H-9β, -19	H-19	H-9β, -19
C-10	H-9, -19	H-9, -19		H-9
C-11	H-16, -17, -18	H-1, -9, -16, -17, -18	H-1, -16, -17, -18	H-16, -17, -18
C-12	H-18	H-13β, -18	H-13β, -18	H-18
C-13	H-18	H-14, -18	H-18	H-13, -18
C-14	H-1	H-14	H-1, -13β	
C-15	H-1, -10, -16, -17	H-1, -16, -17	H-1, -16, -17	H-16, -17
C-16	H-16, -17	H-16, -17	H-1, -16, -17	H-16, -17
C-17	H-16, -17	H-16, -17	H-16, -17	H-16, -17
C-18	H-13α, -18	H-18		H-18
C-19	H-7α, -19	H-19	H-3, -19	H-7β, -19
C-20	H-20	H-3, -5, -20	H-5, -20a	
C-1′			H-3′, -4′	
C-2′		H-3′	H-3′, -4′	
C-3′			H-3′, -4′	
C-4′			H-3′, -4′	
2-OAc-CH_3	H-2-OAc	H-2-OAc	H-2-OAc	
2-OAc-C=O ...	H-2-OAc	H-2-OAc	H-2-OAc	
5-OAc-CH_3	H-5-OAc			H-5-OAc
5-OAc-C=O ...	H-5, 5-OAc			H-5, 5-OAc

group and Me-16 in a NOESY spectrum of **3** (Table 4). The structure of **3** was thus assigned as 5,10,14-trideacetyl-14-isobutyryltaxuyunnanine C.

Taxuyunnanine J [**4**] showed a molecular formula of $C_{22}H_{34}O_4$ by hreims (found $[M]^+$ *m/z* 362.25182, calcd 362.24571). The ^{1}H- and ^{13}C-nmr spectral data (Tables 1 and 2) revealed that **4** possessed four methyls, five methylenes, one olefinic methylene, two methines, three secondary oxymethines, two quaternary carbons, three olefinic quaternary carbons, and one acetyl. These conclusions as well as a consideration of known taxane structures from the genus *Taxus*, indicated a taxane diterpenoid skeleton for **4**, which was confirmed by the analysis of 2D nmr spectra (Tables 3–5).

Further 2D nmr spectral analysis determined the location of functional groups in **4**. The long-range correlation of δ_C 140.4 (s) and 132.8 (s) to Me-18 [δ_H 1.92 (3H, s)] observed in the COLOC spectrum established a double bond as $\Delta^{11,12}$, and the signal of δ_C 140.4 was assigned to C-11 due to its three-bond couplings to Me-16 and Me-17. Another double bond was shown to be an exocyclic double bond, which was assigned to $\Delta^{4,20}$ due to the observation of long-range couplings between H-3 [δ_H 2.57 (1H, d, J=5.1 Hz)] and H_2-20 [δ_H 5.10 (1H, br s); δ_H 4.77 (1H, br d, J=1.2 Hz)] in the ^{1}H-^{1}H COSY spectrum. The 2D COSY spectrum also showed long-range correlations between Me-18 and the signal at δ_H 2.47 (2H, d, J=7.1 Hz), and the latter signal coupled with the signal of δ_H 3.71 (1H, t, J=7.1 Hz). These observations suggested that C-14 was a secondary oxymethine. The sequence -CH_2-CH_2-CH(OR)- [δ_H 1.16 (1H, m), 1.88 (1H, m), 1.73 (2H, m), and 5.27 (1H, br t, J=2.8 Hz); δ_C 34.0 (t), 28.1 (t), and 76.5

(d)] revealed by ^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR nmr spectra permitted the assignment of a second secondary oxymethine at C-5. The COLOC spectrum established the correlations of C-7 (δ_C 34.0) to H-9 [δ_H 2.24 (1H, dd, J=14.4 and 11.9 Hz)], and the correlation to this H-9 assigned the signal at δ_H 5.11 (1H, dd, J=11.8 and 5.6 Hz) as H-10. The last secondary oxymethine in **4** was therefore assigned to C-10. Furthermore, the nOes observed between H-10 and Me-18 in a ^{1}H-^{1}H NOESY spectrum (Table 3) assigned the proton at C-10 to the α- position. In addition, H-5 and H-14 were assigned as β and α, respectively, on the basis of their coupling constants. Consequently, the structure of taxuyunnanine J was identified as **4**.

In summary, the ^{1}H- and ^{13}C-nmr assignments of all four new taxanes were confirmed by 2D nmr experiments. Compounds **1–3** had only four oxygenated sites in their skeletons (at C-2, 5, 10, and 14), and **4** showed only three oxygenated sites in its skeleton (at C-5, 10, and 14). To the best of our knowledge, only eleven compounds, including those reported in this paper, have been demonstrated to be substituted by an oxygenated group at C-14 but not at C-13 (5–8); and, interestingly, except for taxuyunnanines C, G [**1**], and J [**4**], the remaining compounds possess unusual acyl groups at C-14.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Prep. hplc was performed using a Cosmosil 10 C_{18} packed column, 20×250-mm i.d. Optical rotations were measured on Jasco Dip-369 and Dip-360 digital polarimeters. Ir spectra were recorded with Perkin-Elmer 577 and Shimadzu ir-400 spectrometers. Nmr spectra were obtained on Bruker AM-400 and JEOL JNM GSX-400 Fourier transform spectrometers operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. The chemical shifts were expressed in ppm with reference to the solvent signals: 7.24 ppm/77.0 ppm for $CDCl_3$. Mass spectra were recorded on VG Auto Spec-3000 and JEOL D-300 spectrometers.

PLANT MATERIAL.—The roots of *T. yunnanensis* were collected in the suburbs of Kunming, Yunnan, People's Republic of China. A voucher specimen is kept at the Yunnan Academy of Forestry, Kunming, Yunnan, People's Republic of China.

EXTRACTION AND ISOLATION.—Dried powdered roots (40 kg) of *T. yunnanensis* were extracted with Et_2O (6×100 liters) at room temperature over 3 weeks to give 650 g of crude extract. The Et_2O extract was chromatographed on a Si gel column [2 kg of Kieselgel 60 (0.04–0.063 mm)], and eluting with $CHCl_3$ with increasing amounts of Me_2CO; $CHCl_3$-Me_2CO (5:1) gave fraction 54 and with $CHCl_3$-Me_2CO (4:1) gave fraction 58. Fractions 54 and 58 were directly subjected to prep. hplc, eluting with MeOH-H_2O (65:35). Fraction 54 yielded taxuyunnanines H (**2**, 15.2 mg), I (**3**, 7.8 mg), and J (**4**, 13.4 mg), and fraction 58 yielded taxuyunnanine G (**1**, 11.6 mg).

Taxuyunnanine G [**1**].—White powder, $[\alpha]^{26}D$ +40.6° (c=0.8, $CHCl_3$); ir (KBr) ν max 3555, 3420, 3000, 2968, 2920, 2880, 1725, 1635, 1430, 1380, 1370, 1333, 1305, 1280, 1245, 1200, 1170, 1155, 1015, 998, 975, 960, 945, 937, 905, 875, 835, 755, 670, 605 cm^{-1}; hreims *m/z* 420.24807 (M^+, $C_{24}H_{36}O_6$ requires 420.25119); eims *m/z* 420 (M^+, 4), 402 (M^+-H_2O, 5), 384 (M^+-2H_2O, 9), 342 ($M^+-CH_3COOH-H_2O$, 3), 300 (M^+-2CH_3COOH, 33), 282 ($M^+-2CH_3COOH-H_2O$, 18), 256 (24), 135 (100), 95 (95), 43 (CH_3CO^+, 66); ^{1}H- and ^{13}C-nmr data, see Tables 1 and 2, respectively.

Taxuyunnanine H [**2**].—White powder, $[\alpha]^{22}D$ +101.8° (c=0.7, $CHCl_3$); ir (KBr) ν max 3400, 2915, 2840, 1725, 1450, 1370, 1245, 1190, 1015 cm^{-1}; hreims *m/z* 361.23376 ($M^+-CH_3CH_2COO$, $C_{22}H_{33}O_4$ requires 361.23788), 57.02459 ($CH_3CH_2CO^+$ requires 57.03404); eims *m/z* 416 (M^+-H_2O, 6), 374 (M^+-CH_3COOH, 25), 360 ($M^+-CH_3CH_2COOH$, 7), 300 ($M^+-CH_3CH_2COOH-CH_3COOH$, 15), 282 ($M^+-CH_3CH_2COOH-CH_3COOH-H_2O$, 22), 256 (12), 238 (20), 57 ($CH_3CH_2CO^+$, 100), 43 (CH_3CO^+, 54); fabms *m/z* 541 (M^++thioglycerol− H, ca. 0.2), 483 (M^++thioglycerol−CH_3CH_2CHO−H, 9), 451 (M^++thioglycerol−$CH_3CH_2COOH-H_2O$+H, 4), 391 (M^++thioglycerol−$CH_3CH_2COOH-CH_3COOH-H_2O$+H, 22), 343 ($M^+-CH_3CH_2COOH-H_2O$+H, 55), 283 ($M^+-CH_3CH_2COOH-CH_3COOH-H_2O$+H, 56), 265 ($M^+-CH_3CH_2COOH-CH_3COOH-2H_2O$+H, 100); ^{1}H- and ^{13}C-nmr data, see Tables 1 and 2, respectively.

Taxuyunnanine I [**3**].—White powder, $[\alpha]^{19}D$ +27.1° (c=0.5, $CHCl_3$); ir (KBr) ν max 3440, 2915, 2840, 1725, 1455, 1370, 1242, 1160, 1015 cm^{-1}; hreims *m/z* 360.23028 ($M^+-(CH_3)_2CHCOOH$,

$C_{24}H_{32}O_4$ requires 360.230061), 71.05096 $(CH_3)_2CHCO^+$, $C_4H_7O_2$ requires 71.04969); eims *m/z* 360 ($M^+-(CH_3)_2CHCOOH$, 6), 342 ($M^+-(CH_3)_2CHCOOH-H_2O$, 1), 300 ($M^+-(CH_3)_2CHCOOH-CH_3COOH$, 15), 282 ($M^+-(CH_3)_2CHCOOH-CH_3COOH-H_2O$, 20), 256 (12), 238 (16), 71 $(CH_3)_2CHCO^+$, 26), 43 (CH_3CO^+, 100); fabms *m/z* 557 (M^++thioglycerol+ H, ca. 0.05), 451 (M^++thioglycerol$-(CH_3)_2$ CHCOOH$-H_2O+H$, 0.5), 391 (M^++thioglycerol$-(CH_3)_2CHCOOH-CH_3COOH-H_2O+H$, 94), 343 ($M^+-(CH_3)_2CHCOOH-H_2O+H$, 100), 283 ($M^+-(CH_3)_2CHCOOH-CH_3COOH-H_2O+H$, 52), 265 ($M^+-(CH_3)_2CHCOOH-CH_3COOH-2H_2O+H$, 81); ^1H- and ^{13}C-nmr data, see Tables 1 and 2, respectively.

Taxuyunnanine J [**4**].—White powder, $[\alpha]^{24}D$ +71.3° (*c*=0.6, $CHCl_3$); ir (KBr) ν max 3460, 3400, 2910, 2840, 1710, 1440, 1375, 1255, 995 cm^{-1}; hreims *m/z* 362.25182 (M^+, $C_{22}H_{34}O_4$ requires 362.24571); eims *m/z* 362 (M^+, 3), 302 (M^+-CH_3COOH, 6), 284 ($M^+-CH_3COOH-H_2O$, 6), 244 (8), 226 (35), 171 (13), 145 (22), 137 (27), 119 (43), 107 (44), 95 (45), 80 (43), 55 (100), 42 ($CH_2=C=O^+$, 66); ^1H- and ^{13}C-nmr data, see Tables 1 and 2, respectively.

ACKNOWLEDGMENTS

The authors are grateful to Mr. Xiang Wei, Yunnan Academy of Forestry, for providing the plant material and to the members of the analytical group in the Phytochemistry Laboratory of Kunming Institute of Botany, Academia Sinica, for measuring the mass spectra, ir, and optical rotation data. We also wish to thank the Nmr Laboratory of Kunming Institute of Botany, Academia Sinica, for opportunities to record nmr spectra. This work was supported in part by the Goho Life Science International Fund of Japan.

LITERATURE CITED

1. M.C. Wani, H.L. Taylor, M.E. Wall, P. Coggon, and A.T. McPhail, *J. Am. Chem. Soc.*, **93**, 2325 (1971).
2. D.G.I. Kingston, A.A. Molinero, and J.M. Rimoldi, in: "Progress in the Chemistry of Organic Natural Products." Ed. by W. Herz, G.W. Kirby, R.E. Moore, W. Steglich, and Ch. Tamm, Springer-Verlag, New York, 1993, Vol. 61, pp. 1–206.
3. H.J. Zhang, Y. Takeda, Y. Minami, K. Yoshida, N. Unemi, Q. Mu, W. Xiang, and H.D. Sun, *Acta Bot. Yunn.*, **15**, 424 (1993).
4. H.J. Zhang, Y. Takeda, T. Matsumoto, Y. Minami, K. Yoshida, W. Xiang, Q. Mu, and H.D. Sun, *Heterocycles*, **38**, 975 (1994).
5. H.J. Zhang, Y. Takeda, Y. Minami, K. Yoshida, T. Matsumoto, W. Xiang, Q. Mu, and H.D. Sun, *Chem. Lett.*, 957 (1994).
6. W.W. Ma, R.W. Stahlhut, T.L. Adams, G.L. Park, W.A. Evans, S.G. Blumenthal, G.A. Gomez, M.H. Nieder, and P.J. Hylands, *J. Nat. Prod.*, **57**, 1320 (1994).
7. W.M. Chen, P.L. Chang, B. Wu, and Q.T. Zheng, *Chin. Chem. Lett.*, **2**, 441 (1991).
8. T.I. Ho, Y.C. Lin, G.H. Lee, S.M. Peng, M.K. Yeh, and F.C. Chen, *Acta Cryst.*, **C43**, 1380 (1987).

Received 9 September 1994