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Four New Taxoids from the Barks of *Taxus yunnanensis*

Sheng Hong LI[1], Hong Jie ZHANG[1]*, Ping YAO[2], Han Dong SUN[1]

[1]Phytochemistry Laboratory, Kunming Institute of Botany, Academia Sinica, Kunming 650204
[2]Guizhou Institute of Traditional Chinese Medicine, Guiyang 550002

Abstract: From the barks of *Taxus yunnanensis*, a new paclitaxel-related compound, 7-xylosyl-taxol D (**1**), and three new 11(15→1)-*abeo*taxoids, taxuyunnanines P-R (**2-4**) have been isolated. Their structures were determined on the basis of spectral methods. Taxuyunnanines P-R are a rare type of naturally occurring *abeo*taxoids with an opened D-ring system.

Keywords: *Taxus yunnanensis*, barks, 11(15→1)-*abeo*taxoids, 7-xylosyl-taxol D, taxuyunnanines P-R.

The ongoing study of our previous work[1-4] led to the isolation of four new taxoids from the barks of *Taxus yunnanensis*. One of them belonged to a paclitaxel analogue named 7-xylosyl-taxol D, the others were 11(15→1)-*abeo*taxoids with an opened D-ring system, named taxuyunnanines P-R respectively. Their structures were determined by means of spectral methods including 1D and 2D NMR spectroscopy.

7-Xylosyl-taxol D (**1**), white powder, has a molecular formula, $C_{49}H_{61}NO_{18}$, from its positive HRFABMS (Found: *m/z* 952.4054 $[M+H]^+$, calcd: 952.3967). The ^1H NMR data of **1** closely resembled those of 7-xylosyl-10-deacetyl-taxol D[5] except that **1** possessed an extra acetyl. The downfield shift of H-10α from δ 5.37 (1H, s) to 6.50 (1H, s) readily assigned that the extra acetoxyl was located at C-10. Accordingly, **1** was identified as 7-xylosyl-taxol D.

Taxuyunnanine P (**2**) was isolated as white powder. Its molecular formula, $C_{24}H_{38}O_{10}$, was established by HRFABMS (Found: *m/z* 485.2401, calcd: 485.2387). The ^1H and ^{13}C NMR spectra were very similar to those of taxuyunnanine N[6], an *abeo*taxoid we reported earlier. Compound **2** differed from taxuyunnanine N only by lacking of an acetoxy group. The ^1H NMR signal of H-5β resonated at δ 3.97 (1H, brd, 2.2) suggesting that the hydroxyl group was attached to C-5. Thus **2** was established as 5-deacetyl-taxuyunnanine N, named taxuyunnanine P.

Taxuyunnanine Q (**3**) was obtained as white powder. Its negative FABMS showed a molecular ion peak at *m/z* 527 $[M-H]^+$, corresponding to a molecular formula $C_{26}H_{40}O_{11}$, which was proved by HRFABMS (Found: *m/z* 527.2464, calcd: 527.2492). Comparison of the ^1H and ^{13}C NMR data of **3** with those of **2** revealed that **3** was an analogue of **2** having an additional acetoxyl. The extra acetoxyl was assignable to C-10 due to the obviously downfield chemical shift of H-10α at δ 6.17 (1H, d, 10.7). Therefore, **3** was

deduced as 10-acetyl-taxuyunnanine P, named taxuyunnanine Q.

Table 1 ^{13}C NMR data of compound **1-4** (125 MHz, δ_C in ppm)

Carbon	**1**[a,b]	**2**[b]	**3**[b]	**4**[b]
1	78.8 s	69.5 s	69.3 s	69.5 s
2	76.1 d	66.6 d	67.3 d	69.5 d
3	47.9 d	41.7 d	41.1 d	44.8 d
4	82.1 s	47.2 d	47.2 d	77.6 s
5	85.4 d	68.9 d	68.8 d	69.8 d
6	36.5 t	33.6 t	33.4 t	34.9 t
7	80.6 d	71.5 d	71.3 d	70.5 d
8	58.8 s	45.1 s	45.3 s	44.1 s
9	204.6 s	81.2 d	78.4 d	81.7 d
10	77.2 d	68.2 d	70.4 d	70.1 d
11	134.8 s	140.0 s	135.9 s	139.9 s
12	142.0 s	145.8 s	151.3 s	145.9 s
13	72.3 d	78.5 d	77.8 d	78.3 d
14	36.5 t	40.3 t	40.6 t	39.8 t
15	44.6 s	77.3 s	77.9 s	77.6 s
16	22.1 q	27.0 q	27.3 q	26.6 q
17	26.9 q	28.0 q	28.0 q	28.2 q
18	14.9 q	11.3 q	11.9 q	11.3 q
19	11.8 q	14.5 q	14.4 q	15.3 q
20	77.5 t	63.5 t	63.5 t	67.0 t
OBz	167.6 s			168.2 s
	131.3 s			131.4 s
	131.2 C×2, d			130.7 C×2, d
	129.7 C×2, d			129.5 C×2, d
	134.6 d			134.3 d
OAc	172.0 s; 171.7 s	173.0s; 172.1 s	172.1s; 171.8 s; 170.2 s	
	23.2 q; 21.1 q	21.8 q; 21.5 q	21.6 q; 21.0 q; 20.8 q	

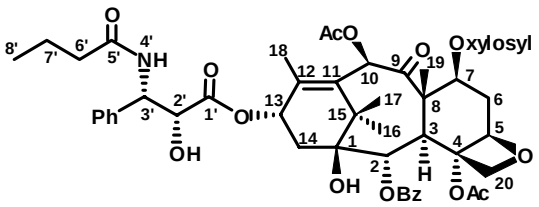
a) Signals of C-13 side chain moiety: 174.4 (s, C-1′), 74.7 (d, C-2′), 56.8 (d, C-3′), 175.9 (s, C-5′), 20.4 (t, C-6′),38.9 (t, C-7′), 14.0 (q, C-8′); 3′-Ph: 140.2 s, 129.7 C×2, d, 128.4 C×2, d, 128.9 d; Signals of 7-xylosyl moiety: 104.9 (d, C-1″), 74.8 (d, C-2″), 77.4 (d, C-3″), 70.9 (d, C-4″), 66.8 (t, C-5″).

b) The data were measured in CD_3OD with reference to the center peak of CD_3OD (δ 49.0 ppm).

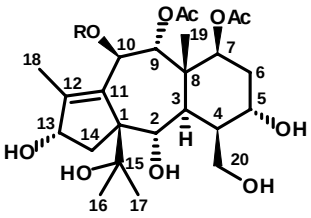
Taxuyunnanine R (**4**) was isolated as white powder. Its negative FABMS gave a molecular ion peak at *m/z* 521 $[M-H]^+$, consistent with a molecular formula $C_{27}H_{38}O_{10}$, which was verified by HRFABMS (Found: *m/z* 521.2371, calcd: 521.2387). The ^{1}H and ^{13}C NMR data indicated that it was an analogue of taxuyunnanine K[6]. Compound **4** differed from taxuyunnanine K only by the absence of an acetyl, which was assigned at C-5 due to the upfield signal of H-5β at δ 3.98 (1H, brs). Thus, compound **4** was determined as 5-deacetyl-taxuyunnanine K, named taxuyunnanine R.

Taxuyunnanines P-R are a rare type of *abeo*taxoids having an opened D-ring system. Furthermore, taxuyunnanine R is a high oxygenated but low esterified *abeo*taxoid.

Scheme

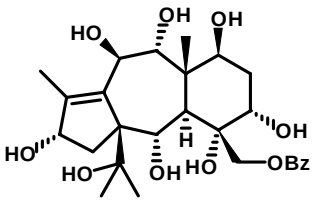


1



2 R = H

3 R = OAc



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7. ^{1}H NMR data of **1** (500MHz, CD_3OD, δ_H in ppm and J in Hz): 5.65 (1H, d, 7.1, H-2); 3.82 (1H, d, 7.5, H-3); 4.97 (1H, d, 8.0, H-5); 2.68 (1H, m, H-6a); 1.92 (1H, m, H-6b); 4.27 (1H, dd, 6.9, 10.6, H-7); 6.50 (1H, s, H-10); 6.11 (1H, t, 9.2, H-13); 2.25 (1H, m, H-14a); 2.04 (1H, m, H-14b); 1.17 (3H, s, CH_3-16); 1.16 (3H, s, CH_3-17); 1.95 (3H, s, CH_3-18); 1.72 (3H, s, CH_3-19); 4.19 (2H, m, H_2-20); 4.58 (1H, d, 4.6, H-2′); 5.45 (1H, d, 4.6, H-3′); 1.61 (2H, m, H_2-6′); 2.27 (2H, m, H_2-7′); 0.91 (3H, t, 7.5, CH_3-8′); 2.34 (3H, s, 4-OAc); 2.18 (3H, s, 10-OAc); 3′-Ph: 7.41 (4H, m), 7.27 (1H, t, 7.0); 2-OBz: 8.10 (2H, dd, 1.5, 8.5), 7.66 (1H, t, 7.5), 7.56 (2H, t, 7.5); 7-xylosyl: 4.24 (1H, d, 7.3, H-1″), 3.06 (1H, dd, 7.4, 8.9, H-2″), 3.28 (1H, t, 8.9, H-3″), 3.42 (1H, ddd, 5.3, 8.8, 10.0, H-4″), 3.81 (1H, dd, 5.2, 11.5, H-5″a), 3.18 (1H, dd, 10.2, 11.5, H-5″b).
8. ^{1}H NMR data of **2** (400MHz, CD_3OD, δ_H in ppm and J in Hz): 4.47 (1H, d, 8.2, H-2); 2.57 (1H, dd, 4.7, 8.2, H-3); 2.19 (1H, m, H-4); 3.97 (1H, brd, 2.2, H-5); 1.88 (1H, m, H-6a); 1.67 (1H,

m, H-6b); 5.38 (1H, dd, 4.8, 11.5, H-7); 5.55 (1H, brd, 10.0, H-9); 4.58 (1H, d, 10.1, H-10); 4.41 (1H, t, 7.5, H-13); 2.08 (1H, m, H-14a); 1.71 (1H, dd, 7.7, 14.6, H-14b); 1.40 (3H, s, CH_3-16); 1.03 (3H, s, CH_3-17); 1.85 (3H, s, CH_3-18); 1.02 (3H, s, CH_3-19); 3.84 (1H, dd, 5.4, 10.6, H-20a); 3.48 (1H, dd, 8.4, 10.5, H-20b); 2.07 (3H, s, OAc); 2.06 (3H, s, OAc).

9. ^{1}H NMR data of **3** (400MHz, CD_3OD, δ_H in ppm and J in Hz): 4.52 (1H, d, 8.2, H-2); 2.50 (1H, dd, 4.7, 8.3, H-3); 2.18 (1H, m, H-4); 3.99 (1H, brd, 2.3, H-5); 1.87 (1H, m, H-6a); 1.76 (1H, m, H-6b); 5.45 (1H, dd, 4.9, 11.4, H-7); 5.66 (1H, brd, 10.1, H-9); 6.17 (1H, d, 10.7, H-10); 4.43 (1H, t, 7.4, H-13); 2.33 (1H, dd, 7.7, 15.3, H-14a); 1.78 (1H, dd, 8.1, 14.3, H-14b); 1.28 (3H, s, CH_3-16); 1.25 (3H, s, CH_3-17); 1.85 (3H, s, CH_3-18); 1.03 (3H, s, CH_3-19); 3.86 (1H, dd, 6.0, 11.0, H-20a); 3.47 (1H, dd, 8.6, 10.4, H-20b); 2.03 (3H, s, OAc); 1.97 (3H, s, OAc); 1.92 (3H, s, OAc).

10. ^{1}H NMR data of **4** (500MHz, CD_3OD, δ_H in ppm and J in Hz): 4.49 (1H, d, 7.7, H-2); 2.62 (1H, d, 7.4, H-3); 3.98 (1H, brs, H-5); 1.91 (2H, m, H_2-6); 4.16 (1H, dd, 5.2, 11.0, H-7); 4.00 (1H, d, 10.4, H-9); 4.45 (1H, d, 10.0, H-10); 4.47 (1H, t, 8.8, H-13); 2.05 (1H, dd, 6.9, 14.0, H-14a); 1.82 (1H, dd, 7.6, 14.1, H-14b); 1.36 (3H, s, CH_3-16); 1.08 (3H, s, CH_3-17); 1.86 (3H, s, CH_3-18); 1.29 (3H, s, CH_3-19); 4.96 (1H, d, 12.1, H-20a); 4.65 (1H, d, 12.0, H-20b); 8.03 (2H, d, 7.4, H-2′, 6′); 7.59 (1H, t, 7.4, H-4′); 7.46 (2H, t, 7.5, H-3′, 5′).

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