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# 云南红豆杉根中的紫杉烷类化合物

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# TAXANES FROM THE ROOTS OF TAXUS YUNNANENSIS

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**关键词** 云南红豆杉; 紫杉烷; 二萜化合物; 云南红豆杉素
**Key words** *Taxus yunnanensis;* Taxane; Diterpenoid; Taxuyunnanine

The discovery of taxol (2) possessing clinical activities against ovarian and breast cancer has stimulated a wide interest in the various *Taxus* species. Current interest in *Taxus* plants focuses on needles and barks of the plant in order to obtain taxol (2) and 10-deacetylbaccatin Ⅲ. Recently, we got an opportunity to investigate the constituents of hte root of *Taxus yunnanensis*. From the ethereal extract of the root of titled plant, we isolated a new compound, named taxuyunnanine (1), $[\alpha]_D^{25}$-45.4° (c=1.67, MeOH) together with six known taxane diterpenoids, which were identified as baccatin-Ⅰ [1], 1β-hydroxy-baccatin-Ⅰ [1], 9-dihydro-10,13-diacetylbaccatin-Ⅲ [2], 1-deoxy-baccatin-Ⅳ [3], baccatin Ⅵ [3] and 7-(β-xylosyl)-10-deacetyl taxol C [4], respectively. The $^1$H- and $^{13}$C NMR spectra of 1 are very similar to those of taxol (2) except for the fact that the siganls arising from NHCO-phenyl group in 2 is replaced by those from NHCO-$(CH_2)_4CH_3$ group in 1 (see Table 1). This was confirmed by two dimensional $^1$H-$^1$H COSY, $^1$H-$^{13}$C COSY and COLOC experiments. Thus the structure of taxuyunnanine was elucidated as 1. Taxuyunnanine (1) showed a comparative cytotoxity ($IC_{50}$ 0.0066μg/ml) with that ($IC_{50}$ 0.0017μg/ml) of taxol (2) against humam nasopharyngeal carcinoma KB cells.

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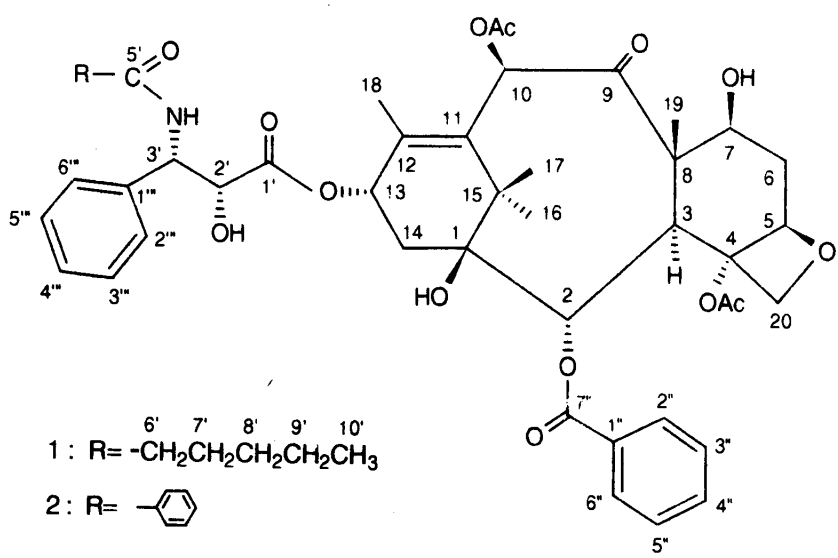
**Table 1 The $^1H$–and $^{13}C$ NMR data① of Taxuyunnanine (1)**

| Position | $^1H$ | $^{13}C$ | Position | $^1H$ | $^{13}C$ |
|---|---|---|---|---|---|
| 1 | | 78.8 | 2′ | | |
| 2 | 5.67 d(7.1) | 75.0 | 3′ | 4.67 d(2.8) | 73.1 |
| 3 | 3.78 d(7.1) | 45.6 | 4′ | 5.56 dd(2.8,9.1) | 54.5 |
| 4 | | 81.1 | 5′ | | 173.1 |
| 5 | 4.92 br.dd (9.6,2.3) | 84.4 | 6′ | 2.18 t(7.3) | 36.5 |
| 6 | 2.52 ddd(6.6,9.6,14.8) | 35.6 | 7′ | 1.56 m | 25.3 |
| | 1.87 dd (2.3,10.9,14.8) | | 8′ | 1.23 m | 31.3 |
| 7 | 4.38 dd(6.6,10.9)* | 72.0 | 9′ | 1.23 m | 22.3 |
| 8 | | 58.5 | 10′ | 1.83 t(7.0) | 13.8 |
| 9 | | 203.6 | 1″ | | 129.2 |
| 10 | 6.28 s | 75.6 | 2″,6″ | 8.10 dd(1.3,7.3) | 130.2 |
| 11 | | 133.2 | 3″,5″ | 7.6 br.t(7.3) | 128.7 |
| 12 | | 141.9 | 4″ | 7.49 t(7.3) | 133.6 |
| 13 | 6.19 br.t (8.4) | 72.3 | 7″ | | 166.8 |
| 14 | ca. 2.32 overlap | 35.6 | 1‴ | | 138.1 |
| | ca. 2.29 overlap | | 2‴,6‴ | 7.38 m | 126.9 |
| 15 | | 43.2 | 3‴,5‴ | 7.38 m | 128.9 |
| 16 | 1.15 s | 21.9 | 4‴ | 7.32 m | 128.2 |
| 17 | 1.25 s | 26.8 | 1–OH | 2.22 br.s | |
| 18 | 1.82 d(1.3) | 14.7 | 7–OH | 2.61 br.d (3.9) | |
| 19 | 1.67 s | 9.6 | 2′–OH | 3.78 br.s | |
| 20 | 4.27 d(8.3) | 76.5 | 3′–OH | 6.36 d(9.1) | |
| | 4.19 d(8.3) | | 4–OAc | 2.35 s | 22.5,170.2 |
| 1′ | | 172.8 | 10–OAc | 2.23 s | 20.8,171.2 |

① The $^1H$ NMR sprectrum was recorded at 399.7 MHz while the $^{13}C$ NMR spedtrum was recorded at 100.4 MHz for $CDCl_3$solution. The chemical shifts are given in $\delta$(ppm) from TMS as internal standard and doupling constants are given in Hz.

* After $D_2O$ treatment.



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8. 元素分析表示法，如：已知化合物(Found: C, 62.9; H, 5.4. Calc. for $C_{13}H_{13}ON_4$: C, 62.9; H, 5.3%)。新化合物(Found: C, 62.9; H, 5.4. $C_{13}H_{13}ON_4$requires: C, 62.9; H, 5.3%)。

9. 比旋度的表示法：$[\alpha]_D^{温度}$ 测定值 ° (所用溶剂；c 指 100ml 溶剂里化合物的克数)，如$[\alpha]_D^{23}$+32.2 ° (EtOH; c 0.3210)。

旋光色散谱 (ORD)可用一系列不同波长下的[α]值或分子比旋[θ]值表示。

园二色散谱 (CD) 可用分子椭率值如$[\theta]_{256}$+21780, $[\theta]_{307}$−16113 或微分子色散吸收值如Δε253−1.02(MeOH; c 0.164)表示。

10. NMR 表示为$^1$H NMR 或$^{13}$C NMR，须注明仪器的频率，溶剂及内标物。化学位移以 δ 值(对TMS)表示，注明峰形，如：单峰(s)，宽单峰(brs)，双峰(d)，双二重峰(dd)，复峰(m)等。$^{13}$C NMR 及$^1$H NMR 数所须注明所对应的碳和氢的位置，采用 IUPAC 定位，标为 C-1, C-2; H-1, H-2。例如：$^{13}$C NMR(21.15Mz, $CDCl_3$): δ30.1(t, C-5), 74.1(d, C-6), 121.3(d, C-3), 144.2(s, C-4)。$^1$H NMR(100MHz, $CDCl_3$): δ0.681(3H, s, H-18), 0.884(6H, d, J=6.0Hz, H-26 and H-27), 0.901(3H, d, J=5.0Hz, H-21), 4.342(1H, q, J6α, 7α=4.5Hz, J6α, 7β=2.0Hz, H-6), 4.211(1H, m, $W_{1/2}$=18.0Hz, H-3α)。所用仪器频率及溶剂若在实验部分的总论中已注明，则以下皆可省略。

11. 质谱须注明所用的方法，如(EIMS, CIMS, GC-MS, FABMS 等)及离解能，只须给出分子离子峰及重要的特征碎片峰(相对强度)，如：EIMS(70eV m/z(%): 386[$M^+$](36), 368[$M-H_2O$]$^+$ (100), 275[M−111]$^+$(35) 等。高分辨质谱(HRMS)若有必要可多给一些信息。

12. 紫外光谱表示法，如 UV$\lambda_{max}^{EtOH}$nm(lgε): 203(4.17)。

13. 红外光谱表示法，如 IR$\nu_{max}^{KBr}$$cm^{-1}$: 1740。官能团的指定放在圆括号内，如：1740(>C=O)。若要标明吸收带的强度，则采用以下缩写符号：w (弱)，m (中等)，v (可变)，s (强)，vs(很强)。

14. 有机化合物和无机化合物及有关的缩写符号须规范化(参考 CA)，如氘代溶剂 $CDCl_3$, DMSO-$d_5$, $D_2O$, pyridine-$d_5$ 等。常见化学试剂在文中均以化学符号表示，如：MeOH, EtOH, n-BuOH, PrOH, iso-PrOH, PhOH(苯酚), petrol (石油醚), $CHCl_3$, $CCl_4$, $C_6C_6$, $Et_2O$, $Me_2CO$, HOAc, EtOAc, THF, $Ac_2O$, NaOMe, $CH_2N_2$, $HCO_2H$(甲酸), TCA(三氯乙酸), TFA(三氟乙酸), NaOAc, NaOH, HCl, $H_2SO_4$, $CO_2$, $H_3BO_3$, $NH_3$, $N_2$ 等。

15. 制备薄层析须注明(1) 薄层厚度；(2) 样品的量；(3) 确定带的方法；(4) 从吸附剂上洗脱下化合物所用的溶剂。特殊 TLC 的吸附剂须注明，如：$AgNO_3$-硅胶(1 : 9)。

16. 气相色谱 (GC)须注明检测器(FID,EC 等)，载气及流速，操作温度，柱子情况等。

17. 高压液相(HPLC) 须注明(1) 柱子情况，如大小、型号；(2) 压力及溶剂；(3) 检测方法，如 UV 或折射率。

18. X-衍射只须给出立体结构图(最好有键长)及必要的数据，详细记录可指明在什么地方储存。