

中国红豆杉中一个新的紫杉烷二萜

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摘要: 从中国红豆杉 (*Taxus chinensis*) 枝叶中分离得到 4 个紫杉烷二萜, 通过波谱分析分别确定为: 1 β -羟基-2 α , 7 β -二去乙酰基巴卡亭 I (1), 1 β -羟基巴卡亭 I (2), 2 α , 5 α , 7 β , 9 α , 10 β , 13 α -六乙酰氧基紫杉-4 (20), 11-二烯 (3) 和 2-去乙酰氧基-5-去肉桂酰 taxinine J (4), 其中化合物 1 为新化合物。

关键词: 中国红豆杉; 红豆杉科; 紫杉烷二萜; 1 β -羟基-2 α , 7 β -二去乙酰基巴卡亭 I (1)

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A New Taxoid from *Taxus chinensis*WANG Fu-Sheng², PENG Li-Yan¹, ZHAO Yu¹, GU Kun³,ZHAO Qin-Shi^{1*}, SUN Han-Dong¹

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Abstract: Four taxoids, 1 β -hydroxy-2 α , 7 β -deacetylbaicatin I (1), 1 β -hydroxybaicatin I (2), 2 α , 5 α , 7 β , 9 α , 10 β , 13 α -hexaacetoxy-4 (20), 11-taxadiene (3) and 2-deacetoxy-5-decinnamoyl taxinine J (4), among which compound 1 was a new one, were isolated from the leaves and stems of *Taxus chinensis*. The structures of the compounds were elucidated by spectroscopic techniques.

Key words: *Taxus chinensis*; *Taxaceae*; Taxoids; 1 β -hydroxy-2 α , 7 β -deacetylbaicatin I (1)

The discovery of the natural product paclitaxel and its clinically useful anticancer activity, has encouraged several groups all over the world to isolate potentially more effective paclitaxel derivatives for the treatment of various cancers or as starting materials for semisynthesis (Baloglu *et al*, 1999; Kingston 2000). As a consequence, nearly 400 taxane-type diterpenoids have been isolated from various *Taxus* plants (Baloglu *et al*, 1999), and some of them possess interesting anticancer activity. An evergreen tree, *Taxus chinensis* (Pilg) Rehd, indigenous to China, is considered as a promising source of taxane-type diterpenoids (Fuji *et al*, 1993; Li *et al*, 1993), and the ethanolic extracts of

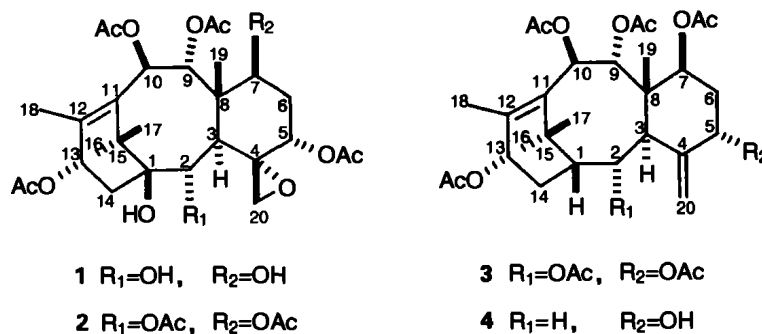
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needles of *Taxus chinensis* showed activity against several tumor cell lines *in vitro* (Fang WS *et al*, 1995). Because they can be collected without destruction of the trees, we have further investigated the chemical constituents of the branches and leaves from *Taxus chinensis* collected in Sichuan province. In continuation of our research, we obtained a new taxane, 1 β -hydroxy-2 α , 7 β -deacetylbaccatin I (1), together with the known compounds 1 β -hydroxybaccatin I (2), 2 α , 5 α , 7 β , 9 α , 10 β , 13 α -hexaacetoxy-4 (20), 11-taxadiene (3) and 2-deacetoxy-5-decinnamoyl taxinine J (4). Their structures were determined by means of spectroscopic methods and confirmed by comparison of spectral data with literature report.



Results and Discussion

Compound 1 was obtained as an amorphous solid, $[\alpha]_D^{21.7} + 63.83$ (c 0.047, acetone). Its molecular formula was deduced as $C_{28}H_{40}O_{12}$ on the basis of 1H , ^{13}C , DEPT NMR and positive FABMS, which showed a quasi-molecular peak at m/z 569 $[M + H]^+$. The ^{13}C and DEPT NMR spectra of 1 showed 28 carbon signals which were composed of four ester carbonyls, two olefinic carbons, four methyls, three methylenes, seven methines (including six oxygenated methines), four quaternary carbons (including two oxygenated ones), and four acetyl methyls, which suggested 1 as a taxoid. Furthermore, compound 1 was suggested to possess a skeleton of 6/8/6 ring-system and an epoxide located on C-4 and C-20, which deduced from the characteristic NMR signals at δ 76.4 (s, C-1), 40.6 (d, C-3), 48.1 (s, C-8), 136.6 (s, C-11), 141.4 (s, C-12), 43.7 (s, C-15); and the signals at δ 59.9 (s, C-4), 78.8 (d, C-5) and 50.9 (t, C-20), respectively. The NMR data (table 1) indicated that 1 was very similar to 1 β -hydroxybaccatin I (2), a known taxoid isolated from the same plant in this time. Comparison of the 1H and ^{13}C NMR spectral data of 1 with 1 β -hydroxybaccatin I (2), revealed that 1 was 1 β -hydroxy-2 α , 7 β -deacetylbaccatin I, which was confirmed by the relational HMBC experimental results. The OH-2 α and OH-7 β were determined by the HMBC correlations of H-2 β [δ_H 4.09 (1H, dd, 3.7, 4.0)] with C-14 (δ_C 39.2) and C-8 (δ_C 48.1), and H-7 α [δ_H 4.23 (1H, dd, 5.3, 11.3)] with C-6 (δ_C 33.5) and C-19 (δ_C 12.9); OH-2 α (δ_H 4.63) with C-2 (δ_C 73.7), and OH-7 β (δ_H 3.73) with C-7 (δ_C 69.5). Meanwhile, the upfield shift of H-2 β from 5.46 (1H, d, 3.6) in 2 to 4.09 (1H, dd, 3.7, 4.0) in 1, and H-7 α from 5.48 (1H, dd, 5.0, 12.2) in 2 to 4.23 (1H, dd, 5.3, 11.3) in 1 also indi-

cated that **1** was 1 β -hydroxy-2 α , 7 β -deacetylbaaccatin I.

Table 1 NMR data of the compound **1**

Position	δ_C	δ_H	Position	δ_C	δ_H
1	76.4 s		16	28.7 q	1.26 (3H, s)
2	73.7 d	4.09 (1H, dd, 3.7, 4.0)	17	22.6 q	1.53 (3H, s)
3	40.6 d	3.18 (1H, d, 3.7)	18	15.8 q	2.14 (3H, d, 1.5)
4	59.9 s		19	12.9 q	1.17 (3H, s)
5	78.8 d	4.05 (1H, dd, 2.8, 3.3)	20	50.9 t	3.84 (1H, d, 5.8), 2.22 (1H, d, 5.8)
6	33.5 t	1.88 (1H, m), 1.83 (1H, m)	OAc	170.9 s	
7	69.5 d	4.23 (1H, dd, 5.3, 11.3)		170.1 s	
8	48.1 s			170.1 s	
9	78.0 d	6.01 (1H, d, 11.4)		170.1 s	
10	71.3 d	6.15 (1H, d, 11.4)	OAc	21.9 q	2.21 (3H, s)
11	136.6 s			21.5 q	2.11 (3H, s)
12	141.4 s			20.9 q	2.08 (3H, s)
13	72.0 d	6.03 (1H, ddd, 1.5, 6.6, 9.8)		20.6 q	1.99 (3H, s)
14	39.2 t	2.42 (1H, dd, 9.8, 11.1)			4.27 (1H, s, OH-1 β)
		1.92 (1H, dd, 6.6, 12.1)			4.63 (1H, d, 4.3, OH-2 α)
15	43.7 s				3.73 (1H, d, 1.8, OH-7 β)

¹H, ¹³C NMR data were measured at 400, 100 MHz, respectively, in acetone-*d*₆ (δ in ppm, *J* in Hz)

The three known taxoids, isolated from the same plant were identified as 1 β -hydroxybaaccatin I (**2**) (Luciano *et al*, 1993), 2 α , 5 α , 7 β , 9 α , 10 β , 13 α -hexa-acetoxy-4 (**20**), 11-taxadiene (**3**) (Miller, 1980), and 2-deacetoxy-5-decinnamoyl taxinine J (**4**) (Chen *et al*, 1994) by spectroscopic techniques and confirmed by comparison of spectral data with literature report.

Experimental

General The NMR spectra were performed on a Bruker AM-400 MHz and DRX-500 MHz spectrometer. FABMS was taken on a VG Auto Spec-3000 or on a Finnigan MAT 90 instrument. Optical rotations were measured with a HORIBA SEPA-300 High Sensitive Polarimeter. Column chromatography was performed ether on 200 - 300 mesh silica gel and 10 - 40 μ m silica gel H; 43 - 63 μ m Lichroprep RP-18 and Sephadex LH-20 were used for column chromatography.

Plant material The leaves and stems of *Taxus chinensis* (Pilg) Rehd were collected in Liangshan prefecture of Sichuan Province. A voucher specimen has been deposited at the Kunming Institute of Botany, Kunming, Yunnan, People's Republic of China.

Extraction and isolation The dried plant material (15 kg) was extracted three times with 95% ethanol to yield a crude extract. After evaporation of the solvent, the residue was dissolved with MeOH/H₂O (9:1), and the MeOH-soluble part was further reextracted with chloroform to give the extract. The chloroform extract was chromatographed over a silica gel column using solvents of increasing polarity (petroleum-EtOAc, 9:1 - 2:8, CH₃COCH₃, v/v) to give ten fractions, and the three fractions (petroleum-EtOAc, 6:4; 5:5; 4:6, v/v) was further chromatographed over a silica gel, Sephadex LH-20, Lichroprep RP-18 and HPLC to give the new compound, 1 β -hydroxy-2 α , 7 β -deacetylbaaccatin I (5 mg), and to give the known compounds 1 β -hydroxybaaccatin I (1.2 g), 2 α , 5 α , 7 β , 9 α , 10 β , 13 α -hexa-acetoxy-4 (**20**), 11-taxadiene (8 mg) and 2-deacetoxy-5-decinnamoyl taxinine J (16 mg).

1 β -hydroxy-2 α , 7 β -deacetylbaaccatin I (1), C₂₈H₄₀O₁₂, amorphous solid, $[\alpha]_D^{21.7} + 63.83$ (c 0.047, acetone), positive FABMS *m/z* (%): 569 ([M+H]⁺, 75), 509 (100), 479 (12), 449 (22), 419 (9), 329 (9).

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更 正

吴征镒等于2003年25卷(3)期刊登的文章“世界种子植物科的分布区类型系统”,在第253页续表1右下部分,(3f)类型后漏排了(3g)类型5个科,它们是:

(3g)

Malesherbiaceae

Vivianiaceae

Misodendraceae

Tribelaceae

Sclerophyllaceae

Total

5