Chinese Journal of Chemistry, **2004**, *22*, 751—756 **Article**

Isolation and Structure of 1-Deoxybaccatin VI from the Root of *Taxus chinensis, Rehd. var. mairei*

LIN, Hai-Xia[a](林海霞) LI, Ming[a](李明) CHEN, Jian-Min*,[a](陈建民)
CHEN, Min-Qin[b](陈民勤)

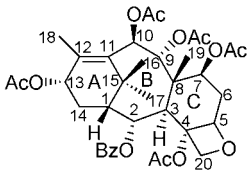
[a]*Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China*
[b]*Research Center of Analysis and Measurement , Fudan University, Shanghai 200433, China*

Deoxybaccatin VI (4*α*,7*β*,9*α*,10*β*,13*α*-penta-acetoxy-2*α*-benzoyloxy-5*β*,20-epoxytax-11-ene) was isolated from the roots of *Taxus chinensis, Rehd. var. mairei.* The structural assignments of the compound were based on their spectral data, including 2D NMR experiments and chemical correlation. The X-ray crystallographic analysis of 1-deoxybaccatin VI provided unambiguous characterization for the structures. In the structure, the six-membered A ring exhibits boat conformation, the eight-membered B ring adopts boat-chair conformation, and the six-membered C ring exhibits a sofa conformation.

Keywords crystal structure, conformation, 1-deoxybaccatin VI

Introduction

The natural diterpenoid paclitaxel (Taxol) has become a major anticancer drug, with U.S. sales in 2000 estimated at over $ 1.5 billion.[1] Its interesting mechanism of action as a promoter of tubulin polymerization[2] and its commercial success have combined to maintain a high level of interest in the preparation of paclitaxel analogues with improved bioactivity, and large numbers of analogues have been prepared.[3,4] Furthermore, the success of paclitaxel and docetaxe (taxotere) as anticancer drugs has prompted the study of the structures of these and related taxanes. There is much hot debate regarding the active conformation of these drugs and numerous X-ray investigations have been performed on paclitaxel,[5] docetaxel,[6] baccatin III,[7] baccatin V,[8] 10-deacetyl baccatin III,[9] 9-dihydro-13-acetylbaccatin III,[10] 7-mesyl-paclitaxel,[11] and 10-deacetyl-7-epitaxol,[12] which share a common tetracyclic ring structure. However, no studies have yet appeared describing the crystal structure of 1-deoxybaccatin VI. The structure-activity studies have led to the conclusion that 1-hydroxyl group is not necessary for the activity of paclitaxel.[13] In addition, it has not proved possible to prepare 1-deoxypaclitaxel analogues from paclitaxel.[14-16] So 1-deoxybaccatin VI was the crucial starting material for the preparation of selected 1-deoxy-analogues with potentially greater therapeutic benefits. Besides, the knowledge of the spatial structure of either active or inactive compounds in this series is important in order to establish structure-activity relationships. A description of the structure of 1-deoxybaccatin VI is therefore of interest.



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Experimental

Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker DM-500 MHz spectrometer at 500.134 MHz and 125.771 MHz, respectively in $CDCl_3$ with TMS as the internal standard. HPLC analysis was performed on an Agilent 1100 series LC system connected to a G1322A vacuum degasser, a G1311A quaternary pump, a G1313A autosampler, a G1316A thermostatted column compartment, a G1314A variable wavelength detector and an Agilent chemostation software. Prep. HPLC was carried out on a Waters PrepLCTM 4000 instrument connected to a Waters 2487 Dual λ Absorbance Detector. FI-IR spectra were recorded on a NICOLET Avatar 360 spectrophotometer. LC/MS/MS were recorded on a Finnigan LCQ advantage system with an electrospray interface (ESI). UV spectra were taken on a Thermo UV 500 spectrometer. Melting point was determined on a WRS-1 A digital melting point

* E-mail: jmchen@fudan.ac.cn
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apparatus and uncorrected.

Plant materials

Roots of *Taxus chinensis, Rehd. var. mairei* were obtained from Mingxi county, Fujian Province. The roots were air-dried and ground to powder.

Extraction and isolation

1-Deoxybaccatin VI was isolated in the same way as that in Refs. 17 and 18. The ground sample (10 kg) suspended in methanol (50 L) and allowed to stand for 24 h with occasional agitation. The extract was filtered, and the residue was extracted twice. The extracts were combined and concentrated. A semisolid methanol extract was obtained and suspended in water, then extracted three times with chloroform. The organic layer was concentrated under reduced pressure, and the residue obtained was separated by column chromatography on silica gel with 50% EtOAc/hexane as an eluent to give 1-deoxybaccatin VI (12 g) with a chromatographic purity of 85%. The 85% 1-deoxy-baccatin VI was finally purified by the Waters PrepLCTM 4000 high performance preparative chromatography with Symmetry TM C18 column (7 μm, 19 mm×300 mm) and 8 g of 1-deoxybaccatin VI was collected with the purity of 99.8%. The purity of 1-deoxybaccatin VI was determined on the Agilent 1100 C18 column (5 μm, 6 mm×25 cm) eluted with H_2O-CH_3OH-CH_3CN (36∶32∶32). The eluant was monitored at 227 nm. The colorless crystals were obtained by recrystallization from ethyl acetate. m.p. 221—222 ℃ (Lit.[19] m.p. 220—221 ℃); UV-vis ($CHCl_3$) λ_{max}: 244 nm; IR (KBr) v: 1741, 1725, 1455, 1380, 1250, 1080, 1010, 983, 710 cm^{-1}; ESI Full MS m/z: 721 $[M+Na]^+$, 661 $[M+Na-HOAc]^+$, 601 $[M+Na-2HOAc]^+$, 537, 415, 355, 313, 295, 277, 249; ^1H NMR and ^{13}C NMR see Table 1.

X-ray structure determination

A summary of the crystallographic information is given in Table 2, selected bond distances and angles are listed in Table 3, and the atomic coordinates are listed in Table 4. The selected crystal of 1-deoxybaccatin VI was mounted on a SMART CCD diffracto-meter. Diffraction data were measured at 20 ℃ using graphite monochromated Mo Kα (λ=0.071073 nm) radiation. The collected data were reduced by using the program SAINT and empirical absorption correction was made by using the SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares method on F^2_{obs} by using the SHELXTL software package. All non-H atoms were anisotropically refined. The hydrogen atoms were located by geometry calculation and riding on the related parent atoms.

Results and discussion

The compound **1** crystallized in monoclinic system with space group $P2_1$. There are two independent molecules of the compound and a ethyl acetate molecule in the asymmetric unit. The structure of molecule **1** with atomic labeling is shown in Figure 1. The absolute configurations of the two independent molecules are the same, as shown in the figure, and the ethyl acetate molecule was not shown in the figure for the sake of clarity. A perspective view of the crystal packing in the unit cell is shown in the Figure 2.

Table 1 NMR spectral data of 1-deoxybaccatin VI

Position	^{13}C NMR ($CDCl_3$) δ	^1H NMR ($CDCl_3$) δ^a
1	47.0	2.01 (dd, J=9.4, 1.7, 1H)
2	71.8	5.86 (dd, J=5.9, 1.7, 1H)
3	44.2	3.01 (d, J=5.9, 1H)
4	81.2	
5	83.6	5.01 (d, J=8.9, 1H)
6	34.5	β 1.87 (dd, J=15.1, 9.3, 1H) α 2.51 (ddd, J=15.1, 8.9, 8.2, 1H)
7	71.8	5.57 (dd, J=9.3, 8.2, 1H)
8	45.6	
9	75.3	6.01 (d, J=11.2, 1H)
10	70.9	6.19 (d, J=11.2, 1H)
11	133.2	
12	138.7	
13	68.8	5.95 (t, J=8.3, 1H)
14	26.4	α 1.68 (dd, J=15.1, 8.3, 1H); β 2.44 (ddd, J=15.1, 9.4, 8.3, 1H)
15	37.8	
16	26.8	1.89 (s, 3H)
17	31.2	1.14 (s, 3H)
18	14.8	1.98 (s, 3H)
19	12.7	1.59 (s, 3H)
20	76.4	4.13 (d, J=8.4, 1H) 4.39 (d, J=8.4, 1H)
2-CO	164.7	
q-Ph	129.5	
o-Ph	129.7	8.06—8.08 (m, 2H)
m-Ph	128.5	7.46—7.48 (m, 2H)
p-Ph	133.4	7.59—7.62 (m, 1H)
4-, 7-, 9-, 10-, 13-CO	168.8, 168.9, 169.7, 170.0, 170.5	
4-, 7-, 9-, 10-, 13-$COCH_3$	20.7, 20.8, 21.1, 21.3, 22.6,	2.05, 2.10, 2.11, 2.19, 2.29 (s, 5×3H)

[a] J in Hz.

Table 2 Summary of crystallographic data for the complex

Empirical formula	$2C_{37}H_{46}O_{13}•C_4H_8O_2$
Formula weight	742.79
Temperature/K	293(2)
Wavelength/nm	0.071073
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimension	a=1.4373(16) nm, α=90°.
	b=2.0277(2) nm, β=90.114(2)°
	c=1.4404(16) nm, γ=90°
Volume/nm^3	4.1978(8)
Z	2
Calculated density/ (g•cm^{-3})	1.175
Absorption coefficient/mm^{-1}	0.089
F(000)	1584
Crystal size/mm^3	0.45×0.30×0.10
θ range for data collection/(°)	1.41—27.18
Index ranges	$-18\leqslant h\leqslant 17$, $-25\leqslant k\leqslant 25$, $-18\leqslant l\leqslant 12$
Reflections collected/unique	21153/17830 [R(int)=0.0261]
Completeness to 2θ=27.18°	98.9%
Absorption correction	Multiscans
Max. and min. transmission	0.9911 and 0.9610
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17830/11/972
Goodness-of-fit on F^2	0.832
Final R indices [$I>2\sigma(I)$]	R_1=0.0624, wR_2=0.1537
R indices (all data)	R_1=0.1186, wR_2=0.1717
Absolute structure parameter	0.0(9)
Extinction coefficient	0.0017(2)
Largest diff. peak and hole/ (e•nm^{-3})	544 and 207

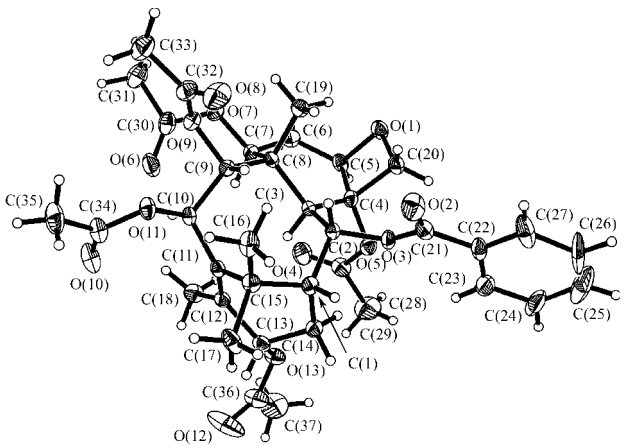

Figure 1 The molecular structure and labeling scheme of compound **1**.

Table 3 Selected bond distances (nm) and angles (°) for the complex

C(1)—C(14)	0.1526(6)	C(6)—C(7)	0.1539(5)
C(1)—C(15)	0.1548(5)	C(7)—C(8)	0.1556(5)
C(1)—C(2)	0.1541(5)	C(8)—C(9)	0.1558(5)
C(2)—C(3)	0.1576(5)	C(9)—C(10)	0.1534(5)
C(3)—C(4)	0.1537(5)	C(10)—C(11)	0.1506(5)
C(3)—C(8)	0.1592(5)	C(11)—C(12)	0.1339(6)
C(4)—C(20)	0.1520(5)	C(11)—C(15)	0.1522(5)
C(5)—O(1)	0.1452(5)	C(12)—C(13)	0.1515(6)
C(5)—C(6)	0.1509(6)	C(13)—C(14)	0.1552(6)
O(1)—C(20)	0.1442(5)		
C(14)-C(1)-C(15)	111.2(3)	C(6)-C(7)-C(8)	114.2(3)
C(14)-C(1)-C(2)	112.6(3)	C(7)-C(8)-C(9)	114.0(3)
C(2)-C(1)-C(15)	114.6(3)	C(19)-C(8)-C(3)	113.5(3)
C(1)-C(2)-C(3)	118.3(3)	C(7)-C(8)-C(3)	104.8(3)
C(4)-C(3)-C(2)	111.2(3)	C(9)-C(8)-C(3)	111.0(3)
C(4)-C(3)-C(8)	111.5(3)	C(10)-C(9)-C(8)	121.6(3)
C(2)-C(3)-C(8)	115.1(3)	C(11)-C(10)-C(9)	112.0(3)
C(20)-C(4)-C(5)	85.2(3)	C(12)-C(11)-C(10)	119.7(3)
C(20)-C(4)-C(3)	121.6(3)	C(12)-C(11)-C(15)	118.5(4)
C(3)-C(4)-C(5)	119.6(3)	C(10)-C(11)-C(15)	120.9(3)
O(1)-C(5)-C(6)	113.9(4)	C(11)-C(12)-C(13)	118.6(4)
O(1)-C(5)-C(4)	90.5(3)	C(12)-C(13)-C(14)	111.8(3)
C(6)-C(5)-C(4)	119.4(3)	C(1)-C(14)-C(13)	114.9(3)
C(20)-O(1)-C(5)	91.6(3)	C(11)-C(15)-C(1)	103.8(3)
C(5)-C(6)-C(7)	115.6(3)	O(1)-C(20)-C(4)	91.9(3)

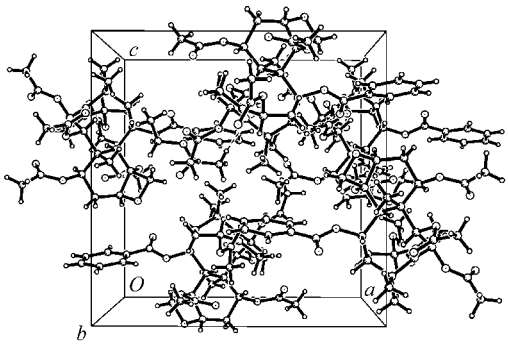

Figure 2 A view of the crystal packing down the *c*-axis.

The cycloctane ring (B) adopts the most stable boat-chair conformation, as shown by the torsion angles with atoms C(1) and C(9) as the ends. This ring is *trans*-fused along the C(3)—C(8) bond to the six-membered ring C, which exhibits a chair conformation flattened in C(4) [atoms C(7) and C(4) deviated by

Table 4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($nm^2 \times 10$)

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
O(1)	−873(2)	8108(2)	5890(2)	61(1)	C(31)	3523(4)	9048(3)	5246(5)	116(2)
O(2)	−2212(2)	8457(2)	2454(3)	87(1)	C(32)	1639(4)	9722(2)	2933(4)	66(1)
O(3)	−1549(2)	7623(1)	3219(2)	47(1)	C(33)	2372(4)	10214(3)	3100(5)	100(2)
O(4)	630(3)	6504(2)	4977(2)	79(1)	C(34)	3052(3)	8327(3)	1527(3)	66(1)
O(5)	−801(2)	6856(1)	4609(2)	53(1)	C(35)	3426(4)	8794(3)	815(4)	101(2)
O(6)	3189(2)	8040(2)	4424(3)	82(1)	C(36)	1071(5)	5301(3)	2585(5)	88(2)
O(7)	2016(2)	8620(2)	5073(2)	60(1)	C(37)	1011(5)	4778(3)	3298(5)	115(2)
O(8)	952(3)	9822(2)	2505(3)	99(1)	C(51)	6870(3)	7796(2)	7035(2)	44(1)
O(9)	1812(2)	9140(1)	3369(2)	56(1)	C(52)	7092(2)	7374(2)	7926(3)	45(1)
O(10)	3416(2)	7809(2)	1747(3)	92(1)	C(53)	6445(2)	7463(2)	8803(2)	41(1)
O(11)	2245(2)	8517(1)	1871(2)	57(1)	C(54)	7018(3)	7668(2)	9673(2)	47(1)
O(12)	1456(5)	5258(2)	1861(4)	163(3)	C(55)	6594(3)	7562(2)	10635(3)	55(1)
O(13)	695(2)	5872(1)	2862(2)	62(1)	C(56)	5630(3)	7272(2)	10709(3)	54(1)
O(21)	7342(2)	7071(2)	10873(2)	71(1)	C(57)	5125(2)	7163(2)	9778(2)	43(1)
O(22)	8648(2)	6733(2)	7383(3)	92(1)	C(58)	5759(3)	6881(2)	9013(2)	40(1)
O(23)	8032(2)	7568(2)	8190(2)	51(1)	C(59)	5221(3)	6664(2)	8120(3)	41(1)
O(24)	6018(3)	8770(2)	9948(2)	71(1)	C(60)	4639(3)	7153(2)	7570(2)	42(1)
O(25)	7391(2)	8326(2)	9563(2)	56(1)	C(61)	5190(2)	7698(2)	7160(2)	40(1)
O(26)	3295(2)	7404(2)	9441(2)	76(1)	C(62)	5096(3)	8320(2)	7466(3)	46(1)
O(27)	4380(2)	6706(1)	10010(2)	51(1)	C(63)	5837(3)	8823(2)	7198(3)	53(1)
O(28)	5389(3)	5416(2)	7443(3)	92(1)	C(64)	6823(3)	8533(2)	7227(3)	54(1)
O(29)	4596(2)	6126(1)	8363(2)	51(1)	C(65)	6004(3)	7545(2)	6509(2)	44(1)
O(30)	3074(2)	7525(2)	6692(3)	96(1)	C(66)	6168(3)	6830(2)	6167(3)	56(1)
O(31)	4199(2)	6768(1)	6833(2)	52(1)	C(67)	5868(3)	7935(2)	5589(3)	59(1)
O(32)	4969(4)	9982(2)	6841(4)	140(2)	C(68)	4295(3)	8571(2)	8065(3)	61(1)
O(33)	5815(2)	9378(2)	7847(2)	66(1)	C(69)	6262(3)	6246(2)	9339(3)	51(1)
C(1)	−402(3)	7437(2)	2073(2)	44(1)	C(70)	7823(3)	7225(3)	10014(3)	63(1)
C(2)	−632(2)	7830(2)	2960(2)	38(1)	C(71)	8751(3)	7225(3)	7829(3)	59(1)
C(3)	28(2)	7750(2)	3827(2)	35(1)	C(72)	9645(3)	7524(3)	8049(3)	61(1)
C(4)	−522(3)	7543(2)	4694(3)	45(1)	C(73)	9703(3)	8179(4)	8299(3)	80(2)
C(5)	−106(3)	7670(2)	5668(2)	50(1)	C(74)	10598(5)	8456(4)	8462(4)	115(2)
C(6)	840(3)	7988(2)	5753(3)	58(1)	C(75)	11367(5)	8090(6)	8366(5)	127(4)
C(7)	1340(3)	8128(2)	4830(3)	45(1)	C(76)	11299(5)	7437(6)	8148(5)	121(3)
C(8)	686(2)	8365(2)	4035(2)	39(1)	C(77)	10441(3)	7164(3)	7980(3)	85(2)
C(9)	1207(3)	8588(2)	3141(3)	41(1)	C(78)	6834(4)	8826(3)	9767(3)	66(1)
C(10)	1823(2)	8111(2)	2589(3)	42(1)	C(79)	7351(5)	9465(3)	9714(4)	100(2)
C(11)	1268(2)	7556(2)	2168(2)	40(1)	C(80)	3496(3)	6900(3)	9834(3)	55(1)
C(12)	1397(3)	6938(2)	2471(3)	44(1)	C(81)	2812(3)	6393(3)	10147(4)	84(2)
C(13)	681(3)	6419(2)	2218(3)	48(1)	C(82)	4768(4)	5527(2)	7974(3)	65(1)
C(14)	−324(3)	6697(2)	2251(3)	53(1)	C(83)	4089(4)	5024(3)	8332(4)	99(2)
C(15)	449(3)	7696(2)	1527(2)	48(1)	C(84)	3441(3)	7035(3)	6419(3)	64(1)
C(16)	264(3)	8415(2)	1187(3)	64(1)	C(85)	3159(4)	6642(3)	5598(4)	90(2)
C(17)	578(3)	7316(3)	586(3)	67(1)	C(86)	5402(5)	9917(3)	7593(5)	98(2)

Continued

Atom	*x*	*y*	*z*	U_{eq}	Atom	*x*	*y*	*z*	U_{eq}
C(18)	2183(3)	6699(2)	3071(3)	61(1)	C(87)	5434(7)	10426(4)	8340(5)	160(4)
C(19)	149(3)	8988(2)	4353(3)	53(1)	*O(41)	2632(8)	4470(6)	5138(8)	151(4)
C(20)	−1348(3)	7941(2)	5038(3)	53(1)	*O(42)	2799(4)	5044(3)	6318(4)	51(1)
C(21)	−2279(3)	7951(3)	2882(3)	56(1)	*O(43)	7356(12)	4982(9)	874(12)	242(7)
C(22)	−3163(3)	7619(3)	3097(3)	68(1)	*O(44)	8587(6)	5352(4)	802(6)	92(2)
C(23)	−3196(4)	6963(4)	3343(4)	89(2)	*C(91)	4157(6)	4749(5)	5555(7)	68(3)
C(24)	−4055(5)	6666(4)	3504(5)	125(3)	*C(92)	3162(7)	4756(5)	5652(7)	77(3)
C(25)	−4874(8)	7012(8)	3441(7)	188(8)	*C(93)	1834(7)	5063(6)	6418(8)	99(4)
C(26)	−4836(5)	7595(7)	3180(5)	153(5)	*C(94)	1588(9)	5367(7)	7181(9)	108(4)
C(27)	−3986(3)	7955(4)	2988(3)	110(2)	*C(95)	7721(12)	5284(8)	2200(11)	144(6)
C(28)	−164(4)	6390(2)	4824(3)	62(1)	*C(96)	7935(11)	5220(8)	1289(10)	123(5)
C(29)	−604(5)	5712(3)	4866(5)	113(2)	*C(97)	8751(8)	5262(6)	−90(8)	95(4)
C(30)	2920(3)	8505(3)	4860(4)	66(1)	*C(98)	9648(8)	5421(7)	−309(9)	108(4)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

−0.063 and 0.019 nm, respectively, from the mean plane of the other four atoms]. Ring A, "double-bridged" to the central ring, exhibits the 1,3-diplanar boat conformation with C(11) only −0.031 nm and C(15) −0.10 nm fully above the mean plane of the atoms C(13), C(12), C(14) and C(1). These conformations are more or less identical for all the baccatin derivatives resolved by X-ray analysis (Table 5).[5-12] The relative orientation of the carboxyl and benzene groups of benzoyl, which has been the subject of discussions in some papers, deviates from coplanarity [atoms O(2) and O(3) deviated by −0.033 and 0.032 nm, respectively, from the plane of atoms C(21), C(22), C(23), C(24), C(25), C(26) and C(27)]. This study, in conjunction with the earlier studies on related baccatin derivatives, reveals that the benzoyl group exhibits an unexpected conformational flexibility that may be relevant to the bioactivity of taxanes. The solid-state conformation of **1** shows that both esterification of the 7-hydroxyl, 9-hydroxyl, 10-hydroxyl and removal of oxygen functionality at 1-position have little effect on the conformation of tetracyclic system.

In the crystal lattice, the hydrophobic interactions include the acetyl moieties at various positions. Consequently, it can be suggested that the driving force of the crystal arrangement is the result of the stacking of the molecules due to intermolecular hydrophobic interactions.[20]

The compound **1** has the composition $C_{37}H_{46}O_{13}$ as derived from ESI mass and ^{13}C NMR spectral data. UV and IR indicated the presence of carboxyl and benzoyl (244 nm, 1741 and 1725 cm^{-1}). The presence of five acetyl groups was verified by observation of ^{1}H NMR and ^{13}C NMR spectral data (Table 1). The characteristic resonances of four methyl singlets (δ 1.14, 1.59, 1.89 and 1.98) indicated that the compound **1** is a taxane. A pair of doublets at δ 4.13 (J=8.4 Hz) and 4.39 (J=8.4 Hz) accounted for the C(20) methylene protons of

Table 5 Selected torsion angles (°) of the compound **1** and Paclitaxel (molecules A and B)

Position	Compound **1**	Paclitaxel A	Paclitaxel B
C(15)-C(1)-C(2)-C(3)	−73	−71	−63
C(14)-C(1)-C(2)-C(3)	55	63	63
C(1)-C(2)-C(3)-C(8)	107	100	99
C(1)-C(2)-C(3)-C(4)	−125	−133	−133
C(8)-C(3)-C(4)-C(5)	−29	−25	−23
C(2)-C(3)-C(4)-C(5)	−159	−155	−154
C(3)-C(4)-C(5)-C(6)	−1	0	−5
C(4)-C(5)-C(6)-C(7)	−3	−8	−5
C(5)-C(6)-C(7)-C(8)	38	43	43
C(6)-C(7)-C(8)-C(3)	−66	−68	−70
C(6)-C(7)-C(8)-C(9)	173	169	168
C(7)-C(8)-C(3)-C(4)	59	56	57
C(9)-C(8)-C(3)-C(2)	−50	−64	−63
C(9)-C(8)-C(3)-C(4)	−178	169	169
C(7)-C(8)-C(3)-C(2)	−173	−177	−175
C(3)-C(8)-C(9)-C(10)	−57	−43	−42
C(7)-C(8)-C(9)-C(10)	61	72	73
C(8)-C(9)-C(10)-C(11)	65	59	59
C(9)-C(10)-C(11)-C(15)	56	50	48
C(9)-C(10)-C(11)-C(12)	−113	−124	−124
C(15)-C(11)-C(12)-C(13)	−5	−6	−5
C(10)-C(11)-C(12)-C(13)	165	168	167
C(11)-C(12)-C(13)-C(14)	−39	−39	−41
C(12)-C(13)-C(14)-C(1)	27	33	37
C(13)-C(14)-C(1)-C(15)	23	14	10
C(13)-C(14)-C(1)-C(2)	−107	−113	−117
C(14)-C(1)-C(15)-C(11)	−62	−55	−53
C(2)-C(1)-C(15)-C(11)	67	70	72
C(1)-C(15)-C(11)-C(12)	55	55	54

oxetane ring. The isolated spin system comprised two doublets at δ 6.01 and 6.19 (J=11.2 Hz) indicative of a *trans*-oriented configuration. The proton signals of H-7, H-9 and H-10 were observed at δ 5.57, 6.01 and 6.19, respectively, suggesting that the acetyl groups were located at C(7), C(9) and C(10), in addition to those on the C(4) and C(13) positions. The structure of **1** was elucidated as 1β-H, 2β-H, 3α-H, 5α-H, 7α-H, 9β-H, 10α-H and 13β-H, which was in good agreement with both X-ray structure and relative ^{1}H NMR signal. The analysis of one and three bond C—H correlations by HMQC and HMBC experiments and DEPT information allowed the unambiguous assignment of all ^{1}H NMR and ^{13}C NMR signals (Table 1) and the assignment of the structure of 1-deoxybaccatin VI for compound **1.**

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