Pergamon

Tetrahedron Vol. 51, No. 37, pp. 10175-10188, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00607-9

STRUCTURES OF NINE NEW DITERPENOIDS FROM *TAXUS CHINENSIS*

Kaoru Fuji*, Kiyoshi Tanaka and Bo Li
Institute for Chemical Research, Kyoto University, Uji 611, Japan

Tetsuro Shingu and Toshio Yokoi
Faculty of Pharmaceutical Sciences, Kobe Gakuin University, Nishi-ku, Kobe 651-21, Japan

Hangdong Sun
Kunming Institute of Botany, Academia Sinica, Kunming 650204, Yunnan, China

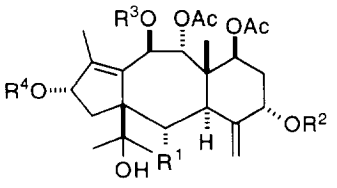
Tooru Taga
Faculty of Pharmaceutical Sciences, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Abstract: The structures of nine new diterpenoids from the leaves and stems of *Taxus chinensis* were elucidated by means of NMR spectroscopy. Some of the new diterpenes were subjected to X-ray crystallographic analysis. Taxchinins D, G, E, H, I, J, K have an 11(15 → 1)-abeotaxane skeleton. Taxchins A and B possess an ordinary taxane skeleton, and belong to the first example of taxoids without an oxygen functionality or the sp^2-hybridized carbon at C-4. Taxchinins D, E, I, and J exist as a mixture of conformational isomers in solution, whose behavior was investigated by variable-temperature NMR spectra and compared with the conformation obtained from X-ray analysis.

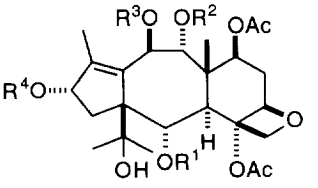
The potent tumor inhibitory properties of taxol have stimulated an extensive search for better source and improved analogues of this type of drug.[1,2] To date over 100 diterpenoids have been isolated from various *Taxus* species.[3] Among them, 11(15→1)-abeotaxoids have been recognized as the rapidly-growing family of diterpenoids since our report on the structure of taxchinin A (**1**) in 1992. Although the first one with this skeleton was a semisynthetic product from taxol,[4,5] about 30 abeotaxoids have recently been isolated from different *Taxus* species, which could be classified into three groups: (A) abeotaxoids with a C-4(20) exocyclic double bond (brevifoliol[6] type or taxchinin A[7] type), (B) abeotaxoids with an oxetane ring (taxchinin B type),[8] and (C) abeotaxoids with an oxirane ring (taxuchin A type).[9] In contrast to the fixed skeletal conformation of taxoids, 11(15→1)-abeotaxoids generally show a slow equilibrium between two or more conformational isomers in solution, which appears to be the characteristic of this type of diterpenoid structure.[10-16]

As the continuation of our ongoing program aimed at investigation of new taxoids of antitumor activities, we reported here a full account for structural elucidation of taxchinins D (**2**), G (**3**), H (**4**), E (**5**), K (**8**), I (**9**), J (**11**), and taxchins A (**13**), B (**14**), mainly based on ^{1}H- and ^{13}C NMR analyses. The conformational study on new diterpenoids by variable-temperature ^{1}H NMR spectroscopy as well as single crystal X-ray analysis are also described. The former seven possess an 11(15 → 1)-abeotaxane skeleton, while the latter two have a usual taxane skeleton. A part of this work has appeared in preliminary forms.[10,11]

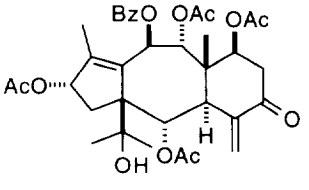
The structure of taxchinin D (**2**) was unequivocally determined by a X-ray analysis.[10] Its ^{1}H NMR spectrum in $CDCl_3$ showed broad signals at an ambient temperature (Figure 1-a), while sharpened upon



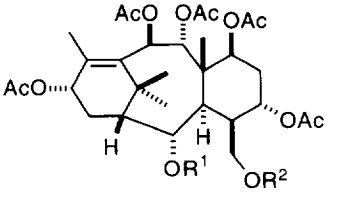
	R^1	R^2	R^3	R^4
1	OAc	H	Bz	H
2	OAc	H	Bz	Ac
3	OAc	H	H	Ac
4	H	Cinn	Bz	H
5	OAc	H	Bz	Cinn



	R^1	R^2	R^3	R^4
6	Ac	Ac	Bz	Cinn
7	Bz	Bz	Bz	Ac
8	Ac	Bz	Bz	Ac
9	Bz	Bz	H	Ac
10	Bz	Bz	Ac	Ac
11	Ac	Bz	H	Cinn



12



13 R^1 = H, R^2 = Ac
14 R^1 = Ac, R^2 = Cinn

cooling. At -10°C, signal for each proton appeared as two resonances (Figure 1-b). Contrary to this, at 150°C in DMSO-d_6, signal for each proton was observed as only one resonance due to fast exchange (weighted average spectrum, Figure 1-c). Such an NMR behavior suggested the presence of a slow equilibrium between two conformational isomers, whereas only one conformation was observed in its crystalline state. Inspection of the conformation by using molecular models implied two preferable conformations, a boat/chair (type A) and a chair/boat (type B) conformation for the B/C ring, respectively. The detailed analysis of the coupling constants observed in the ^{1}H NMR spectra at low temperature was well consistent with these two conformers.[10] The crystalline state of taxchinin D adopts the type A conformation. Oxidation of taxchinin D by pyridinium dichromate gave the ketone **12** with a chair-like conformation for ring B in $CDCl_3$ at room temperature.

The structure of taxchinin G (**3**) was confirmed by X-ray analysis.[10] Its ^{1}H NMR spectrum (Table 1) showed only one set of broad signals at room temperature, corresponding to the type B conformation ($J_{9,10}$ = 3.7 Hz), which was observed in crystalline state.

The ^{1}H- and ^{13}C NMR spectra of taxchinin H (**4**) (Table 1) are very similar to those of brevifoliol,[6] except for the presence of one cinnamoyl. In $CDCl_3$ at an ambient temperature, taxchinin H (**4**) adopts a stable boat/chair conformation for the B/C ring ($J_{9,10}$ = 10.5 Hz). In the ^{13}C-^{1}H LR COSY (12.5 Hz) spectrum, a correlation between cinnamoyl carbonyl signal at δ 165.8 and H-5 signal at δ 5.54 (dd, J = 2.1, 3.9 Hz) established the location of cinnamoyloxy group at C-5.

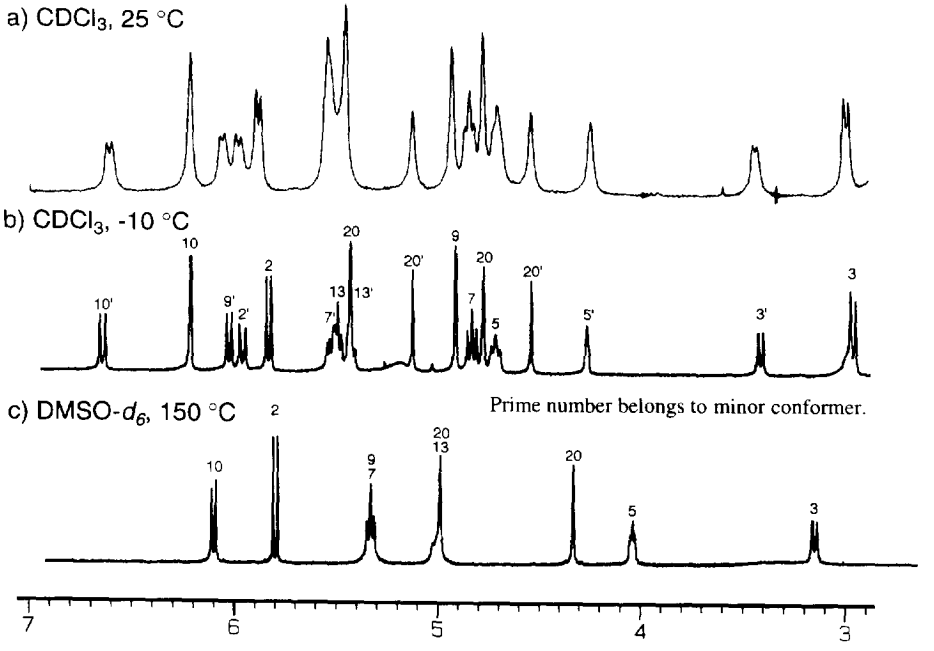


Figure 1. ^{1}H NMR Spectra of Taxchinin D (400 MHz)

Taxchinin E (**5**) showed very similar ^{1}H- and ^{13}C NMR spectra to those of taxchinin D (**2**) both at 25 and -10°C (Table 2). The structure of taxchinin E (**5**) was clearly elucidated by detailed 2D NMR spectral analysis.[11]

The ratio of conformational isomers for a series of taxchinin A type compounds in solution is shown in Table 3. Although it can be seen from the table that the ratio significantly depends upon the acylation pattern on the abeotaxoid skeleton, the effects of these groups on the conformational equilibrium are too complex to be analyzed. However, in the case of taxchinin D (**2**) and taxchinin G (10-debenzoyltaxchinin D) (**3**), it might be explained in terms of both the hydrogen bonding and steric interaction. The X-ray analysis of taxchinin G (**3**) showed the presence of hydrogen bonding between C(15)-O<u>H</u> and C(10)-<u>O</u>H [distance between C(15)-O<u>H</u> and C(10)-<u>O</u>H: 2.653 Å]. Thus, the chair/boat conformation for B/C ring is more stabilized due to the hydrogen bonding. On the other hand, the X-ray analysis of taxchinin D (**2**) revealed a boat/chair conformation for B/C ring [distance between C(15)-O<u>H</u> and C(10)-<u>O</u>Bz: 3.031 Å]. Taxchinin D (**2**) intends to take this arrangement to avoid the repulsive steric interaction between the dimethylcarbinol at C-1 and benzoyloxy group at C-10. Consequently, it seems likely that the cooccurrence and balance of the hydrogen bonding and the steric interaction

in taxchinin D (**2**) result in a conformational equilibrium in $CDCl_3$ at room temperature. Since such an intramolecular hydrogen bonding in taxchinin D (**2**) is somewhat interrupted by the solvation with a polar solvent possessing the larger dielectronic constant, a boat/chair conformation for B/C ring (type A) is favored in

Table 1. ^1H- and ^{13}C NMR Data for Taxchinins G (3) and H (4) ($CDCl_3$, δ in ppm from TMS, at room temperature)

	Taxchinin G (3)[a]		Taxchinin H (4)[b]	
Position	δ_H	δ_C	δ_H	δ_C
1		66.8		63.1
2	5.77 (d, 9.0)	70.5	1.48 (brd, 14.1, Hα) 2.42 (dd, 14.1, 8.9, Hβ)	29.3
3	2.96 (d, 9.0)	44.9	2.87 (d, 8.9)	39.1
4	c	144.4	c	145.6
5	4.68 (brs)	66.0	5.54 (dd, 2.1, 3.9)	74.2
6	c	35.8	2.08 (ddd, 15.0, 5.4, 2.1, Hα) 1.95 (ddd, 15.0, 11.2, 3.9, Hβ)	34.0
7	4.82 (brs)	71.5	5.67 (dd, 11.2, 5.4)	69.8
8		43.7		44.9
9	4.92 (d, 3.7)	76.3	6.05 (brd, 10.5)	77.3
10	4.82 (brs)	71.5	6.68 (d, 10.5)	70.8
11		137.4		134.2
12		147.5		151.2
13	5.56 (t, 7.2)	80.3	4.49 (t, 7.1)	77.0
14	2.39 (dd, 7.2, 14.7, Hβ)	38.4	1.22 (dd, 14.0, 7.2, Hα) 2.41 (dd, 14.0, 7.2, Hβ)	47.5
15		76.0		75.6
16	1.26 (s)	27.8	1.32 (s)	24.8
17	1.15 (s)	27.1	1.02 (s)	27.1
18	1.66 (s)	12.9	2.16 (brs)	11.9
19	1.59 (s)	14.7	0.94 (s)	13.0
20	4.77 (s, Hα) 5.45 (s, Hβ)	113.9	4.93 (brs, Hα) 5.33 (s, Hβ)	114.2
2OAc (C=O)		171.9		
(Me)	1.98 (s)	21.2		
7OAc (C=O)		171.5		169.95
(Me)	1.96 (s)	21.3	2.07 (s)	21.4
9OAc (C=O)		171.2		169.96
(Me)	1.99 (s)	21.5	1.76 (s)	20.8
13OAc (C=O)		170.9		
(Me)	2.14 (s)	22.0		
5OCi (C=O)				165.8
Ci (α)			6.50 (d, 16.0)	118.3
Ci (β)			7.67 (d, 16.0)	145.2
Ci (1)				134.5
Ci (2,6)			7.55 (m)	128.2
Ci (3, 5)			7.37 (m)	128.9
Ci (4)			7.37 (m)	130.3
10OBz (C=O)				164.2
Bz (1)				129.3
Bz (2,6)			7.88 (dd, 1.2, 7.8)	129.5
Bz (3, 5)			7.43 (brt, 7.5)	128.8
Bz (4)			7.43 (brt, 7.5)	133.3

[a] 200 MHz for ^1H NMR, 50 MHz for ^{13}C NMR. Assigned by HH COSY, HETCOR, NOESY, DEPT spectra.

[b] 500 MHz for ^1H NMR, 125 MHz for ^{13}C NMR. Assigned by HH COSY, CH COSY, DEPT, NOESY, CH Long Range COSY.

[c] Signals are not identified due to the overlap with other signals.

Table 2. ^{1}H- and ^{13}C NMR Data for Taxchinin E (5) ($CDCl_3$, δ in ppm from TMS, at -10°C)[a]

Position	Type A Conformer[b]		Type B Conformer[b]	
	δ_H	δ_C	δ_H	δ_C
1		69.2		66.6
2	6.12 (d, 9.5)	67.2	5.92 (d, 9.5)	70.2
3	3.55 (d, 9.5)	41.6	3.07 (d, 9.5)	44.3
4		144.3		146.8
5	4.33 (brs)	74.4	4.78 (brs)	65.5
6	2.03 (m, Hα)	36.7	2.12(m, Hα)	35.2
	1.80 (m, Hβ)		1.90 (dt, 12.4, 8.5, Hβ)	
7	5.65 (dd, 5.3, 11.1)	68.7	4.93 (t, 8.5)	70.5
8		45.2		43.3
9	6.05 (d, 10.7)	75.8	5.00 (d, 3.5)	73.8
10	6.77 (d, 10.7)	69.3	6.32 (d, 3.5)	69.2
11		134.9		133.0
12		149.2		149.0
13	5.61 (t, 7.3)	79.2	5.72 (t, 7.0)	79.5
14	2.19 (m, Hα)	38.0	2.06 (m, Hα)	38.8
	2.49 (dd, 7.3, 13.3, Hβ)		2.51 (dd, 7.0, 14.9, Hβ)	
15		75.3		75.4
16	1.24 (s)	25.2	1.16 (s)	26.6
17	1.16 (s)	27.5	0.99 (s)	27.6
18	2.18 (s)	12.4	1.95 (s)	13.1
19	1.06 (s)	13.3	1.76 (s)	14.6
20	4.59 (brs, Hα)	112.8	4.86 (brs, Hα)	113.7
	5.18 (brs, Hβ)		5.50 (brs, Hβ)	
2OAc (C=O)		171.4		170.7
(Me)	2.01 (s)	21.9	1.99 (s)	21.8
7OAc (C=O)		170.1		170.5
(Me)	2.10 (s)	21.5	1.98 (s)	21.2
9OAc (C=O)		169.7		169.7
(Me)	1.80 (s)	20.8	2.12 (s)	20.9
10OBz (C=O)		164.0		164.7
Bz (1)		128.6		128.7
Bz (2, 6)	7.89 (d, 7.4)	129.5	8.02 (d, 7.4)	129.7
Bz (3, 5)	7.47 (t, 7.4)	128.8	7.52 (t, 7.5)	128.9
Bz (4)	7.60 (t, 7.5)	133.5	7.65 (t, 7.4)	133.8
13Ci (C=O)		166.8		167.1
Ci (α)	6.46 (d, 16.0)	117.5	6.59 (d, 16.0)	117.4
Ci (β)	7.77 (d, 16.0)	145.4	7.77 (d, 16.0)	145.6
Ci (1)		133.9		134.0
Ci (2, 6)	7.55 (m)	128.2	7.61 (m)	128.2
Ci (3, 5)	7.42 (m)	128.9	7.45 (m)	128.9
Ci (4)	7.42 (m)	130.5		130.6

[a] 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR. Assigned by HH COSY, CH COSY, DEPT, NOESY, CH Long Range COSY.

[b] Type A conformer / type B conformer = 40 / 60

such kinds of solvents. Experimentally, the population of type A conformer of taxchinin D (**2**) increases from 38 % in $CDCl_3$ to 63 % in DMSO-d_6-$CDCl_3$ (5:1).

Table 3. Conformer Ratio of 11(15→1)-Abeotaxa-4(20), 11-diene Diterpenoids in $CDCl_3$

Compound	T (°C)	Type A (%)	Type B (%)
1	r.t.	80	20
2	-10	38	62
3	r.t.	0	100
4	r.t.	100	0
5	-10	40	60
12	r.t.	0	100

Both the ^1H- and ^{13}C NMR spectra of taxchinin K (**8**) (Table 4) are considerably similar to those of taxchinins B (**6**) and C (**7**).[8] The difference is the presence of two benzoyls and four acetyls in taxchinin K (**8**). The upfield shifts of H-2 and H-3, as well as downfield shift of H-20α, comparing with those of taxchinin C (**7**) suggested the location of two benzoyloxy groups at C-9 and C-10. The ^1H NMR spectrum at an ambient temperature in $CDCl_3$ indicated one biased conformation with boat/half-boat for B/C ring ($J_{9,10}$ = 11.0 Hz).

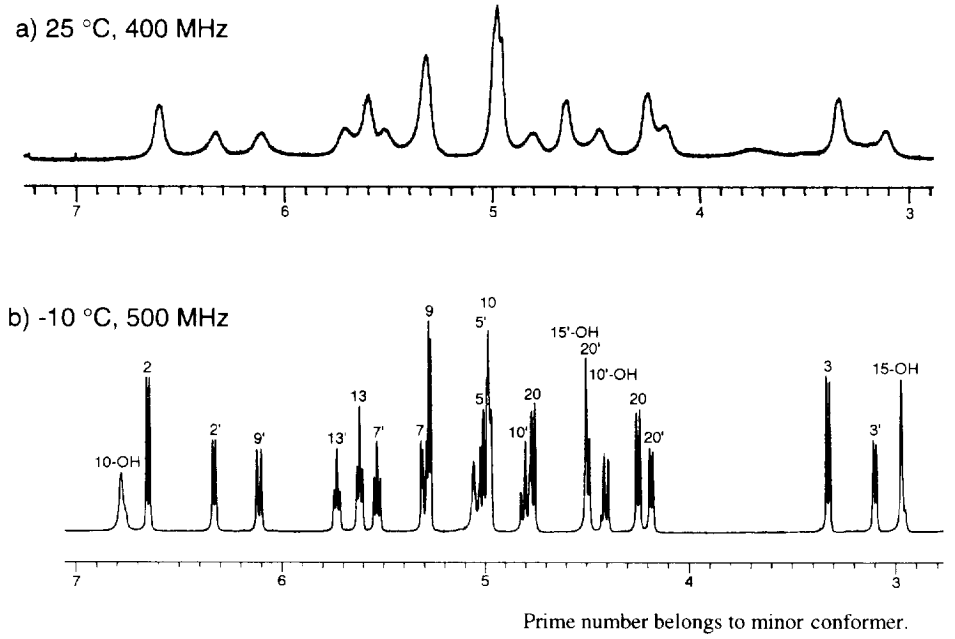
Table 4. ^1H- and ^{13}C NMR Data for Taxchinin K (8) ($CDCl_3$, δ in ppm from TMS, at room temperature)

Position	δ_H[a]	δ_C[b]	Position	δ_H[a]	δ_C[b]
1		67.9	15-OH	2.62 (brs)	
2	6.26 (d, 7.4)	68.4	OAc (C=O)		171.2
3	3.06 (d, 7.4)	44.3			170.9
4		79.2			170.6
5	5.01 (d, 7.3)	85.2			169.6
6	2.70 (m)	34.9	OAc (Me)	2.13 (s)	22.1
7	5.63 (m)	70.8		2.04 (s)	21.8
8		44.0		1.84 (s)	21.7
9	6.48 (d, 11.0)	77.6			21.2
10	6.73 (d, 11.0)	68.6	9OBz (C=O)		167.0
11		136.4	10OBz (C=O)		164.8
12		148.2	Bz (1)		129.6
13	5.63 (m)	79.0			129.3
14	2.34 (dd, 7.4, 14.3, Hβ)	37.0	Bz (2, 6)	7.34 (m)	130.0
15		76.0		7.23 (m)	129.8
16	1.24 (s)	27.8	Bz (3, 5)		129.2
17	1.21 (s)	25.4			129.0
18	1.94 (s)	12.0			128.7
19	1.80 (s)	13.2	Bz (4)	7.74 (d, 7.0)	133.4
20	4.50 (d, 7.6, Hα)	74.8		7.63 (d, 7.1)	133.3
	4.53 (d, 7.6, Hβ)				

[a] 200 MHz, [b] 50 MHz.

The ^1H- and ^{13}C NMR spectra of taxchinin I (**9**) at 25°C and -10°C (Figure 2 and Table 5) suggested that taxchinin I (**9**) exists as an equilibrium mixture of two conformers in $CDCl_3$. ^{13}C NMR signals at δ 66.0 and 75.1 (C-1 and C-15, major conformer) and δ 67.2, 76.2 (C-1 and C-15, minor conformer) indicated an 11(15→1)-abeotaxane skeleton. The presence of an oxetane ring was confirmed by both the ^1H NMR signal at δ 4.25,

4.76 (each 1H, d, J = 8.4 Hz, major conformer) , as well as δ 4.18, 4.49 (each 1H, d, J = 7.7 Hz, minor conformer) and ^{13}C NMR signals at δ 78.4 (CH_2, major conformer) and δ 74.4 (CH_2, minor conformer). The upfield shift of H-10 signal [δ 4.98 (d, J = 5.0 Hz, major conformer), 4.80 (t, J = 10.5 Hz, minor conformer)] suggested a free hydroxyl group at C-10. The ^{13}C-^1H LR COSY spectra established the location of benzoyloxy groups at C-2 and C-9, two acetoxyls at C-7 and C-13. The major conformer of taxchinin I (**9**) adopts a chair/half-chair conformation for B/C ring, which could be easily characterized by the ^1H NMR signal at δ 5.01 (t, J = 8.4 Hz, H-5), 5.30 (dd, J = 4.0, 13.2 Hz, H-7), 5.27 (d, J = 5.0 Hz, H-9) and 4.98 (d, J = 5.0 Hz, H-10). This was also supported by the observation of the cross peak between H-9 and H-10 in the NOESY spectrum. The minor conformer possesses a boat/half-boat conformation for B/C ring, which was revealed by the ^1H NMR signals at δ 4.98 (d, J = 7.0 Hz, H-5), 5.53 (t, J = 7.9 Hz, H-7), 6.11 (d, J = 10.2 Hz, H-9) and 4.80 (t, J = 10.5 Hz, H-10). The cross peaks between H-3 and H-10 as well as H-7 and H-10 in the NOESY spectrum confirmed this type of conformation. Furthermore, taxchinin I (**9**) was proven to be 10-debenzoyl taxchinin C, since benzoylation of taxchinin I (**9**) with benzoyl chloride in pyridine gave an identical compound with taxchinin C (**7**), whose structure had already been established.[8]



Prime number belongs to minor conformer.

Figure 2. ^1H NMR Spectra of Taxchinin I ($CDCl_3$)

The ^1H- and ^{13}C NMR spectra of taxchinin J (**11**) (Table 6) at -10°C are similar to those of taxchinin I (**9**). The difference is the presence of one benzoyl, one cinnamoyl and three acetyl groups in taxchinin J (**11**). The location of acyl groups was consistently determined by ^{13}C-^1H LR COSY spectrum. Conformational bias

in taxchinin I (**9**) and taxchinin J (**11**) in $CDCl_3$ at -10°C is very alike, appearing as a mixture of two conformers with a ratio of 46/54 (boat/half-boat:chair/half-chair) for taxchinin J (**11**).

Table 5. ^1H- and ^{13}C NMR Data for Taxchinin I (9) ($CDCl_3$, δ in ppm from TMS, at -10°C)[a]

	Chair/Half-chair Conformer[b]		Boat/Half-boat Conformer[b]	
Position	δ_H	δ_C	δ_H	δ_C
1		66.0		67.2
2	6.65 (d, 8.0)	70.7	6.33 (d, 7.5)	68.5
3	3.32 (d, 8.0)	42.8	3.10 (d, 7.5)	44.3
4		82.5		78.8
5	5.01 (t, 8.4)	84.0	4.98 (d, 7.0)	84.7
6	2.39	30.9	2.63	34.7
	(ddd, 4.0, 9.6, 13.3, Hα)		(dt, 8.0, 16.4, Ha)	
	2.11		1.82	
	(td, 7.5, 13.3, Hβ)		(m, Hβ)	
7	5.30 (dd, 4.0, 13.3)	70.0	5.53 (t, 8.0)	70.5
8		44.4		43.2
9	5.27 (d, 5.0)	75.3	6.11 (d, 10.3)	80.7
10	4.98 (d, 5.0)	67.7	4.80 (t, 10.3)	66.3
11		137.8		139.7
12		140.8		142.6
13	5.62 (t, 6.6)	80.9	5.73 (t, 7.0)	79.3
14	1.94	36.4	1.80	36.3
	(dd, 6.6, 14.8, Hα)		(m, Hα)	
	2.58		2.34	
	(dd, 7.4, 14.8, Hβ)		(dd, 8.1, 15.8, Hβ)	
15		75.1		76.2
16	1.16 (s)	27.9	1.21 (s)	25.2
17	0.98 (s)	30.4	1.12 (s)	27.7
18	1.25 (s)	13.3	1.90 (s)	11.4
19	1.86 (s)	13.8	1.81 (s)	13.3
20	4.25 (d, 8.4, Hα)	78.4	4.18 (d, 7.7, Hα)	74.4
	4.76 (d, 8.4, Hβ)		4.49 (d, 7.7, Hβ)	
10-OH	6.78 (brs)		4.40 (d, 10.3)	
15-OH	2.97 (brs)		4.50 (brs)	
4OAc (C=O)		169.6		169.2
(Me)	2.32 (s)	22.2	2.22 (s)	22.1
7OAc (C=O)		169.7		170.8
(Me)	1.91 (s)	21.0	1.80 (s)	22.0
13OAc (C=O)		170.9		171.1
(Me)	2.18 (s)	21.1	2.21 (s)	21.3
2OBz (C=O)		167.1		165.9
2OBz (1)		129.3		129.5
2OBz (2, 6)	8.10 (d-like, 7.2)	130.0	8.02 (d-like, 7.2)	129.6
2OBz (3, 5)	7.53 (t-like, 8.0)	128.9	7.51 (t-like, 7.8)	128.7
2OBz (4)	7.67 (t-like, 7.5)	134.1	7.65 (t-like, 8.1)	133.7
9OBz (C=O)		165.0		168.0
9OBz (1)		129.1		130.2
9OBz (2, 6)	8.14 (d-like, 7.3)	129.9	7.98 (d-like, 7.1)	129.7
9OBz (3, 5)	7.47 (t-like, 7.7)	128.3	7.45 (t-like, 7.4)	128.3
9OBz (4)	7.59 (t-like, 7.4)	133.4	7.57 (t-like, 7.3)	133.0

[a] 500 MHz for ^1H NMR. 125 MHz for ^{13}C NMR. Assigned by HH COSY, CH COSY, NOESY, DEPT, CH LR COSY.
[b] Boat/half-boat conformer : chair/half-chair conformer = 40 : 60

Table 6. ^{1}H- and ^{13}C NMR Data for Taxchinin J (11) ($CDCl_3$, δ in ppm from TMS, at -10°C)[a]

	Chair/half-chair Conformer [b]		Boat/half-boat Conformer [b]	
Position	δ_H	δ_C	δ_H	δ_C
1		65.8		67.0
2	6.40 (d, 7.8)	70.7	6.06 (d, 7.8)	68.2
3	3.31 (d, 7.8)	42.6	3.02 (d, 7.8)	43.8
4		82.7		78.6
5	5.06 (t, 9.0)	84.2	5.01 (d, 7.1)	84.9
6	2.45 (ddd, 4.0, 9.0, 13.1, Hα)	30.9	2.69 (dt, 16.1, 8.0, Hα)	34.6
	2.15 (m, Hβ)		1.80 (m, Hβ)	
7	5.34 (dd, 4.0, 13.1)	70.1	5.54 (t, 7.4)	70.4
8		44.4		43.3
9	5.26 (d, 4.7)	75.8	6.06 (d, 9.7)	80.7
10	4.97 (d, 4.7)	67.7	4.80 (brt, 9.7)	66.3
11		137.7		139.6
12		140.9		142.6
13	5.82 (t, 7.1)	80.4	5.64 (t, 7.0)	79.7
14	1.80 (m, Hα)	36.4	1.63 (dd, 7.1, 14.6, Hα)	37.0
	2.50 (dd, 7.1, 15.1, Hβ)		2.36 (dd, 7.1, 14.6, Hβ)	
15		74.9		76.2
16	1.30 (s)	27.8	1.27 (s)	25.2
17	1.02 (s)	30.4	1.16 (s)	27.6
18	1.27 (s)	13.3	1.95 (s)	11.5
19	1.81 (s)	14.1	1.77 (s)	13.5
20	4.45 (d, 7.6, Hα)	78.5	4.43 (d, 7.3, Hα)	74.6
	4.81 (d, 7.6, Hβ)		4.52 (d, 7.3, Hβ)	
10-OH			4.43 (d, 11.4)	
15-OH	2.85 (brs)			
2OAc (C=O)		172.2		170.7
(Me)	2.16 (s)	22.8	2.04 (s)	21.7
4OAc (C=O)		170.2		169.2
(Me)	2.13 (s)	22.1	2.01 (s)	22.0
7OAc (C=O)		169.7		170.8
(Me)	1.90 (s)	21.0	1.81 (s)	22.0
9OBz (C=O)		165.1		168.0
Bz (1)		129.0		130.2
Bz (2, 6)	8.13 (d-like, 7.4)	129.7	7.50 (m)	129.7
Bz (3, 5)	7.30 (t-like, 7.6)	128.3	7.99 (d-like, 7.3)	128.3
Bz (4)	7.39 (t-like, 7.4)	133.4	7.56 (t-like, 7.4)	133.1
13OCi (C=O)		166.3		166.9
Ci (α)	6.51 (d, 16.1)	117.6	6.51 (d, 16.1)	117.2
Ci (β)	7.91 (d, 16.1)	145.3	7.82 (d, 16.1)	145.9
Ci (1)		134.0		133.8
Ci (2, 6)	7.74 (m)	128.2	7.50 (m)	128.2
Ci (3, 5)	7.52 (m)	129.2	7.50 (m)	129.0
Ci (4)	7.52 (m)	130.8	7.50 (m)	130.7

[a] 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR. Assigned by HH COSY, CH COSY, NOESY, DEPT, CH Long Range COSY.

[b] Boat/half-boat conformer : chair/half-chair conformer = 46 : 54

The ratios of conformational isomers of some 11(15→1)-abeotaxoids with an oxetane ring are shown in Table 7. Comparing to 11(15→1)-abeotaxoids without an oxetane ring, a relatively small conformational change has been observed probably due to a constraint on conformation by the oxetane ring. It also seems likely that the conformational equilibrium is mainly affected by acyl groups on B ring. Similar to the case of taxchinin A type compounds, the hydrogen bonding between the hydroxy group at C-15 and the oxygen functionality at C-10 as well as the steric repulsive interaction between the dimethylcarbinol moiety at C-1 and acyl group at C-10 again

account for the observed conformational bias. Thus, in the case of taxchinin C (**7**), 10-acetyltaxchinin I (**10**) and taxchinin I (**9**), the boat/half-boat conformation for B/C ring is favored by the presence of a bulky acyl group at C-10 (Table 7).

Table 7. Conformer Ratio of 5β, 20-Epoxy-11(15→1)-abeotaxa-11-ene Diterpenoids in $CDCl_3$

Compound	T (°C)	Boat/half-boat conformer (%)	Chair/half-chair conformer (%)
6	r.t.	100	0
7	r.t.	91	9
8	r.t.	100	0
9	-10	40	60
10	-10	86	14
11	-10	46	54

Taxchin A (**13**) was determined to have a molecular formula of $C_{32}H_{46}O_{13}$ by analyses of the ^{13}C NMR and HRMS data. The ^{13}C NMR signals at δ 38.0 (C-15) and δ 52.1 (C-1) suggested taxchin A possesses a usual taxane skeleton. Taxchin A showed a similar ^{1}H NMR spectrum to those of baccatin I[17] and 1-dehydroxyl baccatin IV.[18] Its ^{1}H- and ^{13}C NMR data are listed in Table 8. ^{1}H NMR signals at δ 2.23 (1H, m, H-4), 3.93 (1H, dd, J = 8.8, 10.4 Hz, H-20α), 4.53 (1H, d, J = 10.4 Hz, H-20β) and ^{13}C NMR signals at δ 42.0 (CH, C-4), 66.8 (CH_2, C-20) indicated the presence of a " $>CHCH_2OAc$ " structural unit. The secondary alcohol at C-2 was confirmed by the ^{1}H NMR signals at δ 4.24 (brs, H-2) and 1.37 (d, J = 4.4 Hz, disappeared with D_2O, C2-OH). The correlation peak between Me-19 and C20-2H in the NOESY spectrum indicated the β-orientation of $-CH_2OAc$ at C-4. Finally, a single crystal X-ray analysis confirmed the structure deduced from the NMR spectroscopic data.

The ^{1}H- and ^{13}C NMR spectra of taxchin B (**14**) (Table 8) indicated a structural similarity of taxchin B (**14**) to taxchin A (**13**). The difference in these two diterpenoids is the presence of six acetyls and one cinnamoyl group in taxchin B (**14**). Taking ^{13}C-^{1}H LR COSY spectrum, it turned out that the location of acetyl groups are at C-2, C-5, C-7, C-9, C-10 and C-13, and the cinnamoyoxyl was connected at C-20. The cross peak between H-3 and H-7, as well as H-7 and H-10 in the NOESY spectrum suggested that taxchinin B (**14**) adopts a boat form for ring A, boat-like form for ring B and chair form for ring C. To the best of our knowledge, isolation of the taxoids possessing no oxygen functionality or the sp^2-hybridized carbon at C-4 is the first example.

Table 8. ^1H- and ^{13}C NMR Data for Taxchin A (13) and B (14) ($CDCl_3$, δ in ppm from TMS, at room temperature)

	Taxchin A (**13**)[a]		Taxchin B (**14**)[b]	
Positon	δ_H	δ_C	δ_H	δ_C
1	1.90 (m)	52.1	2.01 (brd, 9.4)	47.7
2	4.24 (brs)	68.6	5.43 (dd, 2.2, 5.7)	70.9
3	2.63 (m)	40.6	2.83 (t, 5.4)	39.5
4	2.23 (m)	42.0	2.35 (m)	42.2
5	5.00 (brd, 2.1)	70.8	5.10 (q, 2.6)	70.7
6	1.90 (m, Hα, β)	29.8	1.85 (brd, 15.0, Hα)	29.8
			1.95 (ddd, 3.2, 11.8, 15.0, Hβ)	
7	5.39 (dd, 4.9, 11.5)	69.9	5.44 (dd, 4.0,11.8)	69.5
8		45.7		45.6
9	5.78 (d, 11.0)	75.9	5.89 (d, 11.0)	75.6
10	6.16 (d, 11.0)	71.9	6.18 (d, 11.0)	71.8
11		133.7		133.7
12		138.0		137.8
13	5.95 (t, 8.2)	70.8	5.95 (brt, 7.9)	70.5
14	1.47 (dd, 7.7, 15.0, Hα)	27.7	1.46 (dd, 7.9, 15.0, Hα)	27.9
	2.63 (m, Hβ)		2.63 (dt, 9.4, 15.0, Hβ)	
15		38.0		37.9
16	1.68 (s)	27.4	1.76 (s)	27.0
17	1.16 (s)	31.9	1.15 (s)	31.6
18	2.21 (d, 1.5)	15.0	2.24 (d, 1.3)	14.9
19	0.96 (s)	14.3	0.96 (s)	14.3
20	3.93 (dd, 8.8, 10.4, Hα)	66.8	3.94 (d, 11.0, Hα)	65.5
	4.53 (d, 10.4, Hβ)		4.11 (dd, 8.1, 11.4, Hβ)	
2-OH	1.37 (d, 4.4, disappeared with D_2O)			
2OAc (C=O)				169.8
(Me)			2.07 (s)	21.4
5OAc (C=O)		171.9[d]		169.92
(Me)	1.68 (s)[c]	21.9[e]	2.26 (s)	21.8
7OAc (C=O)		170.9[d]		169.5
(Me)	1.97 (s)[c]	21.7[e]	1.98 (s)	21.0
9OAc (C=O)		170.9[d]		169.9
(Me)	2.03 (s)[c]	21.5[e]	2.04 (s)	20.8
10OAc (C=O)		170.6[d]		169.2
(Me)	2.05 (s)[c]	21.1[e]	1.98 (s)	20.9
13OAc (C=O)		170.3[d]		170.4
(Me)	2.12 (s)[c]	21.0[e]	2.14 (s)	21.6
20OAc (C=O)		169.6[d]		
(Me)	2.23 (s)[c]	20.9[e]		
20OCi (C=O)				166.9
20OCi (α)			6.43 (d, 16.0)	117.1
20OCi (β)			7.73 (d, 16.0)	145.9
20OCi (1)				134.7
20OCi (2, 6)			7.53 (m)	128.2
20OCi (3, 5)			7.39 (m)	130.0
20OCi (4)			7.39 (m)	130.6

[a] 400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR. Assigned by HH COSY, DEPT, HETCOR, NOESY spectra.

[b] 500 MHz for ^1H NMR, 125 MHz for ^{13}C NMR. Assigned by HH COSY, CH COSY, NOESY, DEPT, and CH Long Range COSY.

[c, d, e] May be exchangeable in any vertical columns.

EXPERIMENTAL

General Experimental Procedures — The general procedures used were as previously described.[6] Some ^{1}H- and ^{13}C NMR spectra were recorded using Bruker ARX-500 instrument. From the leaves and stems of *Taxus chinensis*, taxchinins D (**2**), G (**3**), H (**4**), E (**5**), K (**8**), I (**9**), J (**11**), and taxchins A (**13**), B (**14**) were isolated in yields of 1.8 x 10^{-3}, 8.0 x 10^{-5}, 1.8 x 10^{-4}, 1.1 x 10^{-3}, 4.0 x 10^{-5}, 6.1 x 10^{-4}, 3.4 x 10^{-4}, 3.2 x 10^{-4}, and 8.3 x 10^{-5} %, respectively.

Taxchinin D (**2**)—Colorless plates from *n*-hexane-acetone, mp 138-141°C; $[\alpha]^{18}_D$ +10.0 (*c* 0.11, $CHCl_3$); IR (KBr) ν_{max}: 3450, 3050, 2980, 1740, 1380, 1250, 1040, 710 cm^{-1}; EIMS *m/z* 538 (M-2OAc)$^+$, 520, 477, 418, 374, 358, 254, 236, 207, 122, 105, 91, 77; HRMS *m/z* 538.2553 (M-2OAc)$^+$, $C_{31}H_{38}O_8$ requires 538.2566. ^{1}H NMR (DMSO-d_6-$CDCl_3$, 5:1, at -3°, 400 MHz): δ 6.00 (d, *J* = 9.5, H-2), 3.44 (d, *J* = 9.5, H-3), 4.10 (brs, H-5), 5.44 (dd, *J* = 5.0, 10.0, H-7), 5.91 (d, *J* = 10.6, H-9), 6.39 (d, *J* = 10.6, H-10), 5.35 (brt, *J* = 7.5, H-13), 4.38 (brs, H-20α), 5.09 (brs, H-20β), major conformer (63 %); δ 5.78 (d, *J* = 9.9, H-2), 2.93 (d, *J* = 8.8, H-3), 4.47 (brt, *J* = 7.5, H-5), 4.73 (t, *J* = 8.8, H-7), 4.83 (d, *J* = 2.8, H-9), 5.76 (brs, H-10), 5.51 (brt, *J* = 7.5, H-13), 4.71 (brs, H-20α), 5.38 (brs, H-20β), minor conformer (37 %); ^{1}H NMR (DMSO-d_6, at 150°, 400 MHz): δ 5.98 (d, *J* = 9.2, H-2), 3.35 (d, *J* = 9.2, H-3), 4.23 (t, *J* = 4.6, H-5), 5.52 (t, *J* = 6.6, H-7), 5.53 (d, *J* = 7.3, H-9), 6.28 (d, *J* = 8.4, H-10), 5.18 (m, H-13), 4.53 (brs, H-20α), 5.18 (brs, H-20β), 1.117, 1.124, 1.76, 1.857, 1.860, 1.91, 1.93, 2.03 (each 3H, s, Me). Signals for H-6 and H-14 are not identified due to the complex overlap with other signals.

X-Ray Analysis of Taxchinin D (**2**)—Crystallized as orthorhombic, space group $P2_12_12_1$ with *a* = 18.350 (2), *b* = 19.148 (3), *c* = 10.105 (2) Å, V = 3550.6 Å^3, Z = 4, *D*x = 1.262 gcm^{-3}. The structure was refined to R = 0.0547, Rw = 0.0492, S = 1.48.[10]

Oxidation of Taxchinin D (**2**)—23 mg of **2** was dissolved in 20 ml of dry CH_2Cl_2, and 73 mg of PDC was added. After stirring at room temperature for 24 h, the mixture was filtered and evaporated. The residure was purified by silica gel column chromatography (CH_2Cl_2-Me_2CO, 93:7) to give 12.5 mg of **12** (yield 54 %). Amorphous powder, mp 120-123°C, EIMS *m/z* 595, 536, 476, 416, 356, 252, 234, 223, 122, 105, 77; ^{1}H NMR (200 MHz, $CDCl_3$, rt): δ 0.97 (3H, s, Me-19), 1.17 (3H, s, Me-16), 1.74 (3H, s, Me-17), 1.95, 1.98, 2.01, 2.08 (each 3H, s, 4 x OCOMe), 2.16 (3H, s, Me-18), 3.28 (1H, d, *J* = 8.1, H-3), 5.20 (2H, m, H-7 and H-9), 5.64 (1H, brt, *J* = 8, H-13), 5.88 (1H, d, *J* = 8.1, H-2), 6.30 (1H, d, *J* = 3.9, H-10), 7.49 [2H, m, Bz (3, 5)], 7.62 [1H, m, Bz (4)], 8.01 (2H, dd, *J* = 1.2, 7.6 , Bz (2, 6)]. ^{13}C NMR (50 MHz, $CDCl_3$, rt): δ 12.7 (C-18), 12.9 (C-19), 20.7, 20.9, 21.1, 21.8 (OCO<u>Me</u>), 27.7 (C-16), 28.1 (C-17), 38.4 (C-6), 38.5 (C-14), 41.8 (C-3), 42.9 (C-8), 65.9 (C-1), 69.2 (C-7), 69.5 (C-2), 70.1 (C-10), 73.8 (C-9), 75.3 (C-15), 80.1 (C-13), 129.1 (C-20, Bz), 129.2, 129.9 (Bz), 133.9 (C-11, Bz), 144.2 (C-4), 148.2 (C-12), 165.3 (O<u>C</u>OPh), 169.7, 170.4, 170.6, 171.3 (4 x O<u>C</u>OMe), 198.7 (C-5).

Taxchinin G (**3**)—Colorless plates from Et_2O, mp 140-143°C, $[\alpha]^{19}_D$ +61.7 (*c* 0.12, $CHCl_3$). IR (KBr) ν_{max}: 3250, 3175, 2975, 2925, 1740, 1700, 1650, 1430, 1380, 1270, 1240, 1210, 1170, 1040, 1000, 970, 920, 600 cm^{-1}; EIMS *m/z* 534 (M-H_2O)$^+$, 519, 516, 492 (M-HOAc)$^+$, 474, 456, 434, 416, 374, 314, 254, 149, 85; HRMS *m/z* 534.2478 (M-H_2O)$^+$, $C_{28}H_{38}O_{10}$ requires 534.2465; ^{1}H- and ^{13}C NMR: Table 1.

X-Ray Analysis of Taxchinin G (**3**)—Crystallized as orthorhombic, space group $P2_12_12_1$ with *a* = 11.909 (5), *b* = 22.430 (6), *c* = 11.104 (3) Å, V = 2966.1 Å^3, Z = 4, *D*x = 1.237 gcm^{-3}. The structure was refined to R = 0.0469, Rw = 0.0460, S = 1.43.[10]

Taxchinin H (**4**)—Amorphous powder, mp 115-118°C; $[\alpha]^{19}_D$ -65.3 (*c* 0.17, $CHCl_3$); IR (KBr) ν_{max}: 3450, 3050, 2975, 2925, 1730, 1640, 1440, 1380, 1260, 1240, 1170, 1020, 710 cm^{-1}; EIMS *m/z* 686 (M)$^+$, 664 (M-H_2O)$^+$, 649, 626 (M-HOAc)$^+$, 604 (664-HOAc)$^+$, 562, 546, 537, 521, 504, 461, 446, 298, 238, 148, 147 (PhCH=CHCOO)$^+$, 131 (PhCH=CHCO)$^+$, 122 (PhCOOH)$^+$, 105, 91, 77; HRMS *m/z* 686.3134 (M)$^+$, $C_{40}H_{46}O_{10}$ requires 686.3091; ^{1}H- and ^{13}C NMR: Table 1.

Taxchinin E (**5**)—Amorphous powder, mp 134-136°C; $[\alpha]^{19}_D$ -17.5 (*c* 0.12, $CHCl_3$); Anal. Found C 67.24, H 6.55; Calcd for $C_{42}H_{48}O_{12}$, C 67.74, H 6.45. IR (KBr) ν_{max}: 3420, 3050, 2975, 2925, 1730, 1630, 1450, 1380, 1300, 1270, 1230, 1160, 1020, 710 cm^{-1}; EIMS *m/z* 623 $(M\text{-}PhCOO)^+$, 622 $(M\text{-}PhCOOH)^+$, 504, 491 $(622\text{-}PhCH{=}CHCO)^+$, 356, 314, 296, 254, 236, 148 $(PhCH{=}CHCOOH)^+$, 147, 131 $(PhCH{=}CHCO)^+$, 122 $(PhCOOH)^+$, 105 $(PhCO)^+$, 91, 77; HRMS *m/z* 622.2738 $(M\text{-}PhCOOH)^+$, $C_{35}H_{42}O_{10}$ requires 622.2777; ^1H- ,^{13}C NMR: see Table 2.

Taxchinin K (**8**)—Colorless needles from *n*-hexane-Et_2O, mp 217-219°C, $[\alpha]^{18}_D$ -30.0 (*c* 0.05, $CHCl_3$); IR (KBr) ν_{max}: 3450, 3025, 2925, 1740, 1630, 1600, 1450, 1370, 1280, 1240, 1100, 1060, 1020, 700 cm^{-1}; EIMS *m/z* 758 $(M\text{-}H_2O)^+$, 698 $(M\text{-}HOAc)^+$, 654 $(M\text{-}PhCOOH)^+$, 638 $(698\text{-}HOAc)^+$, 598, 537, 476, 416, 356, 252, 234, 122, 105, 77; FABMS *m/z* 777 $(M+H)^+$; HRMS *m/z* 758.2970 $(M\text{-}H_2O)^+$, $C_{42}H_{46}O_{13}$ requires 758.2939; ^1H- and ^{13}C NMR: see Table 4.

Taxchinin I (**9**)—Colorless needles from Et_2O, mp 235-237°C, $[\alpha]^{19}_D$ -6.1 (*c* 0.115, $CHCl_3$); IR (KBr) ν_{max}: 3425, 3060, 2980, 1740, 1600, 1450, 1370, 1260, 1170, 1100, 1060, 1020, 980, 710 cm^{-1}; EIMS *m/z* 732, 717, 716, 701, 674, 657, 616, 594, 552, 494, 372, 312, 297, 252, 223, 149, 133, 122, 105, 91, 77; HRMS *m/z* 716.2854 $(M\text{-}H_2O)^+$, $C_{40}H_{44}O_{12}$ requires 716.2833; ^1H-, ^{13}C NMR: see Table 5.

Acetylation of Taxchinin I (**9**)—A mixture of 19.8 mg of **9** and 0.6 ml each of pyridine and Ac_2O was allowed to stand at room temperature overnight. Usual work-up procudure gave the residue, which was purified by silica gel column chromatography (CH_2Cl_2-Me_2CO, 96:4) to yield 11 mg of taxchinin I acetate (**10**). Amorphous powder, mp 134-136°C, EIMS *m/z* 717, 716, 701, 659, 658, 638, 598, 536, 494, 339, 252, 122, 105, 77; HRMS *m/z* 717.2888 $(M\text{-}HOAc)^+$, $C_{40}H_{45}O_{12}$ requires 717.2910; ^1H NMR (400 MHz, $CDCl_3$, at -10°, major conformer): δ 1.16 (6H, s, Me-16, 17), 1.67 (3H, s, OCOMe), 1.85 (6H, s, Me-19, OCOMe), 1.91 (3H, s, Me-20), 2.20 (6H, s, 2 x OCOMe), 2.41 (dd, *J* = 7.3, 14.3, H-14β), 2.59 (1H, brs, C-15-OH), 2.69 (1H, m, H-6α), 3.10 (H, d, *J* = 7.7, H-3), 4.19 (1H, d, *J* = 8.1, H-20α), 4.50 (1H, d, *J* = 7.7, H-20β), 4.96 (1H, d, *J* = 7.0, H-5), 5.60 (1H, t, *J* = 7.9, H-7), 5.72 (1H, t, *J* = 7.4, H-13), 6.42 (1H, d, *J* = 11.0, H-9), 6.45 (1H, d, *J* = 8.1, H-2), 6.52 (1H, d, *J* = 11.0, H-10), 7.49 (4H, m, OBz), 7.62 (2H, m, OBz), 7.95 (2H, d, *J* = 7.3, OBz), 8.03 (2H, d, *J* = 7.0, OBz).

Taxchinin J (**11**)—Colorless needles from Et_2O, mp 238-240°C, $[\alpha]^{19}_D$ +23.4 (*c* 0.11, $CHCl_3$); Anal. Found C 65.85, H 6.42; Calcd for $C_{42}H_{48}O_{13}$, C 66.32, H 6.32. IR (KBr) ν_{max}: 3450, 3025, 2975, 2925, 1720, 1640, 1450, 1380, 1265, 1240, 1160, 1020, 710 cm^{-1}; EIMS *m/z* 742 $(M\text{-}H_2O)^+$, 724 $(742\text{-}H_2O)^+$, 684 $(724\text{-}HOAc)^+$, 625, 507, 372, 312, 252, 147 $(PhCH{=}CHCOO)^+$, 131, 122 $(PhCOOH)^+$, 105, 77; HRMS *m/z* 742.2942 $(M\text{-}H_2O)^+$, $C_{42}H_{46}O_{12}$ requires 742.2988; ^1H-, ^{13}C NMR: see Table 6.

Taxchin A (**13**)—Colorless needles from Et_2O, mp 284-286°C, $[\alpha]^{21}_D$ +64.5 (*c* 0.11, $CHCl_3$), , IR (KBr) ν_{max}: 3590, 3450, 3025, 2950, 1740, 1640, 1440, 1380, 1250, 1010 cm^{-1}; EIMS *m/z* 578, 536, 518 $(578\text{-}HOAc)^+$, 476 $(536\text{-}HOAc)^+$, 458 $(518\text{-}HOAc)^+$, 416 $(476\text{-}HOAc)^+$, 398 $(458\text{-}HOAc)^+$, 356 $(416\text{-}HOAc)^+$, 338 $(398\text{-}HOAc)^+$, 264, 255 (base peak), 222, 193, 151, 105, 95, 81; HRMS *m/z* 578.2743 $(M\text{-}HOAc)^+$, $C_{30}H_{42}O_{11}$ requires 578.2728; ^1H- and ^{13}C NMR: see Table 8.

X-Ray Analysis of Taxchin A (**13**)—Crystallized as orthorhombic, space group $P2_12_12_1$ with *a* = 15.419 (2), *b* = 19.511 (3), *c* = 11.119 (2) Å. V = 3345.0 $Å^3$, Z = 4, *D*x =1.268, The struture was refined as R = 0.0670, Rw = 0.0490, S = 2.38.[10]

Taxchin B (**14**)—Amorphous powder, mp 124-126°C, $[\alpha]^{19}_D$ +39.7 (*c* 0.15, $CHCl_3$); IR (KBr) ν_{max}: 3420, 3010, 2950, 1730, 1630, 1450, 1370, 1250, 1220, 1160, 1020 cm^{-1}; EIMS *m/z* 726 $(M\text{-}CH_2CO)^+$, 724, 708 $(M\text{-}HOAc)^+$, 666, 648 $(M\text{-}2HOAc)^+$, 606, 546, 535, 263, 255, 221, 147 $(PhCH{=}CHCO)^+$, 131, 103, 91, 77; HRMS *m/z* 708.3155 $(M\text{-}HOAc)^+$, $C_{39}H_{48}O_{12}$ requires 708.3154; ^1H-, ^{13}C NMR: see Table 8.

Acknowledgements: A part of this work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

REFERENCES AND NOTES

1. Wani, M. C., Taylor, H. L.,Wall, M. E., Coggon, P., McPhail, A. T. *J. Am. Chem. Soc.* **1971**, *93*, 2325-2327.
2. Borman, S., *Chem. & Eng. News* **1991**, 69, 11-18.
3. Kingston, D. G. I., Molinero, A. A., Rimoldi, J. M. *Progress in the Chemistry of Organic Natural Products* **1993**, *61* , 1-206.
4. Kingston, D. G. I., Samaranayake, G., Ivey, C. A. *J. Nat. Prod.* **1990**, *53*, 1-12.
5. Samaranayake, G., Magri, N. F., Jitrangsri, C., Kingston, D. G. I. *J. Org. Chem* . **1991**, *56*, 5114-5119.
6. Balza, F., Tachibana, S., Barrios, H., Towers, G. H. N. *Phytochemistry* **1991**, *30*, 1613-1614. Brevifoliol was initially assigned a normal taxane skeleton, which was latter corrected to the abeotaxoid; Georg, G. I., Gollapudi, S. R., Grunewald, G. L., Gunn, C. W., Rao, B. K., Liang, X.-Z., Mirhom, Y. W., Mitscher, L. A., Vander Veld, D. G., Ye, Q.-M. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 1345-1348; see also references 14 and 16.
7. Fuji, K., Tanaka, K., Li, B., Shingu, T., Sun, H. D., Taga, T. *Tetrahedron Lett.* **1992**, *33*, 7915-7916.
8. Fuji, K., Tanaka, K., Li, B., Shingu, T., Sun, H. D., Taga, T. *J. Nat. Prod.* **1993**, *56*, 1520-1531.
9. Zhang, S.-X., Lee, C. T.-L, Chen, K., Kashiwada, Y., Zhang, D. -C., Mcphail, A. T., Lee, K. H. *J. Chem. Soc. Chem. Commun.* **1994**, 1561-1562.
10. Li, B., Tanaka, K., Fuji, K., Sun, H. D., Taga, T. *Chem. Pharm. Bull.* **1993**, *41*, 1672-1673; For erratum: *ibid.* **1993**, *41*, 2200; The conformation (chair- or boat-like) of the C-ring was deduced from the NOESY analysis and inspection of molecular model. Both the coupling constants and the chemical shifts of H-5 and H-7 in ^{1}H NMR are also informative.
11. Tanaka, K., Fuji, K., Yokoi, T., Shingu, T., Li, B., Sun, H. D. *Chem. Pharm. Bull.* **1994**, *42*, 1539-1541.
12. Barboni, L., Garibold, P., Torregiani, E., Appendino, G., Grabetta, B., Zini, G., Bombardelli, E. *Phytochemistry* **1993**, *33*, 145-150.
13. Appendino, G., Tagliapietra, S., Ozen, H. C., Gariboldi, P., Gabetta, B., Bombardelli, E. *J. Nat. Prod.* **1993**, *56*, 514-520.
14. Appendino, G., Barboni, L., Gariboldi, P., Bombardelli, E., Gabetta, B., Viterbo, D. *J. Chem. Soc. Chem. Commun.* **1993**, 1587-1589.
15. Barboni, L., Gariboldi, P., Torregiani, E., Appendino, G., Crravotto, G., Bombardelli, E., Gabetta, B., Viterbo, D. *J. Chem. Soc. Perkin Trans. 1* **1994**, 3233-3238.
16. Chen, R., Kingston, D. G. I. *J. Nat. Prod.* **1994**, *57*, 1017-1021.
17. Della Casa De Marcano, D. P., Halsall, T. G. *J. Chem. Soc. Chem. Commun.* **1970**, 1381-1383.
18. Della Casa De Marcano, D. P., Halsall, T. G. *J. Chem. Soc. Chem. Commun.* **1975**, 365-366.

(*Received in Japan* 14 *June* 1995; *accepted* 20 *July* 1995)