Taxumairols X—Z, New Taxoids from Taiwanese *Taxus mairei*

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In addition to 19-dydroxybaccatin III, 1β-hydroxy-5α-deacetylbaccatin I, taxayuntin G and 13-*O*-deacetyltaxumairol Z (4), three new taxane diterpenoids, taxumairols X (1), Y (2), Z (3) have been isolated from extracts of the Formosan *Taxus mairei* (LEMEE & LEVL.) S. Y. HU. Compounds 1—2 belong to the 11(15→1)-*abeo*-taxane system, having a tetrahydrofuran ring at C-2, C-3, C-4 and C-20. The new compound 3 and 4, which was misidentified previously are derivatives of 11(15→1)-*abeo*-taxane with an intact oxirane system. The structures of compounds 1—4 were elucidated on the basis of extensive two dimensional (2D)-NMR analysis.

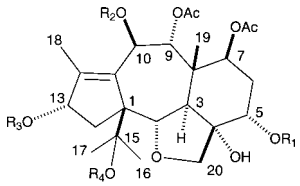
Key words *Taxus mairei*; Taxaceae; taxoid; taxumairols X—Z; 13-*O*-deacetyltaxumairol Z

The unique structure of Taxol and its novel action mechanism have attracted many scientists to study the taxane diterpenoids from various yew trees.[1,2] Although more than 400 taxoids have been found and their structures characterized, still many new taxoids continued to be discovered recently from different parts of yew trees.[3—5] Taiwan yew is an evergreen growing at high altitudes in northern and central parts of Taiwan. Recent studies on the taxane diterpenoids of *Taxus mairei* have resulted in the isolation of taxumairols G—J and L from the roots,[6] taxumairol M and taxumairone A from the seeds,[7,8] and taxumairols U—W from the stem bark.[9] As part of our investigation of taxoids, we now report the isolation and structure elucidation of three additional new taxoids (**1**—**3**) along with 19-hydroxybaccatin III, taxayuntin G and compound **4**, which were isolated for the first time from Taiwanese *T. mairei*.

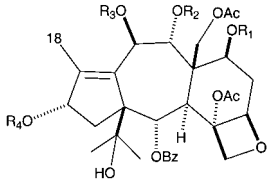
Results and Discussion

Extensive column chromatography, preparative TLC (Si gel and RP-C_{18}) and reversed-phase HPLC of the extracts of *T. mairei* yielded taxumairols X (**1**) and Y (**2**) from the roots, and taxumairol Z (**3**) together with compound **4**,[10] 19-hydroxybaccatin III,[11,12] 1β-hydroxy-5α-deacetylbaccatin I[13] and taxayuntin G[14] from the small twigs and needles.

Taxumairol X (**1**), $[\alpha]$ +14.6° (CH_2Cl_2), had a molecular formula of $C_{24}H_{36}O_{10}$ as derived from a fragment at *m/z* 466 ($[M-H_2O]^+$) in the electron impact (EI)-MS. Its IR bands indicated the presence of hydroxyl (3450 cm^{-1}) and acetyl (1738 cm^{-1}) groups. The ^{1}H-NMR data of **1** (Table 1) exhibited two acetyl singlets (δ 1.94, 1.95), four methyl singlets (δ 0.99, 1.38, 1.39, 1.62), two pairs of coupled doublets at δ 3.72, 3.65 (H-20, J=10 Hz), 4.77 (H-9) and 4.67 (H-10, J=3.8 Hz), and four additional oxygenated methine protons at δ 4.08 (H-5, dd, J=6.9, 10.9 Hz), δ 4.49 (H-13, t, J=7.6 Hz), δ 4.83 (H-2, d, J=7.6 Hz) and δ 4.84 (H-7). The connectivities of H-2/H-3, H-5/H-6/H-7, H-9/H-10 and H-13/H-14 were established by a correlation spectroscopy (COSY) spectrum of **1**. Analysis of the ^{13}C-NMR and heteronuclear single quantum coherence (HSQC) spectra (Table 1) revealed that **1** is a 11(1→15)-*abeo*-taxane with a novel 2,20-tetrahydrofuran ring.[15,16] The dimethyl carbinol group at C-1 was observed from the adjacent quaternary carbons at δ 64.5 (C-1) and δ 75.0 (C-15), and cross-peaks from Me-16 (δ 1.39) and Me-17 (δ 0.99) to C-15 in the heteronuclear multiple bond connectivity (HMBC) spectrum (Table 1). Moreover, HMBC data of C-3/H-2, H-7, H-9, Me-19 and C-11/ H-9, H-10, Me-18 fully supported the structure of **1**, having a rearranged 5/7/6-membered ring with a tetrahydrofuran ring. Two acetoxyl groups were assigned at C-7 and C-9 due to HMBC correlations of their methine protons with corresponding carbonyl signals. The remaining five hydroxyl groups should be located at C-4, C-5, C-10, C-13 and C-15. Upon acetylation taxumairol X (**1**) yielded a triacetylated compound (**5**), in which signals of H-5, H-10 and H-13 were shifted downfield from 4.08, 4.67 and 4.49 ppm in **1** to 5.28, 5.98 and 5.70 ppm in **5**, respectively. The relative stereochemistry of **1** was determined from nuclear Overhauser effect spectroscopy (NOESY) experiment. The NOE correlations of H-2/Me-16, H-13/Me-17 and H-9/Me-19 in **1** suggested that H-2, H-9, H-13, Me-19 and the dimethyl carbinol group were in β-orientation. Correlations between H-3/H-7 and H-10/Me-18 agreed with α-configuration of H-3, H-7 and H-10. The small coupling constant between H-9 and H-10 (J=3.8 Hz) and intense cross peaks between H-9 and H-10 in the NOESY spectrum of **1** suggested a dihedral angle



1 $R_1 = R_2 = R_3 = R_4 = H$
2 $R_1 = R_2 = R_4 = H$, $R_3 = Ac$
5 $R_1 = R_2 = R_3 = Ac$, $R_4 = H$
7 $R_1 = R_2 = R_3 = Ac$, $R_4 = Bz$



3 $R_1 = R_2 = R_3 = H$, $R_4 = Ac$
4 $R_1 = R_2 = R_3 = R_4 = H$
6 $R_1 = R_2 = R_3 = R_4 = Ac$

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Table 1. ^{1}H- and ^{13}C-NMR ($CDCl_3$) Spectral Data of Taxumairol X (**1**)

Position	^{13}C	Carbon type[a)]	^{1}H[b)]	COSY	HMBC
1	64.5	S			H16, Me17,
2	80.0	D	4.83 (d, 7.6)	H3	
3	51.0	D	2.09 (d,7.6)	H2	H2, H7, H9, Me19
4	82.3	S		H20	
5	74.0	D	4.08 (dd, 10.9, 6.9)	H6	
6	30.8	T	1.84 m, 1.75 m	H5, H7	
7	71.0	D	4.84 (overlap)	H6	Me19
8	43.0	S			H2, H7, H9, Me19
9	76.0	D	4.77 (d, 3.8)	H10	H10, Me19
10	68.3	D	4.67 (d, 3.8)	H9	H9
11	136.0	S			H9, H10, Me18
12	144.5	S			Me18
13	79.0	D	4.49 (t, 7.6)	H14	Me18
14	38.2	T	2.17 m, 1.89 m	H13	
15	75.0	S			
					H16, Me17
16	26.5	Q	1.39 s		Me17
17	27.0	Q	0.99 s		
18	11.8	Q	1.62 s	H13	
19	14.2	Q	1.38 s		
20 A	75.7	T	3.72 (d, 10)	H20	
20 B			3.65 (d, 10)	H20	
7-OA[c)]	170.9	S	1.94 s		H7
	20.9[c)]	Q			
9-OA[c)]	170.4	S	1.95 s		H9
	20.6[c)]	Q			

a) S=C, D=CH, T=CH_2, Q=CH_3. Multiplicities and assignments made by the HSQC and HMBC techniques. *b*) Multiplicities and coupling constants in Hz in parentheses. *c*) Data interchangeable.

Table 2. ^{1}H- and ^{13}C-NMR ($CDCl_3$) Spectral Data of Taxumairol Y (**2**)

Position	^{13}C	Carbon type[a)]	^{1}H[b)]	COSY	HMBC
1	64.0	S			H3, H16, Me17
2	79.5	D	4.88 (d, 7.5)	H3	
3	51.7	D	2.13 (d, 7.6)	H2	H2, H9, H20
					Me19
4	82.8	S		H20	H20
5	73.2	D	4.30 (dd, 11.5, 7.2)	H6	H6
6	31.0	T	1.95 m, 1.80 m	H5, H7	H5, H7
7	70.2	D	4.94 (overlap)	H6	Me19
8	43.2	S			H2, H7, H9, H10
					Me19
9	75.5	D	4.92 (d, 3.8)	H10	H10, Me19
10	68.5	D	4.79 (d, 3.8)	H9	H9
11	138.6	S			H9, H10, Me18
12	141.0	S			H10, Me18
13	81.0	D	5.66 (t, 7.0)	H14	H14, Me18
14	36.0	T	2.34 m, 1.87 m	H13	H13
15	76.0	S			
					H16, Me17
16	27.8	Q	1.56 s		Me17
17	27.6	Q	1.19 s		Me16
18	12.0	Q	1.62 s	H13	H13
19	14.5	Q	1.47 s		
20 A	76.0	T	3.80 (d, 10)	H20	H2, H3
20 B			3.73 (d, 10)	H20	
7-OAc	171.0	S	2.10 s		H7
	20.8[c)]	Q			
9-OAc	170.8	S	2.00 s		H9
	20.5[c)]	Q			
13-OAc	169.5	S	2.04 s		H13
	20.5[c)]	Q			

a) S=C, D=CH, T=CH_2, Q=CH_3. Multiplicities and assignments made by the HSQC and HMBC techniques. *b*) Multiplicities and coupling constants in Hz in parentheses. *c*) Data interchangeable.

Table 3. ^{1}H- and ^{13}C-NMR ($CDCl_3$) Spectral Data of Taxumairol Z (**3**)

Position	^{13}C	Carbon type[a]	^{1}H[b]	COSY	HMBC
1	69.9	S			Me16, Me17
2	70.0	D	6.22 (d, 6.5)	H3	
3	43.2	D	3.13 (d, 6.5)	H2	H2
4	79.2	S			H3, H2
5	84.0	D	5.00 (d, 9)	H6	H20
6	35.8	T	2.58 m, 1.78 m	H5, H7	
7	72.5	D	4.45 (dd, overlap)	H6	H9
8	46.5	S			
9	74.1	D	4.73 (d, 10.3)	H10	H10, Me19
10	69.8	D	5.05 (d, 10.3)	H9	
11	136.0	S			
					Me18
12	137.8	S			H10
					Me18
13	81.4	D	6.18 (t, 9.3)	H14	
14	37.2	T	2.20 m, 1.87 m	H13	
15	76.0	S			
					Me16, Me17
16	22.7	Q	1.71 s		Me17
17	28.3	Q	1.32 s		Me16
18	14.9	Q	1.86 s	H13	
19 A	62.2	T	5.38 (d, 13)	H19 B	H3
19 B			5.22 (d, 13)	H19 A	
20 A	74.7	T	4.40 (d, 8.5)	H20 B	
20 B			4.14 (d, 8.5)	H20 A	
4-OAc	169.4	S	2.30 s[c]		
	21.0	Q			
13-OAc	170.3	S	2.36 s[c]		H13
	21.2	Q			
19-OAc	172.8	S	2.19 s[c]		H9
	21.5	Q			
$OCOC_6H_5$	167.1	S			*o*-C_6H_5
i	133.6	S			
o	129.3	D	8.10 (d, 7.3)	*m*-C_6H_5	*p*-C_6H_5, *m*-C_6H_5
m	128.6	D	7.47 (t, 7.3)	*o*,*p*-C_6H_5	
p	130.0	D	7.61 (t, 7.3)	*m*-C_6H_5	*o*-C_6H_5

a) S=C, D=CH, T=CH_2, Q=CH_3. Multiplicities and assignments made by the HSQC and HMBC techniques. *b*) Multiplicities and coupling constants in Hz in parentheses. *c*) Data interchangeable.

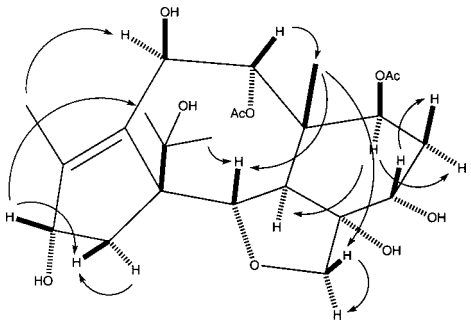

Fig. 1. NOE Correlations of Taxumairol X (**1**)

of 45° between H-9 and H-10 as in taxumairol G (**7**).[6,17] The large coupling constants of H-5 (J=6.9, 10.9 Hz) indicated that the C-5 hydroxyl group is at α-orientation. A chair-like conformation of rings B and C consistent with the results from NOESY experiments is given in Fig. 1.

Taxumairol Y (**2**), [α] +72.6° (CH_2Cl_2), had similar ^{1}H- and ^{13}C-NMR spectral data to those of **1**. The presence of four methyl singlets (δ 1.19, 1.47, 1.56, 1.62), three acetyls (δ 2.00, 2.04, 2.10), and two pairs of doublet (δ 3.73, 3.80, J=10 Hz, H-20; 4.79, 4.92, J=3.8 Hz, H-10, H-9) indicated that compound **2** was a close analog of **1** (Table 2). Detailed comparison of the ^{1}H- and ^{13}C-NMR spectra of **2** with those of taxumairol X (**1**) revealed that the two compounds differ at C-13. The proton signal of H-13 was observed at δ 5.66, suggesting that the hydroxyl group of C-13 in **1** was replaced by an acetoxyl in **2**. These findings were collaborative with the chemical shift difference of C-11, C-12, C-13 and C-14 between **2** and **1** (+2.6, −3.5, +2.0 −2.2 ppm). The assignment of ^{1}H- and ^{13}C-NMR data of **2** were determined by COSY, HSQC and HMBC. The HMBC spectrum of **2** showed very similar correlations to those of **1**, confirming the location of the acetoxyl groups at C-7, C-9 and C-13. The stereochemistry of **2** was established by comparison of the observed chemical shifts and coupling constants with those of compound **1**. The coupling constants of H-2, H-3, H-5, H-9, H-10 and H-20 in **2** were similar to those of compound **1**, suggested that **2** has the same configuration at each chiral center as **1**. Acetylation of **2** yielded a compound identical with **5**.

Taxumairol Z (**3**), [α] −25° (CH_2Cl_2), exhibited similar ^{1}H- and ^{13}C-NMR spectra to those of compound **4**, which was also isolated from the twigs and needles of *T. mairei*. Its IR absorptions indicated the presence of benzoyl (1437, 1373 cm^{-1}), hydroxyl (3450 cm^{-1}), and acetyl (1736, 1720

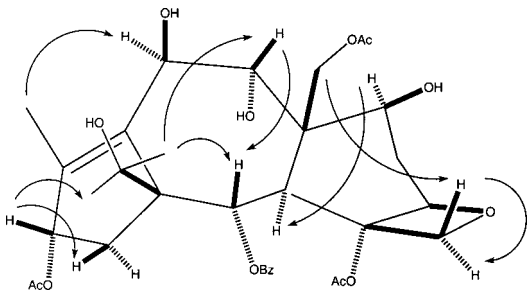

Fig. 2. NOE Correlations of Taxumairol Z (**3**)

cm^{-1}) groups. The presence of benzoyl and acetoxyls was verified from the ^{1}H- and ^{13}C-NMR spectral data of **3**. A taxene skeleton was inferred from the observation of three methyl singlets (δ 1.32, 1.71, 1.86), three acetoxyls (δ 2.19, 2.30, 2.36) and the corresponding ^{13}C-NMR signals. The COSY spectrum established the connectivities of H-2/H-3, H-5/H-6/H-7, H-9/H-10, H-13/H-14, H19A/H19B and H20A/H20B in **3**. The signals of δ 6.22 (H-2) and δ 6.18 (H-13) suggested that they were attached with acetoxyl and benzoyl groups while signals of δ 4.45 (H-7), δ 4.73 (H-9) and δ 5.05 (H-10) had hydroxyl groups connected. This structural assignment was similar to the reported structure of **4**, which has a hydroxyl group at C-13 rather than an acetoxyl group in **3**. Compound **4** was previously isolated from the needles of *T. baccata* and its structure was revised in 1995 by the same research group without detailed spectral and chemical evidence.[10,18,19] The assignment of ^{1}H- and ^{13}C-NMR spectra of **4**, facilitated by COSY, HSQC and HMBC experiments is thus given in the Experimental section. The above findings suggested that compound **3** is a member of 11(1→15)-*abeo*-taxanes with an intact oxetane ring. Further evidence came from the HMBC spectrum of **3**, which exhibited correlations of H-19/C-9, H-10/C-9, H-2/C-3, C-4, COC_6H_5, Me-16/C-1, C-15, Me-17/C-1, C-15, Me-18/C-12, C-11, H-10/C-12, H-20/C-5 and H-3/C-19, C-4. The relative stereochemistry of **3** was established by NOESY experiment. The results showed correlations of H-2/Me-16, H-2/H-9, H-9/Me16, H-20β/H-19, H-10/Me-18, H-13/Me-17 and H-3/H-7 as illustrated in Fig. 2. Finally, a chemical correlation between **3** and **4** was carried out to confirm the structure of **3**. Acetylation of **3** yielded a product, identical with compound **6**, which was a product derived from acetylation of 13-*O*-deacetyltaxumairol Z (**4**).

Experimental

Optical rotations were measured with a JASCO DIP-1000 polarimeter. IR spectra were recorded with a HORIBA FT-720 spectrophotometer. EI-MS and HR-FAB-MS were measured with a VG Quettro 5022 and JEOL JMS-SX 102 mass spectrometer. ^{1}H-, ^{13}C-NMR, COSY, HSQC, HMBC and NOESY spectra were recorded using a Bruker FT-300 (AVANCE) or a Varian FT-500 (INOVA) NMR instrument.

Plant Material The roots of *Taxus mairei* (Lemee & Levl.) S. Y. Hu were purchased in Kaohsiung, in October 1995. The twigs and needles of this plant were collected in Taichung County, Taiwan, in December 1999. A voucher specimen was kept in the Institute of Marine Resources, National Sun Yat-sen University.

Extraction and Isolation Dried roots (90 kg) were ground and repeatedly extracted with EtOH (300 l) under room temperature. The combined extracts were concentrated to a brown tar (9.5 kg), which was extracted with a solvent mixture of *n*-hex/EtOAc to yield portions A (900 g), B (1080 g), C (1500 g) and D (2500 g) as previously described.[6] The mother liquor (50 g) from extensive chromatography of portion A (500 g) was further chromatographed on a silica gel column (600 g) and eluted with *n*-hexane–CH_2Cl_2–MeOH (70 : 70 : 1, 60 : 60 : 1, 50 : 50 : 1, 40 : 40 : 1, each 4 l) to afford six fractions A (30 g), B (8 g), C (5.6 g), D (2 g), E (1 g) and F (1.2 g). Part of fraction A (1.3 g) was separated by HPLC (RP-C18) using MeOH/H_2O/CH_3CN (6 : 1 : 3; 75 : 10 : 15) as solvent system to afford a residue (132 mg), which was applied on preparative TLC plates, and developed with *n*-hexane–CH_2Cl_2–MeOH (7 : 7 : 1) to give taxumairol X (**1**, 4 mg) and taxumairol Y (**2**, 2 mg).

The twigs and needles (130 g) of *T. mairei* were extracted with four different solvents (*n*-hexane, EtOAc, acetone, MeOH) of increasing polarity afforded five fractions Fr. A (1.92 g), Fr. B (2.70 g), Fr. C (1.22 g), Fr. D (3.14 g) and Fr. E (5.50 g). Fraction D was chromatographed on a Sephadex LH-20 column and eluted with MeOH to afford a taxoid-containing fraction (0.7 g), which was chromatographed on a silica gel column and eluted with a solvent mixture of *n*-hexane/CH_2Cl_2/MeOH (increasing polarity) to yield 15 fractions. Fraction 11 (70 mg) was separated by HPLC (RP-C18) using CH_3CN/MeOH/H_2O (1 : 5 : 4) as solvent system to give 1β-hydroxy-5α-deacetylbaccatin I (3 mg) and taxumairol Z (**3**, 2 mg). 19-Hydroxybaccatin III (7 mg) was directly crystallized from fraction 13 (25 mg). Fractions 14 (41 mg) and 15 (40 mg) were separated by HPLC (RP-C18) using CH_3CN/MeOH/H_2O (1 : 5 : 4) as eluent to give 13-*O*-deacetyltaxumairol Z (**4**, 6 mg) and taxayuntin G (6.2 mg), respectively.

Taxumairol X (**1**): Isolated as an amorphous powder: $[\alpha]_D^{25}$ +14.6° (c=0.2, CH_2Cl_2); IR (neat) ν_{max} 3450, 2924, 2852, 1738, 1456, 1371, 1246, 1167, 1070, 1030 cm^{-1}; ^{1}H- and ^{13}C-NMR ($CDCl_3$/CD_3OD, 10 : 1): Table 1; EI-MS *m/z* (rel. int.) 466 ([M−H_2O]$^+$, 0.1), 410 (0.3), 402 (1), 386 (1), 368 (1), 337 (1), 295 (1), 275 (1), 256 (3), 236 (2), 221 (2), 213 (3), 199 (2), 185 (4), 149 (8), 136 (10), 121 (10), 97 (20), 95 (21), 83 (26), 81 (45), 69 (100), 55 (64), 43 (91); negative high resolution (HR)-FAB-MS *m/z* 483.2238 (Calcd for $C_{24}H_{35}O_{10}$ 483.2236, [M−H]$^-$).

Acetylation of Taxumairol X (**1**): Taxumairol X (1.5 mg) was acetylated with acetic anhydride (0.2 ml) and pyridine (0.2 ml) and after usual work-up furnished a taxumairol X triacetate (**5**, 1.2 mg). ^{1}H-NMR (300 MHz, $CDCl_3$): δ: 4.94 (1H, d, J=8.1 Hz, H-2), 2.27 (1H, d, J=6.6 Hz, H-3), 5.28 (1H, dd, J=12, 3.7 Hz, H-5), 5.03 (1H, dd, J=12.3, 3.3 Hz, H-7), 4.90 (1H, d, J=3.8 Hz, H-9), 5.98 (1H, d, J=3.8 Hz, H-10), 5.70 (1H, t, J=6.0 Hz, H-13), 1.42 (3H, s, Me-16), 1.08 (3H, s, Me-17), 1.72 (3H, s, Me-18), 1.35 (3H, s, Me-19), 3.64 (2H, br s, H-20), 2.18, 2.13, 2.09×2, 1.99 (s, $OCOCH_3$).

Taxumairol Y (**2**): Isolated as an amorphous powder: $[\alpha]_D^{25}$ +72.6° (c=0.2, CH_2Cl_2); IR (neat) ν_{max} 3448, 2983, 2946, 1734, 1716, 1439, 1371, 1254, 1066, 1041, 1026, 858, 737 cm^{-1}; ^{1}H- and ^{13}C-NMR ($CDCl_3$): Table 2; EI-MS *m/z* (rel. int.) 448 ([M−AcOH−H_2O]$^+$, 0.1), 408 (1), 390 (5), 388 ([M−2AcOH−H_2O]$^+$, 0.2), 372 (1), 348 (4), 331 (3), 330 (5), 315 (10), 288 (4), 270 (3), 255 (4), 149 (10), 133 (15), 121 (9), 105 (11), 85 (11), 59 (25), 55; negative HR-FAB-MS *m/z* 483.2233 (Calcd for $C_{24}H_{35}O_{10}$ 483.2232, [M−Ac−H]$^-$).

Acetylation of Taxumairol Y (**2**): Taxumairol Y (1 mg) was acetylated with acetic anhydride (0.1 ml) and pyridine (0.1 ml) and after usual work-up furnished a diacetylated compound (0.8 mg), which was identical with compound **5**.

Taxumairol Z (**3**): Isolated as an amorphous powder: $[\alpha]_D^{25}$ −25° (c=0.2, CH_2Cl_2); IR (neat) ν_{max} 3450, 2924, 2854, 2359, 1736, 1720, 1437, 1373, 1240, 1107, 1026, 737, 712 cm^{-1}; ^{1}H- and ^{13}C-NMR ($CDCl_3$) in Table 2; EIMS *m/z* (rel. int.) 302 (16), 285 (9), 239 (12), 167 (23), 149 (59), 105 (29), 81 (59), 69 (100), 55 (60).

13-*O*-Deacetyltaxumairol Z (**4**): Isolated as an amorphous powder: $[\alpha]_D^{25}$ −42° (c=0.5, $CHCl_3$); ^{1}H-NMR (300 MHz, $CDCl_3$): δ: 6.39 (1H, d, J=7.8 Hz, H-2), 3.06 (1H, d, J=7.8 Hz, H-3), 4.94 (1H, d, J=8.5 Hz, H-5), 1.80, 2.62 (2H, m, H-6), 4.31 (1H, t, J=8.7 Hz, H-7), 4.67 (1H, d, J=9.9 Hz, H-9), 4.73 (1H, d, J=9.9 Hz, H-10), 4.56 (1H, m, H-13), 1.75, 2.26 (2H, m, H-14), 1.05 (3H, s, Me-16), 1.09 (3H, s, Me-17), 1.96 (3H, s, Me-18), 5.37 (1H, d, J=12.9 Hz, H-19a), 5.27 (1H, d, J=12.9 Hz, H-19b), 4.49 (1H, d, J=8.0 Hz, H-20a), 4.17 (1H, d, J=8.0 Hz, H-20b), 2.20, 2.47 (s, $OCOCH_3$), 8.02 (2H, d, J=7.5 Hz, *o*-C_6H_5), 7.46 (2H, t, J=7.5 Hz, *m*-C_6H_5), 7.59 (1H, t, J=7.5 Hz, *p*-C_6H_5); ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 68.7 (s, C-1), 79.2 (d, C-2), 44.2 (d, C-3), 79.9 (s, C-4), 85.1 (d, C-5), 36.9 (t, C-6), 72.0 (d, C-7), 45.2 (s, C-8), 74.0 (d, C-9), 68.0 (d, C-10), 136.6 (s, C-11), 148.1 (s, C-12), 77.3 (d, C-13), 39.8 (t, C-14), 75.9 (s, C-15), 27.7 (q, C-16), 24.7 (q, C-17), 11.5 (q, C-18), 61.2 (t, C-19), 74.2 (t, C-20), 170.9, 174.0 (s, $O\underline{C}OCH_3$), 21.3, 22.3, (q, $OCO\underline{C}H_3$), 165.0 (s, $O\underline{C}OC_6H_5$), 130.3 (s, C_6H_5, *i*), 129.7 (d, C_6H_5, *o*), 128.6 (d, C_6H_5, *m*), 133.4 (d, C_6H_5, *p*); EI-MS *m/z* (rel. int.) 509 (0.2, [M−AcOH−2H_2O+H]$^+$), 490 ([M−AcOH−3H_2O]$^+$, 0.3), 472 ([M−AcOH−4H_2O]$^+$, 1), 430 ([M−AcOH+Ac−4H_2O]$^+$, 2), 412 ([M−

$AcOH-Ac-5H_2O]^+$, 2), 370 (3), 339 (7), 297 (5), 279 (4), 237 (7), 209 (6), 105 (78), 79 (11), 59 (40).

Acetylation of Compound **4**: 13-*O*-Deacetyltaxumairol Z (**4**, 6 mg) was acetylated with acetic anhydride (0.3 ml) and pyridine (0.3 ml) and after usual work-up furnished a tetraacetylated compound (**6**, 7 mg): $[\alpha]_D^{25}$ −50° (c=1.5, $CHCl_3$); IR (neat) ν_{max} 2958, 2930, 1741, 1450, 1371, 1236, 1113, 1039, 970, 758 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ: 6.91 (1H, d, J=7.8 Hz, H-2), 3.15 (1H, d, J=7.8 Hz, H-3), 4.98 (1H, d, J=8.4 Hz, H-5), 2.56 (1H, m, H-6), 5.63 (1H, t, J=8.4 Hz, H-7), 6.39 (1H, d, J=11.1 Hz, H-9), 6.50 (1H, d, J=11.1 Hz, H-10), 5.70 (1H, t, J=8.2 Hz, H-13), 1.14 (3H, s, Me-16), 1.20 (3H, s, Me-17), 1.96 (3H, s, Me-18), 5.28 (1H, d, J=12.6 Hz, H-19a), 4.76 (1H, d, J=12.6 Hz, H-19b), 4.44 (1H, d, J=8.1 Hz, H-20a), 4.18 (1H, d, J=8.1 Hz, H-20b), 2.43, 2.19, 2.16, 2.11, 2.01, 1.88 (s, $OCOCH_3$), 8.00 (2H, d, J=7.3 Hz, o-C_6H_5), 7.47 (2H, t, J=7.3 Hz, m-C_6H_5), 7.60 (1H, t, J=7.3 Hz, p-C_6H_5).

Acetylation of Taxumairol Z (**3**): Taxumairol Z (**3**, 0.5 mg) was acetylated with acetic anhydride (0.1 ml) and pyridine (0.1 ml) and after usual work-up furnished a product identical with compound **6**.

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