Structure Determination of New Texanes from *Taxus wallichana* Zucc.

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Summary: Three new rearranged texane diterpenoids, 5α, 7β, 10β, 13α-tetrahydroxy-2α, 9α, 15-triancetoxy-11(15→1)–*abeo-texa*-4(20), 11–diene (1), 5α,9α,10β,13α tetraacetoxy-15-hydroxy-11 (15→1)–*abeo-texa*-4(20), 11–diene (2) and 7,9,10,13-tetradeacetyle-abeo-baacatin IV (3) have been isolated from Himalayan yew, Texus wallichiana. The structure of these compounds has been confirmed by modern spectroscopic techniques.

Introduction

Texus wallichina Zucc. is a member of the family Texaccae which is commonly known as the Himalyan yew [1]. The plant is widely distributed in Pakistan and India. In Pakistan, it is found in Chitral, Swat, Hazara, Muree Hills and Poonch which is. widely used in the traditional system of medicine [2]. Its leaves are reported to have sedative, antispasmodic, and aphrodisiac properties and they have also been used for the treatment of asthma, indigestion and epilepsy. A water extract of the leaves is also reported to have tranquillizing effects [1]. The importance of the investigation of the genus *Taxus* is mainly due to isolation of taxol from the pacific yew, *Taxus* brevifolia and lactron from *T. wallichiana* which is clinically used against ovarian and breast cancers [3,4]. There are several compre-hensive reviews which cover almost all phytochemistry *Taxus* species [5-8]

Results and Discussion

The concentrated $CHCl_3$ fraction (47 g) of the crude methanolic extract of *T. wallichiana* was loaded onto a silica gel (650 g) column and eluted with *n*-hexane-$CHCl_3$ followed by $CHCl_3$-MeOH. A fraction eluted with *n*-hexane-$CHCl_3$ was subjected to a preparative. TLC purification using $CHCl_3$-MeOH (9:1) This afforded compound **1** as a colorless gum. The EI MS of **1** showed the M^+-CH_3COOH ion at m/z 450. In the FAB MS the $(M+1)^+$ion appeared at m/z 511. The HREI MS showed the M^+-CH_3COOH-H_2O ion at *m/z* 432.2087 ($C_{24}H_{32}O_7$, calcd. 432. 2079). The molecular formula was therefore deduced to be $C_{26}H_{38}O_{10}$ corresponding to eight degrees of unsatutration in the molecule. The UV. Spectrum of **1** in MeOH showed only the end of absorptions. The IR spectrum displayed intense absorptions at 1735 (CO), 3194 (C-H) and 3628 (OH) cm^{-1}.

The ^{1}H-NMR spectrum of 1 showed seven methyle singles at δ1.56 (Me-19), 1.70 (Me-18), 1.04 (Me-16), 1.19 (Me-17), 1.92 (-OCOMe), 1.93 (-OCOMe) and 1.95 (-OCOMe) along with eight downfield proton signals, out of which six protons were inferred to be geminal to the oxygen functions based on their chemical shifts (δ 4.52, 4.59, 4.79, 4.80, 4.98, 5.83) while two were vinylic in nature. The exomethylenic protons resonated as broad singlets at δ 4.90 (11-20a) and 5.40 (II-20b), while H-5β and H-7α appeared each as double doublets at β 4.80 ($J_{5\beta6\alpha}$ = 8.5H_Z, $J_{5\beta6\alpha}$ = 6.0 Hz, H-5β) and 4.59 ($J_{7\alpha,\ 6\beta}$ =9.5 Hz $_{7\alpha,\ 6\beta}$ = 9.5Hz H-7α). Furthermore, a triplet resonated at δ 5.52 was assigned H-13β ($J_{3\ \beta,14}$ = 7.5 Hz,H- 13 β). The spectrum also exibited three 1H doublets resonating at δ 5.83 ($J_{2\ \beta,3\alpha}$ = 9.5 Hz,H-2 β), 4.98 ($J_{9\ \beta,10\alpha}$ = 4.0Hz, H-9) and 4.76 ($J_{10\alpha\ ,\ 9\ \beta}$= 9.5 Hz, H2 β), 4.98 ($J_{9\ \beta,10\alpha}$ = 4.0 Hz, H-9 β) and 4.76 ($J_{10\alpha\ ,\ 9\ \beta}$ = 4.0 Hz, H-10 α). H-2 (δ 5.83) and H-9β (δ 4.98), both gemenal to acetoxy groups showed strong HMBC correlations with ester carbonylel carbons. In the case of third acetoxy group the ^{1}H-NMR spectrum showed that there was no protons geminal to it, and it was accordingly placed at C-15 (δ 76.3). The coupling constants of H-9β and H-10α were found to be 4.0 Hz due to small dihedral angle wich was supported by the model and the data of reported conformer related skeleton [9-10] Further-more, a characteristic signal of the H-3α methine appeared at δ 2.30 ($J_{14\beta,\ 14\alpha}$=14.5 Hz $J_{14\ \beta,\ 13\ \beta}$ = 7.0Hz H-14β) was assinged to H-14β and overlaping signals at δ 1.70 was assigned to H-14β wherese a multiplet resonating at δ 2.02 and 1.71 was due to H-6 β H-6α respectively. The COSY-45° spectrum revealed the presence of four isolated spin systems in the molecule. The H-5 β (δ 2.01) and H-6α(δ 1.71) which were in turned coupled with H-7α (δ 4.76)

whereses H-13 β (δ 4.52)showed coupling with H-14α (1.70) and H-14 β (δ 2.30). The coupling of H-2 β (δ 5.83) with H-3α (δ 3.04) indicated the presence of an acetoxy group at C-2.

The ^{13}C-NMR spectra (broadband, DEPT) of **1** showed the resonences of for all twenty six carbon atoms in the molecule corresponding to seven methyle. Three methylene, seven methline and nine quaternary carbons atoms (Table-**1**). Another compound, 9-deacetyle-9-benzoyl-10-debenzoyl-5-cinnamonyl-taxchinin. A that had been recently isolated from taxus mairei has spectral data closely comparable to that of compound **1** [9]. The HMBC spectrum was recorded to locate the quatenary carbons and confirm various chemicals shift assign-ments. The spectrum showed that proton resonating at δ 4.80 (H-5 β) displayed heteronuclear shift correlation (^{3}*J*c-H) with the carbons at δ 45.9) and C-10 (δ 66.5) which allowed the placement of one of the three acetoxy groups at C-9 (δ 77.4). The exomethylene protons at δ 4.90 (H-20a) and 5.15 (H-20b) exhibited shift correlationn with the C-4 (δ 149.3). The protons at δ 4.76 (H-10α) geminal to the hydroxy group displayed interactions with C-12 (δ 135.0), (δ 77.4) and C-1 (δ 67.3) which evidenced that C-11 is linked with C-10, C-12 and C-1. The protons at δ 4.52 (H-13 β) showed long- range heteronuclear corrolations with the carbons resonated at δ 148.8 (C-12), 135.0 (C-11) and 67.3 (C-1). Furthermore, H-2 β (δ 5.83) exhibited coupling with the C-1 (δ 67.3) and C-3 (δ 45.9) which concluded that one acetoxy group located between C-1 and C-3. A literature survey revealed that C-1 of an abeo-taxane generally resonates between δ 67.0-68.0 when acetoxy group present at C-2, whereases C-1 resonates between δ 63.0-64.5 in the absence of and acetoxy group [11-12]. Another strong evidence of the presence of an abeo-taxane skeleton was provided by the long-range interactions of both Me-16 (δ 1.04) and Me-17 (δ 1.19) with C-15 (δ 76.3) and C-1 (δ 67.3).

The relative stereochemistry at various chiral centers of taxoid **1** was established by NOESY experiment and coupling constants. The protons resonating at δ 1.56 (Me-19) showed correlations with H-2β, H-6β and H-9β resonating at δ 5.83, 2.01 and 4.98 respectively. Similarly, H-5β, (δ 4.80) also exhibited strong vicinal coupling with H-6β and resonating at δ 2.01 Based on these studies, the structure of 1 was deduced to be 5α ,7 β,10 β,13α-tetrahydroxy-2α,9α15-triacetoxy-11(15→1) abeo-texa-4(20), 11-diene.

The EI MS of **2** showed the M^+-CH_3COOH ion at *m/z* 460. The HREI MS showed the loss of three OAc group, affording an M^+- (3xOAc) ion at *m/z* 521 which indicated the loss of one molecule of acetic acid in the EI MS. On the basis of mass,^{1}H-, NMR and ^{13}C-NMR studies the moleculer formula of **2** was concluded to be $C_{28}H_{40}O_9$ with nine degrees of unsaturation in the molecule. The UV spectrum of **2** showed only the end absorption.The IR spectrum ($CHCl_3$) displayed absorptions at 1742 (-CO-), 2953 (CH) and 3589 (-OH)cm^{-1}.

The ^{1}H-NMR spectrum of **2** displayed eight 3H singlets for eight methyl groups at δ 0.78 (Me-19), 1.21 (Me-17), 1.35 (Me-16), 1.76 (Me-18), 1.99 (-OCOMe), 2.01 (-OCOMe), 2.02 (-OCOMe) and 2.03 (OCOMe). The exomethylenic protons resonated at δ 4.80 and 5.15 as broad singlets, while H-5 β appeared as double doublet at δ 5.34($J_{5\beta,6\alpha}$= 8.6 Hz, $J_{5\beta,6\beta}$=6.4 Hz, H-5 β) wherease H-13 β appeared as a triplet at δ 5.57 ($J13_{\beta,14}$= 7.3 Hz,H-13β). The spectrum also exhibited two 1Hdoublets at δ 5.75 ($J_{9\beta,10\alpha}$=10.5 Hz) and 6.16 ($J_{10\alpha,9\beta}$ = 10.5 Hz) which were assinged to H-9 β and H-10α respectively.The trans orientation of H-9 β and H-10α was infered from their large vicinal coupling constants($J_{9\beta,10\alpha}$ = 10.5 Hz) due to large dihedral angle between H-9 β and H-10α with reduces the coupling constant to 4.0 Hz which was supported by the Direding model and reported data of closely related skeleton.Some naturally occuring taxane diterpinoids can existd in either one or two conformational isomers which can be distinguished on the basis of small (4.0 Hz) and large (10.5 Hz)coupling constants [9,10]. Further more a characteristic signal of H-3α appeared at δ 2.74 as a broad doublet ($J2_{\alpha,3\beta}$ = 8.2 Hz). In the COSY-45° spectrum of **2** the H-5 β (δ 5.34) displayed a cross peak with the H-6α (δ 1.91) and H-6 β (δ 2.31) which were in turned coupled with H-7α (δ 1.93) and H-7 β (δ 2.30). Vicinal coupling with Me-18-(δ 1.78). The couplings of H-2β (δ 2.01) and H-2α (δ 1.71) with the methine H-3α (δ 2.74) was also observed in the COSY-45° spectrum.

The ^{13}C-NMR data of **2** showed resonances for all twenty eight carbon atoms with eight methyl, five methylene, five methane and ten quaternary carbon atoms (Table-**1**). An other compound, 5,10, 13,10-debenzoyl brevifoliol that had been recetly isolated has spectral data closely comparable to that of compound **2** [12].

Table-1: ^{1}H- and ^{13}C-NMR chemical shift assignments of **1-3**.

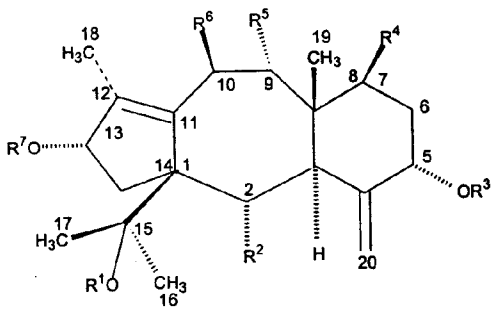
Carbon no.	1		2		3	
	^{1}H-NMR,500 MHz δ (ppm), J= Hz	^{1}H-NMR,500 MHz δ (ppm), J= Hz	^{13}C-NMR,125 MHz, δ (ppm), J = Hz	^{13}C-NMR,125 MHz, δ (ppm), J = Hz	^{1}H-NMR,500 MHz δ (ppm), J= Hz	^{13}C-NMR,125 MHz, δ (ppm), J = Hz
1	-	67.3	-	64.1	-	68.5
2	5.83 (*d, j* = 9.5)	71.7	1.90-2.01 (*m*)	30.5	5.79 (*d, j,* = 7.5)	70.1
3	3.04 (*d, j* = 9.5)	45.9	2.74 (*br, d,* = 8.2)	41.4	2.87 (*d, J* = 7.5)	43.4
4	-	149.3		148.7	-	80.9
5	4.80 (*d d, J* = 8.5, 6.0)	68.8	5.34 (*dd, J* = 8.6,6.4)	76.6	4.95 (*dd, J* = 7.6, 6.2)	86.5
6	6β 2.02 (*m*) 6α 1.71 (*m*)	36.6	1.90-2.01 (*m*)	28.2	6	6β 1.70 (*m*) 6α 2.07 (*m*)
7	4.59 (*d d, J* = 9.5, 7.5)	72.7	1.90-2.01 (*m*)	28.6	41.4 (dd,J = 8.5, 5.8)	38.2
8	-	43.0	-	42.9	-	45.9
9	4.86 (*d, J* = 4.0)	77.4	5.75 (*t, J* = 7.3)	79.2	4.16 (*d, J* = 10.0)	81.8
10	4.76 (*d, J* = 4.0)	66.5	6.16 (*d, J* = 10.5)	69.9	4.45 (*d, J* = 10.0)	69.8
11	-	135.0	-	139.3	-	138.4
12	-	148.	-	146.8	-	147.6
13	4.52 (*t, J* = 7.5)	77.9	5.75 (*t, J* = 7.3)	80.7	4.49 (*t, J* = 7.5)	77.8)
14	14α 1.70 (overlapping signal) 14α 2.30 (*dd, J* = 14.5, 7.0)	41.7	14α 2.01 (overlapping signals) 14α 2.60 (*dd, J* = 13.6, 7.1)	45.2	14α 1.71 (overlapping signals) 14α 2.46 (*dd, J* = 15.0, 8.5)	40.3
15	-	76.3	-	76.7	-	76.9
16	1.04 (*s*)	21.0	1.35 (*s*)	26.0	1.10 (*s*)	22.2
17	1.19 (*s*)	21.21.7	1.21 (*s*)	27.1	1.04 (*s*)	21.7
18	1.70 (*s*)	12.7	1.76 (*s*)	11.6	1.82 (*s*)	11.2
19	1.56 (*s*)	14.9	0.78 (*s*)	17.2	1.72 (*s*)	12.6
20	20a 4.90 (*br.s*) 20b 5.40 (*br..s*)	114.1	20a 4.80 (*br..s*) 20b 5.15 (*br..s*)	112.8	20a 4.38 (*d, J* = 7.5) 20b 4.39 (d, J = 7.5)	75.7
OCOMe	1.92 (s)	28.1#	1.99 (s)	20.6	1.98 (s)	28.2#
OCOMe	-	173.0 *	-	171.5 *	-	28.2#
OCOMe	1.93 (s)	28.2 *	2.01 (s)	20.7#	2.11 (s)	172.2#
OCOMe	-	172.0 *	-	171.6 *	-	171.9 *
OCOMe	1.95 (s)	26.8#	2.02 (s)	21.3#	-	-
OCOMe	-	172.1 *	-	170.9*	-	-
OCOMe	-	-	2.03 (s)	20.9#	-	-
OCOMe	-	-	2.03 (s)	20.9#	-	-
	-	-	-	172.4*	-	-

#Exchangeable assignments

[1] H- and ^{13}C-NMR technique was performed in CD_3OD.

In the HMBC spectrum of **2,** H-5β (δ 5.34) showed interaction with C-20 (δ 112.8), C-7 (δ 28.6) and with the geminal ester carbonyl carbon (δ 171.5). H-9β (δ 5.75) displayed Cross- peaks with C-10 (δ 69.9) and with the carbonyl carbon (δ 171.6) of the geminal acetoxy group, whereas H-10α (δ 6.16) showed couplings with C-11 (δ 139.3), C-1 (δ 64.1) and carbonyl carbon (δ 170.9) of the acetoxy group. The exomethylene protons. H-2a (δ 4.80) and H-20b (δ 5.15) both showed long-range coupling with C-3 (δ 41.4) and C-5 (δ 76.6) The NOESY spectrum of **2** showed interactions of Me-19β (δ 0.78) with H-2β (δ1.80), H-6β (δ 1.78). On the basis of the above spectroscopic evidences, structure **2** was assigned to 5α,9α,10β,13α-tetraacetoxy-15-hydroxy-11 (15 1)-abeo-texa-(20),11-diene.

The EI MS of **3** showed the M^{+}-CH_3COOH-H_2O ion at *m/z* 408. The HREI MS showed the M^{+}-$C_2H_4O_3$ ions at m/z 408.17862 ($C_{22}H_{32}O_7$, Calcd. 408.1779). The molecular ion was identified by FAB MS $(M+1)^{+}$ to be at *m/z* 485. On the basis of mass,



(1) R^1 = Ac, R^2 = OAc, R^3 = H, R^4= OH, R^5 = OAc, R^6 = OH, R^7 =H
(2) R^1 = H, R^2 = H, R^3 = Ac, R^4 = H, R^5 = OAc, R^6 = OAc, R^7 = Ac

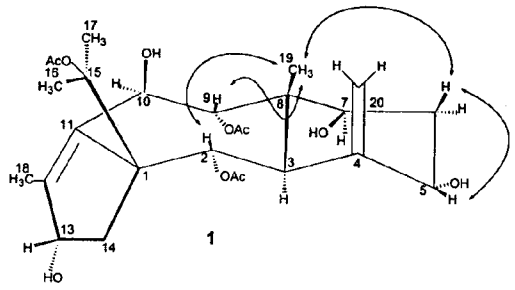


Fig. 1: Some important NOESY interactions in **1**

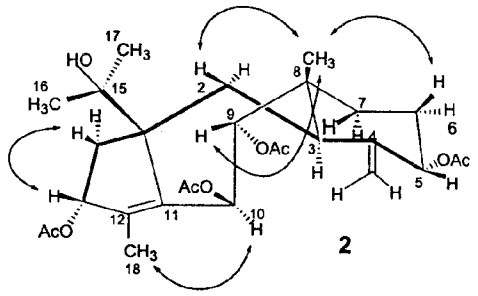


Fig. 2; Some important NOESY interactions in **2**

^{1}H-NMR and ^{13}C-NMR techniques the molequler formula of **3** was concluded to be $C_{24}H_{36}O_{10}$ which indicated seven degrees of unsaturation in the molecules. The UV spectrum (MeOH) of **3** showed only the absorption. The IR Spectrum ($CHCl_3$) displayed absorptions at 3552(-OH), 2947 (C-H), 1739(C-O)cm^{-1}.

The ^{1}H-NMR spectrum of **3** exibited the presence of four tertiary methyl singlets at (δ 1.04) (Me-17), 1.10 (Me-16), 1.72 (Me-19) and 1.98 and 2.11 were assingned to the acetyle methyle groups. The two pairs of AB at (δ 4.38/4.39 and 4.16/4.45 were assigned to the H-20a/H-20b and H-9 β/H-10α, respectively other signals appeared at δ 4.95 (1H, dd,$J_{5\alpha,6\beta}$ = 7.6 Hz, $J_{5\alpha,6\beta}$ = 6.2 Hz, H-5α),4.14 (1H, dd,$J_{7\alpha,6\beta}$ = 8.5 Hz, $J_{7\alpha,6\beta}$ = 5.8 Hz, H-7α) 4.49,(1H,t, $J_{13\beta,14}$ = 7.5 Hz,H-13 β) and 5.79 (1H, d, $J_{2\beta,3\alpha}$ = 7.5 Hz,H-2β) which were assinged to the protons geminal to the oxygen functionalities. The down field chemical shift of H-2 β (δ 5.79) indicated that there is an acetoxy group geminal to this proton which was further confirmed by the COSY-45° and HMBC techniques. In addition, the upfield signals at δ 2.87 (1H, d, $J_{3\alpha,2\beta}$ = 7.5 Hz) was assigned to H-3α. The COSY-45° spectrum of **3** revealed the presence of four isolated spin systems. H-5α(δ 4.95) displayed cross-peaks with the H-6α (δ 1.60)and H-6β (δ 2.04), which was in turned coupled with H-7α (δ 4.14). Strong vicinal coupling were also observed between H-9β(δ 4.16) and H-10α (δ 4.45), and between and between H-13 β (δ 4.49) and H-14 β (δ 2.46)/H-14α (δ 1.71). The coupling of the downfield H-2β (δ 5.79) with H-3α (δ 2.87) indicated the presence of an acetoxy group at C-2.

The ^{13}C-NMR data of **3** showed resonances for all twenty four carbon atoms including six methyl, 3 methylene, seven methine and eight quaternary carbon atoms in the molecule (Table-1). Another compound taxuspine Q that had been isolated from *taxus cuspidata* has spectral data closely comparable to that of compound **3** (Wang et al., 1996). In the HMBC spectrum H-5α (δ 4.95) exhibited coupling with C-4 (δ 80.9) and C-7 (δ 73.8). H-9 β (δ 4.16) and H-3α (δ 2.87) exhibited HMBC interaction with C-7(δ 73.8) and C-4 (δ 80.9), respectively. Furthermore, H-9β displayed cross-peak with C-3 (δ 43.4) and C-10 (δ 69.8), wherease H-10 (δ 4.45) was coupled with C-9 (δ 81.8). H-2 (δ 5.79) exhibited coupling with C-3 (δ 43.4) and C-8 (δ 45.9). In addition, H-3 showed interaction with C-4 (δ 80.9), C20 (δ 75.7) and C-19 (δ 12.6). The methylene proton, H-20a (δ 4.38) of the oxetane ring also displayed coupling with C-5 (δ 86.5) and C-3 (δ 43.4). H-13 (δ 4.49) showed long-range coupling with C-1 (δ 68.5), wherease Me-18 (δ 1.82) displyed coupling with C-11 (δ 138.4), C-12 (δ 147.6) and C-13 (δ 77.8) Me-16 (δ 1.10) and Me-17 (1.04) showed the coupling with C-1 (δ 68.5) and C-15 (δ 76.9). Furthermore, H-3 (δ 2.87) and H-10 (δ 4.45) both showed interaction with C-1 (δ 68.5) The NOESY

experiment was also used to develop the relative stereochemistry of taxoids **3.** Me-19 (δ 1.72) showed strong interactions with H-2 β (δ 5.79) and H-9β (δ 4.16). In addition,H-3α (δ 2.87) and H-10α (δ 4.45) exhibited interaction with H-5α (δ 4.95) and Me-18 (δ 1.82) respectively. Furthermore, a proton at δ 4.49 (H-13β) displayed coupling cross-peak with Me-16 (δ 1.10). Based on the above mentioned spectros-copic evidence structure **3** was elucidated for 7,9,10,13-tetradeacetyl-abeobaccatin IV. The relative stereo-chemistry at different chiral centers of taxoids **1-3** is also supported by coupling constants and comparable study with the literature [3,9].

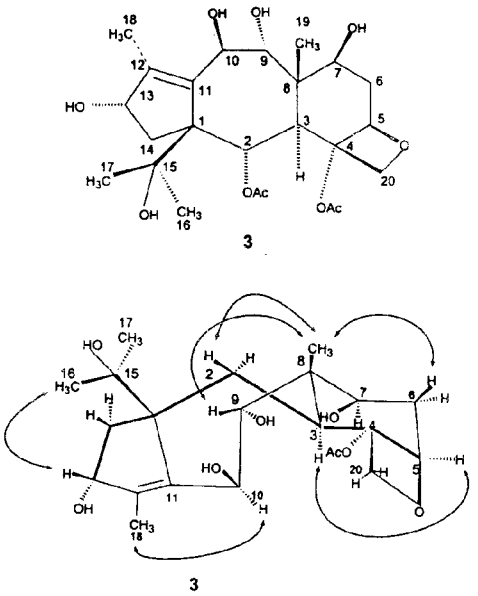


Fig. 3: Some important NOESY interactions in **3**

Experimental

General Experimental Procedures

Optical rotations were measured on JASCO-DIP-360 digital polarimeter in MeOh. The IR spectra were recorded on a JASCO A-302 spectrophoto-meter. The UV spectra were measured Hitachi U-3200 spectrophotometer. The ^{1}H-NMR spectra were recorded on Burker AM-300, AM-400 and AMX-500 spectrometer using UNIX data system at 300, 400 and 500 MHz, respectively, while ^{13}C-NMR spectra were recorded at 75, 100 and 125 MHz, on the same instruments. The EI and HREI MS were recorded on JMS HX 110 with the data system DA 5000 and on MAT 112S mass spectrometers.

Plant Material

The bark of *T .wallichiana* ZUCC. Was collected from Hainah in Leepa Valley, 2900 meters above the sea level, District Muzaffarabad, Azad Kashmir (Pakistan) in December, 1996. The plant was identified by Prof. Shafiq-ur-Rahman and a specimen was deposited in the Herbarium of the Botany Department, University of Azad Jammu and Kashmir, Muzaffarabad, Pakistan.

Extraction and Isolation

Powdered dried bark (23 kg) of *T. wallichiana* was soaked in methanol (40 lit., 3 times) for one week.The methanolic extract was filtered and then evaporated under vacuum. The residue (1150 g) was partitioned between water (2 lit.) and *n*-hexane (5 lit.). The water layer was extracted with $CHCl_3$ (5 lit., 3 times).The $CHCl_3$ extract (47 g) was subjected to column chromatography on silica gel (70-230 mesh size). The elution of the column with *n*-hexane-EtOAc and EtOAc yielded three major fractions which were subjected to preparative TLC using $CHCl_3$–MeOH (9:1), n-hexane-$CHCl_3$-EtOAc-NH_4OH (1:8:1:3.drops) and $CHCl_3$- EtOAc-MeOH (8:1:1.) as solvent system which afforded compounds **1-3**, respectively.

5α, 7β,10 β,13α-Tetrahydroxy-2α,9α,15-tetrace-toxy-11(15→1)-abeo-taxa-4(20),11-diene (1):

Oily compound (15.4 mg, Yield 6.6×10^{-5} %); R_f = 0.53; $[\alpha]_D^{20}$ 112 (MeOH): IR V_{max}^{CHCl3} cm^{-1}: 17.35 (-CO-), 3194 (C-H), 3628 (-0H): UV λ_{max}^{MeOH}; 206 nm (log ε = 4.8): ^{1}H-NMR (CD_3OD, 500 MHz) and ^{13}C-NMR (CD_3OD, 75 MHz) δ; see Table-1: EI MS *m/z* : 450 (6 %, M^+-HOAc), 432 (9), 390 (75), 254 (100); FAB MS m/z 511 $(M+1)^+$; HREI MS m/z 432.2087 ($C_{24}H_{32}O_7$, calcd. 432.2079, M^+-$C_2H_6O_3$).

5α, 9α, 10β, 13α-Tetraacetoxy-15hydroxy-11(15→1) abeo-taxa-4(20), 11-diene (2):

Oily compound (11.5 mg, yield 5.0×10^{-5} %); R_f= 0.42; $[\alpha]_D^{20}$ 85 (MeOH): IR $V_{max}^{CHCl_3}$ cm^{-1}: 1742 (-CO-), 2952 (C-H), 3589 (-H); UV λ_{max}^{MeOH} : 201 nm (log ε = 4.7); ^{1}H-NMR (CD_3OD, 400 MHz) and ^{13}C-NMR (CD_3OD, 125 MHz) δ: See Table-1; EI MS *m/z* : 460 (6 %, M^+-HOAc), 400 (1), 343 (8), 300 (100), 240 (78); FAB MS $(M+1)^+$ *m/z* : 521; HREI MS *m/z* 343.1949 ($C_{21}H_{27}O_4$, calcd. 343..1909, M^+-OAcx3).

7,9,10,13-Tetradeacetyl-abeo-baccatin IV (3):

Amorphous solid (9.4 mg, yield 4.0 x10^{-5} %); R_f = 0.62; $[\alpha]_D^{20}$-22 (MeOH);IR $\nu_{max}^{CHCl_3}$ 1739 (-CO-), 2947 (C-H), 3552 (-OH), 1018 (C-O); UV λ_{max}^{MeOH}: 203 nm (log ε = 4.6); ^{1}H-NMR(CD_3OD, 500 MHz) and ^{13}C-NMR (CD_3OD, 75 MHz) δ: See Table-**1**; E1 MS *m/z* : 460 (3 % M^+-HOAc-H_2O), 367 (54), 306 (100), 288 (83), 270 (39), 252 (11); FAB MS $(M+1)^+$- *m/z* 485; HREI MS *m/z* 408.1786 ($C_{22}H_{31}O_7$, cacld.408.1779, M^+-HOAc-H_2O)

Acknowledgement

The financial assistance from the University Grants Commission, Islamabad is gratefully acknowledged.

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