

Constituents with a Novel Skeleton Isolated from *Amentotaxus formosana*

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A novel compound consisting of two diterpenoid substructures, amentotaxin BA (**1**), and two novel terpenoids with a new skeleton, amentotaxins WA (**2**) and WB (**3**), were isolated from the barks and heart woods of *Amentotaxus formosana*, respectively. Their structures, including the relative configuration, were elucidated from spectroscopic data and a computer-generated plot for the 3D structure.

1. Introduction. – *Amentotaxus formosana* Li (Amentotaxaceae) is a tree endemic to southeastern Taiwan. Recently, two new lanostanoids, isolated from the leaf of *Amentotaxus formosana*, have been reported [1]. As part of a continued search for novel bioactive constituents from this plant, a novel compound consisting of two diterpenoid substructures, amentotaxin BA (**1**), and two novel terpenoids with a new skeleton, amentotaxins WA (**2**) and WB (**3**), were isolated from the CHCl₃ extract of air-dried barks and heart woods of *A. formosana*, respectively. In the present paper, the structure elucidations of the novel compounds are reported.

2. Results and Discussion. – Amentotaxin BA (**1**), a colorless, optically active oil, revealed a M^+ at m/z 614.3975 in the high-resolution MS, which corresponds to the molecular formula C₄₀H₅₄O₅. The IR absorption of **1** implied the presence of an OH (3440 cm⁻¹) and two carbonyl groups (1713 and 1650 cm⁻¹), which were confirmed by ¹³C-NMR data (off-resonance s at δ 213.4 and 221.5), and an aromatic ring (1620 cm⁻¹) moiety. The proposed structure for amentotaxin BA (**1**; see *Fig. 1*) was deduced from extensive analysis of the 1D and 2D NMR data, including those from COSY, HMQC, HMBC, and NOESY experiments in CDCl₃ (*Table 1*).

The ¹H- and ¹³C-NMR spectra of **1** displayed signals of a moiety with three angular Me groups at δ (H) 0.80, 0.86, and 1.07, an sp³ CH₂ group δ (H) 1.85 (d , $J = 12.6$ Hz, H _{β} -C(14)) and 2.41 (d , $J = 12.6$ Hz, H _{α} -C(14)), an olefinic proton at δ (H) 6.65 (d , $J = 6.8$ Hz), and a carbonyl group at δ (C) 221.5, and were similar to those of *ent*-

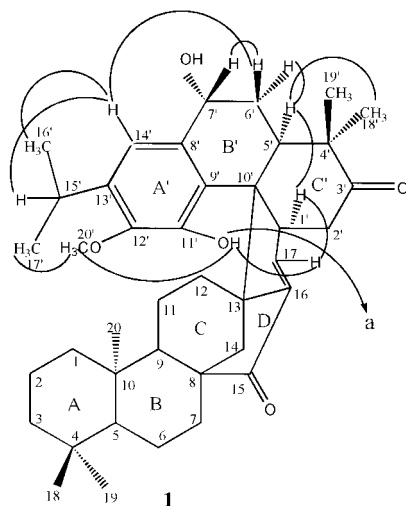


Fig. 1. Structure of **1** including selected NOESY correlations, relative configuration, and major MS fragmentation pattern. Arbitrary numbering.

kaur-16-en-15-one, except for the absence of signals of an exocyclic methylene and a cyclic skeletal methine group [2]. In addition to the above evidence, the ^1H - and ^{13}C -NMR data (Table 1) revealed signals due to a pentasubstituted benzene ring, an ^iPr , two tertiary Me, a phenolic OH and a MeO group, and two sp^3CH_2 , two sp^3CH , an OCH, a quaternary, and a carbonyl C-atom. The HMBC correlations $\text{Me}(16')/\text{C}(13')$, $\text{C}(15')$, and $\text{C}(17')$, $\text{Me}(17')/\text{C}(13')$ and $\text{C}(15')$, $\text{H}-\text{C}(14')/\text{C}(7')$, $\text{C}(8')$, $\text{C}(9')$, and $\text{C}(12')$, and $\text{Me}(20')\text{O}/\text{C}(12')$, and the NOESY cross-peak $\text{H}-\text{C}(14')/\text{Me}(16')$ established the pentasubstituted benzene moiety. The COSY correlations $\text{H}-\text{C}(7')/\text{CH}_2(6')$ and $\text{CH}_2(6')/\text{H}-\text{C}(5')$, and the HMBC correlation $\text{C}(7')/\text{H}-\text{C}(14')$ established the connection between $\text{C}(5')$ to $\text{C}(8')$. The HMBC correlation $\text{C}(10')/\text{H}_\alpha-\text{C}(6')$ and the $\text{C}(10')$ being a quaternary C-atom established that $\text{C}(5')$ was linked *via* $\text{C}(10')$ to $\text{C}(9')$. The COSY correlation $\text{H}-\text{C}(1')/\text{CH}_2(2')$, the HMBC correlations $\text{C}(3')/\text{H}-\text{C}(1')$, $\text{Me}(19')/\text{C}(3')$, $\text{C}(18')$, and $\text{C}(4')$, $\text{Me}(18')/\text{C}(4')$ and $\text{C}(19')$, and $\text{C}(10')/\text{H}_\alpha-\text{C}(6')$, and the $\text{C}(10')$ being a quaternary C-atom established the connectivity of ring C'. The HMBC correlations $\text{H}-\text{C}(1')/\text{C}(16)$ and $\text{C}(17)$, and $\text{C}(1')/\text{H}-\text{C}(17)$, the COSY correlation $\text{H}-\text{C}(1')/\text{H}-\text{C}(17)$, and both the $\text{C}(10')$ and $\text{C}(13)$ being quaternary C-atoms established the connection between $\text{C}(10')$ to $\text{C}(13)$ and that of $\text{C}(1')$ to $\text{C}(16)$ *via* $\text{C}(17)$. In the EI-MS of **1** (Fig. 1), significant peaks at m/z 596 ($[\text{M}-\text{H}_2\text{O}]^+$), 330 ($[\text{M}-\text{a}]^+$), 310 ($[\text{596}-\text{a}-2\text{H}]^+$), and 270 ($[\text{330}-\text{H}_2\text{O}-\text{CH}(\text{CH}_3)_2+\text{H}]^+$) also supported the structure of **1**. The NOESY experiment of **1** showed cross-peaks as shown in the computer-generated 3D drawing. The relative configurations at $\text{C}(1')$, $\text{C}(5')$, and $\text{C}(7')$ were deduced from the NOESY cross-peaks $\text{H}_\alpha-\text{C}(6')/\text{H}-\text{C}(5')$, $\text{H}-\text{C}(5')/\text{Me}(18')$, and $\text{H}-\text{C}(1')/\text{H}-\text{C}(5')$, establishing that $\text{H}-\text{C}(1')$ and $\text{H}-\text{C}(5')$ are on the α -side. The NOESY cross-peak $\text{H}_\beta-\text{C}(6')/\text{H}-\text{C}(7')$ suggested that $\text{OH}-\text{C}(7')$ adopted the α -configuration.

Based on the information from ^1H , ^1H -COSY, and NOESY data of **1**, a computer-assisted 3D structure was obtained with the molecular-modeling program CS CHEM 3D V3.5.1, by means of a MM2 force-field calculation for energy minimization. The calculated distances between $\text{H}_\alpha-\text{C}(1')/\text{H}-\text{C}(17)$ (2.651 Å), $\text{H}_\alpha-\text{C}(1')/\text{H}_\alpha-\text{C}(5')$ (3.981 Å), $\text{H}_\alpha-\text{C}(5')/\text{H}_\alpha-\text{C}(6')$ (2.309 Å), $\text{H}_\alpha-\text{C}(5')/\text{Me}(18')$ (2.418 Å), $\text{H}_\beta-\text{C}(6')/\text{H}_\beta-\text{C}(7')$ (2.461 Å), $\text{H}_\beta-\text{C}(7')/\text{H}-\text{C}(14')$ (2.275 Å), $\text{H}-\text{C}(14')/\text{H}-\text{C}(15')$ (2.236 Å), $\text{H}-\text{C}(14')/\text{Me}(16')$ (3.640 Å), $\text{Me}(17')/\text{Me}(12')\text{O}$ (2.848 Å), $\text{Me}(12')\text{O}/\text{OH}-\text{C}(11')$ (2.019 Å), and $\text{OH}-\text{C}(11')/\text{H}-\text{C}(17)$ (3.326 Å) are all less than 4.00 Å, which is

Table 1. ^1H - and ^{13}C -NMR Data (δ in ppm, J in Hz) of **1** in CDCl_3 ^a. Arbitrary numbering (see Fig. 1).

	$\delta(\text{H})$	$\delta(\text{C})$	HMBC (^1H)		$\delta(\text{H})$	$\delta(\text{C})$	HMBC (^1H)
2 H–C(1)	1.70 (<i>m</i>)	39.3	1.07 (Me(20))	H–C(1')	3.26 (<i>ddd</i> , $J = 13.1, 13.1, 6.8$)	53.2	6.65 (H–C(17))
2 H–C(2)	1.69 (<i>m</i>)	18.6		2 H–C(2')	1.27 (<i>dd</i> , $J = 13.1, 6.8$)	29.7	
2 H–C(3)	1.35 (<i>m</i>), 1.09 (<i>m</i>)	41.8	0.86 (Me(19))	C(3')		213.4	3.26 (H–C(1')), 0.95 (Me(19'))
C(4)		33.2	0.80 (Me(18))	C(4')		47.1	1.04 (Me(18')), 0.95 (Me(19'))
H–C(5)	3.29 (<i>dd</i> , $J = 13.1, 6.8$)	55.2	1.07 (Me(20)), 0.86 (Me(19))	H–C(5')	2.15 (<i>br. s</i>)	38.6	
2 H–C(6)	1.69 (<i>m</i>)	18.6		H $_{\alpha}$ –C(6')	1.80 (<i>m</i>)	38.0	
2 H–C(7)	1.83 (<i>m</i>)	27.7		H $_{\beta}$ –C(6')	2.00 (<i>dd</i> , $J = 13.4, 4.1$)		
C(8)		52.2		H $_{\beta}$ –C(7')	4.87 (<i>dd</i> , $J = 12.0, 4.1$)	66.8	7.06 (H–C(14'))
H–C(9)	1.04 (<i>m</i>)	52.9	1.07 (Me(20))	C(8')		138.0	7.06 (H–C(14'))
C(10)		39.8		C(9')		117.1	7.06 (H–C(14'))
2 H–C(11)	1.32 (<i>m</i>)	18.3		C(10')		46.4	6.65 (H–C(17)), 0.95 (Me(19')), 1.80 (H $_{\alpha}$ –C(6'))
				C(11')		146.4	
2 H–C(12)	2.15 (<i>m</i>)	34.7		OH–C(11')	6.09 (<i>s</i>)		
C(13)		51.6		C(12')		143.4	7.06 (H–C(14')), 3.80 (Me(20')O)
H $_{\alpha}$ –C(14)	2.41 (<i>d</i> , $J = 12.6$)	35.1		C(13')		140.1	1.25 (Me(16'))
H $_{\beta}$ –C(14)	1.85 (<i>m</i>)			H–C(14')	7.06 (<i>s</i>)	114.4	
C(15)		221.5	2.41 (H $_{\alpha}$ –C(14))	H–C(15')	3.26 (<i>m</i>)	26.8	1.25 (Me(16'))
C(16)		142.4	3.26 (H–C(1'))	Me(16')	1.25 (<i>d</i> , $J = 6.8$)	23.5	
H–C(17)	6.65 (<i>d</i> , $J = 6.8$)	120.0	3.26 (H–C(1'))	Me(17')	1.25 (<i>d</i> , $J = 6.8$)	23.8	1.25 (Me(16'))
Me(18)	0.80 (<i>s</i>)	21.5		Me(18')	1.04 (<i>s</i>)	20.2	0.95 (Me(19'))
Me(19)	0.86 (<i>s</i>)	33.4	0.80 (Me(18))	Me(19')	0.95 (<i>s</i>)	24.6	1.04 (Me(18'))
Me(20)	1.07 (<i>s</i>)	17.5		Me(20')O	3.80 (<i>s</i>)	61.9	

^a) All assignments were confirmed by HMQC, HMBC, and NOESY data.

consistent with the well-defined NOEs observed for each of these proton pairs (Fig. 1). Thus, the structure **1** for amentotaxin BA, with a configuration as shown in Fig. 1, was confirmed.

The molecular formula of amentotaxin WA (**2**; $\text{C}_{18}\text{H}_{20}\text{O}_3$) was established by HR-EI-MS (m/z 284.1409, M^+). The IR absorptions of **2** implied the presence of an OH (3171 cm^{-1}), a C=O (1720 cm^{-1}), and an α,β -unsaturated carbonyl group (1636 cm^{-1}), besides an aromatic ring (1600 cm^{-1}). The structure proposed for **2** (Fig. 2) was deduced from extensive analysis of 1D and 2D NMR data, including those from COSY, HMQC, HMBC, and NOESY experiments in $(\text{CD}_3)_2\text{CO}$ (Table 2).

The ^1H -NMR spectrum of **2** showed signals for two tertiary Me groups at δ 1.59 and 1.60, and a *cis*-disubstituted olefin moiety at δ 6.13 (*d*, $J = 9.6\text{ Hz}$, 1 H) and 7.68 (*d*, $J = 9.6\text{ Hz}$, 1 H), an aromatic proton at δ 7.32 (*s*), and a phenolic OH at δ 8.63 (*br. s*). The above evidence suggested that **2** contained a phenolic OH group at a disubstituted 1,1-dimethylnaphthalene-2(1*H*)-one moiety [3]. The ^1H -NMR spectrum of **2** also

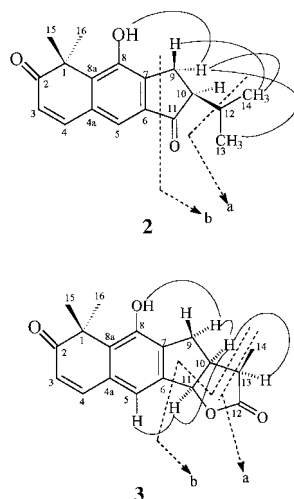


Fig. 2. Structure of **2** and **3**, with major MS fragmentations and NOESY correlations. Arbitrary numbering.

revealed signals for two secondary Me groups at δ 0.80 ($d, J = 6.8$ Hz) and 1.05 ($d, J = 6.8$ Hz), a CH_2 group at δ 2.94 ($dd, J = 17.6, 3.6$ Hz, 1 H) and 3.23 ($dd, J = 17.6, 8.0$ Hz, 1 H), and two CH protons at δ 2.31 (m) and 2.72 (m). The ^{13}C -NMR spectrum showed signals for four Me, a CH_2 , and two CH groups and for two olefinic, a tertiary aromatic, and eight quaternary C-atoms. The HMBC correlations of $\text{H}-\text{C}(5)/\text{C}(4)$, $\text{C}(6)$, $\text{C}(7)$, and $\text{C}(11)$ (Table 2), and the NOESY cross-peak of $\text{OH}-\text{C}(8)/\text{H}_\alpha-\text{C}(9)$ (Fig. 2) confirmed the presence of a 6,7-disubstituted 8-hydroxy-1,1-dimethylnaphthalene-2(1H)-one moiety in **2**. The COSY correlations $\text{CH}_2(9)/\text{H}-\text{C}(10)$, $\text{H}-\text{C}(10)/\text{H}-\text{C}(12)$, $\text{H}-\text{C}(12)/\text{Me}(13)$ and $\text{Me}(14)$, and HMBC correlations (Table 2) established the 2-isopropylcyclopentan-1-one moiety. The EI-MS of **2** showed significant peaks at m/z 242 ($[M - a + \text{H}]^+$), 214 ($[242 - \text{CO}]^+$), and 181 ($[M - b - 2 \text{H}]^+$) which also supported the structure of **2**.

The molecular formula of amentotaxin WB (**3**; $\text{C}_{18}\text{H}_{18}\text{O}_4$) was established by HR-EI-MS (m/z 298.1209, M^+). The IR absorptions of **3** implied the presence of an OH group (3244 cm^{-1}), a γ -lactone ring (1743 cm^{-1}), an α,β -unsaturated carbonyl group (1652 cm^{-1}), and an aromatic ring (1562 cm^{-1}). The proposed structure of **3** (Fig. 2) was deduced from extensive analysis of 1D and 2D NMR data, including those from COSY, HMQC, HMBC, and NOESY experiments in $(\text{CD}_3)_2\text{CO}$ (Table 2).

The ^1H -NMR spectrum of **3** showed signals for two tertiary Me groups at δ 1.54 and 1.55, and a *cis*-disubstituted olefin moiety at δ 6.07 ($d, J = 9.6$ Hz, 1 H) and 7.60 ($d, J = 9.6$ Hz, 1 H), an aromatic proton at δ 7.18 (*s*), and a phenolic OH at δ 8.36 (*br. s*). The above evidence suggested that also **3** contained a phenolic OH group at a disubstituted 1,1-dimethylnaphthalene-2(1H)-one moiety [3]. The ^1H -NMR spectrum of **3** also revealed signals for a secondary Me group at δ 1.25 ($d, J = 7.2$ Hz), a CH_2 group at δ 2.87 ($dd, J = 17.2, 4.8$ Hz, 1 H) and 3.16 ($dd, J = 17.2, 8.8$ Hz, 1 H), three CH groups at δ 3.13 (*m*), 3.47 (*m*), and 5.67 ($d, J = 6.0$ Hz). The ^{13}C -NMR spectrum showed signals for three Me, a CH_2 , and three CH groups and for two olefinic, a tertiary aromatic, and eight quaternary C-atoms. The HMBC correlations $\text{H}-\text{C}(5)/\text{C}(4)$, $\text{C}(7)$, and $\text{C}(8a)$ (Table 2), and the NOESY cross-peak $\text{OH}-\text{C}(8)/\text{H}_\alpha-\text{C}(9)$ (Fig. 2) confirmed the presence of a 6,7-disubstituted 8-hydroxy-1,1-dimethylnaphthalene-2(1H)-one moiety in **3**. The COSY correlations $\text{CH}_2(9)/\text{H}-\text{C}(10)$, $\text{H}-\text{C}(10)/\text{H}-\text{C}(11)$ and $\text{H}-\text{C}(13)$, and $\text{H}-\text{C}(13)/\text{Me}(14)$ confirmed the connectivities between $\text{C}(9)$ to $\text{C}(11)$, $\text{C}(10)$ to $\text{C}(13)$, and $\text{C}(13)$ to $\text{C}(14)$. The HMBC correlations $\text{H}_\beta-\text{C}(9)/\text{C}(6)$, $\text{C}(7)$, and $\text{C}(8)$, and $\text{H}_\alpha-\text{C}(9)/\text{C}(7)$ established the connectivity between $\text{C}(7)$ and $\text{C}(9)$. The HMBC correlations $\text{Me}(14)/\text{C}(13)$ and $\text{C}(12)$ established the connectivity between $\text{C}(12)$ and $\text{C}(13)$. The HMBC correlations $\text{H}-\text{C}(5)/\text{C}(11)$ and $\text{H}-\text{C}(11)/\text{C}(7)$, and NOESY cross-peak $\text{H}-\text{C}(5)/\text{H}-\text{C}(11)$ established the connectivity between $\text{C}(6)$ and $\text{C}(11)$. In addition to the above HMQC, COSY, and HMBC correlations, the ^{13}C -NMR spectrum of **3** revealed a

Table 2. ^1H - and ^{13}C -NMR Data (δ in ppm, J in Hz) of **2** and **3** in (D_6)Acetone. Arbitrary numbering (see Fig. 2).

	2			3		
	$\delta(\text{H})$	$\delta(\text{C})$	HMBC (^1H)	$\delta(\text{H})$	$\delta(\text{C})$	HMBC (^1H)
C(1)		47.5	6.13 (H–C(3)), 1.60 (Me(15)), 1.60 (Me(16))		47.1	6.07 (H–C(3)), 1.54 (Me(15)), 1.54 (Me(16))
C(2)		203.7	7.68 (H–C(4)), 1.60 (Me(15)), 1.60 (Me(16))		204.3	7.60 (H–C(4)), 1.54 (Me(15)), 1.54 (Me(16))
H–C(3)	6.13 (<i>d</i> , $J=9.6$)	125.1		6.07 (<i>d</i> , $J=9.6$)	124.3	
H–C(4)	7.68 (<i>d</i> , $J=9.6$)	146.2	7.32 (H–C(5))	7.60 (<i>d</i> , $J=9.6$)	146.5	7.18 (H–C(5))
C(4a)		135.1	6.13 (H–C(3)), 7.68 (H–C(4))		131.2	6.07 (H–C(3))
H–C(5)	7.32 (<i>s</i>)	117.1	7.68 (H–C(4))	7.18 (<i>s</i>)	120.7	7.60 (H–C(4))
C(6)		143.7	7.32 (H–C(5))		140.6	3.16 (H $_{\beta}$ –C(9))
C(7)		138.2	7.32 (H–C(5))		134.4	7.18 (H–C(5)), 2.87 (H $_{\alpha}$ –C(9)), 3.16 (H $_{\beta}$ –C(9)), 5.67 (H $_{\alpha}$ –C(11))
C(8)		153.9			152.8	3.16 (H $_{\beta}$ –C(9))
HO–C(8)	8.63 (<i>br. s</i>)			8.36 (<i>br. s</i>)		
C(8a)		138.5	7.68 (H–C(4)), 1.60 (Me(15)), 1.60 (Me(16))		135.0	7.60 (H–C(4)), 7.18 (H–C(5)), 1.54 (Me(15)), 1.54 (Me(16))
H $_{\alpha}$ –C(9)	2.94 (<i>dd</i> , $J=17.6, 8.0$)	26.1	2.72 (H $_{\alpha}$ –C(10))	2.87 (<i>dd</i> , $J=17.2, 4.8$)	29.7	
H $_{\beta}$ –C(9)	3.23 (<i>dd</i> , $J=17.6, 3.6$)			3.16 (<i>dd</i> , $J=17.2, 8.8$)		
H $_{\alpha}$ –C(10)	2.72 (<i>m</i>)	53.8	2.94 (H $_{\alpha}$ –C(9)), 3.23 (H $_{\beta}$ –C(9)), 0.80 (Me(13)), 1.05 (Me(14))	3.47 (<i>m</i>)	44.3	1.25 (Me(14))
C(11)		207.4	7.32 (H–C(5)), 3.23 (H $_{\beta}$ –C(9))			
H $_{\alpha}$ –C(11)				5.67 (<i>d</i> , $J=6.0$)	85.8	3.16 (H $_{\beta}$ –(9)), 7.18 (H–C(5)), 3.13 H $_{\alpha}$ –C(13))
H–C(12)	2.31 (<i>m</i>)	29.6	2.94 (H $_{\alpha}$ –C(9)), 0.80 (Me(13)), 1.05 (Me(14))			
C(12)					178.8	3.47 (H $_{\alpha}$ –C(10)), 1.25 (Me(14))
Me(13)	0.80 (<i>d</i> , $J=6.8$)	17.9	1.05 (Me(14))			
H $_{\alpha}$ –C(13)				3.13 (<i>m</i>)	38.8	2.87 (H $_{\alpha}$ –C(9)), 1.25 (Me(14))
Me(14)	1.05 (<i>d</i> , $J=6.8$)	20.8	0.80 (Me(13))	1.25 (<i>d</i> , $J=7.2$)	12.1	
Me(15)	1.60 (<i>s</i>)	24.1	1.59 (Me(16))	1.55 (<i>s</i>)	24.4	1.54 (Me(16))
Me(16)	1.59 (<i>s</i>)	24.1	1.60 (Me(15))	1.54 (<i>s</i>)	24.2	1.54 (Me(15))

tertiary O-substituted C-atom at δ 85.8 and a quaternary C-atom at δ 178.8, and its IR spectrum indicated the presence of a γ -lactone ring. The EI-MS spectrum of **3** showed significant peaks at m/z 283 ($[M - \text{Me}]^+$), 255 ($[283 - \text{CO}]^+$), 240 ($[M - a - 2\text{H}]^+$), and 211 ($[M - b - 2\text{H}]^+$) in accordance with the proposed structure. The relative configurations at C(10), C(11), and C(13) were deduced from the NOESY cross-peaks H–C(10)/H $_{\alpha}$ –C(9), H–C(11), and H–C(13), establishing that H–C(10), H–C(11), and H–C(13) are on the α -side (Fig. 2).

The uncommon structure of amentotaxin BA (**1**) results from the spiro-annulation of an abietane-type diterpene and a kaurane-type diterpene. The terpenoid **3** can be biologically derived from **2** by lactonization of OH–C(11) and COOH–C(12), the latter being formed in **2** by reduction at C(11) and oxidation at C(13).

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Experimental Part

General. M.p.: uncorrected. Optical rotations: *Jasco DIP-370* digital polarimeter. UV Spectra: *Jasco UV/VIS* spectrophotometer; λ_{\max} (log ϵ) in nm. IR Spectra: *Perkin Elmer 200 FT-IR* spectrophotometer; ν in cm^{-1} . ^1H - and ^{13}C -NMR Spectra: *Varian Unity-400* spectrometer; at 400 and 100 MHz, resp.; δ in ppm, J in Hz. MS: *JMSHX100*-mass spectrometer; m/z (rel. %).

Plant Material. Whole plants of *A. formosana* were collected at Kaohsiung Hsien, Taiwan, R. O. C., during July 1990, and a voucher specimen (9001) has been deposited at the Department of Medical Chemistry, School of Pharmacy, Kaohsiung Medical University.

Extraction and Isolation. CHCl_3 extract (15.7 g) of air-dried barks (0.7 kg) of *A. formosana* was chromatographed over silica gel. Elution with $\text{CH}_2\text{Cl}_2/\text{Me}_2\text{CO}$ 50:1 yielded **1** (5 mg). The CHCl_3 extract (6.5 g) of the heart woods (1.6 kg) of *A. formosana* was chromatographed over silica gel. Elution with hexane/acetone 1:0 \rightarrow 0:1, gave a 1st fraction with hexane/acetone 6:1, which was purified by column chromatography (silica gel, CH_2Cl_2) to afford **2** (8 mg), and a 2nd fraction with hexane/acetone 3:1, which was also purified by column chromatography (silica gel, hexane/AcOEt 3:4) to afford **3** (15 mg).

Amentotaxin BA (= 3',4'-Dihydro-7'' α ,11''-dihydroxy-12''-methoxy-13H-abieta-8'',11'',13''-trien[10'',1'':3',4']cyclopenta[2',1':13,16]ent-17-norkaur-13(16)-ene-3'',15-dione = 1,2,2a,3,5,5a,9,9a,10,11,12,13,13a,13b,14,15-hexadecahydro-1,16-dihydroxy-18-isopropyl-17-methoxy-3,3,10,10,13a-pentamethyl-8H-7a,15a-methano-[2',1':5,6]azuleno[2,1-a]phenanthrene-4,7-dione; **1**): Colorless oil. $[\alpha]_{\text{D}}^{25} = -36$ ($c = 0.20$, CHCl_3). IR (KBr): 3440, 1713, 1650. ^1H -NMR (CDCl_3 , 400 MHz): *Table 1*. ^{13}C -NMR (CDCl_3 , 100 MHz): *Table 1*. EI-MS (70 eV): 614 (22), 596 (1), 330 (0.3), 310 (16), 270 (66). HR-EI-MS: 614.3975 ($\text{C}_{40}\text{H}_{54}\text{O}_5$; calc. 614.3971).

Amentotaxin WA (= (2R)- or (2S)-2,3-Dihydro-4-hydroxy-2-isopropyl-5,5-dimethyl-1H-cyclopenta[b]naphthalen-1,6(5H)-dione; **2**): White powder from CHCl_3 . $[\alpha]_{\text{D}}^{25} = -2.4$ ($c = 0.1$, acetone). UV (MeOH): 219 (4.19), 238 (3.83), 270 (4.32), 307 (3.93), 350 (sh, 3.54). IR (KBr): 3171, 1720, 1636, 1600. ^1H -NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): *Table 2*. ^{13}C -NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): *Table 2*. EI-MS (70 eV): 284(2), 242(19), 241 (2) 227(11), 214(33), 199(17), 172(12), 185(7), 181(5), 141(36), 128(14), 115(62), 55(100). HR-EI-MS: 284.1409 ($\text{C}_{18}\text{H}_{20}\text{O}_3$; calc. 284.1412).

Amentotaxin WB (= rel-(3R,3aS,10bR)-3a,4,6,10b-Tetrahydro-5-hydroxy-3,6,6-trimethyl-2H-benzo[5,6]indeno[1,2-b]furan-2,7(3H)-dione; **3**): White powder from hexane/acetone. $[\alpha]_{\text{D}}^{25} = -48.4$ ($c = 0.1$, acetone). UV (MeOH): 212 (4.13), 225 (4.24), 312 (4.74). IR (KBr): 3244, 1743, 1652, 1562. ^1H -NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$): *Table 2*. ^{13}C -NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$): *Table 2*. EI-MS (70 eV): 298(6), 283(3), 270(7), 255 (3), 240 (1), 239(6), 226(17), 211(61), 197(26), 181(40), 172(35), 165(52), 141(44), 128(73), 115(87), 91(51), 55(100). HR-EI-MS: 298.1209 ($\text{C}_{18}\text{H}_{18}\text{O}_4$; calc. 298.1205).

REFERENCES

- [1] H. J. Su, S. H. Day, S. Z. Yang, M. Y. Chiang, C. N. Lin, *J. Nat. Prod.* **2002**, 65, 79.
- [2] U. Langenbahn, G. Burkhardt, H. Becker, *Phytochemistry* **1993**, 33, 1173.
- [3] D. P. Kelly, D. R. Leslie, B. D. Smith, *J. Am. Chem. Soc.* **1984**, 106, 687.

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