Five New Diterpenoids from the Bark of *Taiwania cryptomerioides*

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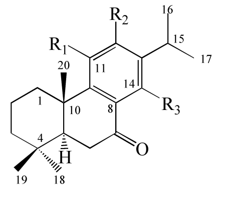
Five new diterpenoids, 11-hydroxyabieta-8,11,13-trien-7-one (1), 11,12,14-trihydroxyabieta-8,11,13-trien-7-one (2), 6β,7α-diacetoxyroyleanone (3), 7β-hydroxymanoyl oxide (4), and 9α-hydroxyisopimara-8(14),15-dien-7-one (5) were obtained from the bark of *Taiwania cryptomerioides*. The structures of the new compounds 1—5 were elucidated on the basis of spectral analysis and chemical evidence.

Key words *Taiwania cryptomerioides*; 6β,7α-diacetoxyroyleanone; 7β-hydroxymanoyl oxide; 11-hydroxyabieta-8,11,13-trien-7-one; 11,12,14-trihydroxyabieta-8,11,13-trien-7-one; 9α-hydroxyisopimara-8(14),15-dien-7-one

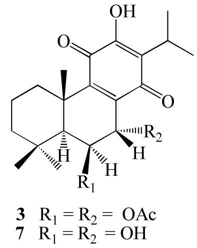
Taiwania cryptomerioides HAYATA (Taxodiaceae) is a decay-resistant, endemic tree that grows at elevations from 1800 to 2600 m in the central mountains of Taiwan. It is an economically important tree species in Taiwan. In previous phytochemical investigations, various sesquiterpenes, lignans, diterpenes, and bisflavones were isolated from the heartwood,[1—3] bark,[4,5] and leaves[6—9] of this plant. Recently, we reinvestigated the constituents of the bark of *T. cryptomerioides*, resulting in the discovery of several new diterpenes with 5(6→7)abeoabietane and podocarpane skeletons.[10—17] In continuing work on the same extracts of the plant, we also obtained five new diterpenoids, designated as 11-hydroxyabieta-8,11,13-trien-7-one (**1**), 11,12,14-trihydroxyabieta-8,11,13-trien-7-one (**2**), 6β,7α-diacetoxyroyleanone (**3**), 7β-hydroxymanoyl oxide (**4**), and 9α-hydroxyisopimara-8(14),15-dien-7-one (**5**). In this paper, we describe the isolation and structural elucidation of the above new diterpenes.

Compound **1** was isolated as an amorphous solid. The high resolution electron impact mass spectrum (HR-EI-MS) afforded a molecular ion at 300.2080, consistent with the molecular formula $C_{20}H_{28}O_2$ and indicated seven degrees of unsaturation. The IR spectrum of **1** showed characteristic absorptions at 3430 (hydroxyl group), 1505, 1625 (aromatic groups), and 1660 (conjugated carbonyl group) cm^{-1}. The UV absorptions at λ_{max} 225 and 267 nm were attributable to the benzoyl moiety. The ^{1}H-NMR (Table 1) spectrum displayed three singlets of methyl groups at δ_H 0.93, 0.96 and 1.38 (each 3H, H-18, H-19, H-20), an isopropyl group attached to a phenyl group at δ_H 2.82 (1H, sep, J=6.8 Hz, H-15) and 1.19 (6H, d, J=6.8 Hz, H-16, 17), a hydroxyl group at δ_H 4.98 (1H, br s, disappeared on D_2O exchange), and two *meta* aromatic protons at δ_H 6.69 (1H, d, J=1.6 Hz, H-12) and 7.55 (1H, d, J=1.6 Hz, H-14). The above data suggested that **1** is an 7-oxodehydroabietane skeleton derivative. An ABX system at δ_H 1.81 (1H, dd, J=3.2, 13.0 Hz), 2.54 (1H, dd, J=13.0, 17.0 Hz) and 2.64 (1H, dd, J=3.2, 17.0 Hz) was observed, and it was assigned to H-5 and H_2-6, respectively. A downfield H_β-1 signal appeared at δ_H 3.16 (1H, br d, J=13.4 Hz) and could be reasonably explained in terms of strong deshielding by a phenol group located at C-11.[18] The ^{13}C-NMR spectrum (Table 2) exhibited twenty signals including a conjugated carbonyl (δ_C 200.1) and six aromatic carbons (δ_C 118.3, 120.5, 133.1, 138.2, 147.8, 153.4). The spectral characteristics were similar to the known compound **6**, 11-hydroxysugiol.[19] By comparison of ^{1}H- and ^{13}C-NMR signals between **6** and **1**, the only difference was a proton attached to C-12 in **1** instead of a hydroxyl group attached to C-12 in **6**. Thus, compound **1** was determined as 11-hydroxyabieta-8,11,13-trien-7-one.

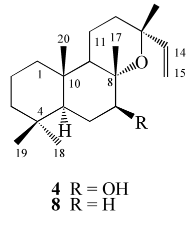
Compound **2** was obtained as a yellowish amorphous solid. Its molecular formula $C_{20}H_{28}O_4$ was determined from an $[M]^+$ ion at m/z 332.1996 in the HR-EI-MS and indicated seven degrees of unsaturation. Analysis of the IR spectrum of **2** suggested that it contained a hydroxyl group (3396 cm^{-1}), aromatic groups (1510, 1610 cm^{-1}), and a conjugated carbonyl group (1666 cm^{-1}). The UV spectrum of **2** showed conjugated carbonyl absorption bands at λ_{max} 220 and 253 nm. The ^{1}H-NMR (Table 1) signals included three methyl groups [δ_H 0.92, 0.94, 1.34 (each 3H, s)], an isopropyl group [δ_H 3.42 (1H, sep, J=6.8 Hz, H-15) and 1.32 (6H, d, J=6.8 Hz, H-16, 17)], and a downfield H_β-1 signal [δ_H 2.98 (1H, br d, J=12.4 Hz)]. Three singlets at δ_H 4.83, 6.33 and 12.16 (each 1H, br s, disappeared on D_2O exchange) were attributed to phenolic hydroxyl groups. The ^{13}C-NMR (Table 2) spectrum showed 20 carbons including a conjugated carbonyl (δ_C 204.5) and six aromatic carbons (δ_C 108.8, 118.4, 132.7, 137.3, 151.8, 159.5). From the above characteristics, compound **2** was similar to the structure of **1** with the abieta-8,11,13-trien-7-one skeleton. The only difference was that two *meta*-phenyl protons in **1** were



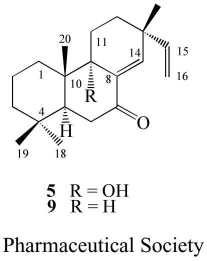
1 R_1 = OH, R_2 = R_3 = H
2 R_1 = R_2 = R_3 = OH
6 R_1 = R_2 = OH, R_3 = H



3 R_1 = R_2 = OAc
7 R_1 = R_2 = OH



4 R = OH
8 R = H



5 R = OH
9 R = H

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Table 1. ^{1}H-NMR Spectral Data of Compounds **1**—**5** (300 MHz in $CDCl_3$)

No.	**1**	**2**	**3**	**4**	**5**
1	1.38 m	1.53 m	1.20 m	1.50 m	1.44 m
	3.16 br d (13.4)	2.98 br d (12.4)	2.64 br d (12.6)	1.54 m	1.61 m
2	1.50 m	1.42 m	1.56 m	1.20 m	1.20 m
	1.71 m	1.72 m	1.60 m	1.51 m	1.56 m
3	1.21 m	1.24 m	1.22 m	1.10 m	1.24 m
	1.43 m	1.44 m	1.45 m	1.36 m	1.43 m
5	1.81 dd (3.2,13.0)	1.78[a]	1.51[a]	0.98 m	2.34 dd (2.6, 12.2)
6	2.54 dd (13.0, 17.0)	2.57 m	5.48 br s	1.30 m	2.21 dd (2.6, 15.8)
	2.64 dd (3.2, 17.0)			1.80 m	2.54 dd (12.2, 15.8)
7			5.69 d (2.0)	3.59 dd (4.8, 12.7)	
9				1.18 m	
11				1.58 m	1.60 m (α)
				1.60 m	1.92 m (β)
12	6.69 d (1.6)			1.70 m	1.62 m (α)
				1.78 m	1.68 m (β)
14	7.55 d (1.6)			5.82 dd (10.5, 17.1)	6.66 s
15	2.82 sep (6.8)	3.42 sep (6.8)	3.14 sep (7.0)	4.88 d (10.5)	5.82 dd (10.5, 17.4)
				5.09 d (17.1)	
16	1.19 d (6.8)	1.32 d (6.8)	1.17 d (7.0)	1.23 s	5.00 d (10.5)
					5.04 d (17.4)
17	1.19 d (6.8)	1.32 d (6.8)	1.20 d (7.0)	1.24 s	1.07 s
18	0.93 s	0.92 s	0.97 s	0.86 s	0.88 s
19	0.96 s	0.94 s	0.97 s	0.79 s	0.90 s
20	1.38 s	1.34 s	1.57 s	0.77 s	0.96 s
6-OCOC$\underline{H}_3$			2.01 s		
7-OCOC$\underline{H}_3$			2.02 s		
11-OH	4.98 br s	4.83 br s			
12-OH		6.33 br s	7.19 s		
13-OH		12.16 br s			

[a] Obscured by another singal.

replaced by two phenolic hydroxyl groups (δ_H 6.33, 12.16). Thus, compound **2** was identified as 11,12,14-trihydroxyabieta-8,11,13-trien-7-one. The conclusion was fully confirmed by COSY, HMQC, HMBC, and NOESY spectral data. In the HMBC spectrum of **2**, the methine proton H-5 (δ_H 1.78) showed correlations with quaternary carbon C-4 (δ_C 33.4), C-18 (δ_C 33.0) and C-20 (δ_C 19.0), and methylene proton H-6 (δ_H 2.57) exhibited correlation signals with C-7 (δ_C 204.5) to further confirm the structure of the AB ring. The isopropyl group attached to C-13 was confirmed by the correlations, and methine proton H-15 (δ_H 3.42) exhibited coupling with C-12 (δ_C 151.8), C-13 (δ_C 118.4), and C-14 (δ_C 159.5).

Compound **3** was obtained as a yellowish amorphous solid. The HR-EI-MS showed a molecular ion at *m/z* 432.2156, consistent with the molecular formula $C_{24}H_{32}O_7$ and indicated nine degrees of unsaturation. Two absorption bands at 1655 and 1665 cm^{-1} in the IR spectrum, the yellowish color, and λ_{max} 272 nm in the UV spectrum, together with the observation of signals at δ_C 124.8, 137.0, 149.3, 150.8, 183.2 and 185.3 in the ^{13}C-NMR spectrum (Table 2) indicated the presence of quinone moiety. The ^{1}H- and ^{13}C-NMR spectra of **3** (Tables 1, 2) showed signals due to an isopropyl group [δ_H 3.14 (1H, sep, $J=7.0$ Hz, H-15), 1.17 (3H, d, $J=7.0$ Hz, H-16) and 1.20 (3H, d, $J=7.0$ Hz, H-17)] bonded to a quinone ring, three tertiary methyls [δ_H 0.97 (6H, s),

Table 2. ^{13}C-NMR Spectral Data of Compounds **1**—**5** (75 MHz in $CDCl_3$)

No.	**1**	**2**	**3**	**4**	**5**
1	36.4	37.4	38.3	38.7	31.5
2	19.0	19.1	18.9	18.5	18.5
3	41.2	40.8	42.4	41.9	41.2
4	33.4	33.4	33.5	33.2	33.1
5	50.2	49.4	48.9	54.1	40.8
6	35.7	35.5	67.1	26.8	37.7
7	200.1	204.5	65.2	81.1	201.8
8	133.1	108.8	137.0	78.4	137.4
9	138.2	137.3	149.3	53.8	74.3
10	40.0	40.3	38.7	37.2	40.3
11	153.4	132.7	183.2	14.8	25.7
12	120.5	151.8	150.8	35.7	30.0
13	147.8	118.4	124.8	73.1	38.5
14	118.3	159.5	185.3	147.7	146.1
15	33.2	24.3	24.1	110.1	145.7
16	23.6	21.5	19.7	28.3	112.3
17	23.6	21.6	19.8	20.2	23.7
18	33.2	33.0	33.2	33.3	32.9
19	21.5	20.3	22.9	21.4	21.3
20	17.9	19.0	20.8	15.5	16.9
6-OCO$\underline{C}H_3$			21.2		
6-O$\underline{C}OCH_3$			169.0		
7-OCO$\underline{C}H_3$			21.2		
7-O$\underline{C}OCH_3$			168.1		

1.57 (3H, s)], two lowfield methyl signals of acetyl groups [δ_H 2.01 (3H, s), 2.02 (3H, s)], two methine protons in proximity to the ester groups [δ_H 5.48 (1H, br s, H-6), 5.69 (1H, d, J=2.0 Hz, H-7)], and a singlet at δ_H 7.19 (1H, s, disappeared on D_2O exchange) was attributed to a *para*-quinone hydroxyl group. An obvious characteristic signal at δ_H 2.64 was assigned as an H_β-1 signal. The ^{1}H- and ^{13}C-NMR spectra of **3** (Tables 1, 2) showed a great similarity to the known compound **7**, $6\beta,7\alpha$-dihydroxyroyleanone,[4] except for two acetyl groups in **3** instead of two hydroxyl groups in **7** attached to C-6 and C-7. Saponification of **3** under basic conditions gave the product which was identified as compound **7**. Complete ^{1}H and ^{13}C chemical shifts (Tables 1, 2) were obtained from COSY, HMQC, HMBC and NOESY spectra.

Compound **4** was obtained as an amorphous solid. The IR spectrum revealed the presence of a hydroxyl absorption band (3456 cm^{-1}) and a monosubstituted double bond (1646, 983, 910 cm^{-1}). The HR-EI-MS showed a molecular ion at *m/z* 306.2567, together with twenty carbon signals in the ^{13}C-NMR spectrum, indicated the molecular formula $C_{20}H_{34}O_2$ for **4** with an unsaturation index of four. The ^{1}H- and ^{13}C-NMR spectra of **4** showed signals assignable to five tertiary methyl groups [δ 0.77, 0.79, 0.86, 1.23, 1.24 (each 3H, s)] and an ABX system of a vinyl group [δ_H 4.88 (1H, d, J=10.5 Hz, H-15a), 5.09 (1H, d, J=17.1 Hz, H-15b), 5.82 (1H, dd, J=10.5, 17.1 Hz, H-14); δ_C 110.1 (C-15), 147.7 (C-14)]. A signal at δ_H 3.59 (1H, dd, J=4.8, 12.7 Hz, H-7) was attributable to an axial proton geminal to a hydroxyl group and coupled with two other vicinal protons observed from the COSY correlations. Additionally, two downfield quaternary carbons [δ_C 73.1 (C-13), 78.4 (C-8)] and a tertiary carbon [δ_C 81.1 (C-7)] were attached to the oxygen atom in the ^{13}C-NMR spectrum. From these characteristics, compound **4** was considered as a manoyl oxide (**8**) derivative with an extra hydroxyl group located on C-7 by comparison of its ^{13}C-NMR data with those of **8**.[20] Based on the multiplicity and J values of the cabinol methine proton at δ_H 3.59 (1H, dd, J=4.8, 12.7 Hz), the hydroxyl group neighboring the methylene group could be placed at either C-1, C-3, C-7, or C-17. From the HMBC correlations, methine proton H-7 (δ_H 3.59) showed cross-peaks with quaternary carbon C-8 (δ_C 78.4) and methylene carbon C-6 (δ_C 26.8), and methine carbon C-9 (δ_C 53.8) supported the hydroxyl group attached to C-7. The relative stereochemistry was established by NOESY. In the NOESY spectrum, the correlations as below H-7/H_α-5, H_α-6 (δ_H 1.80); H_β-1 (δ_H 1.54)/H-20; H_β-11 (δ_H 1.58)/H-16, -17, -20 and no correlation between H_α-5 and H-20 indicated that H-20, H-17, and H-16 are all in axial orientation, and the AB ring is *trans*-fused. Thus, compound **4** was identified as 7β-hydroxymanoyl oxide.

Compound **5** was obtained as an amorphous solid and had the molecular formula $C_{20}H_{30}O_2$ which was established by its HR-EI-MS spectrum with an $[M]^+$ ion at *m/z* 302.2233 with six degrees of unsaturation. The IR spectrum of **5** exhibited a hydroxyl group (3460 cm^{-1}), a monosubstituted double bond (1640, 980, 910 cm^{-1}), and a conjugated carbonyl group (1680 cm^{-1}). A conjugated carbonyl absorption band appeared at λ_{max} 242 nm in the UV spectrum. The ^{1}H-NMR spectrum showed signals for four tertiary methyl groups [δ_H 0.88, 0.90, 0.96, 1.07 (each 3H, s)], a β-H of α,β-unsaturated double bond [6.66 (1H, s, H-14)], and two ABX coupling system. Among the ABX coupling systems, one belongs to a vinyl group [5.00 (1H, d, J=10.5 Hz, H-16a), 5.04 (1H, d, J=17.4 Hz, H-16b), 5.82 (1H, dd, J=10.5, 17.4 Hz, H-15)], the other was contributed by the coupling between the methine and methylene neighboring a carbonyl group [δ_H 2.21 (1H, dd, J=2.6, 15.8 Hz), 2.34 (1H, dd, J=2.6, 12.2 Hz) and 2.54 (1H, dd, J=12.2, 15.8 Hz)]. The ^{13}C-NMR (Table 2) spectrum displayed 20 carbons including a conjugated carbonyl (δ_C 201.8) and four olefinic carbon signals (δ_C 112.3, 137.4, 145.7, 146.1). From the above observations, compound **5** was similar to the characteristics of the known compound, isopimara-8(14),15-dien-7-one (**9**).[21] The only difference was that H-9 in **9** was replaced by a hydroxyl group in **5**, resulting in the absence of an allylic coupling of H-14 with H-9 in **9** and the presence of a downfield carbon signal C-9 (δ_C 74.3) in **5**. Further evidence was provided by the correlations between H-20/C-9 and H-14/C-9. The NOESY correlations between H-18/H-5, H_α-6 (δ 2.21); H_β-6 (δ 2.54)/H-19, H-20, and H_β-11 (δ 1.92)/H-17, H-20 confirmed the relative stereochemistry of **5**. Thus, compound **5** was identified as 9α-hydroxyisopimara-8(14),15-dien-7-one.

Experimental

General Experimental Procedures Melting points were determined with a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AM-300 at 300 and 75 MHz in $CDCl_3$, with tetramethylsilane as an internal standard. EI-MS, IR, UV, and specific rotations were recorded on a Finnigan TSQ-46 C, Perkin-Elmer 983, a Hitachi S-3200 spectrometer, and a JASCO DIP-180 digital polarimeter, respectively. Extracts were chromatographed on silica gel (Merck 70—230 mesh, 230—400 mesh, ASTM).

Plant Material The bark of *T. cryptomerioides* was collected in Tai-Chun, Taiwan, in 1996. The plant material was identified by Mr. Muh-Tsuen Gun, formerly a technician of the Department of Botany, National Taiwan University. A voucher specimen (no. 013542) has been deposited at the Herbarium of the Department of Botany, National Taiwan University, Taipei, Taiwan.

Extraction and Isolation Air-dried pieces of *T. cryptomerioides* bark (12 kg) were extracted three times with acetone (60 l) at room temperature (7 d each time). The acetone extract was evaporated *in vacuo* to leave a black residue, which was suspended in H_2O (8 l), and then partitioned (3×) with 1 l of ethyl acetate. The EtOAc fraction (360 g) was chromatographed on Si gel using *n*-hexane and EtOAc of increasing polarity as eluent and further purified by HPLC eluted with *n*-hexane : EtOAc (75 : 25). Five components, 11-hydroxyabieta-8,11,13-trien-7-one (**1**) (8.2 mg), 11,12,14-trihydroxyabieta-8,11,13-trien-7-one (**2**) (6.8 mg), $6\beta,7\alpha$-diacetoxyroyleanone (**3**) (10.2 mg), 7β-hydroxymanoyl oxide (**4**) (7.8 mg), and 9α-hydroxyisopimara-8(14),15-dien-7-one (**5**) (18.2 mg) were obtained in the pure form.

11-Hydroxyabieta-8,11,13-trien-7-one (**1**): Amorphous solid; $[\alpha]_D^{23}$= +22.3° (c=0.3, $CHCl_3$); UV λ_{max}^{MeOH} nm (log ε) 327 (3.1), 267 (3.5), 225 (4.0, sh), 211 (4.2); IR (dry film) ν_{max} 3430, 1660, 1625, 1600, 1505 cm^{-1}; ^{1}H- and ^{13}C-NMR, see Tables 1 and 2; EI-MS (70 eV) (rel. int. %) *m/z* 300 (M^+, 71), 285 (100), 243 (23), 215 (100), 203 (65), 189 (36); HR-EI-MS *m/z* 300.2080 (Calcd for $C_{20}H_{28}O_2$, 300.2090).

11,12,14-Trihydroxyabieta-8,11,13-trien-7-one (**2**): Yellowish solid; $[\alpha]_D^{23}$=+92.0° (c=0.4, $CHCl_3$); UV λ_{max}^{MeOH} nm (log ε), 253 (3.4, sh), 318 (3.6), 344 (3.5, sh); IR (dry film) ν_{max} 3396, 1666, 1610, 1510, 1447, 1288, 1182, 903 cm^{-1}; ^{1}H- and ^{13}C-NMR, see Tables 1 and 2; EI-MS (70 eV) (rel. int. %) *m/z* 332 (M^+, 100), 317 (66), 247 (18), 235 (15), 203 (10); HR-EI-MS *m/z* 332.1996 (Calcd for $C_{20}H_{28}O_4$, 332.1988).

$6\beta,7\alpha$-Diacetoxyroyleanone (**3**): Yellowish solid; $[\alpha]_D^{23}$=−56.7° (c=0.3, $CHCl_3$); UV λ_{max}^{MeOH} nm (log ε) 272 (3.3), 403 (3.2); IR (dry film) ν_{max} 3397, 1732, 1665, 1655, 1600, 1460, 1367, 1228, 1023, 897 cm^{-1}; ^{1}H- and ^{13}C-NMR, see Tables 1 and 2; EI-MS (70 eV) (rel. int. %) *m/z* 432 (M^+, 2), 372 (6), 330 (78), 314 (100), 299 (30), 245 (58), 232 (62); HR-EI-MS *m/z* 432.2156 (Calcd for $C_{24}H_{32}O_7$, 432.2149).

7β-Hydroxymanoyl Oxide (**4**): Amorphous solid; $[\alpha]_D^{23}$=+35.2° (c=0.5, $CHCl_3$); IR (dry film) ν_{max} 3456, 1646, 1069, 983, 910 cm^{-1}; ^{1}H- and ^{13}C-

NMR, see Tables 1 and 2; EI-MS (70 eV) (rel. int. %) m/z 306 (M^+, 18), 291 (100), 273 (39), 177 (48), 123 (100); HR-EI-MS m/z 306.2567 (Calcd for $C_{20}H_{34}O_2$, 306.2560).

9α-Hydroxyisopimara-8(14),15-dien-7-one (**5**): Amorphous solid, $[\alpha]_D^{23} = -30.0°$ (c=0.6, $CHCl_3$); IR ν_{max} 3460, 1680, 1640, 980, 910 cm^{-1}; ^{1}H- and ^{13}C-NMR, see Tables 1 and 2; UV λ_{max}^{MeOH} nm (log ε) 242 (3.1) nm; EI-MS (70 eV) (rel. int. %) m/z 302 (M^+, 6), 284 (50), 269 (91), 234 (19), 178 (100), 160 (60); HR-EI-MS m/z 302.2233 (Calcd for $C_{20}H_{30}O_2$, 302.2247).

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