

DITERPENOIDS AND STEROIDS FROM *TAIWANIA*
CRYPTOMERIOIDES

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Key Word Index—*Taiwania cryptomerioides*; Taxodiaceae; leaves; diterpenes; sterols.

Abstract—Five new diterpenes and four uncommon sterols were isolated from the leaves of *Taiwania cryptomerioides*. Their structures were determined by chemical, spectroscopic and X-ray diffraction methods. The terpenes are 8,9-epoxy-7-oxoroyleanone methyl ether, 1,13,14-trihydroxypodocarpa-8,11,13-trien-7-one, 7 α ,8 α -dihydroxyabda-13(16),14-dien-19-yl *cis*-4-hydroxycinnamate, 7 α ,8 α -dihydroxyabda-13(16),14-dien-19-yl *trans*-4-hydroxycinnamate and beyer-15-en-18-carboxy β -D-glucopyranoside pentaacetate. The sterols, namely taiwaniasterols A–D, exhibit an uncommon skeleton of 6-5-6-5 fused rings. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

There are several studies on the chemical constituents of *Taiwania cryptomerioides* [1–6]. We recently found the constituents of diterpenoid quinols (taiwaniaquinols A–B) and quinones (taiwaniaquinones A–E) of uncommon 6-5-6 fused-ring skeleton [4–6]. A series of [4+2] and [5+2] products (taiwaniadducts A–I) derives from the additions of taiwaniaquinone A with β -myrcene or *trans*-ozic acid were also isolated [4–6]. In this paper, we report nine novel compounds, including an abietane (**1**), a trinorabietane (**2**), two labdanes (**3–4**), a beyerane (**5**) and four sterols (**6–9**) which contain uncommon 6-5-6-5 fused rings.

RESULTS AND DISCUSSION

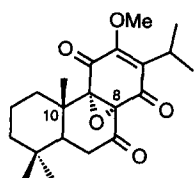
Compound **1** showed a molecular ion at m/z 360.1937 corresponding to a molecular formula $C_{21}H_{28}O_4$. The 1H NMR spectrum (Table 1) exhibited characteristic signals for an isopropyl group at δ 1.11 (d , $J = 6.8$ Hz), 1.16 (d , $J = 6.8$ Hz) and 3.02 (*sept*, $J = 6.8$ Hz). Three methyl groups, positioned on tertiary carbons, appeared at δ 0.84 (*s*), 0.87 (*s*) and 1.27 (*s*). A methoxy group occurred at a relatively low field of δ 3.80 (*s*). The carbon resonance at δ 197.9 in the ^{13}C NMR spectrum was attributable to a carbonyl group, whereas the resonances at δ 134.1, 156.6, 187.1 and 188.3 were attributable to a conjugated 1,4-dione fragment (Table 1). The signals at δ_C 60.7 and 69.9

might be ascribed to two epoxy carbons. The structure of compound **1** was assigned to 8,9-epoxy-7-oxoroyleanone methyl ether. The stereochemistry was confirmed by a chemical correlation with a known compound, 7-hydroxyroyleanone [4], which was previously isolated from the leaves of *T. cryptomerioides* in this laboratory. Thus, 7-hydroxyroyleanone (**10**, a mixture of 7-epimers) was treated with diazomethane to give a methyl ether **11** (Scheme 1). Oxidation of **11** with pyridinium dichromate afforded a ketone **12**, which reacted with *tert*-butyl hydroperoxide to give an epoxide identical to abietane **1**. Due to the steric hindrance of the C-10 methyl group, the epoxidation should occur at the less hindered α -face.

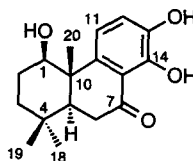
Based on spectroscopic and X-ray analyses (Fig. 1), the structure of a novel trinorabietane **2** ($C_{17}H_{22}O_4$) was determined to be 1,13,14-trihydroxypodocarpa-8,11,13-trien-7-one. The UV absorption at λ_{max} 278 nm was attributable to the phenone moiety. Two aromatic protons occurred at δ 7.03 (d , $J = 8.7$ Hz) and 7.64 (d , $J = 8.7$ Hz), indicating their *ortho*-relationship. H-5 (at δ 1.79) was axially oriented because it appeared as a double of doublet ($J = 13.0, 4.7$ Hz). An NOE experiment indicated that the carbonyl proton (H-1) was oriented on the α -face. Thus, irradiation of H-1 at δ 3.98 caused a significant enhancement (20%) of the H-5 resonance.

The 1H NMR spectrum of compound **3** ($C_{29}H_{40}O_5$) showed the proton resonances at δ 5.78 (d , $J = 12.5$ Hz), 6.82 (d , $J = 12.5$ Hz), 6.75 (d , $J = 8.6$ Hz) and 7.53 (d , $J = 8.6$ Hz) attributable to a *cis-p*-hydroxycinnamic ester. Three olefinic protons of a conjugated diene appeared at δ 5.04 (d , $J = 11.0$ Hz), 5.26 (d , $J = 17.5$ Hz) and 6.33 (*dd*, $J = 17.5, 11.0$ Hz). The

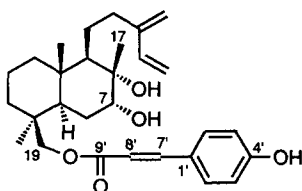
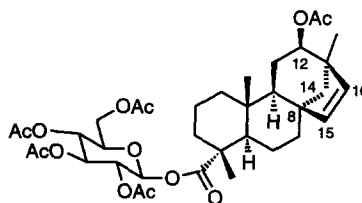
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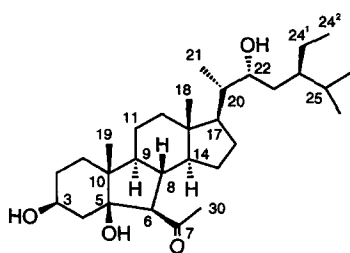
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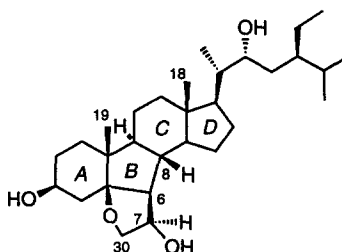
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3 (*cis*)4 (*trans*)

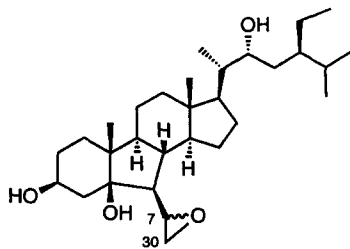
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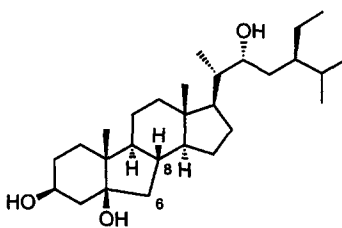
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7



8



9

signals at δ 0.76 (*s*), 0.88 (*s*) and 1.10 (*s*) were ascribed to three methyl groups on tertiary carbons. The ^{13}C NMR spectrum showed two methine signals at δ 46.9 (C-5) and 54.4 (C-9), characteristic of a labdane-type diterpene. Three carbonyl resonances occurred at δ 74.2 (CH), 75.0 (C) and 67.3 (CH_2). The structure of compound 3 was assigned as $7\alpha,8\alpha$ -dihydroxyabda-13(16),14-dien-19-yl *cis*-4-hydroxycinnamate. The assignments of carbon and proton resonances (Table 1) were confirmed by the HMQC and HMBC spectra. The stereochemistry was determined by NOE studies. Thus, irradiation of H-7 at δ_{H} 3.62 caused enhancements of C-8 and C-10 methyl groups (at δ_{H} 1.10 and 0.76). Irradiation of 10-Me caused an enhancement of one H-19 (at δ 4.15).

Compound 4 ($\text{C}_{29}\text{H}_{40}\text{O}_5$) is an isomer of compound 3. The ^1H NMR and ^{13}C NMR spectra of 4 (Table 1) were similar to those of 3, except for two olefinic

protons of cinnamate in 4 exhibiting a large coupling constant of 16.1 Hz. The structure of 4 was thus assigned as $7\alpha,8\alpha$ -dihydroxyabda-13(16),14-dien-19-yl *trans*-4-hydroxycinnamate.

A portion of the plant extract was subjected to peracetylation (Ac_2O , pyridine), after which the product mixture was chromatographed to give a peracetylated diterpene glycoside 5. The structure of compound 5 was unambiguously determined at 12-acetoxybeyer-15-ene-18-carboxy β -D-glucopyranoside pentaacetate by an X-ray analysis (Fig. 2). The ^1H NMR and ^{13}C NMR spectral data (Table 1) are in agreement with this structure, in which two *cis* olefinic protons occurred at δ 5.53 and 5.74 with a coupling constant of 5.7 Hz. To our knowledge, beyeranes are not so often found in nature [7] as those of *ent*-beyeranes (also known as stachanes) [8–10].

Compound 6 gave rise to a molecular ion $[\text{M}]^+$

Table 1. ^{13}C NMR and ^1H NMR data of compounds 1–4 and 5 (CDCl_3 , δ in ppm)

1 ^a	2		3		4		5 ^b
	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	
1	34.4	1.42 (m)	76.4	3.98 (br t, 8.3)	39.3	1.05 (m)	35.9†*
2	18.3	2.73 (br d, 12.4)‡	29.9	1.80 (m)*	18.0	1.68 (m)	17.4
3	40.9	1.62 (m)	39.1	1.28 (m)	36.3	1.55 (m)	1.45 (m)*
4	33.5	1.46 (m)	33.1	1.44 (m)	36.3	1.03 (m)	37.8
5	42.9	1.82 (dd, 12.5, 5.6)	48.7	1.79 (dd, 13.0, 4.7)	46.9	1.63 (m)	0.92 (m)
6	37.6	2.29 (dd, 17.2, 12.5)	35.8	2.78 (dd, 19.0, 13.0)	26.2	1.58 (m)	1.62 (m)
7	197.9	2.51 (dd, 17.2, 5.6)	206.2	2.66 (dd, 19.0, 4.7)	74.2	1.85 (dd, 11.8, 2.7)	1.04 (m)
8	60.7		115.3		74.2	3.62 (br s)	1.42 (m)
9	69.9		146.9		75.0		35.5†*
10	37.5		43.7		54.4	1.42 (m)	47.1
11	187.1		116.6	7.64 (d, 8.7)	38.4		51.5
12	156.6		121.0	7.03 (d, 8.7)	24.1	1.41 (m)	1.20 (m)
13	134.1		143.1		24.1	1.57 (m)	48.4
14	188.3		149.4		34.9	2.28 (m)	26.5
15	25.6	3.02 (sept, 6.8)	138.7	6.33 (dd, 17.5, 11.0)	147.1		1.90 (m)
16	19.5	1.11 (d, 6.8)	113.5	5.04 (d, 11.0)	138.7	6.33 (dd, 17.5, 11.0)	76.2
17	20.4	1.16 (d, 6.8)	115.8	5.26 (d, 17.5)	113.5	5.04 (d, 11.0)	47.4
18	32.9	0.84 (s)	22.9	1.10 (s)	115.8	4.99 (s)	1.14 (m)
19	20.9	0.87 (s)	27.0	0.88 (s)	23.0	1.13 (s)	1.50 (m)
20	16.0	1.27 (s)	67.3	3.92 (d, 11.0)	27.1	0.98 (s)	5.74 (d, 5.7)
1'			4.15 (d, 11.0)		67.3	3.98 (d, 11.1)	5.53 (d, 5.7)
2'			15.3	0.76 (s)	15.3	0.79 (s)	21.1
3'			126.9		126.4		0.94 (s)
4'			132.1	7.53 (d, 8.6)	130.0	7.37 (d, 8.4)	16.5
5'			115.1	6.75 (d, 8.6)	114.9	6.83 (d, 8.4)	15.1
6'			157.3		158.7		0.71 (s)
7'			115.1	6.75 (d, 8.6)	114.9	6.83 (d, 8.4)	5.63 (d, 9.1)
8'			132.1	7.53 (d, 8.6)	130.0	7.37 (d, 8.4)	70.0
9'			143.8	6.82 (d, 12.5)	144.9	7.57 (d, 16.1)	5.13 (t, 9.1)
			116.7	5.78 (d, 12.5)	116.0	6.24 (d, 16.1)	5.18 (t, 9.1)
			167.4		168.1		72.4†
							68.0
							5.09 (t, 9.1)
							72.7†
							3.78 (m)
							61.5
							4.05 (dd, 12.1, 2.1)
							4.21 (dd, 12.1, 4.4)

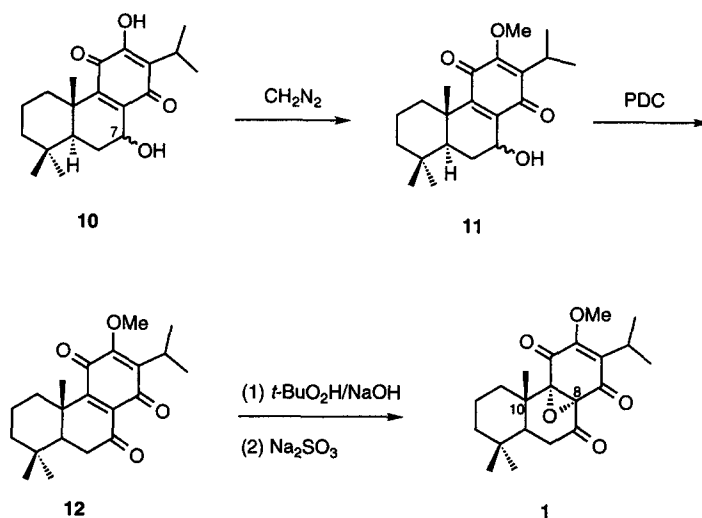
^aThe resonance of OMe group appeared at δ_{C} 59.5 and δ_{H} 3.80 (s).

^bThe resonance of OAc groups appeared at δ_{C} 20.4, 20.5, 20.6, 169.0, 169.3, 170.0, 170.4 and 170.9, as well as δ_{H} 2.01 (s), 1.98 (s) and 1.97 (s) and 1.96 (s). The signal of one or both protons was too weak to be assigned.

*The signal of one or both of the protons was too weak to be assigned.

†Assignments can be exchanged.

‡Coupling constants (*J* in Hz) in parentheses.



Scheme 1.

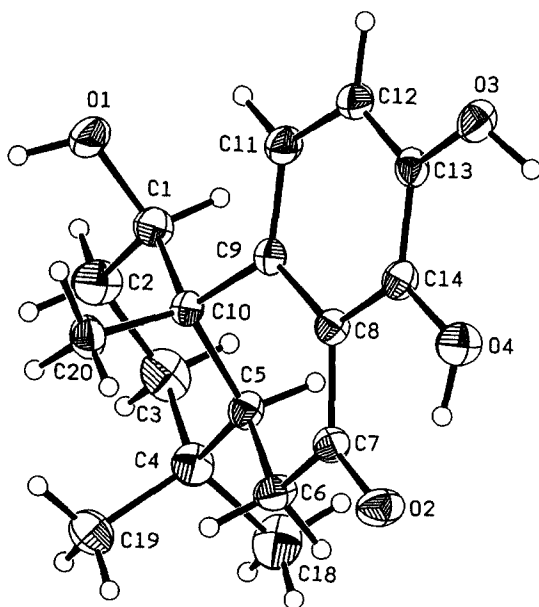


Fig. 1. ORTEP drawing of compound 2.

at m/z 476.3868 consistent with a molecular formula $C_{30}H_{52}O_4$. This compound had five degrees of unsaturation. Besides a carbonyl group appearing at δ_C 210.8, compound 6 contained four rings as those found in steroids. The signal at δ_H 2.17 (*s*) was attributable to an acetyl group. Two resonances at δ_H 0.68 (*s*) and 0.90 (*s*) were attributable to two methyl groups positioned on tertiary carbons. Compound 6, m.p. 89–91°, $[\alpha]_D^{25} + 80$ ($CHCl_3$; c 0.2), was crystallised from $CHCl_3$ -hexane. The X-ray analysis (Fig. 3) revealed that compound 6 has an unprecedented skeleton of 6-5-6-5 fused rings. Accordingly, compound 6 (namely

taiwaniasterol A) has the (3*S*,5*R*,6*R*,8*S*,9*S*,10*R*,13*S*,14*S*,17*R*,20*S*,22*R*,24*R*)-configuration (the numbering for compounds 6–9 is used by analogy to that of other steroids). The carbon and proton resonances (Table 2) were assigned by assistance of H–H COSY, HMQC and HMBC spectra.

By comparison of the 1H NMR and ^{13}C NMR spectra, the structures of compounds 7 ($C_{30}H_{52}O_4$) and 8 ($C_{30}H_{52}O_4$) appeared to be similar to that of taiwaniasterol A (6), except for the substituents on B-rings. Compounds 7 or 8 did not give rise to the signal for an acetyl group on the B-ring. Instead, compound 7 showed an ABX pattern of three protons at δ 3.83 (*dd*, $J = 10.0, 2.7$ Hz), 4.00 (*dd*, $J = 10.0, 4.3$ Hz) and 4.18 (*m*) attributable to a moiety of β -hydroxy tetrahydrofuran. Compound 8 showed an ABX pattern of three protons at δ 2.37 (*dd*, $J = 5.4, 3.0$ Hz), 2.74 (*dd*, $J = 4.5, 4.5$ Hz) and 2.88 (*ddd*, $J = 9.0, 4.5, 3.0$ Hz) attributable to a moiety of oxirane. Thus, the structures of compounds 7 (namely taiwaniasterol B) and 8 (namely taiwaniasterol C) were deduced. Assignments of 1H and ^{13}C resonances were made according to their H–H COSY, HMQC and HMBC spectra. The stereochemistry was supported by their NOESY spectra. For instance in taiwaniasterol B (7), H-19 (δ 0.91) was correlated to H-8 (δ 1.90) and H-30 β (δ 3.83), H-6 (δ 1.80) to H-30 α (δ 4.00), H-18 (δ 0.71) to H-8 and H-20 (δ 1.70), as well as H-7 (δ 4.18) to H-4 (δ 1.55). Similarly, the NOESY spectrum of taiwaniasterol C (8) showed that H-7 (δ 2.88) and H-30 (δ 2.37 and 2.74) have correlations with H-19 (δ 0.95). An attempt to convert 8 to 7 by treatment with NaH/THF (room temperature, 4 h) failed. Compound 8 probably has the 7*R*-chirality by analogy to that in 7.

Compound 9 gave rise to a molecular ion $[M]^+$ at m/z 434.3764 consistent with a molecular formula $C_{28}H_{50}O_3$. This lacks two carbon atoms by comparison with taiwaniasterols A–C. Compound 9 had four

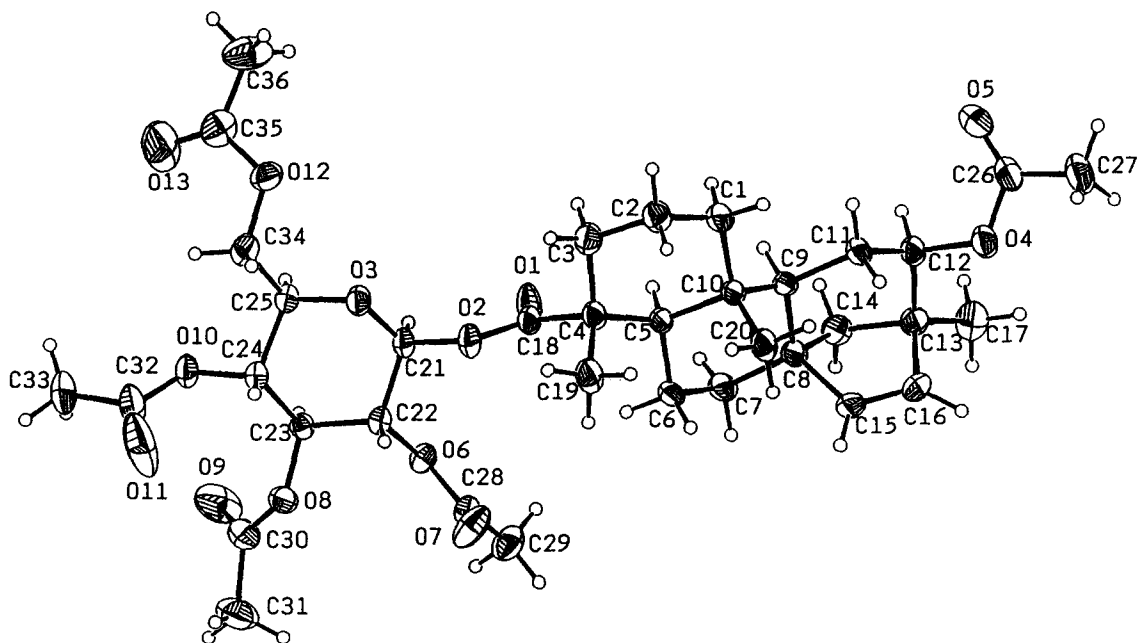


Fig. 2. ORTEP drawing of compound 5.

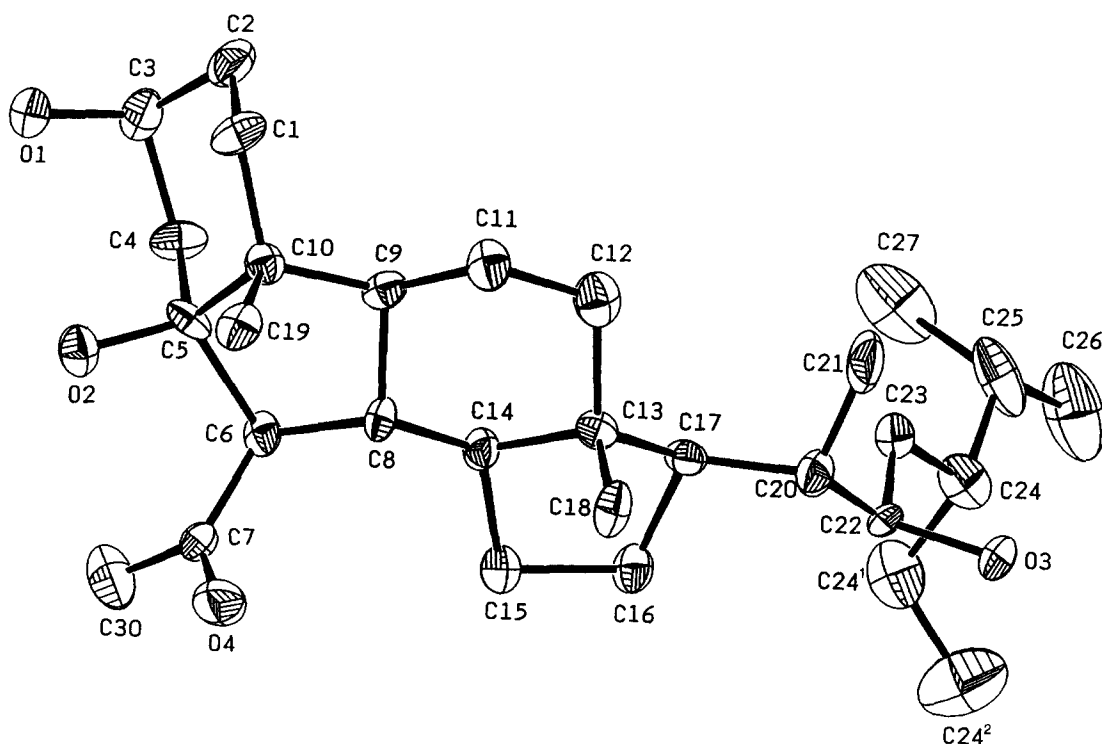


Fig. 3. ORTEP drawing of taiwaniasterol A (6).

degrees of unsaturation. As its IR or NMR spectra did not show any signal attributable to carbonyl group or double bond, compound **9** must have a skeleton of four rings. By detailed analyses of its ^1H NMR, ^{13}C NMR, HMQC, HMBC and NOESY spectra, the structure of **9** (namely taiwaniasterol D) was deter-

mined. Correlations of C-5 (δ 81.5) with H-3 (δ 4.03) and H-19 (δ 0.89) as well as C-22 (δ 71.3) with H-21 (δ 0.89) strongly supported the assigned structure.

In summary, five new diterpenoids of royleanone, norabietane, labdane and beyerane types were isolated from the leaves of *T. cryptomerioides*. The finding of

Table 2. ^{13}C NMR and ^1H NMR data of compounds 6–9 (CDCl_3 , δ in ppm)

	6		7		8		9	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	27.9	1.20–1.80 (<i>m</i>)	31.2	1.08 (<i>m</i>) 1.46 (<i>m</i>)	26.8	1.35 (<i>m</i>),*	26.5	1.32 (<i>m</i>) 1.64 (<i>m</i>)
2	28.2	1.20–1.80 (<i>m</i>)	29.5	1.42 (<i>m</i>) 1.95 (<i>m</i>)	27.8	1.60 (<i>m</i>),*	28.1	1.62 (<i>m</i>),*
3	67.2	4.01 (<i>br s</i>)	67.7	3.93 (<i>br m</i>)	67.1	3.97 (<i>br s</i>)	67.4	4.03 (<i>m</i>)
4	44.1	1.75 (<i>m</i>) 2.15 (<i>m</i>)	39.4	1.55 (<i>m</i>) 1.85 (<i>m</i>)	45.4	1.60 (<i>m</i>) 1.92 (<i>br d</i> , 15.0)‡	43.2†	1.65 (<i>m</i>) 1.95 (<i>br d</i> , 13.0)
5	83.2		95.7		82.7		81.5	
6	65.6	2.50 (<i>d</i> , 9.5)	59.0	1.80 (<i>mm</i>)	56.9	0.94 (<i>m</i>)	43.3†	1.30 (<i>m</i>) 1.73 (<i>m</i>)
7	210.8		71.0	4.18 (<i>br m</i>)	54.1	2.88 (<i>ddd</i> , 9.0, 4.5, 3.0)		
8	42.1	2.12 (<i>m</i>)	36.3	1.90 (<i>m</i>)	41.6	1.65 (<i>m</i>)	37.3	1.79 (<i>m</i>)
9	50.7	1.15 (<i>m</i>)	57.8	1.16 (<i>m</i>)	50.4	1.26 (<i>m</i>)	51.9	1.25 (<i>m</i>)
10	44.8		44.5		44.7		44.8†	
11	21.4	1.40 (<i>m</i>),*	21.5	1.38 (<i>m</i>),*	21.3	1.40 (<i>m</i>),*	21.7	1.28 (<i>m</i>) 1.35 (<i>m</i>)
12	39.6	1.12 (<i>m</i>) 2.02 (<i>br d</i> , 13.0)	39.6	1.09 (<i>m</i>) 2.01 (<i>br d</i> , 13.0)	39.7	1.15 (<i>m</i>) 2.03 (<i>br d</i> , 13.0)	40.0	1.12 (<i>m</i>) 2.00 (<i>br d</i> , 13.0)
13	45.6		44.5		45.1		44.9†	
14	56.0	1.10 (<i>m</i>)	56.0	1.07 (<i>m</i>)	55.5	1.16 (<i>m</i>)	56.5	1.13 (<i>m</i>)
15	24.6	1.10 (<i>m</i>) 1.38 (<i>m</i>)	25.1	1.22 (<i>m</i>) 1.54 (<i>m</i>)	25.3	1.36 (<i>m</i>) 1.50 (<i>m</i>)	24.4	1.12 (<i>m</i>) 1.52 (<i>m</i>)
16	27.6	1.20–1.80 (<i>m</i>)	27.5	1.34 (<i>m</i>) 1.72 (<i>m</i>)	27.7	1.34 (<i>m</i>) 1.70 (<i>m</i>)	27.7	1.35 (<i>m</i>) 1.72 (<i>m</i>)
17	52.5	1.12 (<i>m</i>)	52.5	1.10 (<i>m</i>)	52.4	1.10 (<i>m</i>)	52.6	1.10 (<i>m</i>)
18	12.5	0.68 (<i>s</i>)	12.4	0.71 (<i>s</i>)	12.4	0.68 (<i>s</i>)	12.5	0.66 (<i>s</i>)
19	17.4	0.90 (<i>s</i>)	15.9	0.91 (<i>s</i>)	18.7	0.95 (<i>s</i>)	18.3	0.89 (<i>s</i>)
20	42.4	1.70 (<i>m</i>)	42.4	1.70 (<i>m</i>)	42.3	1.70 (<i>m</i>)	42.4	1.70 (<i>m</i>)
21	12.3	0.88 (<i>d</i> , 7.0)	12.3	0.90 (<i>d</i> , 7.0)	12.3	0.90 (<i>d</i> , 7.0)	12.3	0.89 (<i>d</i> , 7.0)
22	71.2	3.68 (<i>br d</i> , 11.8)	71.2	3.69 (<i>br d</i> , 8.3)	71.2	3.67 (<i>br d</i> , 9.8)	71.3	3.68 (<i>br d</i> , 10.3)
23	29.8	0.98 (<i>m</i>) 1.24 (<i>m</i>)	29.8	0.97 (<i>m</i>) 1.22 (<i>m</i>)	29.8	1.00 (<i>m</i>) 1.22 (<i>m</i>)	29.8	1.00 (<i>m</i>) 1.22 (<i>m</i>)
24	41.3	1.25 (<i>m</i>)	41.3	1.24 (<i>m</i>)	41.3	1.24 (<i>m</i>)	41.4	1.25 (<i>m</i>)
25	28.7	1.75 (<i>m</i>)	28.7	1.75 (<i>m</i>)	28.6	1.75 (<i>m</i>)	28.7	1.75 (<i>m</i>)
26	17.6	0.75 (<i>d</i> , 7.0)	17.6	0.77 (<i>d</i> , 7.0)	17.5	0.75 (<i>d</i> , 7.0)	17.6	0.76 (<i>d</i> , 7.0)
27	20.5	0.85 (<i>d</i> , 7.0)	20.5	0.86 (<i>d</i> , 7.0)	20.5	0.86 (<i>d</i> , 7.0)	20.5	0.86 (<i>d</i> , 7.0)
241	23.5	1.23 (<i>m</i>) 1.35 (<i>m</i>)	23.5	1.20 (<i>m</i>) 1.34 (<i>m</i>)	23.5	1.22 (<i>m</i>) 1.35 (<i>m</i>)	23.5	1.24 (<i>m</i>) 1.35 (<i>m</i>)
242	11.7	0.84 (<i>t</i> , 7.0)	11.7	0.86 (<i>t</i> , 7.0)	11.7	0.85 (<i>t</i> , 7.0)	11.8	0.85 (<i>t</i> , 7.0)
30	33.1	2.17 (<i>s</i>)	76.6	3.83 (<i>dd</i> , 10.0, 2.7) 4.00 (<i>dd</i> , 10.0, 4.3)	47.0	2.37 (<i>dd</i> , 4.5, 3.0) 2.74 (<i>dd</i> , 4.5, 4.5)		

*The signal of one or both protons was too weak to be assigned.

†Assignments can be exchanged.

‡Coupling constants (*J* in Hz) in parentheses.

four novel steroids 6–9 with an uncommon skeleton of 6-5-6-5 fused rings is most remarkable, though the biogenesis of these sterols awaits further investigation.

EXPERIMENTAL

General

HPLC: Hibar Lichrosorb Si 60 column (10 μm , 25 $\text{cm} \times 1 \text{ cm}$ *i.d.*); TLC: Merck silica gel 60F sheets.

Plant material

The dried leaves (1.75 kg) of *T. cryptomerioides* were exhaustively extracted with Me_2CO (7 l \times 3). The combined extracts were concd to approximately 0.8 l and taken up with CHCl_3 (0.8 l \times 3). The CHCl_3 -soluble portion was concd (55 g) and subjected to silica-gel CC. The portion obtained from elution of EtOAc-hexane (10%–100%) was further subjected to flash chromatography and HPLC to give compounds 1 (11

mg), **2** (20 mg), **3** (53 mg), **4** (20 mg), **6** (22 mg), **7** (11 mg), **8** (9 mg) and **9** (9 mg). The portion obtained from the Me₂CO-EtOAc (10%–50%) eluant was subjected to peracetylation (Ac₂O, pyridine). Compound **5** (20 mg) was isolated from the product mixture by chromatography.

8,9-Epoxy-7-oxoroleanone methyl ether (1). Solid, m.p. 65–67°, $[\alpha]_D^{25} - 113.2$ (CHCl₃; *c* 0.55). TLC (10% EtOAc in hexane) *R_f* 0.37. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 1724, 1692, 1669. UV $\lambda_{\max}^{\text{MeOH}}$ nm (ϵ): 303 (5163), 216 (10,000). EIMS (70 eV) *m/z* (rel. int.) 360 [M]⁺ (2), 332 (4), 256 (8), 235 (4), 223 (4), 55 (100). HRMS for C₂₁H₂₈O₄ requires 360.1937; Found: 360.1937.

Preparation of 1. A soln of 7-hydroxyroleanone (a mixture of 7-epimers, 38 mg, 0.115 mmol) in Et₂O (10 ml) was treated with CH₂N₂ to give a methyl ether **11**. The crude product **11** was dissolved in CH₂Cl₂ (5 ml) and treated with pyridinium dichromate (86.5 mg, 0.23 mmol) and molecular sieves (4 Å, 1 g) at room temp for 6 h. After which, the mixture was subjected to silica-gel CC by elution with CH₂Cl₂ to give a ketone **12** (28 mg). To a soln of **12** (28 mg, 0.081 mmol) in MeOH (5 ml) was added aq NaOH (0.05 N, 1 ml), followed by aqueous *t*-BuOOH (70% soln, 1 ml). The mixture was stirred at room temp for 8 h, cooled to 0°, and quenched with a soln of Na₂SO₃ (90 mg) in water (5 ml). The mixture was stirred at room temp for 3 h, concd, and chromatographed on a silica-gel column by elution with EtOAc-hexane (1:39) to give epoxide **1** (11 mg) in 27% overall yield.

1,13,14-Trihydroxypodocarpa-8,11,13-trien-7-one (2). Crystals from EtOAc-hexane (1:9), m.p. 188–189°, $[\alpha]_D^{25} - 37.3$ (CHCl₃; *c* 1.02). TLC (30% EtOAc in hexane) *R_f* 0.23. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3478, 3417, 3333, 1620. UV $\lambda_{\max}^{\text{MeOH}}$ nm (ϵ): 364 (2617), 278 (10,069). EIMS (70 eV) *m/z* (rel. int.) 290 [M]⁺ (100), 258 (12), 232 (28), 190 (38), 173 (30), 161 (18), 145 (10). HRMS for C₁₇H₂₂O₄ requires 290.1519; Found: 290.1516.

7 α ,8 α -Dihydroxyabda-13(16),14-dien-19-yl cis-4-hydroxycinnamate (3). Solid, m.p. 155–157°, $[\alpha]_D^{27} + 1.1$ (MeOH; *c* 2.6). TLC (25% EtOAc in hexane) *R_f* 0.12. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 1693. UV $\lambda_{\max}^{\text{MeOH}}$ nm (ϵ): 309 (19,815), 226 (100,296). EIMS (70 eV) *m/z* (rel. int.) 450 [M–H₂O]⁺ (2), 339 (4), 286 (4), 268 (4), 203 (3), 187 (4), 147 (100). HRMS for C₂₉H₃₈O₄ [M–H₂O]⁺ requires 450.2771; Found: 450.2804.

7 α ,8 α -Dihydroxyabda-13(16),14-dien-19-yl trans-4-hydroxycinnamate (4). Solid, m.p. 165–167°, $[\alpha]_D^{27} + 1.4$ (MeOH; *c* 1.0). TLC (25% EtOAc in hexane) *R_f* 0.12. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 1689. UV $\lambda_{\max}^{\text{MeOH}}$ nm (ϵ): 312 (24,338), 213 (42,567). EIMS (70 eV) *m/z* (rel. int.) 450 [M–H₂O]⁺ (1), 369 (1), 386 (3), 203 (2), 187 (3), 147 (100). HRMS for C₂₉H₃₈O₄ [M–H₂O]⁺ requires 450.2771; Found: 450.2774.

12-Acetoxybeyer-15-ene-18-carboxy β -glucopyranoside pentaacetate (5a). Solid, m.p. 192–194°, $[\alpha]_D^{23}$

–3.8 (CHCl₃; *c* 1.0). TLC (25% EtOAc in hexane) *R_f* 0.24. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 1754, 1740, 1227. EIMS (70 eV) *m/z* (rel. int.) 690 [M]⁺ (1), 630 (2), 331 (50), 255 (20), 229 (8), 169 (100), 108 (25). HRMS for C₃₆H₅₀O₁₃ requires 690.3252; Found: 690.3254.

Taiwaniasterol A (6). Crystals from CHCl₃-hexane (1:1), m.p. 89–91°, $[\alpha]_D^{30} + 80$ (CHCl₃; *c* 0.2). TLC (20% EtOAc in hexane) *R_f* 0.20. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3447, 1705. EIMS (70 eV) *m/z* (rel. int.) 476 [M]⁺ (28), 458 (44), 441 (28), 415 (30), 348 (30), 330 (42), 69 (100), 55 (100). HRMS for C₃₀H₅₂O₁₃ requires 476.3868; Found: 476.3868.

Taiwaniasterol B (7). Solid, m.p. 87–89°, $[\alpha]_D^{30} + 47.5$ (CHCl₃; *c* 2.3). TLC (20% EtOAc in hexane) *R_f* 0.35. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3422. EIMS (70 eV) *m/z* (rel. int.) 476 [M]⁺ (2), 458 (4), 348 (48), 330 (32), 304 (74), 275 (64), 55 (100). HRMS for C₃₀H₅₂O₁₃ requires 476.3868; Found: 476.3860.

Taiwaniasterol C (8). Solid, m.p. 89–91°, $[\alpha]_D^{30} + 81.2$ (CHCl₃; *c* 0.62). TLC (20% EtOAc in hexane) *R_f* 0.37. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3423. EIMS (70 eV) *m/z* (rel. int.) 476 [M]⁺ (1), 458 (12), 440 (20), 428 (22), 173 (22), 147 (32), 128 (100). HRMS for C₃₀H₅₂O₁₃ requires 476.3868; Found: 476.3871.

Taiwaniasterol D (9). Solid, m.p. 151–152°, $[\alpha]_D^{30} + 39$ (CHCl₃; *c* 0.4). TLC (20% EtOAc in hexane) *R_f* 0.24. IR $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$: 3396. EIMS (70 eV) *m/z* (rel. int.) 434 [M]⁺ (4), 416 (6), 398 (5), 362 (30), 228 (25), 273 (18), 234 (100). HRMS for C₂₈H₅₀O₃ requires 434.3762; Found: 434.3764.

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