



UNCOMMON DITERPENES WITH THE SKELETON OF SIX-FIVE-SIX FUSED-RINGS FROM *TAIWANIA CRYPTOMERIOIDES*

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Key Word Index—*Taiwania cryptomerioides*, taxodiaceae; leaves; diterpenes.

Abstract—Four diterpenoid aldehydes and one norditerpenoid ketone having the uncommon skeleton of six-five-six fused-rings were isolated from the leaves of *Taiwania cryptomerioides*.

INTRODUCTION

Taiwania cryptomerioides Hayata, is an endemic evergreen species with thick linear-triangular leaves and elongate ovoid cones. The chemical constituents of this plant have been investigated extensively [1-5]. Varied sesquiterpenes, lignans and bisflavones have been found in the essential oil of the leaves and wood. We report herein the isolation of four diterpenes **1-4** and a norditerpene **5**, which have the uncommon skeleton of fused 6-5-6 rings, in addition to known diterpenes.

RESULTS AND DISCUSSION

Four known abietane-type diterpenes, ferruginol (**6**) [6, 7], 6,7-dehydroferruginol (**7**) [6], 7 β -hydroxyroyleanone (**8**) [8], 7 α -hydroxyroyleanone (**9**) [8] and a secoabietane dialdehyde (**10**) [9], were identified by comparison of their physical and spectral data (mp, $[\alpha]$, mass, IR, ^1H and ^{13}C NMR) with those in the literature.

Compound **1**, namely taiwaniaquinone A, was isolated as orange crystals, mp 201-203° (decomposed). Its structure was determined by spectral methods. The exact mass $[\text{M}]^+$ at m/z 330.1825 indicated the molecular formula $\text{C}_{20}\text{H}_{26}\text{O}_4$. The IR absorptions at 1659 and 1639 cm^{-1} , and the UV absorptions at 432 (ϵ 579), 284 (ϵ 6400) and 207 nm (ϵ 12 600) were attributable to the quinone moiety. The ^{13}C signals of the quinone moiety occurred at δ 124.6, 149.2, 151.2, 152.8, 181.0 and 185.3 (Table 1). The proton resonance (Table 2) at δ 9.84 ($d, J = 4$ Hz) and the carbon signal at δ 200.2 were attributable to an aldehyde group. The skeleton of 6-5-6 fused-rings were established by means of the C-H COSY and the HMBC experiment. Irradiation of Me-10 (at δ 1.14) caused 10% nOe of H-7 (at δ 3.76). The stereochemistry of **1** was thus confirmed.

H-5 and H-7 were *trans* oriented and had a large coupling constant 11.5 Hz. Compound **1**, $[\alpha]_D^{25} - 220.6^\circ$, showed a positive Cotton effect with the maximum at 309 nm ($[\theta]$, 22 600). Compound **1** was assigned to have the (5S, 7R, 10S)-configuration by analogy to those abietanes found in the plants of the Taxodiaceae family [4, 5]. The uncommon 6-5-6 rings skeleton was presumably formed (biogenetically) from the pinacol rearrangement of abietane-6,7-diol as depicted in A (Scheme 1).

Table 1. ^{13}C NMR spectral data of **1-5** (δ value in ppm)

C	1*	2†	3†	4*‡	5*§
1	34.4	35.8	37.6	35.6	30.3
2	19.3	20.2	20.4	19.7	17.5
3	41.1	44.1	44.2	41.7	36.5
4	33.6	35.1	35.2	34.0	34.3
5	61.5	62.1	69.6	61.5	65.1
6	200.2	203.7	201.5	205.0	—
7	54.4	88.4	90.2	54.5	211.1
8	149.2	148.8	147.4	113.4	118.3
9	152.8	155.1	154.3	132.3	142.7
10	48.7	50.2	47.3	46.3	42.7
11	181.0	182.8	182.6	135.2	138.4
12	151.2	154.3	153.5	146.8	152.2
13	124.6	125.0	125.6	116.7	126.1
14	185.3	186.1	187.0	146.0	151.1
15	24.2	24.9	24.9	25.1	25.9
16	19.8	20.4	20.5	21.0	20.6
17	19.8	20.4	20.5	21.1	20.6
18	35.0	34.8	33.8	34.4	24.4
19	21.8	23.7	24.6	22.0	33.0
20	20.1	22.8	23.9	22.4	28.8

* Solution in CDCl_3 .

† Solution in acetone- d_6 .

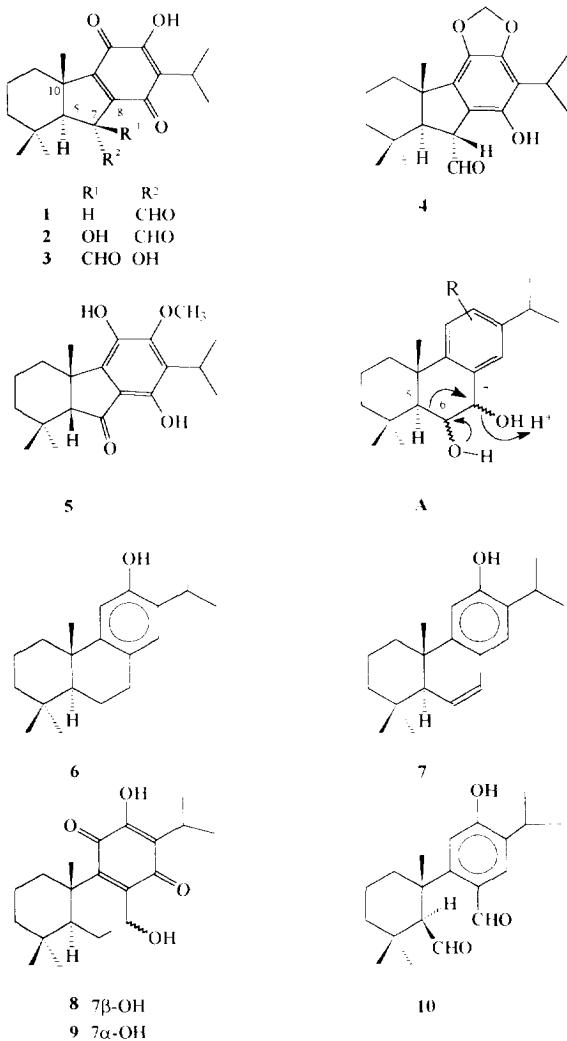
‡ The signal of methylenedioxy group in **4** appeared at δ 100.8.

§ The signal of methoxyl group in **5** appeared at δ 62.1.

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Table 2. ^1H NMR spectral data of **1–5** (δ value in ppm; J value in Hz)

H	1*	2†	3†	4*‡	5*§
5	2.13 (<i>d</i> , $J = 11.5$)	2.04 (<i>s</i>)	2.26 (<i>s</i>)	2.16 (<i>d</i> , $J = 11$)	2.10 (<i>s</i>)
6	9.84 (<i>d</i> , $J = 4$)	9.82 (<i>s</i>)	10.08 (<i>s</i>)	9.47 (<i>d</i> , $J = 5$)	
7	3.76 (<i>dd</i> , $J = 11.5, 4$)			3.77 (<i>dd</i> , $J = 11, 5$)	
15	3.12 (<i>sept</i> , $J = 7$)	3.12 (<i>sept</i> , $J = 7$)	3.14 (<i>sept</i> , $J = 7$)	3.16 (<i>sept</i> , $J = 7$)	3.25 (<i>sept</i> , $J = 7$)
16	1.17 (<i>d</i> , $J = 7$)	1.16 (<i>d</i> , $J = 7$)	1.18 (<i>d</i> , $J = 7$)	1.26 (<i>d</i> , $J = 7$)	1.36 (<i>d</i> , $J = 7$)
17	1.18 (<i>d</i> , $J = 7$)	1.16 (<i>d</i> , $J = 7$)	1.17 (<i>d</i> , $J = 7$)	1.26 (<i>d</i> , $J = 7$)	1.36 (<i>d</i> , $J = 7$)
18	0.79 (<i>s</i>)	0.78 (<i>s</i>)	1.11 (<i>s</i>)	0.89 (<i>s</i>)	0.86 (<i>s</i>)
19	1.05 (<i>s</i>)	1.20 (<i>s</i>)	1.04 (<i>s</i>)	1.06 (<i>s</i>)	1.24 (<i>s</i>)
20	1.14 (<i>s</i>)	1.49 (<i>s</i>)	1.35 (<i>s</i>)	1.10 (<i>s</i>)	1.42 (<i>s</i>)

* Solution in CDCl_3 .† Solution in acetone- d_6 .‡ The signals of methylenedioxy group in **4** appeared at 5.82 (*d*, $J = 1$) and 5.87 (*d*, $J = 1$).§ The signal of methoxyl group in **5** appeared at δ 3.78 (*s*).

Scheme 1.

The structures of two 7-hydroxylated derivatives **2** (namely taiwaniaquinone B) and **3** (namely taiwaniaquinone C) were determined by similar procedures. Their pertinent ^{13}C and ^1H signals are listed in Tables 1 and 2. The formyl group in **3** oriented on the β -face as the proton signal at δ 10.08 showed 10% nOe upon irradiation of Me-10 (at δ 1.35). Compound **2** showed a positive Cotton effect with maximum $[\theta]_{304}$ 21100, whereas the epimer **3** showed a negative Cotton effect with minimum $[\theta]_{316} - 6100$.

The molecular formula $\text{C}_{21}\text{H}_{28}\text{O}_4$ for **4**, which we have named taiwaniaquinol A, was deduced from its parent peak at m/z 344.1979. Compound **4** was colourless and crystalline, mp 158–160 °C. It showed intense IR absorptions at 3335 and 1686 cm^{-1} for the hydroxyl and carbonyl groups. The ^1H NMR spectrum exhibited characteristic signals at δ 5.87 and 5.82 for the methylenedioxy group. The corresponding carbon signal appeared at δ 100.8. The structure of taiwaniaquinol A (**4**) was finally determined by means of the H–H COSY, C–H COSY and HMBC experiments. The nOe effect (13%) of H-7, observed by irradiation of Me-10 (at δ 1.10), was in agreement with the assigned stereochemistry. The large coupling constant 11 Hz between H-5 and H-7 conformed to their *trans*-relationship.

The NMR analysis revealed that compound **5** ($\text{C}_{20}\text{H}_{28}\text{O}_4$) is a norditerpene containing a methoxyl group (δ_{H} 3.78 and δ_{C} 62.1). The conjugated ketone showed IR absorption at 1638 cm^{-1} and a carbon signal at δ 211.1. Compound **5**, named taiwaniaquinol B, has a *cis*-ring junction as revealed by a nOe experiment, i.e. an 18% enhancement of H-5 (at δ 2.10) resulting from irradiation of Me-10 (at δ 1.42).

In summary, compounds **1–4** represent a new class of diterpenes, and **5** is a novel norditerpene. This is the first report of compounds having the uncommon 6–5–6 rings in nature.

EXPERIMENTAL

General and plant material. The dried leaves (1.75 kg) of *T. cryptomerioides* were exhaustively extracted with Me_2CO ($7\text{L} \times 3$). The combined extracts were concd to *ca* 0.81, and taken up with CHCl_3 (0.81×3). The CHCl_3 -soluble portion was concd (55 g) and subjected to silica gel CC. The portion obtained from elution with EtOAc in hexane (5–20%) was further purified by HPLC (Hibar Lichrosorb Si 60, 7 or 10 μm , 25×1 cm) with elution by EtOAc–hexane (1:10) to give compounds **1** (40 mg), **2** (20 mg), **3** (20 mg), **4** (25 mg), **5** (10 mg), **6** (30 mg), **7** (6 mg), **8** (251 mg), **9** (55 mg), **10** (15 mg). Merck Silica gel 60F sheets were used for analyt. TLC (EtOAc–hexane, 1:9).

Taiwaniaquinone A (**1**). Orange crystals from EtOAc–hexane (1:9). Mp 201–203 °C (decomposed). $[\alpha]_D^{25} - 220.6^\circ$ (CHCl_3 ; *c* 1.3). TLC (EtOAc–hexane, 1:9) R_f 0.5. IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3331, 1706, 1659, 1639. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (*ε*): 432 (579), 284 (6400), 207 (12 600). EIMS (70 eV) *m/z* (rel. int.): 330 [M]⁺ (2), 302 (100), 287 (22), 233 (68), 220 (35), 121 (5), 109 (8). HRMS for $\text{C}_{20}\text{H}_{26}\text{O}_4$ requires: 330.1832. Found: 330.1825. CD (MeOH) $[\theta]_{309} + 22600$, $[\theta]_{277} - 1900$, $[\theta]_{267} - 1100$, $[\theta]_{249} - 4400$, $[\theta]_{237} - 3600$.

Taiwaniaquinone B (**2**). Orange crystals from EtOAc–hexane (1:9). Mp 183–185 °C (decomposed). $[\alpha]_D^{25} - 83^\circ$ (CHCl_3 ; *c* 0.27). TLC (EtOAc–hexane, 1:9) R_f 0.43. IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3498, 3376, 1720, 1662, 1664. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (*ε*): 427 (619), 277 (6000), 204 (8900). EIMS (70 eV) *m/z* (rel. int.): 317 [M – CHO]⁺ (56), 299 (4), 209 (100), 187 (5), 115 (10), 109 (68). HRMS for $\text{C}_{20}\text{H}_{26}\text{O}_5\text{–CHO}$ requires: 317.1754. Found: 317.1749. CD (MeOH) $[\theta]_{353} + 1800$, $[\theta]_{304} + 21100$, $[\theta]_{257} - 9800$.

Taiwaniaquinone C (**3**). Orange crystals from EtOAc–hexane (1:9). Mp 210–212 °C (decomposed). $[\alpha]_D^{25} - 266$ (CHCl_3 ; *c* 0.27). TLC (EtOAc–hexane, 1:9) R_f 0.45. IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3497, 3358, 1718, 1648, 1623. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (*ε*): 426 (631), 270 (8300), 220sh (22 000), 202 (123 800). EIMS (70 eV) *m/z* (rel. int.): 317 [M – CHO]⁺ (52), 299 (4), 233 (5), 209 (100), 205 (8), 115 (9), 109 (68). HRMS for $\text{C}_{20}\text{H}_{26}\text{O}_5\text{–CHO}$ requires: 317.1754. Found: 317.1749. CD (MeOH) $[\theta]_{399} + 2600$, $[\theta]_{352} + 6200$, $[\theta]_{316} - 6100$, $[\theta]_{280} + 17700$, $[\theta]_{248} + 4000$, $[\theta]_{228} + 12000$.

Taiwaniaquinol A (**4**). Crystals from EtOAc–hexane (1:9). Mp 158–160 °C. $[\alpha]_D^{25} + 88.2^\circ$ (CHCl_3 ; *c* 0.64). TLC (EtOAc–hexane, 1:9) R_f 0.48. IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3335, 1686. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (*ε*): 293 (4300), 206 (34 200). EIMS (70 eV) *m/z* (rel. int.): 344 (82), 315 (100), 273 (3), 259 (10), 245 (25), 231 (10), 203 (4). HRMS for $\text{C}_{21}\text{H}_{28}\text{O}_4$ requires: 344.1988. Found: 344.1979. CD (MeOH) $[\theta]_{352} + 200$, $[\theta]_{308} + 16800$, $[\theta]_{280} - 6400$, $[\theta]_{260} - 2500$, $[\theta]_{251} - 2800$, $[\theta]_{226} + 2000$, $[\theta]_{210} - 1000$.

Taiwaniaquinol B (**5**). Crystals from EtOAc–hexane (1:9). Mp 142–144 °C. $[\alpha]_D^{31} - 37.7^\circ$ (CHCl_3 ; *c* 0.27). TLC (EtOAc–hexane, 1:9) R_f 0.63. IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3297, 1638. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (*ε*): 350 (4900), 276 (10 000), 238 (14 000), 207 (18 700). EIMS (70 eV) *m/z* (rel. int.): 332 (100), 317 (38), 263 (8), 249 (45), 233 (10), 219 (6), 149 (3). HRMS for $\text{C}_{20}\text{H}_{28}\text{O}_4$ requires: 332.1988. Found: 332.1986.

Ferruginol (**6**). Oil solid. $[\alpha]_D^{20} + 37^\circ$ (CHCl_3 ; *c* 1.2) (lit. [6] $[\alpha]_D^{16} + 40.6^\circ$).

6,7-Dehydroferruginol (**7**). Oil. $[\alpha]_D^{24} - 59^\circ$ (CHCl_3 ; *c* 0.5) (lit. [6] $[\alpha]_D - 60^\circ$).

7β -Hydroxyroyleanone (**8**). Yellow solid. Mp 210–212 °C (lit. [10, 11] 212–214 °C). $[\alpha]_D^{20} + 330^\circ$ (CHCl_3 ; *c* 1.3) (lit. [10, 11] $[\alpha]_D + 340^\circ$ (CHCl_3)).

7α -Hydroxyroyleanone (**9**). Yellow solid. Mp 175–176 °C (lit. [12] 173–175 °C). $[\alpha]_D^{22} - 135^\circ$ (CHCl_3 ; *c* 1.6) (lit. [12] $[\alpha]_D + 132^\circ$ (CHCl_3)).

12-Hydroxy-6,7-secoabiet-8,11,13-triene-6,7-dial (**10**). Solid. Mp 189–191 °C (lit. [9] 191–192 °C). $[\alpha]_D^{30} + 20^\circ$ (MeOH; *c* 0.7) (lit. [9] $[\alpha]_D^{25} + 22^\circ$ (MeOH; *c* 1.2)).

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