

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

WANG-HONG LIN, JIM-MIN FANG and YU-SHIA CHENG\*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

(Received in revised form 21 March 1995)

**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 $\beta$ -hydroxyroyleanone (**8**) [8], 7 $\alpha$ -hydroxyroyleanone (**9**) [8] and a secoabietane dialdehyde (**10**) [9], were identified by comparison of their physical and spectral data (mp,  $[\alpha]$ , mass, IR,  $^1\text{H}$  and  $^{13}\text{C}$  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  $[M]^+$  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  $\text{cm}^{-1}$ , and the UV absorptions at 432 ( $\epsilon$  579), 284 ( $\epsilon$  6400) and 207 nm ( $\epsilon$  12 600) were attributable to the quinone moiety. The  $^{13}\text{C}$  signals of the quinone moiety occurred at  $\delta$  124.6, 149.2, 151.2, 152.8, 181.0 and 185.3 (Table 1). The proton resonance (Table 2) at  $\delta$  9.84 ( $d$ ,  $J = 4$  Hz) and the carbon signal at  $\delta$  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  $\delta$  1.14) caused 10% nOe of H-7 (at  $\delta$  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 (5*S*, 7*R*, 10*S*)-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.  $^{13}\text{C}$  NMR spectral data of **1–5** ( $\delta$  value in ppm)

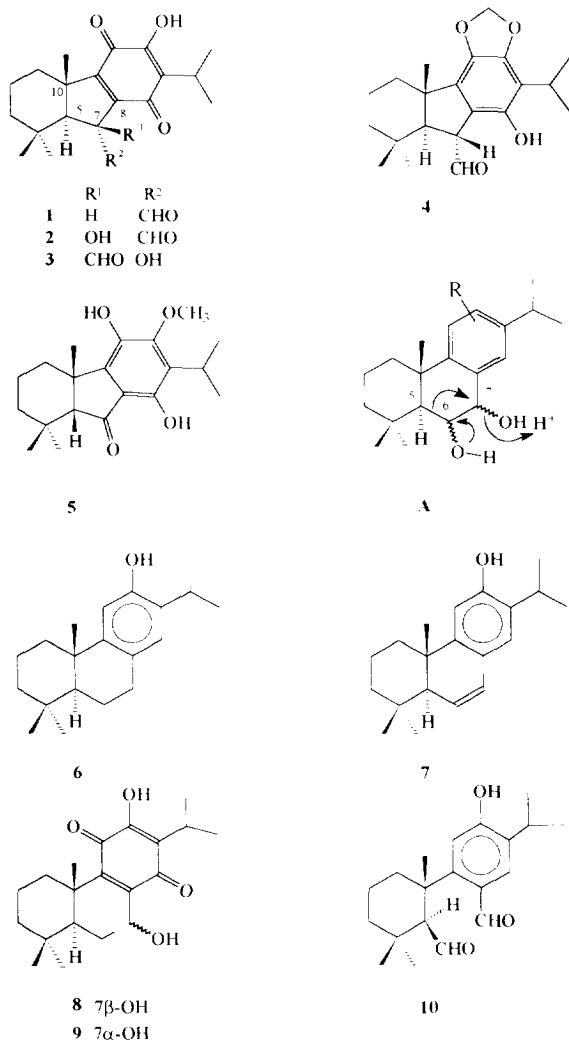
C	<b>1</b> *	<b>2</b> †	<b>3</b> †	<b>4</b> *‡	<b>5</b> *§
1	34.4	35.8	37.6	35.6	30.3
2	19.3	20.2	20.4	19.7	17.5
3	41.1	44.1	44.2	41.7	36.5
4	33.6	35.1	35.2	34.0	34.3
5	61.5	62.1	69.6	61.5	65.1
6	200.2	203.7	201.5	205.0	—
7	54.4	88.4	90.2	54.5	211.1
8	149.2	148.8	147.4	113.4	118.3
9	152.8	155.1	154.3	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  $\text{CDCl}_3$ .† Solution in acetone- $d_6$ .‡ The signal of methylenedioxy group in **4** appeared at  $\delta$  100.8.§ The signal of methoxyl group in **5** appeared at  $\delta$  62.1.

\* Author to whom correspondence should be addressed.

Table 2.  $^1\text{H}$  NMR spectral data of 1–5 ( $\delta$  value in ppm;  $J$  value in Hz)

H	1*	2†	3‡	4*‡	5*§
5	2.13 ( <i>d</i> , $J = 11.5$ )	2.04 (s)	2.26 (s)	2.16 ( <i>d</i> , $J = 11$ )	2.10 (s)
6	9.84 ( <i>d</i> , $J = 4$ )	9.82 (s)	10.08 (s)	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 (s)	0.78 (s)	1.11 (s)	0.89 (s)	0.86 (s)
19	1.05 (s)	1.20 (s)	1.04 (s)	1.06 (s)	1.24 (s)
20	1.14 (s)	1.49 (s)	1.35 (s)	1.10 (s)	1.42 (s)

\*Solution in  $\text{CDCl}_3$ .†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  $\delta$  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  $^{13}\text{C}$  and  $^1\text{H}$  signals are listed in Tables 1 and 2. The formyl group in **3** oriented on the  $\beta$ -face as the proton signal at  $\delta$  10.08 showed 10% nOe upon irradiation of Me-10 (at  $\delta$  1.35). Compound **2** showed a positive Cotton effect with maximum  $[\theta]_{304}^{21\ 100}$ , whereas the epimer **3** showed a negative Cotton effect with minimum  $[\theta]_{316}^{21\ 100}$ .

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  $\text{cm}^{-1}$  for the hydroxyl and carbonyl groups. The  $^1\text{H}$  NMR spectrum exhibited characteristic signals at  $\delta$  5.87 and 5.82 for the methylenedioxy group. The corresponding carbon signal appeared at  $\delta$  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  $\delta$  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 ( $\delta_{\text{H}}$  3.78 and  $\delta_{\text{C}}$  62.1). The conjugated ketone showed IR absorption at 1638  $\text{cm}^{-1}$  and a carbon signal at  $\delta$  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  $\delta$  2.10) resulting from irradiation of Me-10 (at  $\delta$  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<sub>2</sub>CO (7 l × 3). The combined extracts were concd to ca 0.8 l, and taken up with CHCl<sub>3</sub> (0.8 l × 3). The CHCl<sub>3</sub>-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<sub>3</sub>; c 1.3). TLC (EtOAc–hexane, 1:9) *R<sub>f</sub>* 0.5. IR  $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$ : 3331, 1706, 1659, 1639. UV  $\lambda_{\max}^{\text{MeOH}} \text{ nm}$  (ε): 432 (579), 284 (6400), 207 (12 600). EIMS (70 eV) *m/z* (rel. int.): 330 [M]<sup>+</sup> (2), 302 (100), 287 (22), 233 (68), 220 (35), 121 (5), 109 (8). HRMS for C<sub>20</sub>H<sub>26</sub>O<sub>4</sub> 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).  $[\alpha]_D^{31} - 83^\circ$  (CHCl<sub>3</sub>; c 0.27). TLC (EtOAc–hexane, 1:9) *R<sub>f</sub>* 0.43. IR  $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$ : 3498, 3376, 1720, 1662, 1664. UV  $\lambda_{\max}^{\text{MeOH}} \text{ nm}$  (ε): 427 (619), 277 (6000), 204 (8900). EIMS (70 eV) *m/z* (rel. int.): 317 [M – CHO]<sup>+</sup> (56), 299 (4), 209 (100), 187 (5), 115 (10), 109 (68). HRMS for C<sub>20</sub>H<sub>26</sub>O<sub>5</sub>–CHO requires: 317.1754. Found: 317.1749. CD (MeOH)  $[\theta]_{353} + 1800$ ,  $[\theta]_{304} + 21\,100$ ,  $[\theta]_{257} - 9800$ .

**Taiwaniaquinone C (3).** Orange crystals from EtOAc–hexane (1:9). Mp 210–212 °C (decomposed).  $[\alpha]_D^{31} - 266^\circ$  (CHCl<sub>3</sub>; c 0.27). TLC (EtOAc–hexane, 1:9) *R<sub>f</sub>* 0.45. IR  $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$ : 3497, 3358, 1718, 1648, 1623. UV  $\lambda_{\max}^{\text{MeOH}} \text{ nm}$  (ε): 426 (631), 270 (8300), 220sh (22 000), 202 (123 800). EIMS (70 eV) *m/z* (rel. int.): 317 [M – CHO]<sup>+</sup> (52), 299 (4), 233 (5), 209 (100), 205 (8), 115 (9), 109 (68). HRMS for C<sub>20</sub>H<sub>26</sub>O<sub>5</sub>–CHO requires: 317.1754. Found: 317.1749. CD (MeOH)  $[\theta]_{399} + 2600$ ,  $[\theta]_{352} + 6200$ ,  $[\theta]_{316} - 6100$ ,  $[\theta]_{280} + 17\,700$ ,  $[\theta]_{248} + 4000$ ,  $[\theta]_{228} + 12\,000$ .

**Taiwaniaquinol A (4).** Crystals from EtOAc–hexane (1:9). Mp 158–160 °C.  $[\alpha]_D^{31} + 88.2^\circ$  (CHCl<sub>3</sub>; c 0.64). TLC (EtOAc–hexane, 1:9) *R<sub>f</sub>* 0.48. IR  $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$ : 3335, 1686. UV  $\lambda_{\max}^{\text{MeOH}} \text{ nm}$  (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 C<sub>21</sub>H<sub>28</sub>O<sub>4</sub> requires: 344.1988. Found: 344.1979. CD (MeOH)  $[\theta]_{352} + 200$ ,  $[\theta]_{308} + 16\,800$ ,  $[\theta]_{280} - 6400$ ,  $[\theta]_{260} - 2500$ ,  $[\theta]_{251} - 2800$ ,  $[\theta]_{226} + 2000$ ,  $[\theta]_{210} - 1000$ .

**Taiwaniaquinol B (5).** Crystals from EtOAc–hexane (1:9). Mp 142–144 °C.  $[\alpha]_D^{31} - 37.7^\circ$  (CHCl<sub>3</sub>; c 0.27). TLC (EtOAc–hexane, 1:9) *R<sub>f</sub>* 0.63. IR  $\nu_{\max}^{\text{KBr}} \text{ cm}^{-1}$ : 3297, 1638. UV  $\lambda_{\max}^{\text{MeOH}} \text{ nm}$  (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 C<sub>20</sub>H<sub>28</sub>O<sub>4</sub> requires: 332.1988. Found: 332.1986.

**Ferruginol (6).** Oil solid.  $[\alpha]_D^{30} + 37^\circ$  (CHCl<sub>3</sub>; c 1.2) (lit. [6]  $[\alpha]_D^{16} + 40.6^\circ$ ).

**6,7-Dehydroferruginol (7).** Oil.  $[\alpha]_D^{24} - 59^\circ$  (CHCl<sub>3</sub>; c 0.5) (lit. [6]  $[\alpha]_D - 60^\circ$ ).

**7β-Hydroxyroyleanone (8).** Yellow solid. Mp 210–212 °C (lit. [10, 11] 212–214 °C).  $[\alpha]_D^{30} + 330^\circ$  (CHCl<sub>3</sub>; c 1.3) {lit. [10, 11]  $[\alpha]_D + 340^\circ$  (CHCl<sub>3</sub>)}

**7α-Hydroxyroyleanone (9).** Yellow solid. Mp 175–176 °C (lit. [12] 173–175 °C).  $[\alpha]_D^{22} - 135^\circ$  (CHCl<sub>3</sub>; c 1.6) [lit. [12]  $[\alpha]_D + 132^\circ$  (CHCl<sub>3</sub>)].

**12-Hydroxy-6,7-secoabieta-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)}.

**Acknowledgement**—We thank the National Science Council for financial support.

## REFERENCES

1. Fang, J.-M. and Cheng, Y.-S. (1992) *J. Chin. Chem. Soc. (Taipei)* **39**, 647.
2. Kamil, M., Ilyas, M., Rahman, W., Hasaka, N., Okigawa, M. and Kawano, N. (1981) *J. Chem. Soc., Perkin Trans. 1*, 553.
3. Kuo, Y.-H., Chen, W.-C. and Lin, Y.-T. (1987) *Chem. Express* **2**, 105.
4. Su, W.-C., Fang, J.-M. and Cheng, Y.-S. (1993) *Phytochemistry* **34**, 779.
5. Su, W.-C., Fang, J.-M. and Cheng, Y.-S. (1994) *Phytochemistry* **35**, 1279.
6. Bredenberg, J. B. (1957) *Acta Chem. Scand.* **11**, 932.
7. Lin, Y.-T., Kuo, Y.-H. and Chang, B.-H. (1975) *J. Chin. Chem. Soc.* **22**, 331.
8. Hensch, M., Ruedi, P. and Eugster, C. H. (1975) *Helv. Chim. Acta* **58**, 1921.
9. Fang, J.-M., Jan, S.-T. and Cheng, Y.-S. (1986) *J. Chem. Res. (S)* 350.
10. Kupchan, S. M., Karim, A. and Marcks, C. (1969) *J. Org. Chem.* **34**, 3912.
11. Kupchan, S. M., Karim, A. and Marcks, C. (1968) *J. Am. Chem. Soc.* **90**, 5923.
12. Edwards, O. E., Feniak, G. and Los, M. (1962) *Can. J. Chem.* **40**, 1542.