

## New Cadinane-Type Sesquiterpenes from the Roots of *Taiwania cryptomerioides* HAYATA

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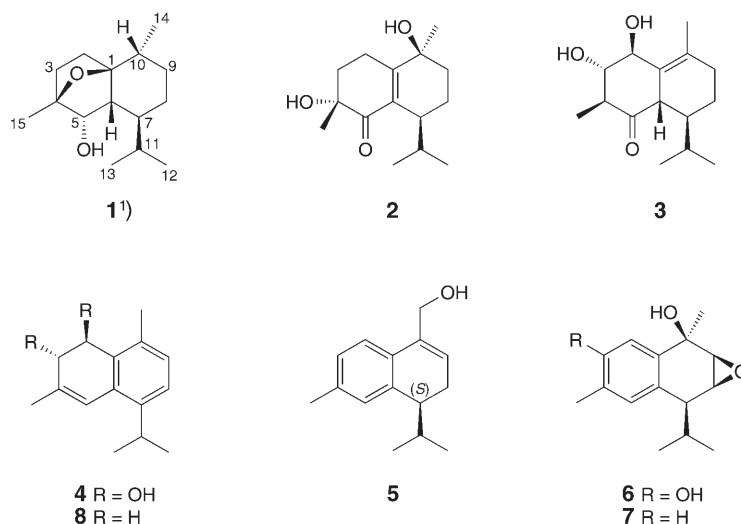
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Six new cadinane-type sesquiterpenes, (1 $\beta$ ,4 $\beta$ ,5 $\alpha$ ,10 $\alpha$ )-1,4-epoxymurolan-5-ol (**1**), (4 $\alpha$ ,10 $\beta$ )-4,10-dihydroxycadin-1(6)-en-5-one (**2**), (2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,6 $\beta$ )-2,3-dihydroxycadin-1(10)-en-5-one (**3**), (2 $\beta$ ,3 $\alpha$ )- $\alpha$ -corocalene-2,3-diol (**4**), (7*S*)- $\alpha$ -calacoren-14-ol (**5**), and (8 $\beta$ ,9 $\beta$ ,10 $\beta$ )-8,9-epoxycalamenene-3,10-diol (**6**) together with one known compound, (8 $\beta$ ,9 $\beta$ ,10 $\beta$ )-8,9-epoxycalamenen-10-ol (**7**), were isolated from the roots of *Taiwania cryptomerioides*. The structures of the new constituents were essentially elucidated by spectral evidence.

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**Introduction.** – *Taiwania cryptomerioides* (Taxodiaceae), an important building material with high value in Taiwan, is taxonomically included in one genus and one species. It is an endemic plant in Taiwan. Its heartwood contains more than 6% of essential oil [1]. Because of the antifungal and decay-resistant characteristics as well as the beautiful yellowish-red color with distinct purplish-pink streaks of the heartwood, we have investigated this plant already previously, and isolated the chemical components of the heartwood [2–4] and bark [5–9].  $\alpha$ -Cadinol, a major component of *T. cryptomerioides*, was found in its essential oil, and shows selectivity for human-colon-tumor cell lines [10]. Also, the oil is a potent agent against wood-decay fungi [11]. In addition, we have isolated lignans and cadinane-type compounds from *T. cryptomerioides*, which exhibit significant cytotoxicity against three human-tumor cell lines [12]. The interesting compounds and those conferring biological activities isolated from the heartwood and bark of *T. cryptomerioides* prompted us to study the chemical components of its roots. Several sesquiterpenes with unique and novel structures have already been obtained, *i.e.*, structures of the cadinane type [13], the secoabeoguaiane type [14], seconorabietane type [15], and the secoabeoabietane type [16].

In this paper, we would like to report on the isolation and characterization of six new cadinane-type sesquiterpenes from the roots of *T. cryptomerioides*, *i.e.*, (1 $\beta$ ,4 $\beta$ ,5 $\alpha$ ,10 $\alpha$ )-1,4-epoxymurolan-5-ol (**1**), (4 $\alpha$ ,10 $\beta$ )-4,10-dihydroxycadin-1(6)-en-5-one (**2**), (2 $\beta$ ,3 $\alpha$ ,4 $\beta$ ,6 $\beta$ )-2,3-dihydroxycadin-1(10)-en-5-one (**3**), (2 $\beta$ ,3 $\alpha$ )- $\alpha$ -corocalene-2,3-diol (**4**), (7*S*)- $\alpha$ -calacoren-14-ol (**5**), and (8 $\beta$ ,9 $\beta$ ,10 $\beta$ )-8,9-epoxycalamenene-3,10-diol (**6**), together with one known compound, (8 $\beta$ ,9 $\beta$ ,10 $\beta$ )-8,9-epoxycalamenen-10-ol (**7**) [17].



**Results and Discussion.** – Compound **1**, isolated as a colorless gum, showed a molecular ion  $M^+$  peak at  $m/z$  238.1934 for  $C_{15}H_{26}O_2^+$ , corresponding to three indices of hydrogen deficiency (IHD). The IR spectrum of **1** displayed an absorption for an OH group ( $3434\text{ cm}^{-1}$ ). The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR (Table 1), COSY, HMBC, and NOESY data (Fig.) established the structure of **1** as ( $1\beta,4\beta,5\alpha,10\alpha$ )-1,4-epoxymuurolan-5-ol<sup>1</sup>.

The  $^1\text{H}$ -NMR spectrum exhibited signals for an  $^i\text{Pr}$  group at  $\delta$  0.95 and 0.90 ( $d, J = 7.2\text{ Hz}$ , 3 H each) and 1.81–1.91 ( $m$ , 1 H), a Me  $s$  at  $\delta$  1.39, a Me  $d$  at  $\delta$  1.06, and a OCH signal at  $\delta$  3.43 (*br. s*). The COSY plot of **1** displayed the connectivities H–C(5)/H–C(6)/H–C(7)/CH<sub>2</sub>(8)/CH<sub>2</sub>(9)/H–C(10)/Me(14), and H–C(5) was also coupled to H <sub>$\beta$</sub> –C(3) ( $\delta$  1.33–1.43 (*m*)) due to a long-range W-coupling. The  $^{13}\text{C}$ -NMR spectrum exhibited 15 signals for four Me, four CH<sub>2</sub>, and four CH groups, and for three oxygenated C-atoms (two C ( $\delta$  87.2 and 86.6) and one CH ( $\delta$  79.0)). Compound **1** contained two O-atoms but three oxygenated C-atoms, suggesting that **1** is a tricyclic compound with two rings and an epoxy bridge. Compound **1** exhibited the following  $^1\text{H},^{13}\text{C}$ -HMBC correlations: Me(14)/C(1), C(9), and C(10), Me(15)/C(3), C(4), and C(5), H–C(6)/C(2), C(4), and C(5). On the above evidence, compound **1** was assumed to be an epicubenol (= (1*S*,4*R*,4*aS*,8*aR*)-1,3,4,5,6,8*a*-hexahydro-4,7-dimethyl-1-(1-methylethyl)naphthalen-4*a*(2*H*)-ol) derivative with an epoxy group located between C(1) and C(4)<sup>1</sup>, and an OH group positioned at C(5)<sup>1</sup>. The NOESY correlations (Fig.) H–C(5)/H–C(6), H–C(11), Me(12), and Me(15), H–C(10)/H–C(6) and H <sub>$\beta$</sub> –C(8), H–C(7)/H <sub>$\alpha$</sub> –C(9), and Me(14)/H <sub>$\beta$</sub> –C(2) and CH<sub>2</sub>(9) confirmed that H–C(5) was in the  $\beta$ -quasi-axial orientation, Me(14) in the  $\alpha$ -quasi-equatorial orientation, H–C(6) in the  $\beta$ -axial orientation, and the  $^i\text{Pr}$ –C(7) in the  $\beta$ -quasi-equatorial orientation.

The HR-EI-MS revealed compound **2** to be a sesquiterpene with the formula  $C_{15}H_{24}O_3$  ( $M^+$  at  $m/z$  252.1726). The IR spectrum suggested that **2** contains an OH group ( $3423\text{ cm}^{-1}$ ) and a conjugated C=O group ( $1670\text{ cm}^{-1}$ ), the latter being confirmed by the UV spectrum ( $\lambda_{\text{max}}$  240.0 and 291.0 nm). The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR (Table 1), HMBC, and NOESY data (Fig.) were compatible with the structure of **2** as ( $4\alpha,10\beta$ )-4,10-dihydroxycadin-1(6)-en-5-one<sup>1</sup>.

<sup>1</sup>) Trivial atom numbering; for systematic names, see *Exper. Part*.

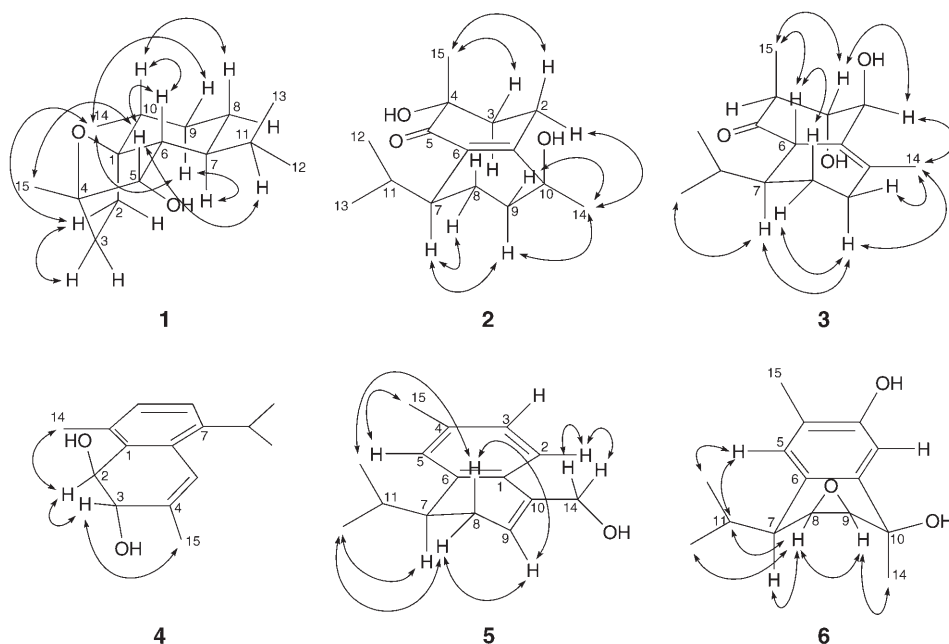


Figure. Key NOESY correlations of compounds 1–6<sup>1)</sup>

The <sup>1</sup>H-NMR spectrum of **2** showed the presence of an <sup>i</sup>Pr ( $\delta$  0.82 and 0.75 ( $d$ ,  $J$  = 7.0 Hz, 3 H each) and 1.85–1.90 ( $m$ , 1 H)) and two Me groups ( $\delta$  1.32 and 1.33 ( $s$ ), the latter two being attached to a quaternary C-atom bearing an OH group. This suggested that **2** was a cadinane-type sesquiterpene. Fifteen <sup>13</sup>C-NMR signals appeared for four Me, four CH<sub>2</sub>, and two CH groups, and for five quaternary C-atoms (including two oxygenated ones at  $\delta$  72.8 and 70.3, two olefinic ones at  $\delta$  158.7 and 133.6, and a conjugated C=O at  $\delta$  204.0). The <sup>13</sup>C,<sup>1</sup>H-HMBC correlations C=O ( $\delta$  204.0)/H–C(3) and Me(15) allowed to position the C=O group at C(5). Considering the skeleton and UV absorption, the location of the C=C bond was assigned between C(1) and C(6). Further evidence came from the following <sup>13</sup>C,<sup>1</sup>H-HMBC correlations: C(1) ( $\delta$  158.7)/H–C(3) and Me(14), and C(6) ( $\delta$  133.6)/H–C(7) and H–C(8). Analysis of the NOESY data (*Fig.*) revealed the following correlations: H–C(7)/H <sub>$\alpha$</sub> –C(8) and H <sub>$\alpha$</sub> –C(9), Me(14)/CH<sub>2</sub>(9) and H <sub>$\alpha$</sub> –C(2), and Me(15)/H <sub>$\beta$</sub> –C(2) and H <sub>$\beta$</sub> –C(3). Thus, the <sup>i</sup>Pr group adopted a  $\beta$ -quasiequatorial, the Me(14) a  $\alpha$ -quasiequatorial, and the Me(15) a  $\beta$ -quasixial orientation.

Based on the HR-EI-MS and <sup>13</sup>C-NMR data (*Table 1*), compound **3** has the molecular formula C<sub>15</sub>H<sub>24</sub>O<sub>3</sub> with an IHD of 4. The IR spectrum of **3** displayed peaks for an OH group (3418 cm<sup>-1</sup>) and a C=O group (1705 cm<sup>-1</sup>), and the <sup>1</sup>H-NMR (*Table 1*), HMBC, COSY, and NOESY (*Fig.*) data confirmed the structure as (*2* $\beta$ ,*3* $\alpha$ ,*4* $\beta$ ,*6* $\beta$ )-2,3-dihydroxycadin-1(10)-en-5-one<sup>1)</sup>.

The <sup>1</sup>H-NMR spectrum of **3** indicated the presence of an <sup>i</sup>Pr group ( $\delta$  0.90 and 0.74 ( $d$ ,  $J$  = 6.8 Hz, 3 H each), and 1.70–1.76 ( $m$ , 1 H)), a Me group ( $\delta$  1.82 ( $s$ )) attached to a C=C bond, another Me group ( $\delta$  1.20 ( $d$ )), and two OCH groups ( $\delta$  4.05 and 4.64). The <sup>13</sup>C-NMR and DEPT showed signals of an <sup>i</sup>Pr group, of two Me groups, of two oxygenated sp<sup>3</sup> C-atoms ( $\delta$  73.8 and 69.7), of a C=O group ( $\delta$  212.9), of two olefinic C-atoms ( $\delta$  128.3 and 137.0), and of two CH<sub>2</sub> and three CH groups. The 15 C-signals including two Me and an <sup>i</sup>Pr group were in accord with a cadinane derivative. Two sets of contiguous protons

Table 1.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR Data ( $\text{CDCl}_3$ , 400 and 100 MHz, resp.) of Compounds **1**–**3**<sup>1</sup>.  $\delta$  in ppm,  $J$  in Hz.

	<b>1</b>		<b>2</b>		<b>3</b>	
	$\delta(\text{H})$	$\delta(\text{C})$	$\delta(\text{H})$	$\delta(\text{C})$	$\delta(\text{H})$	$\delta(\text{C})$
C(1)	–	87.2 (s)	–	158.7 (s)	–	128.3 (s)
CH <sub>2</sub> (2) or H–C(2)	1.27–1.34 (m), 2.04–2.10 (m)	32.5 (t)	2.85 (dd, $J = 17.5, 5.5$ ), 2.33 (ddd, $J = 17.5, 12.0, 5.5$ )	22.5 (t)	4.64 (d, $J = 3.2$ )	69.7 (d)
CH <sub>2</sub> (3) or H–C(3)	1.33–1.43 (m), 1.50–1.60 (m)	35.1 (t)	1.89–1.98 (m), 2.17 (ddd, $J = 13.1, 5.2, 2.0$ )	36.8 (t)	4.05 (t, $J = 3.2$ )	73.2 (d)
C(4) or H–C(4)	–	86.6 (s)	–	72.8 (s)	2.68–2.71 (m)	44.0 (d)
H–C(5) or C(5)	3.43 (br. s)	79.0 (d)	–	204.0 (s)	–	212.9 (s)
H–C(6) or C(6)	1.49–1.55 (m)	55.1 (d)	–	133.6 (s)	3.52 (br. s)	49.7 (d)
H–C(7)	1.36–1.40 (m)	43.5 (d)	2.68–2.74 (m)	37.3 (d)	1.86–1.92 (m)	36.8 (d)
CH <sub>2</sub> (8)	1.33–1.43 (m)	20.7 (t)	1.55–1.62 (m)	19.3 (t)	1.50–1.56 (m), 1.28–1.35 (m)	20.9 (t)
CH <sub>2</sub> (9)	1.18–1.24 (m), 1.48–1.54 (m)	29.3 (t)	1.58–1.65 (m), 1.81–1.88 (m)	36.1 (t)	1.94–2.00 (m)	31.2 (t)
H–C(10) or C(10)	2.07–2.14 (m)	34.9 (d)	–	70.3 (s)	–	137.0 (s)
H–C(11)	1.81–1.91 (m)	30.1 (d)	1.85–1.90 (m)	28.8 (d)	1.70–1.76 (m)	28.2 (d)
Me(12)	0.90 (d, $J = 7.2$ )	17.1 (q)	0.75 (d, $J = 7.0$ )	18.8 (q)	0.74 (d, $J = 6.8$ )	17.2 (q)
Me(13)	0.95 (d, $J = 7.2$ )	21.0 (q)	0.82 (d, $J = 7.0$ )	21.0 (q)	0.90 (d, $J = 6.8$ )	21.4 (q)
Me(14)	1.06 (d, $J = 6.8$ )	13.3 (q)	1.33 (s)	27.0 (q)	1.82 (s)	19.9 (q)
Me(15)	1.39 (s)	16.4 (q)	1.32 (s)	23.7 (q)	1.20 (d, $J = 7.6$ )	11.9 (q)

(H–C(2), H–C(3), and H–C(4); H–C(6), H–C(7), H–C(8), and H–C(9)) were disclosed from the COSY plot. The signals of H–C(3), H–C(6), H–C(7), and Me(15) correlated with that of the C=O group ( $\delta$  212.9) (HMBC), establishing that the C=O group was positioned at C(5). The signal at  $\delta$  1.20 (Me(15)) had HMBC correlations with  $\delta$  73.2 (C(3)) and 44.0 (C(4)), whereas the signal of H–C(2) ( $\delta$  4.64) had HMBC correlations with  $\delta$  128.3 (C(1)), 73.2 (C(3)), 44.0 (C(4)), and 137.0 (C(10)). In accord with the chemical shift of H–C(2), the COSY data (H–C(2)/H–C(3)), and the above HMBC evidence, the two OH groups were positioned at C(2) and C(3). The NOESY correlations (Fig.) Me(15)/H $_{\beta}$ –C(3) and H $_{\beta}$ –C(6), and Me(14)/H–C(2) confirmed that H–C(6) and Me(15) adopted a  $\beta$ -quasiaxial orientation, and that OH–C(3) and OH–C(2) were also in quasiaxial orientation.

Fifteen  $^{13}\text{C}$ -NMR signals (Table 2) and the HR-EI-MS confirmed the molecular formula  $\text{C}_{15}\text{H}_{20}\text{O}_2$  of **4**. Analysis of its IR spectrum suggested that **4** contained OH ( $3360\text{ cm}^{-1}$ ), olefinic ( $1654\text{ cm}^{-1}$ ), and aromatic ( $1625$  and  $1500\text{ cm}^{-1}$ ) moieties. The UV absorption band at  $\lambda_{\text{max}}$  224.0 (4.29) nm indicated the presence of the conjugated C=C bond and a benzene moiety in **4**. The six IHD (from the DEPT experiment), the  $^{13}\text{C}$ -NMR data, and the molecular formula indicated that **4** is a sesquiterpene. Further spectral data (Table 2 and Fig.) established the structure of **4** as ( $2\beta,3\alpha$ )- $\alpha$ -corocalene-2,3-diol<sup>1</sup>.

The  $^1\text{H}$ -NMR signals of **2** (Table 2) at  $\delta$  2.08 (s, 3 H), 2.40 (s, 3 H), and 1.19 and 1.23 (d,  $J = 6.8$  Hz, 3 H each), and 3.26 (H–C(11)), COSY cross-peaks with  $\delta$  1.19 and 1.23) suggested that **4** has an  $^i\text{Pr}$  group

Table 2. <sup>1</sup>H- and <sup>13</sup>C-NMR Data (CDCl<sub>3</sub>, 400 and 100 MHz, resp.) of Compounds **4**–**6**<sup>1</sup>. δ in ppm, J in Hz

	<b>4</b>		<b>5</b>		<b>6</b>	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(1)	–	130.7 (s)	–	135.6 (s)	–	138.4 (s)
H–C(2)	4.89 (d, J=2.0)	69.2 (d)	7.22 (d, J=7.6)	122.6 (d)	7.07 (s)	112.3 (d)
H–C(3) or C(3)	4.05 (d, J=2.0)	71.9 (d)	7.01 (d, J=7.6)	127.0 (d)	–	153.2 (s)
C(4)	–	135.9 (s)	–	136.3 (s)	–	123.9 (s)
H–C(5)	6.66 (s)	120.4 (d)	6.93 (s)	129.8 (d)	6.74 (s)	131.8 (d)
C(6)	–	128.6 (s)	–	139.3 (s)	–	125.5 (s)
C(7) or H–C(7)	–	142.0 (s)	2.32–2.36 (m)	44.1 (d)	3.06 (dd, J=5.4, 1.5)	44.8 (d)
H–C(8) or CH <sub>2</sub> (8)	7.14 (d, J=8.0)	125.6 (d)	2.38–2.42 (m), 2.38–2.42 (m)	25.3 (t)	3.58 (dd, J=4.2, 1.5)	55.7 (d)
H–C(9)	7.04 (d, J=8.0)	129.8 (d)	5.92 (br. s)	124.7 (d)	3.35 (d, J=4.2)	59.6 (d)
C(10)	–	135.4 (s)	–	130.0 (s)	–	70.5 (s)
H–C(11)	3.26 (sept., J=6.8)	28.2 (d)	1.84–1.90 (m)	30.3 (d)	1.89–1.94 (m)	33.3 (d)
Me(12)	1.19 (d, J=6.8)	23.5 (q)	0.88 (d, J=6.8)	20.3 (q)	1.00 (d, J=7.0)	21.5 (q)
Me(13)	1.23 (d, J=6.8)	23.6 (q)	0.80 (d, J=6.8)	21.4 (q)	0.90 (d, J=7.0)	19.9 (q)
Me(14) or CH <sub>2</sub> (14)	2.40 (s)	18.3 (q)	4.42 (d, J=12.4), 4.52 (d, J=12.4)	64.0 (t)	1.53 (s)	27.7 (q)
Me(15)	2.08 (s)	22.2 (q)	2.31 (s)	21.3 (q)	2.15 (s)	15.6 (q)

and two Me groups attached to an olefinic quaternary C-atom. In addition to three CH and two OCH groups (δ 71.9 and 69.2), the structure of **4** was suggested to be a α-corocalene-type sesquiterpene. Comparison of the <sup>1</sup>H- and <sup>13</sup>C-NMR data of **4** with the known α-corocalene (=1,2-dihydro-3,8-dimethyl-5-(1-methylethyl)naphthalene; **8**) [18] suggested that **4** was a derivative of α-corocalene with the two OH groups located at C(2) and C(3). The 1,2-diol moiety was deduced from the <sup>1</sup>H,<sup>13</sup>C-HMBC (Me(15)/C(4) and C(3), H–C(2)/C(3) and C(4)), COSY (H–C(3)/H–C(2)), and NOESY data (H–C(3)/H–C(2)). The NOESY correlations (Fig.) H–C(2)/Me(14) and H–C(3)/Me(15) established the quasiequatorial orientation of the two OCH protons, which was confirmed by the coupling constant J(2,3)=2.0 Hz.

Compound **5** had the molecular ion peak at *m/z* 216.1519 (HR-EI-MS), as analyzed for C<sub>15</sub>H<sub>20</sub>O<sup>+</sup>. The IR spectrum of **5** exhibited the presence of an OH group at 3411 cm<sup>-1</sup> and an aromatic moiety at 1610 and 1500 cm<sup>-1</sup>. The UV absorptions (λ<sub>max</sub> 229.0 and 256.0 nm) confirmed the conjugated C=C bond and an aromatic system. Six IHD were determined from the molecular formula, <sup>13</sup>C-NMR spectrum (Table 2), and DEPT. Further spectral data (Table 2 and Fig.) and comparison with reference compounds [19][20] established the structure of **5** as (7*S*)-calacoren-14-ol<sup>1</sup>.

The <sup>1</sup>H-NMR data of **5** indicated the presence of aromatic protons giving rise to *ABX*-type resonances (δ 7.22 (d, J=7.6 Hz, 1 H), 7.01 (d, J=7.6 Hz, 1 H), 6.93 (s, 1 H)), an <sup>i</sup>Pr group (δ 0.80 and 0.88 (d, J=6.8 Hz, 3 H each) and 1.84–1.90 (m, 1 H)), and a trisubstituted olefinic proton (δ 5.92 (br. s)). The <sup>13</sup>C-NMR and DEPT showed a trisubstituted benzene ring (δ 122.6, 127.0, 136.3, 129.8, 139.3, and 135.6), a trisubstituted olefinic group, and a secondary alcohol (δ 64.0). From the six IHD was deduced that compound **5** contained one trisubstituted benzene ring, one trisubstituted olefinic group, and one ring, which was assumed to be an α-calacorene (= (1*S*)-1,2-dihydro-4,7-dimethyl-1-(1-methylethyl)naph-

thalene) sesquiterpene [19], however, with the C(14) being a CH<sub>2</sub>OH instead of a Me group. The following HMBC correlations were observed: H–C(5)/C(3), C(7), and C(15), and CH<sub>2</sub>(14)/C(9), C(10), and C(1). Comparison with reference compounds [19][20] allowed to determine the absolute configuration (*S*) from the positive specific rotation of **5**.

Based on the HR-EI-MS and <sup>13</sup>C-NMR data (Table 2), compound **6** has the molecular formula C<sub>15</sub>H<sub>20</sub>O<sub>3</sub> with an IHD of 6. The IR spectrum showed absorptions for an OH group (3423 cm<sup>-1</sup>) and an aromatic moiety (1624 and 1507 cm<sup>-1</sup>). Further spectral data (Table 2, Fig.) and comparison with those of (8β,9β,10β)-8,9-epoxycalamenen-10-ol (**7**) [17] allowed to assign to **6** the structure of (8β,9β,10β)-8,9-epoxycalamene-3,10-diol<sup>1</sup>.

The <sup>1</sup>H-NMR data (Table 2) indicated the presence of an <sup>i</sup>Pr group (δ 0.90 and 1.00 (*d*, *J* = 7.0 Hz, 3 H each) and 1.89–1.94 (*m*, 1 H)) and two Me groups (δ 2.15 (*s*) and 1.53 (*s*)). Six aromatic C-atom signals (δ 112.3–153.2) along with the chemical shift of the <sup>i</sup>Pr and a Me group (δ 2.15) suggested that the compound was a derivative of calamenene (= (1*S*,4*S*)-1,2,3,4-tetrahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene). Two *s* of aromatic protons (δ 7.07 and 6.74) in addition to a phenol signal (δ 5.89, exchangeable) and that of an oxygenated C-atom (δ 153.2) were in accord with an OH group at C(3). The proton at δ 6.74 had a NOESY correlation with H–C(7) (δ 3.06) and Me(15), and could thus be assigned to H–C(5). The remaining signal at δ 7.07 must arise from H–C(2). The consecutive protons Me(12) (δ 0.90), H–C(11) (δ 1.89–1.94), H–C(7) (δ 3.06 (*dd*, *J* = 5.4, 1.5 Hz)), H–C(8) (δ 3.58 (*dd*, *J* = 4.2, 1.5 Hz)), and H–C(9) (δ 3.35 (*d*, *J* = 4.2 Hz)) were revealed from COSY and NOESY data. The signal at δ 1.53 was assigned as Me(14) since it had cross-peaks with δ 138.4 (C(1)), 70.5 (C(10)), and 59.6 (C(9)). The quaternary C(10) was considered to be substituted by an OH group. Based on the above analysis, 5 of the 6 IHD were consumed by one aromatic ring and one cyclohexane ring, and the remaining IHD was considered to be an epoxy bridge. The chemical shifts of H–C(8) (δ(H) 3.58, δ(C) 55.7) and H–C(9) (δ(H) 3.35 and δ(C) 59.6) were consistent with an epoxy moiety. Comparison of the physical data of **6** with those of **7** [17] revealed that the only difference was an additional OH group at C(3) in **6**. Although H–C(2) is *ortho*-positioned with respect to the OH group, it showed a lower chemical shift than H–C(5). The reason is that H–C(2) is deshielded by OH–C(10), suggesting that the OH group adopts a β-quasiequatorial position. The relative configuration of **6** was mainly established by a NOESY plot.

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### Experimental Part

*General.* Column chromatography: silica gel (*Merck*; 70–230 mesh, 230–400 mesh, ASTM). Semi-prep. normal-phase HPLC: *LDC-Analytical-III* instrument; 250 × 10 mm column, *LiChrosorb Si 60* (7 μm). M.p.: *Yanagimoto* micro-melting-point apparatus; uncorrected. Specific rotation: *Jasco DIP-180* digital polarimeter. UV Spectra: λ<sub>max</sub> (log ε) in nm. IR Spectra: *Perkin-Elmer 983-G*; in cm<sup>-1</sup>. Spectrophotometer. <sup>1</sup>H- and <sup>13</sup>C-NMR Spectra: *Varian Unity-400* or *Bruker DMX-400* spectrophotometer; δ in ppm, *J* in Hz. EI-MS: *Jeol JMS-HX-300* mass spectrometer; in *m/z* (rel. %).

*Plant Material.* The roots of *T. cryptomerioides* were collected from Taichung, Taiwan, in August 1996. The plant was identified by Dr. *Shang-Tzen Chang*, Professor of the Department of Forestry, National Taiwan University. A voucher specimen (No. 013542) has been deposited in the Herbarium of the Department of Botany of the National Taiwan University, Taipei, Taiwan.

*Extraction and Isolation.* Air-dried root slices of *T. cryptomerioides* (15 kg) were extracted two times with acetone (125 l) at r.t. (twice 7 days). The acetone extract was concentrated, the black residue suspended in H<sub>2</sub>O (7 l) and then extracted with AcOEt (3 × 1 l), and the AcOEt fraction (365 g) subjected to CC (silica gel, hexane/AcOEt of increasing polarity), and each product fraction further

purified by HPLC. Compounds **5** (8.0 mg) and **7** (4.8 mg) were eluted with 30% AcOEt/hexane (HPLC purifications with 10% AcOEt/CH<sub>2</sub>Cl<sub>2</sub> and 20% acetone/hexane). Compound **1** (6.8 mg) was eluted with 40% AcOEt/hexane (HPLC purification with 15% AcOEt/CH<sub>2</sub>Cl<sub>2</sub> and 30% acetone/hexane). Compounds **2** (56 mg), **3** (7.8 mg), **4** (6.8 mg), and **6** (6.5 mg) were eluted with 70% AcOEt/hexane (HPLC purifications with 50% AcOEt/CH<sub>2</sub>Cl<sub>2</sub> and 40% acetone/hexane).

(1*β*,4*β*,5*α*,10*α*)-1,4-Epoxy $\mu$ uroolan-5-ol (= (1*S*,2*S*,4*aS*,5*R*,8*S*,8*aR*)-Octahydro-2,5-dimethyl-8-(1-methylethyl)-2H-2,4a-epoxynaphthalen-1-ol; **1**): Colorless gum.  $[\alpha]_D^{25} = -9.0$  ( $c = 0.14$ , CHCl<sub>3</sub>). IR (KBr): 3434, 2934, 2878, 1462, 1379, 1058. <sup>13</sup>C- and <sup>1</sup>H-NMR: Table 1. EI-MS: 238 (12,  $M^+$ ), 220 (18), 195 (50), 177 (43), 151 (100). HR-EI-MS: 238.1934 (C<sub>15</sub>H<sub>26</sub>O<sub>2</sub><sup>+</sup>; calc. 238.1934).

(4*α*,10*β*)-4,10-Dihydroxycadin-1(6)-en-5-one (= (2*R*,5*S*,8*S*)-3,4,5,6,7,8-Hexahydro-2,5-dihydroxy-2,5-dimethyl-8-(1-methylethyl)naphthalen-1(2H)-one; **2**): Light brown oil.  $[\alpha]_D^{25} = +41.3$  ( $c = 0.32$ , CHCl<sub>3</sub>). UV (MeOH): 242.0 (4.38), 291.0 (3.46). IR (KBr): 3423, 2964, 1670, 1459, 1370, 1170, 1136. <sup>13</sup>C- and <sup>1</sup>H-NMR: Table 1. EI-MS: 252 (1,  $M^+$ ), 234 (100,  $[M - H_2O]^+$ ), 191 (75), 151 (26), 133 (36), 105 (41). HR-EI-MS: 252.1726 (C<sub>15</sub>H<sub>24</sub>O<sub>3</sub><sup>+</sup>; calc. 252.1720).

(2*β*,3*α*,4*β*,6*β*)-2,3-Dihydroxycadin-1(10)-en-5-one (= (2*S*,3*S*,4*S*,8*S*,8*aS*)-3,4,6,7,8,8a-Hexahydro-3,4-dihydroxy-2,5-dimethyl-8-(1-methylethyl)naphthalen-1(2H)-one; **3**): White solid. M.p.: 134–136°.  $[\alpha]_D^{25} = +18.5$  ( $c = 0.80$ , CHCl<sub>3</sub>). IR (KBr): 3418, 2928, 1705, 1464, 1370, 1123, 1002. <sup>13</sup>C- and <sup>1</sup>H-NMR: Table 1. EI-MS: 252 (64,  $M^+$ ), 191 (76), 183 (100), 123 (56). HR-EI-MS: 252.1725 (C<sub>15</sub>H<sub>24</sub>O<sub>3</sub><sup>+</sup>; calc. 252.1720).

(2*β*,3*α*)- $\alpha$ -Corocalene-2,3-diol (= (1*S*,2*S*)-1,2-Dihydro-3,8-dimethyl-5-(1-methylethyl)naphthalene-1,2-diol; **4**): Yellow gum.  $[\alpha]_D^{25} = -63.1$  ( $c = 0.45$ , CHCl<sub>3</sub>). UV (MeOH): 224.0 (4.29), 262.0 (3.88), 282.0 (3.79), 333.0 (3.24). IR (KBr): 3360, 2964, 1654, 1449, 1385, 1249, 1015. <sup>13</sup>C- and <sup>1</sup>H-NMR: Table 2. EI-MS: 214 (44,  $[M - H_2O]^+$ ), 199 (81), 191 (84), 91 (100), 57 (71). HR-EI-MS: 214.1359 ( $[M - H_2O]^+$ , C<sub>15</sub>H<sub>18</sub>O<sup>+</sup>; calc. 214.1352).

(7*S*)- $\alpha$ -Calacoren-14-ol (= (4*S*)-3,4-Dihydro-6-methyl-4-(1-methylethyl)naphthalene-1-methanol; **5**): Yellow gum.  $[\alpha]_D^{27} = +35.7$  ( $c = 0.17$ , CHCl<sub>3</sub>). UV (MeOH): 229.0 (3.59), 256.0 (3.27). IR (KBr): 3411, 2965, 2932, 2877, 1684, 1610, 1500, 1460, 1386, 1254, 1210, 1093. <sup>13</sup>C- and <sup>1</sup>H-NMR: Table 2. EI-MS: 216 (12,  $M^+$ ), 202 (47), 197 (12), 160 (60), 159 (100), 145 (32), 131 (34). HR-EI-MS: 216.1519 (C<sub>15</sub>H<sub>20</sub>O<sup>+</sup>; calc. 216.1510).

(8*β*,9*β*,10*β*)-8,9-Epoxy $\mu$ calamenene-3,10-diol (= (1*aS*,2*R*,7*S*,7*aS*)-1*a*,2,7,7*a*-Tetrahydro-2,5-dimethyl-7-(1-methylethyl)naphth[2,3-*b*]oxirene-2,4-diol; **6**): Amorphous solid.  $[\alpha]_D^{23} = +108.4$  ( $c = 0.66$ , CHCl<sub>3</sub>). UV (MeOH): 219.0 (4.06), 285.0 (3.63). IR (KBr): 3423, 2930, 1624, 1507, 1458, 1377, 1245. <sup>13</sup>C- and <sup>1</sup>H-NMR: Table 2. EI-MS: 248 (30,  $M^+$ ), 230 (28), 205 (53), 187 (100), 159 (50). HR-EI-MS: 248.1414 (C<sub>15</sub>H<sub>20</sub>O<sub>3</sub><sup>+</sup>; calc. 248.1407).

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