New Lignans from the Roots of *Taiwania cryptomerioides* HAYATA

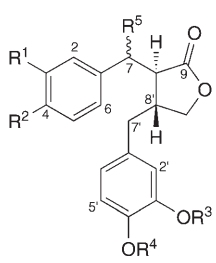
by **Chiou-Fung Chyu**[a]) and **Yueh-Hsiung Kuo***[b])[c])[d])

[a]) Department of Chemistry, National Taiwan University, Taipei 106, Taiwan
[b]) Research Center of Food and Biomolecules, National Taiwan University, Taipei 106, Taiwan
(phone: +886-233661671; fax: +886-2-23636359; e-mail: yhkuo@ntu.edu.tw)
[c]) College of Pharmacy, China Medical University, Taichung, 404, Taiwan
[d]) Agriculture Biotechnology Research Center, Academia Sinica, Taipei, 115, Taiwan

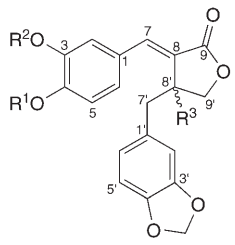
The five new lignans designated 3′,4′-de-*O*-methylenehinokinin (**1**), taiwaninolide (**2**), 8′-hydroxysavinin (**3**), isoguamarol (**4**), and 4′-*O*-methylsalicifolin (**5**), as well as the new 4-(3,4-dimethoxybenzyl)dihydro-3-(4-hydroxybenzyl)furan-2(3*H*)-one (**6**) were isolated from the roots of *Taiwania cryptomerioides*, besides the three known compounds hinokinin (**8**), savinin (**9**), and 3,4-de-*O*-methylenehinokinin (**7**). The structures of the new constituents were elucidated through chemical and spectral studies. A compound previously isolated from the heartwood of *Chamaecyparis obtusa* var. *formosana* was assigned structure **1**; however, this structure has now been revised to be 3,4-de-*O*-methylenehinokinin (**7**).

Introduction. – *Taiwania cryptomerioides* (Taxodiaceae) is taxonomically included in one genus and one species of endemic plants in Taiwan. It contains more than 6% of essential oil in its heartwood [1]. *T. cryptomerioides* is an important building material with high value in Taiwan. Previously, we investigated the chemical components of the heartwood [2–4] and bark [5–9] of this plant because of its antifungal and decay-resistant characteristics as well as of its beautiful yellowish-red color with distinct purplish-pink streaks. α-Cadinol was found as a major component in its essential oil, which showed selectivity for human-colon-tumor cell lines [10]. Also, it has been a potent agent against wood-decay fungi [11]. Besides, we have found lignans and cadinane-type compounds in this essential oil exhibiting significant cytotoxicity against three human-tumor cell lines [12]. Their interesting structures and those conferring biological activities inspired us to study the chemical components of the roots of *T. cryptomeroides*. Several sesquiterpenes with unique structures, including novel secocadinane-type [13], seco-abeoguaiane-type [14], seco-norabietane-type [15], and norabietane-type [16] derivatives, were isolated from these roots and their structures elucidated. In this paper, we would like to report the five new lignans 3′,4′-de-*O*-methylenehinokinin (**1**), taiwaninolide (**2**), 8′-hydroxysavinin (**3**), isoguamarol (**4**), and 4′-*O*-methylsalicifolin (**5**), and the new 4-(3,4-dimethoxybenzyl)dihydro-3-(4-hydroxybenzyl)furan-2(3*H*)-one (**6**), together with the three known lignans 3,4-de-*O*-methylenehinokinin (**7**) [17], hinokinin (**8**) [18], and savinin (**9**) [19][1]). One compound, isolated from the heartwood of *Chamaecyparis obtusa* var. *formosana*,

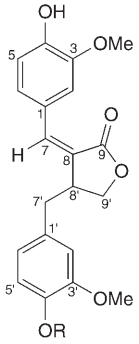
[1]) Trivial names and trivial atom numbering; for systematic names, see *Exper. Part*.



1 R^1–R^2 = OCH_2O, R^3 = R^4 = R^5 = H
2 R^1 = H, R^2 = R^5 = OH, R^3–R^4 = CH_2
6 R^1 = R^5 = H, R^2 = OH, R^3 = R^4 = Me
7 R^1 = R^2 = OH, R^3–R^4 = CH_2, R^5 = H
8 R^1–R^2 = OCH_2O, R^3–R^4 = CH_2, R^5 = H



3 R^1 – R^2 = CH_2, R^3 = OH
4 R^1 = R^3 = H, R^2 = Me
9 R^1 – R^2 = CH_2, R^3 = H
10 R^1 = Me, R^2 = R^3 = H



5 R = Me
11 R = H

was previously assigned the structure **1**; this assignment has now been revised to the structure of 3,4-de-*O*-methylenehinokinin (**7**).

Results and Discussion. – Compound **1** was isolated as a pale yellow gum, which had a molecular formula $C_{19}H_{18}O_6$, as established by analysis of its ^{13}C-NMR spectrum (*Table 1*) and HR-EI-MS. The IR spectrum of **1** confirmed the presence of an OH group (3410 cm^{-1}), a γ-lactone carbonyl group (1745 cm^{-1}), and aromatic moieties (1608, 1489 cm^{-1}). Detailed analysis of the NMR (*Table 1*), MS (*Fig. 1*), HMBC, and NOESY (*Fig. 2*) data established the structure of **1** as (8*R*,8′*R*)-3′,4′-de-*O*-methylenehinokinin[1]). Comparison of the ^{1}H- and ^{13}C-NMR data of **1** and hinokinin (**8**) also verified the structure. The CH_2(9′) protons were nonequivalent [18], as two benzyl groups were in *trans*-configuration. Therefore, compound **1** was in *trans*-configuration. The value of the specific rotation of **1** ($[\alpha]_D = 20.2$) was near that of (−)-hinokinin ($[\alpha]_D = -26.3$) which confirmed the (8*R*,8′*R*) configuration of **1**, and the CD curve of **1** ($[\Delta\varepsilon]_{234}$ −2.12, $[\Delta\varepsilon]_{286}$ −0.25) was closely similar to the ORD curve of (8*R*,8′*R*)-(−)-hinokinin ($[\phi]_{250}$ −10900, $[\phi]_{285}$ +400, $[\phi]_{300}$ −4850) [18][20].

The ^{1}H-NMR spectrum of **1** (*Table 1*) exhibited signals for a methylenedioxy group (δ 5.92 (*d*, *J* = 1.2 Hz, 1 H) and 5.91 (*d*, *J* = 1.2 Hz, 1 H)) at a benzene moiety and CH_2 protons in γ-position of a γ-lactone ring (δ 3.84 (*dd*, *J* = 9.2, 7.2 Hz, 1 H) and 4.09 (*dd*, *J* = 9.2, 7.2 Hz, 1 H)). Also, two *ABX* systems (6 H) of aromatic protons were observed (δ 6.59 (*d*, *J* = 1.6 Hz, 1 H), 6.71 (*d*, *J* = 8.0 Hz, 1 H), and 6.57 (*dd*, *J* = 8.0, 1.6 Hz, 1 H); 6.50 (*d*, *J* = 2.0 Hz, 1 H), 6.74 (*d*, *J* = 8.0 Hz, 1 H), and 6.42 (*dd*, *J* = 8.0, 2.0 Hz, 1 H)), besides four benzylic protons (δ 2.82 (*dd*, *J* = 14.0, 7.2 Hz, 1 H), 2.93 (*dd*, *J* = 14.0, 4.8 Hz, 1 H); 2.38–2.45 (*m*, 1 H), 2.51–2.55 (*m*, 1 H)). The ^{13}C-NMR spectrum and DEPT experiment showed 19 signals including a γ-lactone carbonyl C-atom (δ 179.0), twelve aromatic C-atoms, and four CH_2 (δ 101.0, 71.4, 37.9, 34.7) and two CH groups (δ 46.5, 41.1). The MS of **1** displayed a base peak at *m*/*z* 135 and a peak at *m*/*z* 219 (see *Fig. 1*), in accordance with a fragment ion of an 8-[(3,4-methylenedioxy)benzyl]-substituted lactone moiety. Another peak at *m*/*z* 123 corresponded to a 3,4-dihydroxybenzyl cation. The signals at δ 2.82 and 2.93 were assigned to CH_2(7), due to a lower-field location than those of CH_2(7′) and to the HMBC correlations to the lactone carbonyl group (δ 179.0, C(9)), C(1), C(2), and C(6). The CH_2(7′) also have HMBC correlations to C(1′), C(2′), C(6′), and C(9′). In the HMBC plot, the OCH_2O protons correlated to C(3) and C(4), and the NOESY correlations (*Fig. 2*) (H−C(7)/H−C(2), H−C(6); H−C(7′)/H−C(2′), H−C(6′)) confirmed the structure of **1** as shown.

Table 1. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$, 400 and 100 MHz) *of Compounds* **1**–**3**[1]). δ in ppm, J in Hz.

	1		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(1)		131.3 (*s*)		132.8 (*s*)		127.1 (*s*)
H–C(2)	6.59 (*d*, *J* = 1.6)	109.5 (*d*)	7.12 (*d*, *J* = 8.8)	126.6 (*d*)	7.67 (*d*, *J* = 1.6)	111.3 (*d*)
C(3) or H–C(3)		147.8 (*s*)	6.77 (*d*, *J* = 8.8)	115.4 (*s*)		148.2 (*s*)
C(4)		146.4 (*s*)		155.3 (*s*)		149.9 (*s*)
H–C(5)	6.71 (*d*, *J* = 8.0)	108.3 (*d*)	6.77 (*d*, *J* = 8.8)	115.4 (*d*)	6.84 (*d*, *J* = 8.0)	108.5 (*d*)
H–C(6)	6.57 (*dd*, *J* = 8.0, 1.6)	122.3 (*d*)	7.12 (*d*, *J* = 8.8)	126.6 (*d*)	7.30 (*dd*, *J* = 8.0, 1.6)	128.9 (*d*)
CH_2(7) or H–C(7)	2.82 (*dd*, *J* = 14.0, 7.2), 2.93 (*dd*, *J* = 14.0, 4.8)	34.7 (*t*)	5.27 (*d*, *J* = 3.2)	71.7 (*d*)	7.63 (*s*)	143.0 (*d*)
H–C(8) or C(8)	2.47–2.53 (*m*)	46.5 (*d*)	2.60 (*dd*, *J* = 6.8, 3.2)	52.7 (*d*)		126.2 (*s*)
C(9)		179.0 (*s*)		178.5 (*s*)		171.2 (*s*)
C(1′)		130.7 (*s*)		131.5 (*s*)		128.1 (*s*)
H–C(2′)	6.50 (*d*, *J* = 2.0)	115.6 (*d*)	6.26 (*d*, *J* = 1.6)	108.6 (*d*)	6.68 (*d*, *J* = 1.6)	110.7 (*d*)
C(3′)		143.9 (*s*)		147.7 (*s*)		147.9 (*s*)
C(4′)		142.4 (*s*)		146.2 (*s*)		147.1 (*s*)
H–C(5′)	6.74 (*d*, *J* = 8.0)	115.4 (*d*)	6.60 (*d*, *J* = 8.0)	108.1 (*d*)	6.69 (*d*, *J* = 8.0)	108.4 (*d*)
H–C(6′)	6.42 (*dd*, *J* = 8.0, 2.0)	120.9 (*d*)	6.32 (*dd*, *J* = 8.0, 1.6)	121.5 (*d*)	6.62 (*dd*, *J* = 8.0, 1.6)	123.6 (*d*)
CH_2(7′)	2.38–2.45 (*m*), 2.51–2.55 (*m*)	37.9 (*t*)	2.23 (*dd*, *J* = 14.0, 7.2), 2.34 (*dd*, *J* = 14.0, 8.4)	39.2 (*t*)	2.97 (*d*, *J* = 14.0), 3.22 (*d*, *J* = 14.0)	41.8 (*t*)
H–C(8′) or C(8′)	2.41–2.47 (*m*)	41.1 (*d*)	2.72–2.81 (*m*)	36.4 (*d*)		76.5 (*s*)
CH_2(9′)	3.84 (*dd*, *J* = 9.2, 7.2), 4.09 (*dd*, *J* = 9.2, 7.2)	71.4 (*t*)	3.90 (*dd*, *J* = 8.8, 6.4), 4.26 (*dd*, *J* = 8.8, 8.0)	72.5 (*t*)	3.95 (*d*, *J* = 9.6), 4.45 (*d*, *J* = 9.6)	76.0 (*t*)
OCH_2O	5.91 (*d*, *J* = 1.2), 5.92 (*d*, *J* = 1.2)	101.0 (*t*)			6.01 (*s*)	101.8 (*t*)
OCH_2O			5.88 (*d*, *J* = 1.6), 5.91 (*d*, *J* = 1.6)	101.0 (*t*)	5.91 (*d*, *J* = 1.6), 5.92 (*d*, *J* = 1.6)	101.1 (*t*)
OH	5.52, 6.71 (2 br. *s*)					

Taiwaninolide (**2**) had a molecular ion at *m*/*z* 342.1108 in the HR-EI-MS, as analyzed for $C_{19}H_{18}O_6$. Analysis of its IR spectrum suggested that **2** contains an OH group (3410 cm^{-1}), a γ-lactone carbonyl group (1751 cm^{-1}), and an aromatic moiety (1615, 1492 cm^{-1}). Eleven indices of hydrogen deficiency (IHD) were determined from the molecular formula, the ^{13}C-NMR spectrum (*Table 1*), and the DEPT experiment. Further spectral data (*Table 1*, *Figs. 1* and *2*) established the structure of **2** as *trans*-4-(1,3-benzodioxol-5-ylmethyl)dihydro-3-[hydroxy(4-hydroxyphenyl)methyl]-furan-2(3*H*)-one.

The ^{1}H-NMR spectrum (*Table 1*) of **2** indicated the presence of an *ABX* system (δ 6.32 (*dd*, *J* = 8.0, 1.6 Hz, 1 H), 6.60 (*d*, *J* = 8.0 Hz, 1 H), and 6.26 (*d*, *J* = 1.6 Hz, 1 H)), a symmetrical A_2X_2 pattern for aromatic protons (δ 7.12 (*d*, *J* = 8.8 Hz, 2 H) and 6.77 (*d*, *J* = 8.8 Hz)), and a OCH_2O group (δ 5.88 (*d*,

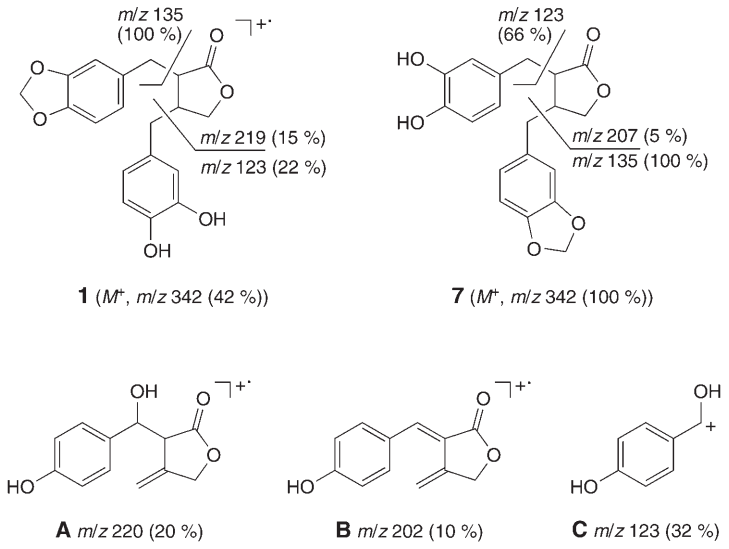


Fig. 1. *MS Fragments*

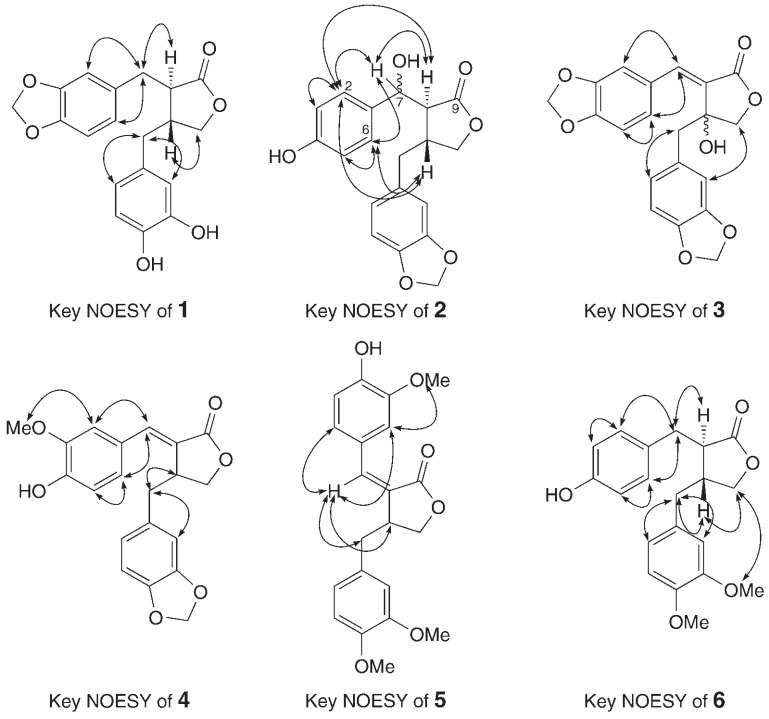


Fig. 2. *Key NOESY correlations of* **1**–**6**

$J = 1.6$ Hz, 1 H) and 5.91 (*d*, $J = 1.6$ Hz, 1 H)). The ^{13}C-NMR and DEPT established the presence of a γ-lactone carbonyl group (δ 178.5), two aromatic rings, and an sp^3-oxygenated C-atom (δ 71.7). The latter and a proton at δ 5.27 (*d*, $J = 3.2$ Hz) were assigned to the benzylic position CH(7). Two CH_2 groups (δ 3.90 (*dd*, $J = 8.8$, 6.4 Hz) and 4.26 (*dd*, $J = 8.8$, 8.0 Hz); δ 2.23 (*dd*, $J = 14.0$, 7.2 Hz) and 2.34 (*dd*, $J = 14.0$, 8.4 Hz)) are characteristic of a CH_2 group of a γ-lactone and of a benzyl group, respectively. From the molecular formula and the spectral evidence, compound **2** was consistent with a dibenzyl-substituted γ-butyrolactone. The base peak in the MS at *m*/*z* 135 and three peaks at *m*/*z* 220, 202, and 123 (see fragment ions **A** – **C** in *Fig. 1*) revealed the presence of a 3,4-(methylenedioxy)benzyl moiety at C(8′) and of a 4,7-dihydroxybenzyl moiety at C(8). The HMBC correlations H–C(7)/C(6), C(2), and C(9), H–C(7′)/C(8), C(8′), C(9′), C(2′), and C(6′) confirmed the gross structure. The NOESY correlations (*Fig. 2*), together with the nonequivalent protons CH_2(9′), suggested that the two benzyl moieties were in *trans*-configuration [18].

The 8′-hydroxysavinin (**3**) was isolated as a yellowish gum; its molecular formula $C_{20}H_{16}O_7$ was established by ^{13}C-NMR and HR-EI-MS data, and the IHD was 13. The IR spectrum of **3** showed absorptions attributable to an OH group (3443 cm^{-1}), to a γ-lactone carbonyl group (1747 cm^{-1}), and to aromatic moieties (1628, 1497 cm^{-1}). The ^{13}C- and ^{1}H-NMR spectrum (*Table 1*) data together with the UV absorption bands at λ_{max} 239, 258, 290, and 336 nm suggested that compound **3** is very similar to savinin (**9**) [19]. Based on further spectral data, the structure of **3** was established to be 8′-hydroxysavinin.

The following HMBC correlations were observed for **3**: H–C(7)/C(2), C(6), C(9), and C(8′); CH_2(7′)/C(2′), C(6′), and C(8′), and H–C(6)/C(4), C(5), and C(7). The NOESY correlations (*Fig. 2*) H–C(7)/H–C(2) and H–C(6), H–C(5)/H–C(6), H–C(6′)/H–C(7′), and H–C(9′)/H–C(2′) confirmed the assigned structure and relative configuration. Thus, the difference between **3** and **9** was that **3** has an additional OH group at C(8′). This caused a shift to lower field of the CH_2(7′) and CH_2(9′) signals as compared to those of **9**, accompanied by a simplification of their pattern to two *AX* systems (δ 2.97, 3.22 (2*d*, $J = 14.0$ Hz, 1 H each, CH_2(7′)) and 3.95, 4.45 (2*d*, $J = 9.6$ Hz, 1 H each, CH_2(9′))) and a low-field shift of the C(7′) and C(9′) signals as compared to those of **9**.

Based on the HR-EI-MS and ^{13}C-NMR data (*Table 2*), isoguamarol (**4**) has the molecular formula $C_{20}H_{18}O_6$, with an IHD of 12. The IR spectrum of **4** displayed peaks for an OH group (3423 cm^{-1}), a γ-lactone carbonyl group (1744 cm^{-1}), and aromatic moieties (1595 and 1518 cm^{-1}). The UV absorption bands at λ_{max} 237, 296, and 332 nm, the ^{13}C-NMR and DEPT data (*Table 2*), in addition to the base peak in the MS at *m*/*z* 135 (3,4-methylenedioxybenzyl cation) indicated that compound **4** is a positional isomer of guamarol (**10**) [21].

The ^{1}H-NMR signals (*Table* 2) of **4** indicated the presence of two *ABX* systems of aromatic protons, an OCH_2O group at a benzene moiety, a proton at a trisubstituted olefin moiety (δ 7.49 (*d*, $J = 1.6$ Hz, 1 H)), an MeO group, and a phenolic proton (δ 6.02 (br. *s*, 1 H; D_2O exchangeable)). The HMBC correlations H–C(7)/C(9), C(2), and C(6), and CH_2(7′)/C(8′), C(2′), and C(6′) confirmed the assigned structure. Based on the NOESY correlations (*Fig. 2*), the MeO group showed a NOESY correlation with H–C(2), which established the position of the MeO group at C(3).

Compound **5** has the formula $C_{21}H_{22}O_6$ according to the HR-EI-MS and ^{13}C-NMR data. It has an IHD of 11 as deduced from its molecular formula. The IR spectrum shows absorptions for an OH group (3418 cm^{-1}), a conjugated γ-lactone carbonyl group (1740 cm^{-1}), and an aromatic moiety (1595 and 1517 cm^{-1}). The UV spectra of **5**

Table 2. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$, 400 and 100 MHz) *of Compounds* **4**–**6**[1]). δ in ppm, J in Hz.

	4		**5**		**6**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
C(1)		126.4 (*s*)		126.5 (*s*)		130.5 (*s*)
H–C(2)	7.00 (*d*, *J* = 2.0)	112.6 (*d*)	8.21 (*d*, *J* = 1.6)	113.3 (*d*)	6.96 (*d*, *J* = 8.4)	130.4 (*d*)
C(3) or H–C(3)		146.5 (*s*)		146.1 (*s*)	6.72 (*d*, *J* = 8.4)	115.5 (*d*)
C(4)		146.7 (*s*)		147.7 (*s*)		154.6 (*s*)
H–C(5)	6.98 (*d*, *J* = 8.0)	115.0 (*d*)	6.84 (*d*, *J* = 8.4)	113.9 (*d*)	6.72 (*d*, *J* = 8.4)	115.5 (*d*)
H–C(6)	7.17 (*dd*, *J* = 8.0, 1.6)	123.8 (*d*)	6.98 (*dd*, *J* = 8.4, 2.0)	126.6 (*d*)	6.96 (*d*, *J* = 8.4)	130.4 (*d*)
H–C(7) or CH_2(7)	7.49 (*d*, *J* = 1.6)	137.6 (*d*)	6.54 (*d*, *J* = 1.6)	141.0 (*d*)	2.85 (*dd*, *J* = 14.2, 7.2), 2.95 (*dd*, *J* = 14.2, 5.6)	34.1 (*t*)
C(8) or H–C(8)		125.3 (*s*)		124.3 (*s*)	2.53–2.56 (*m*)	46.5 (*d*)
C(9)		172.7 (*s*)		169.7 (*s*)		178.7 (*s*)
C(1′)		131.5 (*s*)		130.4 (*s*)		129.7 (*s*)
H–C(2′)	6.63 (*d*, *J* = 1.6)	109.0 (*d*)	6.67 (*d*, *J* = 2.0)	112.9 (*d*)	6.43 (*d*, *J* = 1.6)	111.7 (*d*)
C(3′)		148.0 (*s*)		149.3 (*s*)		149.0 (*s*)
C(4′)		147.5 (*s*)		148.2 (*s*)		147.8 (*s*)
H–C(5′)	6.71 (*d*, *J* = 8.0)	108.5 (*d*)	6.80 (*d*, *J* = 8.0)	111.8 (*d*)	6.74 (*d*, *J* = 8.0)	111.3 (*d*)
H–C(6′)	6.61 (*dd*, *J* = 8.0, 1.6)	122.0 (*d*)	6.71 (*dd*, *J* = 8.0, 2.0)	121.4 (*d*)	6.54 (*dd*, *J* = 8.0, 1.6)	120.6 (*d*)
CH_2(7′)	2.58 (*dd*, *J* = 14.4, 10.4), 3.01 (*dd*, *J* = 14.4, 4.4)	37.4 (*t*)	2.80 (*dd*, *J* = 13.8, 8.6), 2.91 (*dd*, *J* = 13.8, 7.0)	40.8 (*t*)	2.44–2.49 (*m*), 2.57–2.61 (*m*)	38.2 (*t*)
H–C(8′)	3.75–3.79 (*m*)	39.7 (*d*)	3.25–3.31 (*m*)	44.5 (*d*)	2.41–2.47 (*m*)	41.1 (*d*)
CH_2(9′)	4.24 (br. *d*, *J* = 4.0)	69.5 (*t*)	4.10 (*dd*, *J* = 9.0, 3.6), 4.32 (*dd*, *J* = 9.0, 7.2)	70.0 (*t*)	3.86 (*dd*, *J* = 8.8, 7.2), 4.11 (*dd*, *J* = 8.8, 7.2)	71.3 (*t*)
OCH_2O	5.91 (*d*, *J* = 1.2), 5.92 (*d*, *J* = 1.2)	101.1 (*t*)				
MeO–C(3)	3.91 (*s*)	56.0 (*q*)	3.92 (*s*)	56.1 (*q*)		
MeO–C(3′)			3.80 (*s*)	56.0 (*q*)	3.79 (*s*)	55.8 (*q*)
MeO–C(4′)			3.85 (*s*)	56.1 (*q*)	3.84 (*s*)	55.9 (*q*)
OH	6.02 (br. *s*)		5.95 (*s*)			

confirmed the presence of a conjugated carbonyl group (λ_{max} 287 and 336 nm). Analysis of the HMQC, HMBC, and NOESY (*Fig. 2*) data revealed that the structure of **5** was similar to that of salicifoline (**11**) [22], the only difference being an MeO instead of an OH group at C(4′). Therefore, the structure of **5** was elucidated as 4′-*O*-methylsalicifolin.

The ^{1}H-NMR data of **5** (*Table 2*) indicated the presence of a 3,4-dimethoxybenzyl moiety (*ABX* system of aromatic protons), which was confirmed by the presence of the base peak in the MS at *m*/*z*

151), of a 1,3,4-trisubstituted benzene moiety carrying an OH and an MeO group, and a γ-lactone with a methylene group in γ-position. These features are compatible with a dibenzylbutyrolactone lignan. The UV absorption showed a C=C bond linking an aromatic and a lactone carbonyl group, but the olefinic proton (H–C(7)) appeared at higher field than the corresponding proton of compounds **3** and **4**. Due to the deshielding effect of the lactone carbonyl group, H–C(2) was shifted downfield to δ 8.21. These two evidences suggested the (*Z*)-configuration at the exocyclic C(7)=C(8) bond.

Compound **6** exhibited the IR absorption of an OH group (3426 cm^{-1}), a γ-lactone carbonyl group (1765 cm^{-1}), and an aromatic moiety (1615, 1596, and 1517 cm^{-1}), and an M^+ at *m/z* 342.1467 establishing the molecular formula $C_{20}H_{22}O_5$. The specific rotation of **6** was near to that of (–)-(8*R*,8′*R*)-hinokinin (**8**) and the CD curve of **6** closely similar to the ORD curve of **8** [18][20], suggesting that compound **6** has the same (8*R*,8′*R*)-configuration[1]) as **8**. Thus, the new compound **6** was (3*R*,4′*R*)-4-(3,4-dimethoxybenzyl)dihydro-3-(4-hydroxybenzyl)furan-2(3*H*)-one [23].

The ^{1}H-NMR spectrum of **6** (*Table 2*) showed signals of an *ABX* systems of aromatic protons, a symmetrical A_2X_2 pattern of aromatic protons, and two MeO signals. In the MS, the fragment ions at *m/z* 151 and 107 revealed the presence of a 3,4-dimethoxybenzyl and a 4-hydroxybenzyl moiety. The CH_2(9′) were nonequivalent (δ 3.86 (*dd*, *J* = 8.8, 7.2 Hz, 1 H) and 4.11 (*dd*, *J* = 8.8, 7.2 Hz, 1 H)) indicating that the two benzyl moieties were in *trans*-relation to each other [18]. HMBC Correlations (H–C(7)/C(9); H–C(7′)/C(9′)) and NOESY correlations (*Fig. 2*) (H–C(7)/H–C(2), H–C(6); H–C(7′)/H–C(2′), H–C(6′)) determined the correct position of the two benzyl moieties.

The assignments of the ^{13}C- and ^{1}H-NMR data (*Table 3*) of **7** were supported by COSY, HMQC, HMBC, and NOESY data. Compound **7** was assigned as 3,4-de-*O*-

Table 3. *^{1}H- and ^{13}C-NMR Data* ($CDCl_3$, 400 and 100 MHz) *of Compound* **7**[1]). δ in ppm, *J* in Hz.

	7	
	δ(H)	δ(C)
C(1)		130.1 (*s*)
H–C(2)	6.67 (*d*, *J* = 2.0)	116.1 (*d*)
C(3)		143.8 (*s*)
C(4)		142.8 (*s*)
H–C(5)	6.77 (*d*, *J* = 8.0)	115.3 (*d*)
H–C(6)	6.54 (*dd*, *J* = 8.0, 2.0)	121.8 (*d*)
CH_2(7)	2.86 (br. *d*, *J* = 6.0)	34.1 (*t*)
H–C(8)	2.50–2.57 (*m*)	46.5 (*d*)
C(9)		179.3 (*s*)
C(1′)		131.6 (*s*)
H–C(2′)	6.46 (*d*, *J* = 2.0)	108.9 (*d*)
C(3′)		147.8 (*s*)
C(4′)		146.3 (*s*)
H–C(5′)	6.68 (*d*, *J* = 8.0)	108.4 (*d*)
H–C(6′)	6.45 (*dd*, *J* = 8.0, 2.0)	121.6 (*d*)
CH_2(7′)	2.41–2.47 (*m*), 2.57–2.64 (*m*)	38.2 (*t*)
H–C(8′)	2.45–2.52 (*m*)	41.0 (*d*)
CH_2(9′)	3.83 (*dd*, *J* = 9.2, 7.6), 4.07 (*dd*, *J* = 9.2, 7.2)	71.4 (*t*)
OCH_2O	5.91 (*d*, *J* = 1.2), 5.92 (*d*, *J* = 1.2)	101.0 (*t*)
OH	5.60, 6.06 (2 br. *s*)	

methylenehinokinin. To a compound formerly isolated from *Chamaecyparis obtusa* var. *formosana* [17], structure **1** was attributed. But this compound and compound **7** have almost identical physical data (including NMR and $[\alpha]_D$). Thus, the structure of the compound isolated from *Chamaecyparis obtusa* must be revised to that of **7**.

The HMBC correlations (*Fig. 3*) of **7** included those of the methylenedioxy protons to C(3′) and C(4′), and the NOESY correlations (*Fig. 3*) H–C(7)/H–C(2) and H–C(6), and H–C(7′)/H–C(2′) and H–C(6′)) were observed. The MS of **7** displayed peaks at *m*/*z* 123 and 207 (see *Fig. 1*), in accordance with the 3,4-dihydroxybenzyl group at the lactone atom C(8). Another peak at *m*/*z* 135 corresponded to the 3,4-(methylenedioxy)benzyl group.

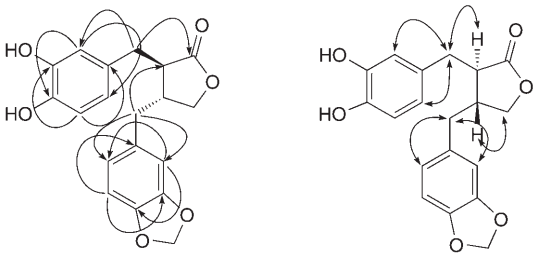


Fig. 3. *Major HMBC and key NOESY correlations for* **7**

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Experimental Part

General. Column chromatography (CC): silica gel (*Merck*; 70–230 mesh, 230–400 mesh, ASTM). Semi-prep. normal-phase HPLC: column *LiChrosorb Si 60* (250 × 10 mm, 7 μm); *LDC Analytical-III* apparatus. M.p.: *Yanagimoto* micro-melting point apparatus; uncorrected. Specific rotation: *Jasco DIP-180* digital polarimeter. IR Spectra: *Perkin-Elmer 983-G* spectrophotometer; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Varian Unity-400* spectrophotometer. EI-MS: *Jeol JMS-HX-300* mass spectrometer.

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. (7 days twice). The acetone extract was concentrated to give a black residue, which was suspended in H_2O (7 l) and then partitioned (3 times) with 1 l of AcOEt. The AcOEt fraction (365 g) was subjected to CC (silica gel, hexane/AcOEt of increasing polarity). The 8′-hydroxysavinin (**3**; 3 mg), isoguamarol (**4**; 10 mg), 3,4-de-*O*-methylenehinokinin (**7**; 8.0 mg), and hinokinin (**8**; 11.2 mg) were obtained with 30% AcOEt/hexane (CC) and purified by HPLC (10% AcOEt/CH_2Cl_2 and 20% acetone/hexane). The 3′,4′-de-*O*-methylenehinokinin (**1**; 8 mg), taiwaninolide (**2**; 10 mg), 4′-*O*-methylsalicifolin (**5**; 13 mg), and 3-(4-hydroxybenzyl)-4-(3,4-dimethoxybenzyl)dihydrofuran-2-one (**6**; 5 mg) were eluted with 50% AcOEt/hexane (CC) and purified by HPLC (25% AcOEt/CH_2Cl_2 and 30% acetone/hexane). Savinin (**9**; 2.3 g) was eluted with 20% AcOEt/hexane (CC).

3′,4′-De-O-*methylenehinokinin* (*=(3*R,*4*R*)-3-(1,3-Benzodioxol-5-ylmethyl)-4-[(3,4-dihydroxyphenyl)methyl]]dihydrofuran-2(3*H*)-one*; **1**): Pale yellow gum. $[\alpha]_D^{25} = -20.2$ ($c = 0.24$, $CHCl_3$). UV (MeOH): 230.0 (3.8), 285.0 (3.7). CD (MeOH): −2.12 (234), −0.25 (286). IR (KBr): 3410, 1745,

1608, 1502, 1489, 1284, 1193. ^{1}H- and ^{13}C-NMR ($CDCl_3$, 400, 100 MHz): *Table 1*. EI-MS: 342 (42, M^+), 219 (15), 218 (24), 192 (12), 135 (100), 123 (22). HR-EI-MS: 342.1108 ($C_{19}H_{18}O_6^+$; calc. 342.1103).

Taiwaninolide (=trans-*4-(1,3-Benzodioxol-5-ylmethyl)dihydro-3-[hydroxy(4-hydroxyphenyl)methyl]furan-2(3*H*)-one*; **2**): Yellow gum. $[\alpha]_D^{25} = -57.2$ ($c = 0.42$, $CHCl_3$). UV (MeOH): 226.5 (4.01), 284.5 (3.65). IR (KBr): 3410, 1751, 1615, 1492, 1446, 1376, 1246. ^{1}H- and ^{13}C-NMR ($CDCl_3$, 400, 100 MHz): *Table 1*. EI-MS : 342 (8, M^+), 324 (26), 220 (20), 202 (10), 123 (32), 189 (6), 135 (100). HR-EI-MS: 342.1108 ($C_{19}H_{18}O_6^+$; calc. 342.1103).

8′-Hydroxysavinin (=*(3*E*)-4-(1,3-Benzodioxol-5-ylmethyl)-3-[(1,3-benzodioxol-5-ylmethylene)dihydro-4-hydroxyfuran-2(3*H*)-one*; **3**): Yellowish gum. $[\alpha]_D^{27} = -34.9$ ($c = 0.12$, $CHCl_3$). UV (MeOH): 238.5 (4.08), 258.0 (3.94), 289.5 (3.93), 336.0 (3.77). IR (KBr): 3443, 1747, 1628, 1497, 1450, 1248, 1039. ^{1}H- and ^{13}C-NMR ($CDCl_3$, 400, 100 MHz): *Table 1*. EI-MS: 368 (7, M^+), 350 (100), 348 (69), 233 (75), 135 (72). HR-EI-MS: 368.0879 ($C_{20}H_{16}O_7^+$; calc. 368.0895).

Isoguamarol (=*(3*E*,4*R*)-4-(1,3-Benzodioxol-5-ylmethyl)dihydro-3-[(4-hydroxy-3-methoxyphenyl)methylene]furan-2(3*H*)-one*; **4**): Yellow gum. $[\alpha]_D^{25} = -67.8$ ($c = 0.40$, $CHCl_3$). UV (MeOH): 237.0 (4.09), 295.5 (4.01), 331.5 (4.16). IR (KBr): 3423, 1744, 1645, 1596, 1518, 1447, 1362. ^{1}H- and ^{13}C-NMR ($CDCl_3$, 400, 100 MHz): *Table 2*. EI-MS: 354 (18, M^+), 219 (78), 135 (100). HR-EI-MS: 354.1113 ($C_{20}H_{18}O_6^+$; calc. 354.1103).

4′-O-*Methylsalicifolin* (=*(3*Z*,4*R*)-4-[(3,4-Dimethoxyphenyl)methyl]dihydro-3-[(4-hydroxy-3-methoxyphenyl)methylene]furan-2(3*H*)-one*; **5**): Yellow gum. $[\alpha]_D^{25} = -26.4$ ($c = 1.08$, $CHCl_3$). UV (MeOH): 286.5 (2.92), 336.0 (3.12). IR: 3418, 1740, 1638, 1595, 1517, 1465, 1387. ^{1}H- and ^{13}C-NMR ($CDCl_3$, 400, 100 MHz): *Table 2*. EI-MS: 370 (24, M^+), 219 (20), 151 (100). HR-EI-MS: 370.1414 ($C_{21}H_{22}O_6^+$; calc. 370.1417).

*(3*R*,4*R*)-4-[(3,4-Dimethoxyphenyl)methyl]dihydro-3-[(4-hydroxyphenyl)methyl]furan-2(3*H*)-one*; (**6**): Yellow gum. $[\alpha]_D^{25} = -25.9$ ($c = 0.20$, $CHCl_3$). UV (MeOH): 226.5 (4.09), 280.0 (3.64). ORD (MeOH, $c = 0.05$; ϕ (λ in nm): +4560 (209), −3090 (231), +3340 (249). IR (KBr): 3426, 1765, 1615, 1596, 1517, 1455, 1266, 1239. ^{1}H- and ^{13}C-NMR ($CDCl_3$, 400, 100 MHz): *Table 2*. EI-MS: 342 (100, M^+), 151 (60), 137 (40), 107 (40). HR-EI-MS: 342.1467 ($C_{20}H_{22}O_5^+$; calc. 342.1468).

3,4-De-O-*methylenehinokinin* (=*(3*R*,4*R*)-4-(1,3-Benzodioxol-5-ylmethyl)-3-(3,4-dihydroxyphenyl)dihydrofuran-2(3*H*)-one*; **7**). Pale yellow gum. $[\alpha]_D^{25} = -13.2$ ($c = 0.32$, $CHCl_3$). UV (MeOH): 285.0 (3.80). ORD (MeOH, $c = 0.07$; ϕ (λ in nm)): −16460 (204), −5120 (235), +40 (256), −1020 (289). IR (KBr): 3445, 1757, 1610, 1492, 1248, 1195. ^{1}H- and ^{13}C-NMR ($CDCl_3$, 400, 100 MHz): *Table 3*. EI-MS: 342 (100, M^+), 218 (5), 192 (16), 135 (100), 123 (66). HR-EI-MS: 342.1110 (calc. for $C_{19}H_{18}O_6$, 342.1103).

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