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Three novel and one new lignan, chamaecypanones A, B, obtulignolide and isootobanone from the heartwood of *Chamaecyparis obtusa* var. *formosana*

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Abstract—Three novel lignans, chamaecypanone A **1**, chamaecypanone B **2**, obtulignolide **4**, and one new lignan, isootobanone **3**, were isolated from the heartwood of *Chamaecyparis obtusa* var. *formosana*, and were elucidated on the basis of 2D NMR techniques. Compounds **1** and **2**, derived from a phenyltetrahydronaphthalene-type lignan by cleavage and cyclization, are anthrone derivatives. Compound **3** is a phenyltetrahydronaphthalene-type lignan, and **4** is a 3,4-secophenyltetrahydronaphthalene-type lignan. The absolute configurations of **3** and otobanone **5** were elucidated by a modified Mosher's method.

Chamaecyparis obtusa var. *formosana* (Taiwan hinoki; Cupressaceae) is an economically important tree species indigenous to Taiwan. Previous chemical studies of the composition of its wood reported only essential oil and acidic components.[1] We have isolated two carbamates from its bark[2] and one novel diterpene, obtunone,[3a] together with three new abietane-type diterpenes[3b] from its heartwood. Further detailed reinvestigation of the same extract from the heartwood has yielded two novel anthrone derivatives, chamaecypanones A **1** and B **2**, a new lignan, isootobanone **3**, and a novel lignan, obtulignolide **4** together with otobanone **5**.[4] The structural elucidation and proposed biosynthetic pathway of these compounds are reported here.

Chamaecypanone A **1**[5] had the molecular formula $C_{20}H_{16}O_6$ on the basis of mass spectroscopy (HRMS). It showed aromatic (3080, 1622, 1600, and 1499 cm^{-1}), isolated carbonyl (1721 cm^{-1}), and conjugated carbonyl (1664 cm^{-1}) absorptions in its IR spectrum. The UV spectrum indicated a benzoyl group (λ_{max} 250, 301, and 345 nm), and the ^1H NMR spectrum revealed two *ortho* aromatic protons [δ 7.88 and 6.92 (both d, $J=8.3$ Hz)], two *para* aromatic protons [δ 7.68 and 6.68 (both s)], and two methylenedioxyl groups attached to different aromatic groups [δ_H 6.02 (2H, s), δ_C 101.8; δ_H 6.08 and 6.16 (both s), δ_C 102.3]. Twelve low field signals between δ_C 105 and 155 (Table 1) and a very low field signal at δ_C 181.8 indicated that **1** contained two aromatic rings and one conjugated carbonyl group. Four downfield ^{13}C NMR signals at δ 151.5, 147.7, 150.9, and 143.4 were assigned as two pairs of vicinal oxygenated phenyl carbons bonded to two methylenedioxyl groups. Two lower field proton signals at δ 7.88 (H-8) and 7.68 (H-1) suggested that they were located *ortho* to the carbonyl group due to deshielding from this functionality. Meanwhile, H-1 and H-8 showed HMBC correlation with the carbonyl group at δ_C 181.8 which revealed the presence of a benzophenone moiety. The remaining four aromatic ^{13}C NMR signals at δ 136.5 (C-4a), 128.7 (C-9a), 127.4 (C-8a) and 125.8 (C-10a) were all quaternary carbons. A methine proton at δ 5.02 (1H, d, $J=2.2$ Hz, H-10; δ_C 37.7) exhibited a NOESY correlation with δ 6.68 (H-4; δ_C 107.8), demonstrating that the signal at δ 5.02 was a benzylic proton. The HMBC correlation was displayed as follows: 7.88/127.4, 181.8; 7.68/128.7, 181.8; 5.02/136.5, 107.8, 125.8, and 143.4. This suggested that it is an anthrone derivative. A C_4 unit was discerned from four other ^{13}C NMR signals at δ_C 28.7 (CH_3), 209.8 (C), 52.9 (CH), and 10.1 (CH_3). Thus, in conjunction with ^1H NMR signals at δ 2.29 (3H, s), 3.02 (1H, qd, $J=7.2$, 2.2 Hz), and 0.58 (3H, d, $J=7.2$ Hz), proved the C_4 alkyl group was 2-oxobut-3-yl. On irradiation at δ 3.02, the signals at δ 5.02 and 0.58 both collapsed to give a singlet. Based on the above evidence and HMBC correlation, **1** could be assigned as 2,3,5,6-dimethylenedioxy-

Keywords: anthrone; 3,4-secophenyltetrahydronaphthalene-type lignan; phenyltetrahydronaphthalene-type lignan; *Chamaecyparis obtusa* var. *formosana*; Mosher ester.

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Table 1. ^{13}C NMR data of **1**, **2**, **3**, **4** and **5** (100 MHz in $CDCl_3$)

No.	**1**	**2**	No.	**3**	**4**	**5**
1	106.6	147.9	1	136.0	135.7	137.6
2	147.7	147.9	2	108.5	108.4	108.7
3	151.5	111.8	3	147.8	147.8	147.5
4	107.8	121.3	4	146.3	146.3	146.0
4a	136.5	132.4	5	108.2	108.1	107.8
5	143.4	143.5	6	121.0	120.8	122.0
6	150.9	151.2	7	45.7	47.9	49.1
7	108.1	108.1	8	43.3	43.1	47.5
8	123.2	123.3	9	12.6	18.7	12.5
8a	127.4	128.1	1′	127.5	123.3	127.8
9	181.8	182.2	2′	123.7	122.8	126.8
9a	128.7	118.1	3′	145.7	146.1	145.1
10	37.7	38.0	4′	151.7	150.5	151.8
10a	125.8	125.4	5′	107.6	107.3	107.6
1′	28.7	28.9	6′	122.7	127.5	122.7
2′	209.8	209.7	7′	198.7	167.6	198.7
3′	52.9	53.6	8′	40.9	159.5	43.5
4′	10.1	10.4	9′	15.4	101.8	17.6
$-OCH_2O-$	101.8, 102.3	102.6, 102.4		102.0, 101.0	101.7, 101.0	101.6, 100.9

10-(2-oxobut-3-yl)anthrone. H-10, seen at lower field (δ 5.02), indicated that the benzylic proton must be in a quasi-equatorial orientation, being deshielded by the oxygen atom of the methylenedioxyl group. H_3-4′ appeared at high field (δ 0.58) due to its quasi-axial orientation and being shielded by a aromatic group.[6]

The MS of **2**[5] gave an identical exact mass to **1** indicating the molecular formula $C_{20}H_{16}O_6$. The IR absorption (1715 and 1670 cm^{-1}) and UV absorption bands (λ_{max} 239, 293 and 331 nm) of **2** were similar to **1** indicating that **2** was an isomer of **1**. The ^1H and ^{13}C NMR (Table 1) spectra showed that **2** contained two methylenedioxyl groups bonded to both aromatic groups [δ_H 6.19, 6.17, 6.12 and 6.09 (each 1H, s); δ_c 102.6 and 102.4], two pairs of *ortho* aromatic protons [δ 7.86, 6.91 (both 1H, d, $J=8.3$ Hz), 6.90, 6.67 (both 1H, d, $J=8.3$ Hz)]. Two aromatic rings, one conjugated carbonyl group (δ 182.2) and C-10 (δ 38.0) revealed an anthrone derivative from its ^{13}C NMR spectrum. The signals at δ 2.25 (3H, s; δ_C 28.9), δ_C 209.7, δ 2.95 (1H, qd, $J=7.1$, 2.8 Hz; δ_C 53.6), and δ 0.63 (3H, d, $J=7.1$ Hz; δ_C 10.4) coincided with the presence of a 2-oxobut-3-yl moiety. The low field benzylic proton H-10 at δ 4.97 (1H, d, $J=2.8$ Hz) displayed strong deshielding from the methylenedioxyl group and had a NOESY correlation with H-4 (δ 6.67). Along with the high field methyl group (δ 0.63) in the C_4 unit, the H-10 and C_4 units can be assigned as having a quasi-equatorial and quasi-axial orientation, respectively. After comparison of spectral data between **2** and **1** and addition of HMBC, NOESY and decoupling techniques, the structure of chamaecypanone B **2** was elucidated as 1,2,5,6-dimethylenedioxy-10-(2-oxobut-3-yl)anthrone. Therefore, compounds **1** and **2** are constitutional isomers.

Isootobanone **3** suggested the presence of the benzoyl moiety in its UV absorption (λ_{max} 235, 285, and 312 nm) and IR absorption bands (3070, 1686, 1626, 1588 and 1505 cm^{-1}). The ^1H NMR spectrum indicated the presence of two secondary methyl groups [δ 1.08 (d, $J=6.9$ Hz), 1.02 (d, $J=7.1$ Hz)], two methylenedioxyphenyl groups [δ 5.93, 5.92 (both 2H, s), 7.73, 6.83 (both 1H, d, $J=8.4$ Hz), 6.70 (1H, d, $J=8.0$ Hz), 6.57 (1H, d, $J=1.7$ Hz), and 6.48 (1H, dd, $J=8.0$, 1.7 Hz)]. Isootobanone **3** had the molecular formula $C_{20}H_{18}O_5$ based on its HRMS and exhibited similar ^1H and ^{13}C NMR (Table 1) spectral signals as otobanone **5** (isolated from the same source). The difference between **3** and **5** was only in the relative configuration of the methyl group. The signal of H-7 in **5**[4] showed a large coupling constant at δ 3.72 (d, $J=9.2$ Hz). The chemical shift of methylenedioxy protons attached on ring A were markedly different [δ 5.66 and 5.74 (d, $J=1.2$ Hz)] and higher field than on ring C [δ 5.90 (2H, s)]. The evidence demonstrated that the aryl group of **5** was in a quasi-equatorial orientation, and exhibited a shielding effect to the methylene protons in ring A. In **3**, H-7 exhibited at low field shift (δ 4.14) with a small coupling constant ($J=2.4$ Hz), which indicated that H-7 was in a quasi-equatorial orientation, being deshielded by the methylenedioxyl group on the ring A. The relative configuration of **3** was determined by a NOESY technique (see structure **6**). The absolute configuration of **5** and **3** were determined by the modified Mosher's method[7] as follows. Sodium borohydride ($NaBH_4$) reduction of **5** gave two products **7a** and **8** (7:1 ratio). Based on the ^1H NMR data analysis,[5] H-7 (d, $J=9.6$ Hz), H-8, H-7′ (d, $J=8.8$ Hz), and H-8′ are all in the axial orientation in **7a**, and **8** [H-7 (d, $J=9.6$ Hz) and H-7′ (br s)] is a C-7′ epimer of **7a**. The reduction of **3** with $NaBH_4$ yielded only one product **9a**, the hydride attacked from the less hindered α-face to produce the axial hydroxyl group. Due to a 1,3-diaxial interaction between C-7′ OH and C-8 CH_3, the conformation of the aryl group was quasi-equatorial in **9a** (Fig. 1). The relative configuration was confirmed by ^1H NMR data [δ 4.87 (d, $J=5.2$ Hz, H-7′), 3.62 (d, $J=8.4$ Hz, H-7), 5.66 and 5.73 (both 1H, s, $-OCH_2O-$

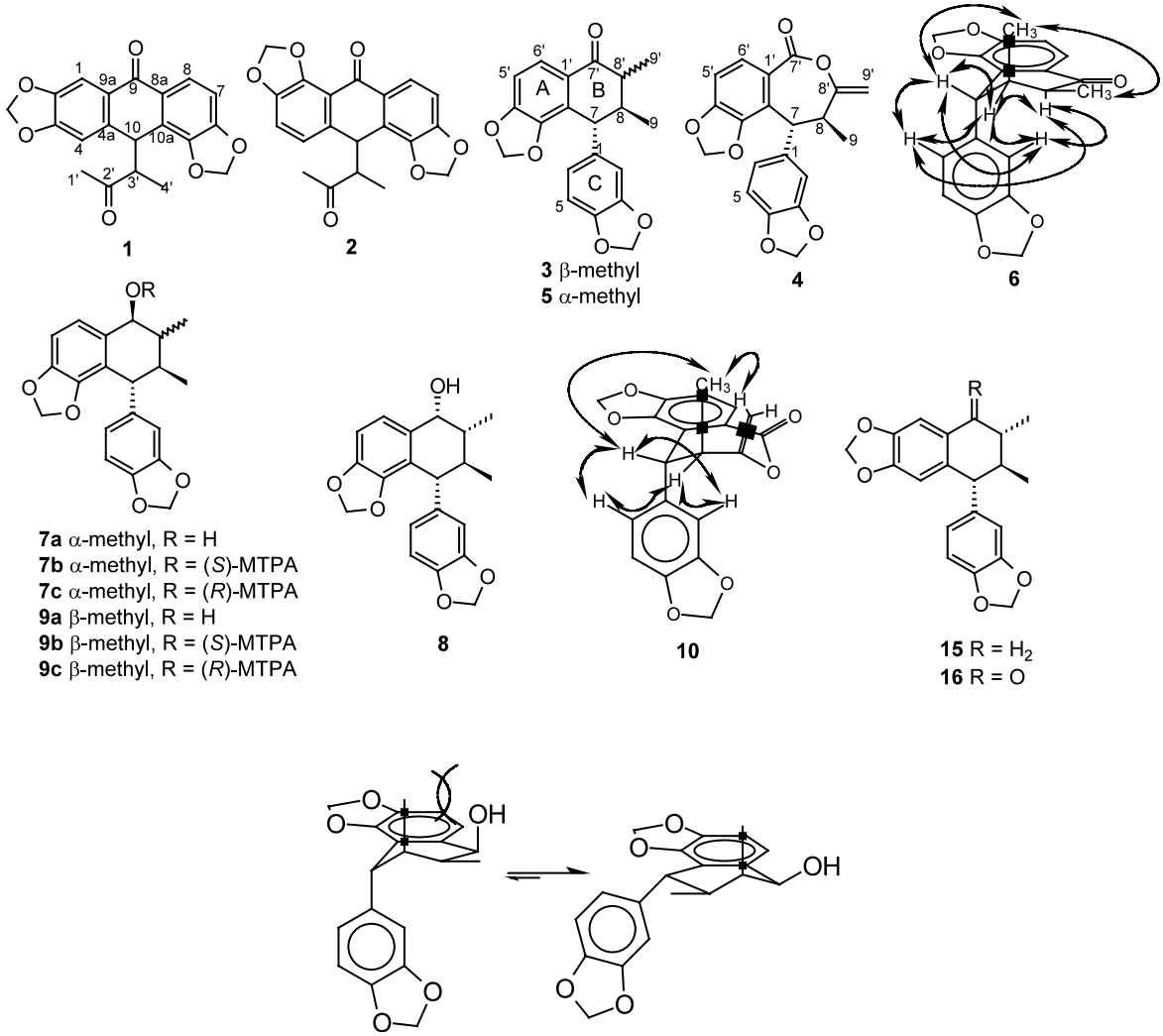


Figure 1. Conformational interconversion of **9a**.

of ring A)]. Treatment of **7a** with (*R*)- and (*S*)-2-methoxy-2-trifluoromethyl-2-phenylacetyl chloride (MTPACl) afforded the (*R*)- and (*S*)-MTPA esters (**7b** and **7c**, respectively). $\Delta\delta$ values (δ_S-δ_R) of H-6′ (+80.0) and H-5′ (+41.2) showed positive values, while those of H-8′ (−3.4), H_3-9′ (−32.6), H-8 (−8.2), and H_3-9 (−15.2) were negative (Fig. 2), thus indicating a 7′*S*-configuration. Therefore, the absolute configurations at C-8′, C-8, and C-7 of **7a** were assigned as *R*, *S*, and *R*, respectively. Thus, the absolute configurations at C-8′, C-8, and C-7 of **5** were the same as those of **7a**. Compound **9a** was converted to (*S*)-MTPA (**9b**) and (*R*)-MTPA (**9c**) as mentioned above. Using the modified Mosher's method,[7] the absolute configuration at C-8′, C-8, and C-7 of **9a** (see Fig. 3) were assigned as *S*, *S*, and *R*, respectively. Therefore, the absolute configuration of **3** was determined. The different conformation of the aryl substituted group in **3** and **9a** was revealed from the coupling constant of H-7 ($J=2.4$ Hz in **3**; $J=8.4$ Hz in **9a**). Based on the above evidence, **3** is a C-8′ epimer of **5**.

Obtulignolide **4** was given the molecular formula $C_{20}H_{16}O_6$, and its IR spectrum shows the presence of an

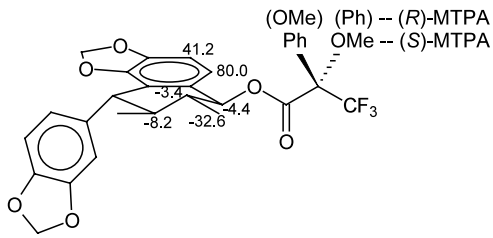


Figure 2. $\Delta\delta$ values [$\Delta\delta$ (in Hz) $=\delta_S$–δ_R] obtained for the (*S*)- and (*R*)-MTPA esters (**7b** and **7c**, respectively).

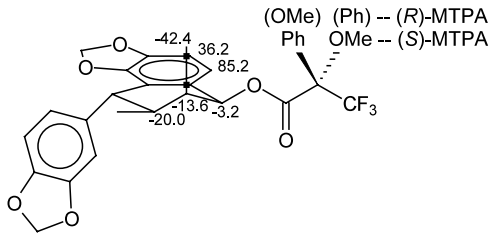
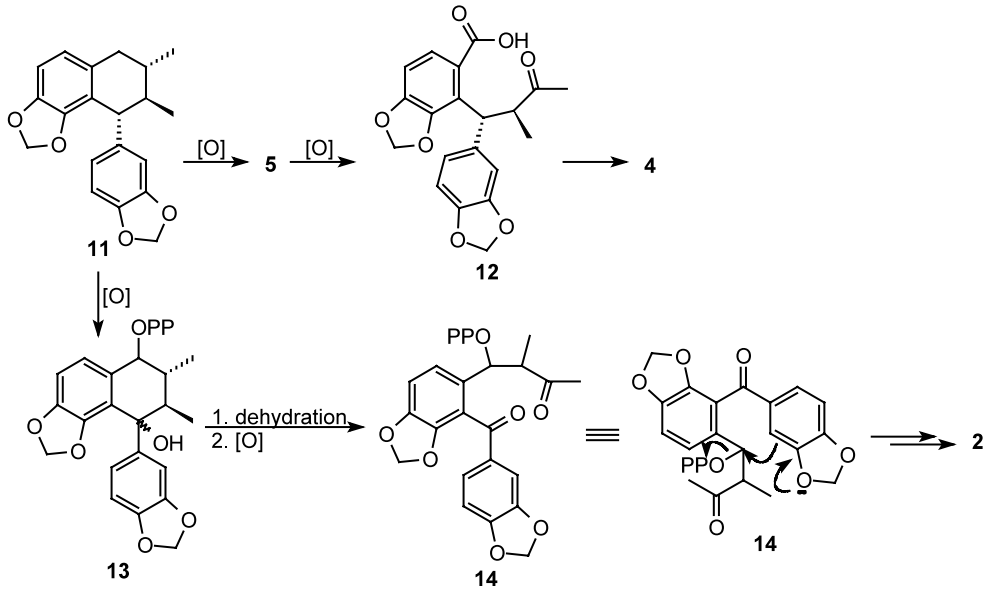


Figure 3. $\Delta\delta$ values [$\Delta\delta$ (in Hz) $=\delta_S$–δ_R] obtained for the (*S*)- and (*R*)-MTPA esters (**9b** and **9c**, respectively).



Scheme 1. Proposed biotransformations leading to **2** and **4**.

ester, a terminal double bond, and aromatic groups (3024, 1735, 1670, 1607, and 1593 cm^{-1}). The ^1H NMR spectrum showed the following: δ 1.27 (3H, d, $J=6.9$ Hz), 3.34 (1H, qd, $J=6.9$, 4.6 Hz, H-8), 4.18 (1H, d, $J=4.6$ Hz, H-7), 4.62 and 4.79 (both 1H, s, H-9′), 6.75, 7.39 (both 1H, d, $J=8.1$ Hz, H-5′, -6′), 6.64 (1H, dd, $J=8.1$, 1.5 Hz, H-6), 6.67 (1H, d, $J=1.5$ Hz, H-2), and 6.68 (1H, d, $J=8.1$ Hz, H-5). The ^1H NMR signals [δ 5.89 (2H, s), 5.95, and 5.97 (both 1H, s)] and ^{13}C NMR signals (Table 1) (δ_C 101.0 and 101.7) indicated that the two methylenedioxyl groups were bonded to different aromatic groups. Removal of $C_2H_4O_4$ (two methylenedioxyl units) from the formula $C_{20}H_{16}O_6$ would afford a phenyltetrahydronaphthalene-type lignan with one lactone, one terminal methylene, and one secondary methyl group. The carbonyl terminal of the lactone was conjugated with the aryl group; this was discerned from the UV absorptions (λ_{max} 291 and 226 nm) and NMR data (δ_C 167.6 and low field aromatic proton δ_H 7.39). The ^{13}C NMR signals of the terminal double bond appeared at δ_C 101.8 and 159.5, this indicated the *O*-terminal of lactone was bonded to the double bond. The low field shift of H-7 (δ 4.18) and methylenedioxyl protons of the A ring at δ 5.95 and δ 5.97 gave the conclusion that H-7 and the aryl groups attached to C-7 were in a quasi-equatorial and quasi-axial orientation, respectively. HMBC analysis confirmed the assigned structure. The relative configuration was elucidated by a NOESY technique (structure **10**), and was ascribed to a 3′,4′-secophenyltetrahydronaphthalene-type lignan, a novel skeleton.

Compounds **2** and **4** are supposed to derive from otobain **11**. The proposed biosynthesis of these compounds is shown in Scheme 1. Oxidation of **11** yields otobanone **5** and then further oxidation gives ketoacid **12**. After enolization and lactonization of **12**, obtulignolide **4** was produced. By another biooxidative pathway, the biotransformation product of **11** was proposed to be **13** which was dehydrated and then subsequently oxidized to yield diketone **14**. **14** produced chamaecypanone B **2** via cyclization. Chamaecypanone A **1** was proposed to derive from cagayanin **15**[4] (cagayanone **16**[4] was also isolated from the same source) by a similar biosynthetic pathway to that shown in Scheme 1.

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4. Kuo, Y. H.; Lin, S. T.; Wu, R. E. *Chem. Pharm. Bull.* **1989**, *37*, 2310.
5. Compound **1**: mp 155–156°C; $[\alpha]_D^{25}$ +7.5 (*c* 0.17, $CHCl_3$); HR-EIMS *m*/*z* 352.0951 (calcd for $C_{20}H_{16}O_6$: 352.0947); IR (KBr) cm^{-1}: 3080, 1721, 1664, 1622, 1600, 1499, 1477; UV (MeOH) λ_{max} nm (log ε): 250 (4.41), 301 (3.86), 345 (4.10). Compound **2**: mp 158–159°C; $[\alpha]_D^{25}$ −37.7 (*c* 0.21, $CHCl_3$); HR-EIMS *m*/*z* 352.0946 (calcd for $C_{20}H_{16}O_6$: 352.0947); IR (KBr) cm^{-1}: 3085, 1715, 1670, 1627, 1594, 1506; UV (MeOH) λ_{max} nm (log ε): 239 (4.16), 293 (3.79), 331 (3.82). Compound **3**: Amorphous; $[\alpha]_D^{26}$ −55.9 (*c* 0.72, $CHCl_3$); HR-EIMS *m*/*z* 338.1147 (calcd for $C_{20}H_{18}O_5$: 338.1154); UV (MeOH) λ_{max} nm (log ε): 235 (4.19), 285 (3.85), 312 (3.67); CD (MeOH): $[\theta]_{224}$ −163996, $[\theta]_{255}$ −16831, $[\theta]_{300}$ −56478, $[\theta]_{334}$ −315950; ^1H NMR (500

MHz, $CDCl_3$): δ 2.31, 2.81 (each 1H, m, H-8, -8′). Compound **4**: Amorphous; $[\alpha]_D^{25}$ −2.8 (*c* 0.25, $CHCl_3$); HR-EIMS *m*/*z* 352.0944 (calcd for $C_{20}H_{16}O_6$: 352.0947); UV (MeOH) λ_{max} nm (log ε): 226 (3.91), 291 (3.57); CD (MeOH): $[\theta]_{248}$ +91520, $[\theta]_{270}$ +399142, $[\theta]_{300}$ −192359. Compound **5**: $[\alpha]_D^{20}$ −27.1 (*c* 0.70, $CHCl_3$); CD (MeOH): $[\theta]_{256}$ +9050, $[\theta]_{273}$ +15870, $[\theta]_{295}$ −8680, $[\theta]_{300}$ −7450, $[\theta]_{330}$ +1570. Compound **7a**: a colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (3H, d, *J*=6.4 Hz, H_3-9), 1.16 (3H, d, *J*=6.4 Hz, H_3-9′), 1.41 (1H, m, H-8′), 1.52 (1H, m, H-8), 3.48 (1H, d, *J*=9.6, H-7), 4.35 (1H, d, *J*=8.8 Hz, H-7′), 5.60, 5.69 (both 1H, d, *J*=1.2 Hz, -OCH_2O-), 5.90 (2H, s, -OCH_2O-), 6.51 (1H, d, *J*=2.0 Hz, H-2), 6.59 (1H, dd, *J*=8.0, 2.0 Hz, H-6), 6.68 (1H, d, *J*=8.0 Hz, H-5), 6.72 (1H, d, *J*=8.0 Hz, H-5′), 7.14 (1H, d, *J*=8.0 Hz, H-6′). Compound **7b**: a colorless oil; EI-MS (70 eV) *m*/*z* (rel. int.%): 556 (M^+, 1), 322 (100), 277 (40); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, d, *J*=6.4 Hz, H_3-9′), 0.91 (3H, d, *J*=6.4 Hz, H_3-9), 1.61 (1H, m, H-8), 1.77 (1H, m, H-8′), 3.49 (1H, d, *J*=10.0 Hz, H-7), 3.56 (3H, br s, OMe), 5.60, 5.68 (both 1H, d, *J*=1.2 Hz, -OCH_2O-), 5.90 (2H, s, -OCH_2O-), 6.03 (1H, d, *J*=9.6 Hz, H-7′), 6.49 (1H, d, *J*=8.0 Hz, H-6′), 6.50 (1H, d, *J*=2.0 Hz, H-2), 6.55 (1H, dd, *J*=8.0, 2.0 Hz, H-6), 6.59 (1H, d, *J*=8.0 Hz, H-5′), 6.68 (1H, d, *J*=8.0 Hz, H-5), 7.42 (3H, m), 7.62 (2H, m). Compound **7c**: a colorless oil; EI-MS (70 eV) *m*/*z* (rel. int.%): 556 (M^+, 1), 322 (100), 277 (37); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, d, *J*=6.4 Hz, H_3-9), 0.97 (3H, d, *J*=7.6 Hz, H_3-9′), 1.63 (1H, m, H-8), 1.78 (1H, m, H-8′), 3.48 (1H, d, *J*=9.6, H-7), 3.59 (3H, br s, OMe), 5.59, 5.65 (both 1H, d, *J*=1.2 Hz, -OCH_2O-), 5.90 (2H, s, -OCH_2O-), 6.04 (1H, d, *J*=9.6 Hz, H-7′), 6.29 (1H, d, *J*=8.0 Hz, H-6′), 6.48 (1H, d, *J*=8.0 Hz, H-5′), 6.50 (1H, d, *J*=2.0 Hz, H-2), 6.55 (1H, dd, *J*=8.0, 2.0 Hz, H-6), 6.68 (1H, d, *J*=8.0 Hz, H-5), 7.43 (3H, m), 7.64 (2H, m). Compound **8**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (3H, d, *J*=6.8 Hz, H_3-9), 1.14 (3H, d, *J*=6.8 Hz, H_3-9′), 1.98 (1H, m, H-8), 1.61 (1H, m, H-8′), 3.38 (1H, d, *J*=9.6 Hz, H-7), 4.53 (1H, br s, H-7′), 5.63, 5.71 (both 1H, d, *J*=1.2 Hz, -OCH_2O-), 5.89 (2H, br s, -OCH_2O-), 6.66 (1H, dd, *J*=8.0, 2.0, H-6), 6.67 (1H, d, *J*=8.0 Hz, H-5′), 6.68 (1H, d, *J*=2.0 Hz, H-2), 6.68 (1H, d, *J*=8.0 Hz, H-5), 6.78 (1H, d, *J*=8.0 Hz, H-6′). Compound **9a**: mp 172–175°C; $[\alpha]_D^{26}$ −35.1 (*c* 0.30, $CHCl_3$); EI-MS (70 eV) *m*/*z* (rel. int.%): 340 (M^+, 20), 322 (46), 277 (16), 61 (100); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (3H, d, *J*=7.2 Hz, H_3-9′), 1.01 (3H, d, *J*=7.2 Hz, H_3-9), 1.94 (1H, m, H-8), 2.11 (1H, m, H-8′), 3.62 (1H, d, *J*=8.4 Hz, H-7), 4.87 (1H, d, *J*=5.2 Hz, H-7′), 5.66, 5.73 (both 1H, d, *J*=1.2 Hz, -OCH_2O-), 5.89 (2H, s, -OCH_2O-), 6.48 (1H, br s, H-2), 6.51 (1H, br d, *J*=8.0 Hz, H-6), 6.67 (1H, d, *J*=8.0 Hz, H-5), 6.75 (1H, d, *J*=8.0 Hz, H-5′), 7.08 (1H, d, *J*=8.0 Hz, H-6′). Compound **9b**: a colorless oil; EI-MS (70 eV) *m*/*z* (rel. int.%): 556 (M^+, 16), 322 (100), 277 (26); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.72 (3H, d, *J*=7.2 Hz, H_3-9′), 0.97 (3H, d, *J*=6.8 Hz, H_3-9), 1.91 (1H, m, H-8), 2.27 (1H, m, H-8′), 3.52 (3H, br s, OMe), 3.88 (1H, d, *J*=4.4, H-7), 5.78, 5.81 (both 1H, d, *J*=1.2 Hz, -OCH_2O-), 5.89 (2H, s, -OCH_2O-), 6.31 (1H, d, *J*=4.4 Hz, H-7′), 6.38 (1H, dd, *J*=8.0, 1.6 Hz, H-6), 6.43 (1H, d, *J*=1.6 Hz, H-2), 6.66 (1H, d, *J*=8.0 Hz, H-5), 6.71 (1H, d, *J*=8.0 Hz, H-5′), 6.86 (1H, d, *J*=8.0 Hz, H-6′), 7.35 (3H, m), 7.51 (2H, m). Compound **9c**: a colorless oil; EI-MS (70 eV) *m*/*z* (rel. int.%): 556 (M^+, 60), 322 (100), 277 (14); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (3H, d, *J*=7.2 Hz, H_3-9′), 0.96 (3H, d, *J*=7.2 Hz, H_3-9), 1.96 (1H, m, H-8), 2.31 (1H, m, H-8′), 3.52 (3H, br s, OMe), 3.75 (1H, d, *J*=6.4, H-7), 5.71, 5.75 (both 1H, d, *J*=1.2 Hz, -OCH_2O-), 5.90 (2H, s, -OCH_2O-), 6.31 (1H, d, *J*=4.4 Hz, H-7′), 6.43 (1H, dd, *J*=8.0, 2.0 Hz, H-6), 6.44 (1H, d, *J*=1.6 Hz, H-2), 6.66 (1H, d, *J*=8.0 Hz, H-5), 6.62 (1H, d, *J*=8.0 Hz, H-5′), 6.64 (1H, d, *J*=8.0 Hz, H-6′), 7.38 (3H, m), 7.55 (2H, m).

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7. Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092.