Four New 2-(2-Phenylethyl)chromone Derivatives from Withered Wood of *Aquilaria sinensis*

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Four new chromone derivatives, 5-hydroxy-6-methoxy-2-(2-phenylethyl)chromone (1), 6-hydroxy-2-(2-hydroxy-2-phenylethyl)chromone (2), 8-chloro-2-(2-phenylethyl)-5,6,7-trihydroxy-5,6,7,8-tetrahydrochromone (3), 6,7-dihydroxy-2-(2-phenylethyl)-5,6,7,8-tetrahydrochromone (4) were isolated from the MeOH extract of withered wood of *Aquilaria sinensis*, together with seven known constituents of agarwood.

Key words *Aquilaria sinensis*; Thymelaeaceae; withered wood; agarwood; chromone derivative

Agarwood ('Jinkoh' in Japanese) is a famous incense and is used as a sedative, analgesic and digestive in Kampo medicine. From agarwood, characteristic sesquiterpenes[2—8)] and chromone derivatives[9—16)] have been isolated. These compounds, together with the pyrolyzation products, constitute a pleasant odor when agarwood is burnt,[17,18)] and combinations of these compounds make up various qualities of agarwood. Although the resinous part of agarwood is formed by decay, injury, *etc.*, of the tree of the *Aquilaria* species (Thymelaeaceae), this process has not been understood in detail. Examination of the chemical constituents of the damaged wood would offer valuable information for understanding the bioorganic process of agarwood formation. In the present paper, we describe the isolation and structure elucidation of four new chromone derivatives (**1**—**4**), together with seven known chromones, from the MeOH extract of withered wood of *A. sinensis*, an original plant of agarwood (Chart 1).

Results and Discussion

Withered wood of *A. sinensis* GILG grown in Taiwan was extracted with MeOH, and the MeOH extract was fractionated to hexane-, AcOEt- and BuOH-soluble fractions. The hexane-soluble fraction was separated by silica gel column chromatography to yield a new 2-(2-phenylethyl)-chromone **1**, together with five known compounds: flindersiachromone,[9)] AH_3,[10)] AH_4,[10)] AH_5[10)] and AH_6.[10)] The AcOEt-soluble fraction was separated by silica gel and reversed-phase silica gel column chromatography to yield a new 2-(2-phenylethyl)chromone **2**, two new 2-(2-phenylethyl)-5,6,7,8-tetrahydrochromones **3** and **4**, and two known dimeric chromones AH_{10}[11)] and AH_{14}[12)] (Chart 1). The structures of the known compounds were confirmed by comparison of the physical and spectral data with those reported.

Compound **1** was obtained as yellow needles with the molecular formula of $C_{18}H_{16}O_4$. The UV absorption maxima at 349 and 242 nm, and the IR absorption at 1655, 1624 and 1585 cm^{-1} suggested the presence of a chromone ring. Its ^{1}H-NMR spectrum (Table 1) showed the presence of a hydroxyl (δ_H 12.77), a methoxyl (δ_H 3.85) and a pair of *ortho*-coupled aromatic (δ_H 6.95, 7.39, each d, J=8.9 Hz) protons. The ^{13}C-NMR spectrum (Table 2) in pyridine-d_5 was in good agreement with that of AH_4[10)] except for the carbons of the chromone system. From the heteronuclear multiple bond connectivity (HMBC) spectrum (Fig. 1), the hydroxyl group was located at C-5 because the hydroxyl proton (δ_H 12.77) and the proton at C-3 (δ_H 6.11) correlated with the same carbon at C-4a (δ_C 111.31). The methoxyl group was located at C-6, because the aromatic carbon (δ_C 144.18) which correlated with the methoxyl protons (δ_H 3.85) also correlated with the hydroxyl proton (δ_H 12.77) at C-5. Thus, compound **1** was determined to be 5-hydroxy-6-methoxy-2-(2-phenylethyl)chromone.

Compound **2** was obtained as a white powder with the molecular formula of $C_{17}H_{14}O_4$. The presence of a chromone ring was suggested from the UV and IR spectra. The ^{13}C-NMR spectrum of **2** (Table 2) was very similar to that of AH_3[10)] except for the methylenes (C-7′, C-8′): one of the methylenes was replaced by an oxymethine group (δ_C 71.37). This was confirmed by the presence of ABX-type signals at δ_H 3.14 (1H, dd, J=14.3, 4.6 Hz), 3.20 (1H, dd, J=14.3, 8.7 Hz) and δ_H 5.53 (1H, dd, J=8.7, 4.6 Hz) in the ^{1}H-NMR (Table 1). The oxymethine group was located at C-7′, because the oxymethine proton (δ_H 5.53) correlated with the C-2′, 6′ carbons (δ_C 126.41) in the HMBC spectrum (Fig. 1). Thus, the structure of **2** was determined to be 6-hydroxy-2-(2-hydroxy-2-phenylethyl)chromone. A reaction of **2** with (*S*)-2-methoxy-2-trifluoromethyl-2-phenylacetic acid (MTPA) in the presence of dicyclohexylcarbodiimide (DCC) gave a mixture of diastereomeric esters **2a** and **2b** (5 : 2), indicating **2** to be a mixture of the enantiomers at C-7′.[19)]

Compound **3** was obtained as a white amorphous solid. High-resolution fast atom bombardment-MS (HR-FAB-MS) analysis revealed the presence of a chlorine atom, and the molecular formula was determined to be $C_{17}H_{17}O_5Cl$ [*m/z*: 337.0833 $[M+H]^+$ (Calcd for $C_{17}H_{18}O_5Cl$: 337.0832)]. The UV and IR spectra suggested the presence of a chromone ring. Its ^{1}H-NMR spectrum (Table 1) showed the signals of four consecutive methine protons [δ_H 5.75 (1H, d, J=3.5 Hz), δ_H 4.92 (1H, dd, J=3.5, 1.6 Hz), δ_H 5.17 (1H, dd, J=7.4, 1.6 Hz) and δ_H 5.62 (1H, d, J=7.4 Hz)]. The ^{13}C-NMR chemical shifts of **3** (Table 2) were similar to those of isoagarotetrol,[13)] except for the carbons of the cyclohexene ring. One methine carbon appeared at higher field (δ_C 59.79) than those of the other methines (δ_C 66.31, 73.70, 74.24), suggesting that this carbon was chlorinated. In the HMBC spectrum (Fig. 2a), the methine proton at δ_H 5.75, which is located at one end of the consecutive methines from the cou-

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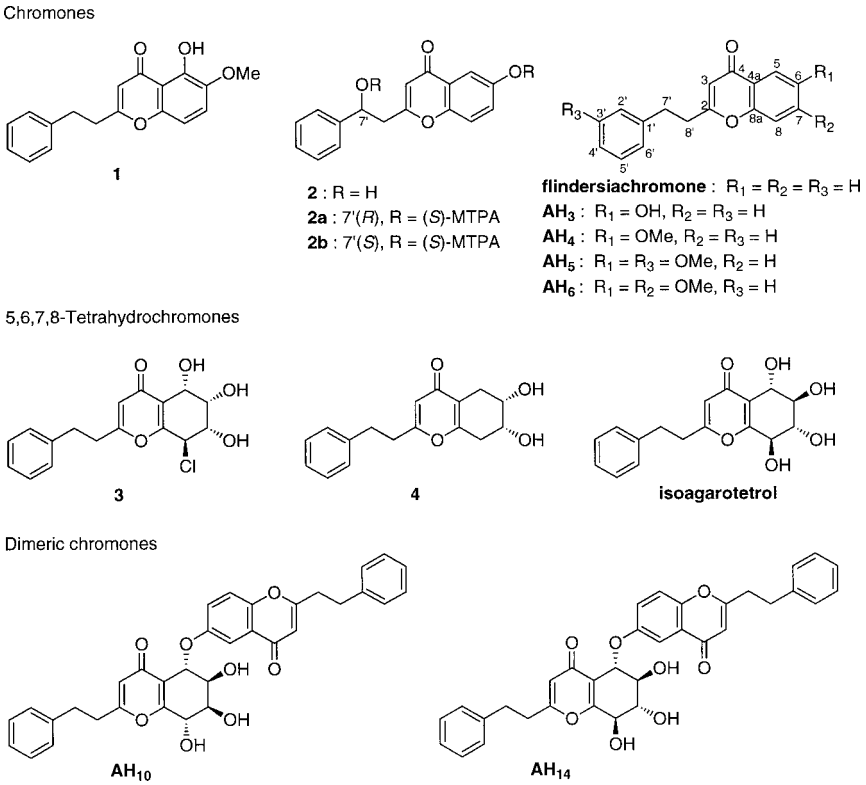

Chart 1. Structures of Chromone Derivatives

Table 1. ^{1}H-NMR Spectra of Compounds **1**—**4**

No.	**1**[a)]	**2**[b)]	**3**[b)]	**4**[b)]
3	6.11 (1H, s)	6.59 (1H, s)	6.27 (1H, s)	6.23 (1H, s)
5		8.02 (1H, m)	5.75 (1H, d, *J*=3.5 Hz)	3.26 (1H, dd, *J*=16.8, 6.0 Hz)
				3.03 (1H, dd, *J*=16.8, 3.4 Hz)
6			4.92 (1H, dd, *J*=3.5, 1.6 Hz)	4.40 (1H, m)
7	7.39 (1H, d, *J*=8.9 Hz)	7.44 (2H, m)	5.17 (1H, dd, *J*=7.4, 1.6 Hz)	4.42 (1H, m)
8	6.95 (1H, d, *J*=8.9 Hz)		5.62 (1H, d, *J*=7.4 Hz)	3.16 (1H, dd, *J*=17.2, 6.1 Hz)
				2.95 (1H, dd, *J*=17.2, 4.3 Hz)
2′, 6′	7.27 (4H, m)	7.69 (2H, d, *J*=7.3 Hz)	7.20 (2H, m)	7.20 (2H, m)
3′, 5′		7.39 (2H, t, *J*=7.3 Hz)	7.28 (2H, t, *J*=7.2 Hz)	7.28 (2H, t, *J*=7.2 Hz)
4′	7.19 (1H, m)	7.29 (1H, t, *J*=7.3 Hz)	7.19 (1H, m)	7.20 (1H, m)
7′	3.08 (2H, t, *J*=7.1 Hz)	5.53 (1H, dd, *J*=8.7, 4.6 Hz)	2.86 (2H, m)	2.83 (2H, t, *J*=7.6 Hz)
8′	3.01 (2H, t, *J*=7.1 Hz)	3.14 (1H, dd, *J*=14.3, 4.6 Hz)	2.71 (2H, m)	2.67 (2H, t, *J*=7.6 Hz)
		3.20 (1H, dd, *J*=14.3, 8.7 Hz)		
6-OMe	3.85 (3H, s)			
5-OH	12.77 (1H, s)			

a) in acetone-d_6, *b*) in pyridine-d_5.

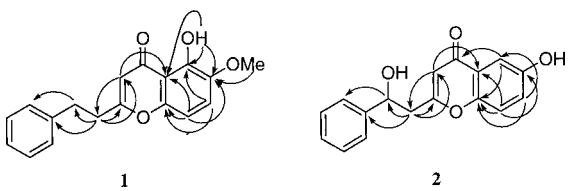

Fig. 1. Selected HMBC Correlations of Compounds **1** and **2**

pling pattern, showed a correlation peak with the carbonyl carbon (δ_C 179.43), indicating that it is located at C-5. The methine proton (δ_H 5.62), which was attached on the chlorinated carbon (δ_C 59.79) and located at the other end of the methines, showed correlation peaks with the carbons at C-8a (δ_C 159.15) and C-4a (δ_C 124.00). This indicated the chlorine atom to be located at C-8. Thus, the structure of **3** was determined to be 8-chloro-2-(2-phenylethyl)-5,6,7-trihydroxy-5,6,7,8-tetrahydrochromone.

The relative stereochemistries of the methine carbons were determined by nuclear Overhauser effect (NOE) experiments and ^{1}H–^{1}H coupling constants. Irradiation of H-7 enhanced the signals of H-5 (1.4%) and H-6 (9.8%) (Fig. 2b), indicating *cis* relationships between these protons. The relatively large coupling constant between H-7 and H-8, together with the absence of NOE between these protons, revealed the *trans* pseudoaxial–axial relationship of these protons. Thus, the sterochemistry of the cyclohexene ring was concluded as shown in Fig. 2b. This was supported by the coupling con-

Table 2. ^{13}C-NMR Spectra of Compounds **1**—**4**

No.	**1**[a)]	**1**[b)]	AH_4[b),10)]	**2**[b)]	AH_3[b),10)]	**3**[b)]	Isoagarotetrol[b),13)]	**4**[b)]
2	171.76	170.76	168.34	166.98	168.32	168.43	169.1	167.29
3	108.27	107.94	109.61	111.11	109.37	113.71	113.6	112.49
4	184.80	184.37	177.35	177.77	177.79	179.43	180.9	178.96
5	150.54	150.34	105.72	108.95	108.96	66.31	71.9	27.51
6	144.18	143.77	157.12	156.21	156.24	74.24	74.8	68.83[c)]
7	121.07	120.55	123.03	123.38	123.48	73.70	75.2	68.55[c)]
8	106.59	106.14	119.73	119.80	119.61	59.79	70.9	33.99
8a	151.32	150.81	151.41	150.69	150.56	159.15	162.5	161.02
4a	111.31	111.21	124.91	125.47	125.29	124.00	121.6	119.57
1′	140.94	140.38	140.57	145.78	140.61	140.41	140.4	140.67
2′,6′	129.21[c)]	128.76	128.67	126.41	128.71	128.69	128.7	128.72
3′,5′	129.29[c)]	129.00	128.91	128.77	128.89	128.91	128.9	128.90
4′	127.15	126.86	126.76	127.73	126.70	126.72	126.8	126.69
7′	33.30	32.76	32.94	71.37	32.95	32.75	32.8	32.99
8′	36.40	35.85	35.76	45.26	35.82	35.17	35.2	35.06
6-OMe	57.27	57.08	55.61					

a) in acetone-d_6, *b*) in pyridine-d_5, *c*) may be interchanged in each column.

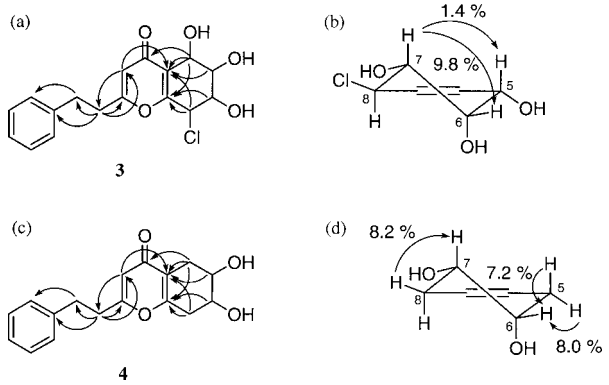

Fig. 2. (a) Selected HMBC Correlations and (b) Conformation of the Cyclohexene Ring of Compound **3** with Observed NOE and (c) Selected HMBC Correlations and (d) Conformation of the Cyclohexene Ring of Compound **4** with Observed NOE

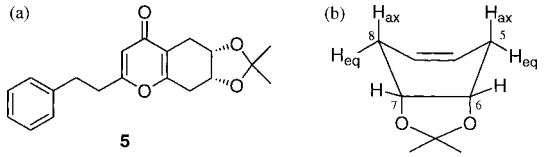

Fig. 3. (a) Structure and (b) Conformation of the Cyclohexene Ring of Acetonide **5**

Table 3. Calculated Dihedral Angles in Cyclohexene Ring of Acetonide **5**

	H_{5ax}-H_6	H_{5eq}-H_6	H_7-H_{8eq}	H_7-H_{8ax}
J (Hz)	4.4	1.8	1.8	4.7
Dihedral angle[a)]	51°	66°	66°	49°
Conduritol[19)]	53°	62°	62°	53°
Orientation	a′e	e′e	ee′	ea′

a) Calculated from *J* value by use of the equation $J=11.0\cos^2\phi$.

stants of the methine protons: they were in good agreement with those reported for the corresponding conduritol isomer.[20)]

Compound **4** was obtained as a brown amorphous solid with a molecular formula of $C_{17}H_{18}O_4$. The ^{13}C-NMR spectrum (Table 2) was similar to that of isoagarotetrol,[13)] except for the cyclohexene ring carbons: instead of four oxymethylenes, two methylenes (δ_C 27.51, 33.99) and two oxymethines (δ_C 68.55, 68.83) were observed. In the HMBC spectrum (Fig. 2c), the protons of one methylene [δ_H 3.03 (1H, dd, J=16.8, 3.4 Hz) and δ_H 3.26 (1H, dd, J=16.8, 6.0 Hz)] showed correlation peaks with the carbonyl carbons (δ_C 178.96) and C-4a (δ_C 119.57), indicating that they are located at C-5. The protons of the other methylenes [δ_H 2.95 (1H, dd, J=17.2, 4.3 Hz) and δ_H 3.16 (1H, dd, J=17.2, 6.1 Hz)] showed correlation peaks with the carbons at C-8a (δ_C 161.02) and C-4a (δ_C 119.57), suggesting that they are located at C-8. Thus, the positions of the hydroxyl groups were concluded to be at C-6 and C-7, and the structure of **4** was determined to be 6,7-dihydroxy-2-(2-phenylethyl)-5,6,7,8-tetrahydrochromone.

The relative stereochemistry of the diol was determined by NOE experiments. The signal intensity of H-6 was increased by irradiation of each of the H-5 protons (Fig. 2d), whereas that of H-7 was enhanced only by irradiation of the H-8 pseudoequatorial proton (δ_H 2.95) (8.2%), and not by that of the H-8 pseudoaxial proton (δ_H 3.16). Thus, the orientations of the hydroxyl groups were 6-axial and 7-equatorial in a half-chair form: *i.e.* 6,7-*cis* diol (Fig. 2d). The ^{1}H–^{1}H coupling constants of the cyclohexene ring protons supported this stereochemistry. To confirm the stereochemistry, **4** was converted to its acetonide **5** (Fig. 3a). The small ^{1}H–^{1}H coupling constants of the cyclohexene ring protons (Table 3) indicated that the ring took a half-boat form, and both H-6 and H-7 were in equatorial orientation (Fig. 3b). Therefore, **4** was determined to be 6,7-*cis*-dihydroxy-2-(2-phenylethyl)-5,6,7,8-tetrahydrochromone.

All of the known chromone derivatives isolated from withered wood of *A. sinensis* in this work were isolated from agarwood. However, none of the compounds including the new ones were detectable by thin-layer chromatography (TLC) in the extract of fresh wood of *A. sinensis*. Therefore, these compounds are assumed to be produced in the process of and/or after the death of the tree. The variety of substitution patterns of the hydroxyl and methoxyl groups[9—16)] and

the presence of a chlorinated compound make the biosynthetic process of these compounds quite interesting.

Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus. Optical rotations were recorded on a JASCO DIP-370 polarimeter. IR spectra were taken with a Shimadzu FT-IR-8700 spectrometer. UV spectra were recorded on a HITACHI U-3210 spectrophotometer. Mass spectra were measured using a JEOL TMS-HX/HX110A spectrometer. *m*-Nitrobenzylalchohol was used as a matrix for FAB-MS measurement. NMR spectra were measured on a JEOL JNM-LA500 (500 MHz for ^{1}H, 125 MHz for ^{13}C) spectrometer with tetramethylsilane as an internal standard and the chemical shifts are given in δ (ppm). Column chromatography was performed on Wakogel C-200 (75—150 μm, Wako) for normal phase and Cosmosil 75C_{18}-PREP (Nacalai Tesque) for reversed-phase. Medium-pressure liquid chromatography was performed on LiChroprep Si 60 (40—63 μm, Merck). For TLC, Silica gel 60 F_{254} and RP-18 F_{254S} precoated plates (Merck) were used and the spots were detected by UV absorption and spraying anisaldehyde-H_2SO_4 reagent or 10% H_2SO_4, followed by heating.

Plant Material A withered wood of *A. sinensis* was provided by T. H. Lo of Oriental Farm Ltd., Taipei, Taiwan.

Extraction and Isolation A withered wood of *A. sinensis* (1.0 kg) was cut into pieces and extracted three times with MeOH at room temperature for 2 d. The MeOH extract was concentrated and diluted with water to *ca.* 300 ml, which was extracted with hexane (300 ml×3) to give a hexane-soluble fraction (4.8 g). The aqueous MeOH layer was extracted with AcOEt and BuOH, to give AcOEt-soluble (12.3 g) and BuOH-soluble (4.0 g) fractions. The aqueous layer was concentrated to dryness to give a water-soluble fraction (5.4 g).

The hexane-soluble fraction (4.5 g) was fractionated by silica gel column chromatography with hexane : AcOEt=9 : 1—1 : 1 into 15 fractions. Further fractionation by silica gel column chromatography afforded compound **1** (17 mg) from fraction 9 with $CHCl_3$: AcOEt=19 : 1, flindersiachromone[9] (87 mg) from fraction 10 with $CHCl_3$: AcOEt=9 : 1, AH_4[10] (239 mg) from fraction 11 with $CHCl_3$: AcOEt=19 : 1, AH_5[10] (52 mg) from fraction 12 with $CHCl_3$: AcOEt=9 : 1, and AH_6[10] (99 mg) and AH_3[10] (33 mg) from fraction 14 with $CHCl_3$: AcOEt=5 : 1. The AcOEt-soluble fraction (11.5 g) was fractionated by silica gel column chromatography ($CHCl_3$: MeOH=9 : 1) into 7 fractions. Rechromatography of fraction 4 (3.78 g) on silica gel with AcOEt afforded three fractions: fraction 4-1—4-3. Fraction 4-2 (440 mg) was subjected to successive column chromatography on silica gel with hexane : acetone=1 : 1 and $CHCl_3$: MeOH=14 : 1, and on ODS with 60% aq. MeOH to give compound **2** (7 mg). Fraction 4-3 (2.93 g) was chromatographed on ODS with 40% aq. to 100% MeOH to afford 13 fractions: fraction 4-3-1—4-3-13. Fraction 4-3-6 (380 mg) was separated by silica gel column chromatography with hexane : acetone=1 : 2 and the resulted fractions were purified by silica gel column chromatography with $CHCl_3$: acetone=8 : 1 and Et_2O : MeOH=9 : 1 to give compound **3** (64 mg) and compound **4** (47 mg), respectively. Fraction 4-3-11 (339 mg) was subjected to silica gel column chromatography (hexane : acetone=3 : 7) and then separated by Lobar column chromatography ($CHCl_3$: MeOH=10 : 1) to afford AH_{10}[11] (62 mg) and AH_{14}[12] (35 mg).

5-Hydroxy-6-methoxy-2-(2-phenylethyl)chromone (**1**): Yellow needles, mp 129 °C. UV λ_{max} (MeOH) nm (log ε): 349 (3.43), 242 (4.32), 202 (4.40). IR (KBr) cm^{-1}: 2936, 1655, 1624, 1585, 1458, 1412, 1281, 1234. HR-EI-MS *m/z*: 296.1056 $[M]^+$ (Calcd for $C_{18}H_{16}O_4$: 296.1049). ^{1}H-NMR (500 MHz): Table 1, ^{13}C-NMR (125 MHz): Table 2.

6-Hydroxy-2-(2-hydroxy-2-phenylethyl)chromone (**2**): White powder, mp 96—98 °C. $[\alpha]_D^{25}$ −3.0° (*c*=0.66, MeOH). UV λ_{max} (MeOH) nm (log ε): 328 (3.83), 240 (4.41), 228 (4.43). IR (KBr) cm^{-1}: 3233, 1628, 1582, 1474, 1404, 1362, 1327, 1234, 1196. HR-EI-MS *m/z*: 282.0898 $[M]^+$ (Calcd for $C_{17}H_{14}O_4$: 282.0892). ^{1}H-NMR (500 MHz): Table 1, ^{13}C-NMR (125 MHz): Table 2.

8-Chloro-2-(2-phenylethyl)-5,6,7-trihydroxy-5,6,7,8-tetrahydrochromone (**3**): White amorphous solid, $[\alpha]_D^{25}$ +7.4° (*c*=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 253 (4.05). IR (KBr) cm^{-1}: 3352, 2928, 1659, 1601, 1435, 1188, 1095, 1041. HR-FAB-MS *m/z*: 337.0833 $[M+H]^+$ (Calcd for $C_{17}H_{18}O_5{}^{35}Cl$: 337.0832). ^{1}H-NMR (500 MHz): Table 1, ^{13}C-NMR (125 MHz): Table 2.

6,7-Dihydroxy-2-(2-phenylethyl)-5,6,7,8-tetrahydrochromone (**4**): Brown amorphous solid, $[\alpha]_D^{25}$ −15.1° (*c*=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 251 (3.87), 203 (4.22). IR (KBr) cm^{-1}: 3360, 2916, 1659, 1605, 1443, 1180, 1084, 1038. HR-FAB-MS *m/z*: 287.1288 $[M+H]^+$ (Calcd for $C_{17}H_{19}O_4$: 287.1283). ^{1}H-NMR (500 MHz): Table 1, ^{13}C-NMR (125 MHz): Table 2.

Reaction of compound **2** with (*S*)-MTPA: A mixture of compound **2** (0.8 mg), (*S*)-MTPA (3.5 mg, 5.3 eq.), DCC (1.7 mg, 2.9 eq.) and DMAP (0.7 mg) in $CHCl_3$ (0.2 ml) was left standing at room temperature for 6 h. The mixture was concentrated under reduced pressure and the residue was separated by preparative TLC to give a mixture of compound **2a** and **2b**.

Compound **2a**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.91 (1H, d, *J*=2.9 Hz, H-5), 7.7—7.1 (17H, m, 3×ArH, H-6, H-7), 6.36 (1H, dd, *J*=9.6, 4.7 Hz, H-7′), 6.16 (1H, s, H-3), 3.71 (3H, s, OMe), 3.36 (3H, s, OMe), 3.26 (1H, dd, *J*=15.3, 9.6 Hz, H-8′), 3.14 (1H, dd, *J*=15.3, 4.7 Hz, H-8′).

Compound **2b**: ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.88 (1H, d, *J*=2.9 Hz, H-5), 7.7—7.1 (17H, m, 3×ArH, H-6, H-7), 6.43 (1H, dd, *J*=9.6, 4.7 Hz, H-7′), 6.02 (1H, s, H-3), 3.71 (3H, s, OMe), 3.37 (3H, s, OMe), 3.23 (1H, dd, *J*=15.3, 9.6 Hz, H-8′), 3.11 (1H, dd, *J*=15.3, 4.7 Hz, H-8′).

Preparation of acetonide of compound **4**: A solution of compound **4** (10 mg), 2,2-dimethoxypropane (13 mg, 3.6 eq.) and *p*-toluenesulfonic acid (3 mg) in dry acetone (0.8 ml) was left standing at room temperature for 8 h. The solution was neutralized with solid $NaHCO_3$, and, after removal of the precipitates by filtration, concentrated to dryness under reduced pressure. The residue was separated by silica gel column chromatography (hexane : cetone=1 : 1) to give the acetonide **5** (3.7 mg).

Compound **5**: Colorless needles, mp 100—102 °C. $[\alpha]_D^{25}$ −13.8° (*c*=0.53, MeOH). UV λ_{max} (MeOH) nm (log ε): 253 (4.05). IR (KBr) cm^{-1}: 2932, 1663, 1624, 1443, 1381, 1207, 1045. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 1.29, 1.32 (each 3H, s, Me), 2.26 (1H, dd, *J*=16.0, 4.4 Hz, H-5), 2.62 (1H, dd, *J*=16.6, 4.7 Hz, H-8), 2.69 (2H, m, H-8′), 2.80 (1H, dd, *J*=16.6, 1.8 Hz, H-8), 2.84 (2H, m, H-7′), 3.41 (1H, dd, *J*=16.0, 1.8 Hz, H-5), 4.54 (1H, m, H-6), 4.60 (1H, m, H-7), 6.27 (1H, s, H-3), 7.23 (5H, m, aromatic H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ: 23.93 (C-5), 24.30 (-Me), 26.83 (-Me), 31.92 (C-8), 32.91 (C-7′), 35.11 (C-8′), 73.19 and 73.83 (C-6, 7), 108.12 (O-C-O), 113.38 (C-3), 117.46 (C-8a), 119.01 (C-4a), 126.72 (C-4′), 128.76 (C-2′, 6′), 128.90 (C-3′, 5′), 140.54 (C-1′), 167.09 (C-2), 177.46 (C-4).

Acknowledgments This research was supported by a Grant-in-Aid for Scientific Research (No. 11793018) from the Ministry of Education, Culture, Sports, Science and Technology Japan. We are grateful to T. H. Lo for a generous gift of plant material.

References and Notes

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