[Chem. Pharm. Bull. 36(7)2417—2422(1988)]

Studies on the Agalwood (Jinkō). VII.[1] Structures of Phenylethylchromone Derivatives AH_7, AH_8 and AH_9

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(Received November 24, 1987)

Three new phenylethylchromone derivatives, tentatively named AH_7, AH_8 and AH_9, were isolated from acetone and pyridine extracts of agalwood (jinkō) from Kalimantan. AH_7 from the pyridine extract was characterized as 5,8-dihydroxy-2-(2-phenylethyl)chromone, and AH_8 from the acetone extract was elucidated to be 6,7-dimethoxy-2-[2-(4-methoxyphenyl)ethyl]chromone. AH_9, acetylated in order to separate it from the mixture, was concluded to be (5*S*,6*S*,7*R*)-5a′,6a,7a-triacetoxy-2-[2-(2-acetoxyphenyl)ethyl]-5,6,7,8,8-pentahydrochromone on the basis of the proton nuclear magnetic resonance (^{1}H-NMR) spectrum, dihedral angle and circular dichroism (CD) spectral data.

Keywords——2-(2-phenylethyl)chromone; agalwood; Aquilariaceae; polyoxylate; ^{1}H-NMR; 2D-COSY; CD; dihedral angle

In the preceding papers of this series[1a–c] it was reported that acetone extract of agalwood (jinkō) contained six 2-(2-phenylethyl)chromone derivatives, tentatively named AH_1 (agarotetrol),[2] AH_2 (isoagarotetrol), AH_3, AH_4, AH_5, and AH_6 along with other related compounds.

This paper deals with the isolation and characterization of three additional minor constituents from the acetone and pyridine extracts, tentatively named AH_7, AH_8 and AH_9. The procedures of isolation are described in the experimental section.

AH_7 (**1**), yellowish needles, mp 198—201 °C, exhibited absorptions due to a trisubstituted γ-pyrone ring, and hydroxyl and phenylethyl groups in the ultraviolet (UV) and infrared (IR) spectra, suggesting it to be a compound closely related to 5,8-dihydroxy-2-(2-phenylethyl)chromone, obtained as a by-product in the acetonide formation of agarotetrol by Yoshii *et al.*,[2] and the structure was further supported by the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra (Table II). In the ^{1}H-NMR spectrum of **1** the doublet signals at δ 6.66 and 7.14 were assigned to 6- and 7-H, respectively, based on the α-effect downfield shifts (*ca.* 0.2—0.3 ppm) following the acetylation at 5- and 8-OH.

Accordingly, AH_7 was concluded to be 5,8-dihydroxy-2-(2-phenylethyl)chromone.

AH_8 (**2**), colorless needles, $C_{20}H_{20}O_5$, mp 139—140 °C, was indicated to be a trimethoxyl derivative of 2-(2-phenylethyl)chromone on the basis of the molecular formula and ^{1}H-NMR spectrum. The structure of the 6,7-dimethoxylate, as in the case of AH_6,[1a] was suggested by the ^{1}H-NMR spectrum, which showed two singlet signals due to aromatic protons at δ 7.07 and 7.77, and another methoxyl group located at the *para*-position with respect to the 1′-carbon of the phenylethyl group was suggested by the appearance of the proton signals of the A^2–B^2 system due to the 1,4-disubstituted benzene ring. In the ^{13}C-NMR spectrum the assignments of carbons at the 5—10 positions were in fairly good accord with the calculated

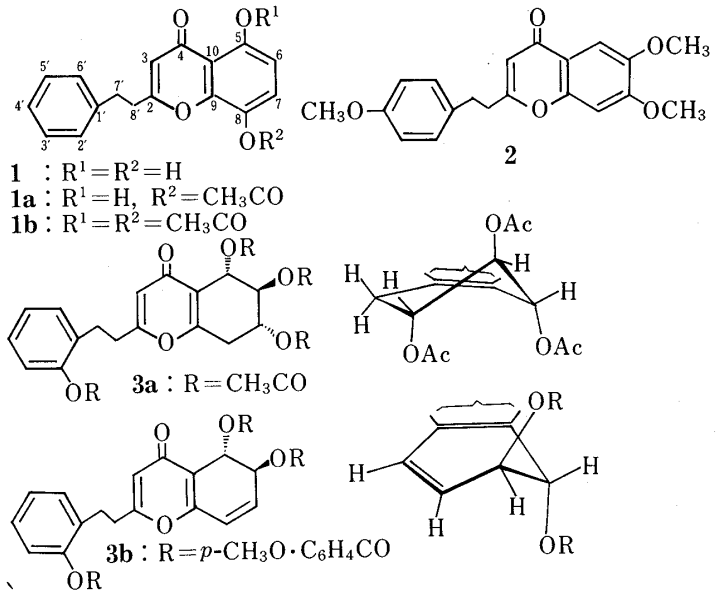

Chart 1

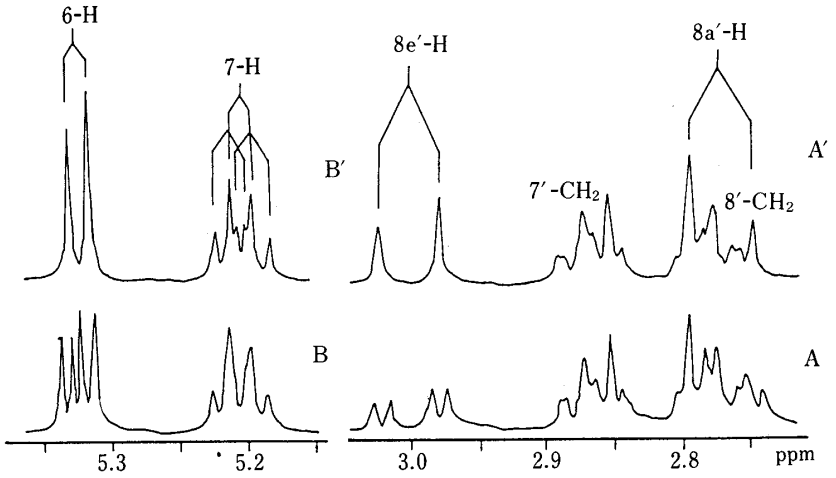

Fig. 1. ^{1}H-NMR Spectra of AH_9 (**3a**)

A and B are normal spectra, and A′ and B′ are spectra irradiated at δ 5.21 and 6.02, respectively.

TABLE I. ^{1}H-NMR Spectral Data for **3a** and Results of ^{1}H-Selective Irradiations

H	(400 MHz, in $CDCl_3$)	
3	6.12 (1H, s)	
5	6.02 (1H, d, J=3.5 Hz)	
6	5.33 (1H, dd, J=6.0, 3.5 Hz)	(d, J=6.0 Hz)[a] (d, J=3.5 Hz)[b]
7	5.21 (1H, bq)	(dt, J=6.0, 5.0, 5.0 Hz)[a]
8a′	2.77 (1H, dd, J=18.0, 5.0 Hz)	(d, J=18.0 Hz)[b]
8e′	2.99 (1H, dd, J=18.0, 5.0 Hz)	(d, J=18.0 Hz)[b]
3′	7.06 (1H, dd, J=8.0, 1.0 Hz)	
4′—6′	7.24 (3H, m)	
7′	2.87 (2H, m)	
8′	2.78 (2H, m)	
CH_3COO	2.05, 2.07, 2.08, 2.33 (each 3H, s)	

a) Selective irradiation at 5-H. *b*) Selective irradiation at 7-H.

TABLE II. ^{13}C-NMR Spectral Data for **1**, **1a**, **1b**, **2** and **3a** (ppm)[a]

Carbon	**1**	**1a**	**1b**	**2**	**3a**[b]
2	170.14	170.67	169.64	168.82	167.94
3	108.82	109.38	111.51	109.65	113.71
4	183.94	183.32	176.20	178.06	176.70
5	158.71	161.30	159.63	104.70 (104.0)[c]	65.99
6	110.53	110.68	118.40	148.09 (148.0)	69.12
7	122.74	127.37	126.25	155.08 (154.2)	66.48
8	138.90	130.53	137.19	100.47 (100.1)	27.71
9	152.92	157.86	156.49	152.99 (152.6)	162.26
10	111.51	110.70	118.40	116.96 (118.1)	117.89
1′	140.23	139.79	139.46	132.59 (133.0)	132.46 (133.0)[d]
2′	128.84	129.00	128.83	129.83 (130.0)	149.74 (151.2)
3′	128.57	128.72	128.73	114.50 (114.4)	123.17 (122.4)
4′	126.75	126.84	126.69	148.09 (158.2)	128.12 (128.0)
5′	128.57	128.72	128.73	114.50 (114.4)	126.53 (126.0)
6′	128.84	129.00	128.83	129.83 (130.0)	130.19 (129.5)
7′	35.69	35.64	35.59	36.02	33.86
8′	32.72	32.54	32.61	32.16	30.11
CH_3O	**2**: 55.32, 56.14, 56.58				
CH_3COO	**1a**: 20.38, 169.85 **1b**: 20.45, 21.01, 166.73, 168.14				
	3a: 20.52 (×2), 20.62 (×2), 169.32 (×2), 169.98 (×2)				

a) The spectrum of **1b** was measured in $CDCl_3$, and others were measured in pyridine-d_5. *b*) Assignments of C_5—C_{10} were established on the basis of the data for AH_2 (isoagarotetrol).[1b] *c*) Calculated values in parentheses have been described in connection with the data for AH_6.[1a,3] *d*) Values in parentheses were calculated by application of monomethoxy substituent effects[3] to the data for AH_1 (agarotetrol) tetraacetate.[1b]

TABLE III. "Observed" and Calculated Dihedral Angles in **3a**

	5-H, 6-H	6-H, 7-H		7-H, 8-H	
	e′e	ee	ea	ea′	ee′
"Observed"	58° (J=3.5 Hz)	42° (J=6.0 Hz)	—	48° (J=5.0 Hz)	48° (J=5.0 Hz)
Conduritols[4]	62°	—	64°	53°	62°
Büchi	70°	56°	64°	50°	70°

values, as shown in Table II.

Therefore, AH_8 was concluded to be 6,7-dimethoxy-2-[2-(4-methoxyphenyl)ethyl]chromone, **2**.

AH_9 (**3a**), colorless needles, $C_{25}H_{26}O_{10}$, mp 147—148 °C, $[\alpha]_D$ −11.1°, exhibited some characteristic absorption maxima due to acetoxyl phenylethylchromones in the UV and IR spectra, suggesting it to be a polyoxyl derivative related to agarotetrol and isoagarotetrol.[1b] The ^{1}H-NMR spectrum indicated the presence of four acetoxyl groups (δ 2.05, 2.07, 2.08 and 2.33) and three methine protons (δ 5.21, 5.33 and 6.02). However, since the methine proton signal at δ 5.21 appeared as a broad quartet-like peak and some signals regarded as being due to methylene protons were very complicated, **3a** was subjected to ^{1}H-selective decoupling experiments. On ^{1}H-selective irradiation at δ 6.02, a signal at δ 5.21 was transformed from the broad quartet into a doublet of triplets (J=6.0, 5.0, 5.0 Hz) and a signal at δ 5.33 from a doublet of doublets into a doublet (J=6.0 Hz). Similarly, at δ 5.21 a pair of geminally coupled methylene protons was clearly confirmed to give two doublet signals (J=18.0 Hz) at δ 2.77

and 2.99 as shown in Fig. 1. Therefore, the hexenyl ring was proved to have three adjacent acetoxyl groups at C_5, C_6 and C_7 or C_6, C_7 and C_8. Two protons at δ 2.77 and 2.99 were ascribable to the methylene protons at C_8 based on the 2D-COSYN spectrum, which showed cross peak signals due to the long-range couplings of $C_{8'}$-methylene (δ 2.78) beyond the γ-pyrone ring. The ^{13}C-NMR spectrum also showed a chemical shift of the C_4 signal analogous with that for isoagarotetrol[1b] while the chemical shift in the case of C_9 showed no effect ascribable to substitution by an acetoxyl group at C_8. Since there was also an upfield shift of about 7.0 ppm in the $C_{1'}$ signal, as shown in Table II, the other acetoxyl group should be attached to the *ortho*-position with respect to 1′-carbon.[3]

By assuming a half-chair conformation with steric and electrostatic repulsion between 4-CO and 5-OAc[2] the vicinal methine protons (C_5—C_7) of the hexenyl ring can be regarded as being pseudoequatorial (e′), equatorial (e) and e, respectively. The dihedral angles calculated by the use of the equation $J = 11.0\cos^2\phi$ and the observed values of $J_{5,6}$, $J_{6,7}$ and $J_{7,8}$ are given in Table III.[4] These values obtained from $J_{5,6\,(e',e)}$ and $J_{7,8\,(e,a')}$ were in good agreement with the corresponding values of conduritols observed by Abraham *et al.*[4] Consideration of the difference of $J_{5,6\,(e',e)}$ and $J_{7,8\,(e,e')}$ values suggested it to be the result of hexenyl ring buckling due to the effects of γ-pyrone ring and three acetoxyl substituents at C_5, C_6 and C_7 in the hexenyl ring. Therefore, the stereochemistry of three vicinal methine protons in the cyclohexenyl moiety was supported as being 5e′, 6e and 7e, respectively.

In order to determine the absolute configuration of **3a**, the *p*-methoxybenzoate (**3b**) was prepared from **3a** followed by hydrolysis of the acetoxyl groups. Compound **3b** showed the three methoxyl group signals at δ 3.83, 3.85 and 3.87 in the ^{1}H-NMR spectrum, suggesting the tri-*p*-methoxybenzoate structure, and further, four methine proton signals at δ 5.62, 6.22, 6.55 and 6.63 were assigned to the vicinal protons at C_5—C_8 based on the coupling systems arising from the 5,6-dioxy-7,9-cyclohexadienyl ring partial structure which was derived by dehydration between 7-OH and 8-H of **3a**.

Accordingly, **3b** was characterized as $\Delta^{7,8}$-5a′,6a,2′-tri-*p*-methoxybenzoate. The circular dichroism (CD) spectrum of **3b** in ethanol showed a positive chirality[5] of the 5,6-dibenzoate groups which was in accordance with the figure of Newman's projection at C_5 and C_6 (Figs. 2 and 3).

Since the conformations of the hexenyl moiety at C_5 and C_6 can be regarded as almost the same in **3a** and **3b**, the drawing shown in Chart 1 represents the absolute structure of **3a**. Consequently, AH_9 was defined as (5*S*,6*S*,7*R*)-2-[2-(2-acetoxyphenyl)ethyl]-5a′,6a,7a-triacetoxy-5,6,7,8,8-pentahydrochromone, **3a**.

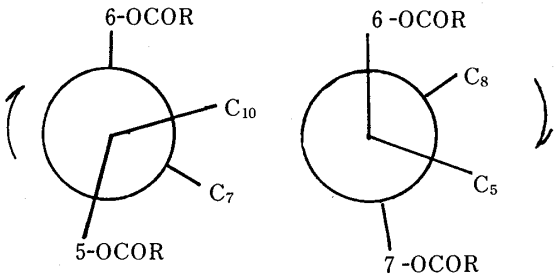

Fig. 2. Newman's Projection Following Büchi's Dreiding Model

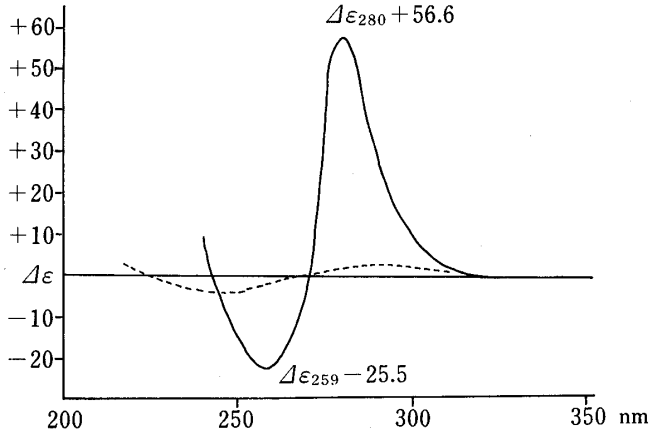

Fig. 3. CD Spectra (MeOH)
3a, ----; **3b**, ——

Compounds **1**, **2** and **3a** were elucidated to be polyoxyl derivatives of 2-(2-phenylethyl)chromone. They are the first to be isolated from agalwood, and the hexenyl ring structure of AH_9 is of interest in connection with that of isoagarotetrol.

Experimental

Melting points were determined on a micro melting point apparatus (Yanagimoto) and are uncorrected. The UV and CD spectra were obtained in EtOH (or MeOH) with a Shimadzu UV-200s spectrometer and a JASCO J-500c spectropolarimeter, respectively, and IR spectra (in KBr disks) with a Shimadzu IR 27G spectrometer. The ^{1}H-NMR spectra were taken on a Varian CFT-20 spectrometer at 79.54 MHz and a JEOL JNM GX-400 spectrometer at 399.65 MHz at 24 °C, and ^{13}C-NMR spectra on the Varian CFT-20 at 20.0 MHz and the JEOL JNM GX-400 at 100.4 MHz. Chemical shifts are given in δ (ppm) with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; dd, double doublet; dt, double triplet; ddd, double double doublet; m, multiplet; br, broad). Column chromatographies were performed on Kieselgel 60 (70—230 mesh, Merck), Kiesel 60 silanisiert (70—230 mesh, Merck) and polyamide (Woelm).

Isolation of AH_7, AH_8 and AH_9——As described previously (refer to Chart 1 in Part I[1a)] of this series) six crystalline compounds, AH_1—AH_6 were isolated from the ethereal and acetone extracts of agalwood from Kalimantan. Fr_2 (35.2 g) was further chromatographed on a polyamide column (MeOH–H_2O, 7:3 v/v) for the isolation of some constituents, with monitoring by thin layer chromatography (TLC) (detection under ultraviolet light). A mixture (20.1 g) of desired constituents was subjected to silica gel chromatography ($CHCl_3$–MeOH, 10:1 v/v) and followed by similar chromatography again but using hexane–AcOEt (1:1 v/v) as the eluent. The fractions of AH_6 (820 mg) and AH_8 (88 mg) were recrystallized from MeOH to give colorless plates (611 mg) and needles (25 mg), respectively. On the other hand, residue 2 (950 g)[1)] was extracted 3 times with pyridine (1 l) under reflux for 5 h. The combined filtrate was concentrated to give a dark viscous extract (300 g), and it was extracted with MeOH under reflux. The MeOH extract (75 g) was chromatographed on a silica gel column by using AcOEt and MeOH eluting solutions successively. The mixture (200 mg) of desired constituents from the AcOEt eluate was subjected to silica gel chromatography (hexane–AcOEt, 1:2 v/v) to give a fraction containing AH_7 (53 mg). The MeOH eluate (66.6 g) was again column-chromatographed on a silica gel column ($CHCl_3$–MeOH–H_2O, 8.5:1.5:0.15 v/v). The eluate (8.6 g) was acetylated with Ac_2O–pyridine by standing overnight and the mixture was evaporated to dryness under reduced pressure. The residue (9.2 g) was chromatographed over a column of silica gel (hexane–AcOEt, 1:1 v/v), and the fractionated AH_9 (324 mg) was further purified by a silanized silica gel chromatography (MeOH–H_2O, 7:3 v/v). AH_7 (40 mg), yellowish needles, was recrystallized from AcOEt and AH_9 (86 mg), colorless needles, recrystallized from an ether solution of the purified AH_9 (139 mg).

AH_7 (1)——Yellowish needles (from AcOEt), mp 198—201 °C. UV λ_{max}^{EtOH} nm (ε): 240.5 (15125), 300.0 (1681), 358.4 (2581). IR (KBr) cm^{-1}: 3120 (OH), 1655, 1615, 1586 (γ-pyrone ring), 852, 822, 749 (phenyl). ^{1}H-NMR ($CDCl_3$) δ: 3.02 (4H, m, CH_2CH_2), 6.05 (1H, s, 3-H), 6.66 (1H, d, J=8.8 Hz, 6-H), 7.14 (1H, d, J=8.8 Hz, 7-H), 7.25 (5H, m, 2′—6′ protons), 1.56, 11.64 (each 1H, s, OH). *Anal.* Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.30; H, 4.75. ^{13}C-NMR: Table II.

Acetylation of 1——a) The 8-Acetate: An Ac_2O–pyridine (1:1, v/v, 5 ml) mixture containing **1** (33 mg) was allowed to stand overnight and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (hexane–AcOEt, 1:1 v/v) and recrystallized from hexane–AcOEt (2:1 v/v) to give colorless needles, mp 100—101 °C. UV λ_{max}^{MeOH} nm (ε): 234 (19395), 257 (11741), 334 (4119). IR (KBr) cm^{-1}: 3500 (OH), 1770 (ester), 1660, 1630, 1600, 1590 (γ-pyrone), 879, 810, 700 (phenyl). ^{1}H-NMR (pyridine-d_5) δ: 2.36 (3H, s, CH_3CO), 2.92 (4H, m, CH_2CH_2), 6.18 (1H, s, 3-H), 6.80 (1H, d, J=8.9 Hz, 6-H), 7.25 (5H, m, 2′—6′ protons), 7.46 (1H, d, J=8.9 Hz, 7-H). *Anal.* Calcd for $C_{19}H_{16}O_5$: C, 70.36; H, 4.97. Found: C, 69.91; H, 4.92. ^{13}C-NMR: Table II.

b) The 5,8-Diacetate (**1b**): An Ac_2O (2 ml)–AcONa (20 mg) solution of **1** (80 mg) was heated on a water bath at 60 °C for 1 h. After addition of ice water, the aqueous mixture was filtered to obtain a precipitate (83 mg). The major product (72 mg) separated from the precipitate by column chromatography (hexane–AcOEt, 2:1 v/v) was recrystallized from acetone to give colorless needles, mp 149—150 °C. UV λ_{max}^{MeOH} nm (ε): 212 (21036), 225 (23570), 256 (4807), 304 (6992). IR (KBr) cm^{-1}: 1770, 1718 (ester), 1665, 1620, 1582 (γ-pyrone), 900, 703 (phenyl). ^{1}H-NMR ($CDCl_3$) δ: 2.38, 2.39 (each, 3H, s, CH_3CO), 2.92 (4H, m, CH_2CH_2), 5.99 (1H, s, 3-H), 6.95 (1H, d, J=8.6, 6-H), 7.22 (5H, m, 2′—6′ protons), 7.38 (1H, d, J=8.6 Hz, 7-H). *Anal.* Calcd for $C_{21}H_{18}O_6$: C, 68.84; H, 4.95. Found: C, 68.68; H, 4.75. ^{13}C-NMR: Table II.

AH_8 (2)——Colorless needles (from hexane–AcOEt, 1:1 v/v), mp 139—140 °C. UV λ_{max}^{MeOH} nm (ε): 230 (31672), 316 (10999). IR (KBr) cm^{-1}: 1640, 1600 (γ-pyrone), 831 (phenyl). ^{1}H-NMR (pyridine-d_5) δ: 2.93 (4H, m, CH_2CH_2), 3.66, 3.76, 3.86 (each 3H, s, CH_3O), 6.35 (1H, s, 3-H), 6.94, 7.25 (each 2H, dt, J=8.7, 3.0, 3.0 Hz, aromatic H), 7.07, 7.77 (each 1H, s, 8- and 5-H). *Anal.* Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.60; H, 5.88. ^{13}C-NMR: Table II.

AH_9 (3a)——Colorless needles (from Et_2O), mp 147—148 °C, $[\alpha]_D^{19}$ −11.1° (c=1.08, MeOH). UV λ_{max}^{MeOH} nm (ε):

249 (12973). IR (KBr) cm^{-1}: 1754 (ester), 1669, 1633, 1613 (γ-pyrone), 822, 724 (phenyl). ^{1}H-NMR ($CDCl_3$) δ: 2.05, 2.07, 2.08, 2.33 (each 3H, s, CH_3CO), 2.78, 2.87 (each 2H, m, CH_2CH_2), 2.77, 2.99 (each 1H, dd, $J=18.0$, 5.0 Hz, 8-a′- and 8-e′-H), 5.21 (1H, br q, $J=10.0$, 5.5 Hz, 7-H), 5.33 (1H, dd, $J=6.0$, 3.5 Hz, 6-H), 6.02 (1H, d, $J=3.5$ Hz, 5-H), 6.12 (1H, s, 3-H), 7.06 (1H, dd, $J=8.0$, 1.0 Hz, 3′-H), 7.24 (3H, m, 4′, 5′, 6′ protons). ^{13}C-NMR: Table II. High-resolution MS *m/z*: Calcd for $C_{25}H_{26}O_{10}$: 486.15242. Found: 486.1531.

Tri-*p*-methoxybenzoate (3b) from 3a——An absolute MeOH solution (5 ml) of **3a** (23 mg) was heated with anhydrous sodium carbonate (50 mg) at 50 °C for 5 h, and the reaction mixture was filtered. The filtrate was evaporated to dryness *in vacuo*. The residue (16.5 mg) was chromatographed on a silica gel column ($CHCl_3$–MeOH, 20 : 1 v/v) to afford a main product (7.2 mg). To a pyridine solution (1 ml) of the product (7.2 mg), *p*-methoxybenzoyl chloride (20 mg) was added and the mixture was allowed to stand overnight at 5 °C. The mixture was then evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column with *n*-hexane–AcOEt (1 : 1, v/v) to afford a powder (4.8 mg) from MeOH: (mp 82—84 °C), $[\alpha]_D^{22}$ +64.4° ($c=1.0$, MeOH). CD ($c=1.37\times10^{-5}$, MeOH) $\Delta\varepsilon^{25}$: −25.5 (259 nm) (negative maximum), +56.6 (280 nm) (positive maximum). ^{1}H-NMR ($CDCl_3$) δ: 2.85, 2.96 (each 2H, m, CH_2CH_2), 3.83, 3.85, 3.87 (each 3H, s, CH_3O), 5.62 (1H, dd, $J=5.1$, 1.7 Hz, 6-H), 6.14 (1H, s, 3-H), 6.22 (1H, d, $J=10.1$ Hz, 8-H), 6.55 (1H, dd, $J=1.7$, 1.3 Hz, 5-H), 6.63 (1H, ddd, $J=10.1$, 5.1, 1.3 Hz, 7-H), 6.84, 6.88, 6.99 (each 2H, d, $J=9.0$ Hz, aromatic H), 7.26 (m, aromatic H), 7.91, 7.93, 8.16 (each 2H, d, $J=9.0$ Hz, aromatic H).

Acknowledgements The authors thank Mr. Yasuhiro Fujiwara of Kyoto Pharmaceutical University and Mr. Masatoshi Nishi of Setsunan University for NMR measurements, and the members of the central analysis room of Kyoto University for elemental analysis. Thanks are also due to Miss Mutsuko Takahashi of Kyoto Pharmaceutical University for high-resolution MS.

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