Studies on the Agalwood (Jinkō). VIII.[1] Structures of Bi-phenylethylchromone Derivatives

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Three new bi-2-(2-phenylethyl)chromones, tentatively named AH_{12}, AH_{13} and AH_{14}, were isolated from agalwood "Jinkō" along with AH_{10}, AH_{11} and AH_{15}. The structures of AH_{12} and AH_{13} were elucidated as (5*S*,6*R*,7*R*,8*S*)-2-(2-phenylethyl)-5,6,7-trihydroxy-5,6,7,8-tetrahydro-8-[2-(2-phenylethyl)-7-methoxychromonyl-6-oxy]chromone and its de-7-methoxylate, respectively. AH_{14} was concluded to be (5*S*,6*S*,7*S*,8*R*)-2-(2-phenylethyl)-6,7,8-trihydroxy-5,6,7,8-tetrahydro-5-[2-(2-phenylethyl)chromonyl-6-oxy]chromone. Elucidation of 5,6′ and 8,6′-ether bonding in bi-2-(2-phenylethyl)chromones was done by detailed analyses of the proton and carbon-13 nuclear magnetic resonance (^{1}H and ^{13}C-NMR) spectra, and measuring nuclear Overhauser effect (NOE) difference values.

Keywords bi-2-(2-phenylethyl)chromone; agalwood; Aquilariaceae; ^{1}H-NMR; ^{13}C-NMR; 2D-COSY; NOE

In the preceding paper of this series,[2] new minor constituents AH_{10}, AH_{15} and AH_{18}, isolated from acetone extract of agalwood from Kalimantan were elucidated as the dimer and trimer of 2-(2-phenylethyl)chromones, formed *via* ether bonds. Three new bi-phenylethychromones, tentatively named AH_{12}, AH_{13} and AH_{14} were isolated from the acetone extract by a combination of repeated column chromatographies on silica gel and other adsorbents. The isolation procedures are described in the experimental section. This paper deals with the characterization of AH_{12}, AH_{13} and AH_{14} in connection with the structures of AH_{10} and AH_{15} on the basis of detailed analyses of the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra by means of two-dimensional (2D) NMR techniques and measurements of the nuclear Overhauser effect (NOE) difference spectra.

AH_{12} (**1**), colorless needles, $C_{35}H_{32}O_9$, mp 227 °C, $[\alpha]_D$ +0.7° was suggested to be a bi-2-(2-phenylethyl) chromone by its infrared (IR) and ultraviolet (UV) spectra which exhibited strong absorption maxima due to a γ-pyrone ring. The ^{1}H-NMR spectrum showed the presence of a pair of singlets at δ 6.13 and 6.18, and two sets of phenylethyl groups. One unit (unit A) of the dimer was considered to be agarotetrol[3] on the basis of the vicinal coupling systems of four protons (δ 3.88, 3.98, 4.44 and 5.30) on the cyclohexene ring moiety of 5,6,7,8-tetrahydrochromone. The doublet signal at δ 6.04 is ascribable to hydrogen-bonded 5-OH, because of its appearance at a lower field than the signals of the other three hydroxyl protons at C_6, C_7 and C_8.[4] Therefore, the proton signals of the cyclohexene ring could be assigned by comparison of the vicinal and geminal coupling constant values with each other based on that of 5-OH, as shown in Table I. Acetylation of **1** afforded a triacetate (**2**). The presence of an ether bond at C_8 of agarotetrol was indicated by the ^{1}H-NMR spectrum, which did not show a considerable downfield shift of the methine proton at C_8 upon acetylation.

The structure of unit B was characterized as 6,7-disubstituted 2-(2-phenylethyl) chromone on the basis of the signals at δ 7.70 and 7.18, which were assumed to be due to protons located at the $C_{5'}$ and $C_{8'}$ positions of the chromone ring. In the ^{13}C-NMR spectrum of **1** the carbon signals of the unit B moiety were in fairly good accord with those of AH_6, 6,7-dimethoxy-2-(2-phenylethyl)chromone,[5] except for the $C_{5'}$ signal, which exhibited a downfield shift of about 3 ppm as shown in the ^{13}C-NMR spectra of AH_{10} and AH_{15}.[2] Therefore, it is suggested that unit B bearing a methoxy group at $C_{7'}$ of phenylethylchromone is linked to unit A through an ether bond between the $C_{6'}$ and C_8 positions. The 8,6′-ether bonding was also supported by measuring the NOE difference spectrum; irradiation of the 8-H at δ 5.30 gave an appreciable NOE increase of the 5′ proton signal at δ 7.70.

Accordingly, the structure of AH_{12} was elucidated as (5*S*,6*R*,7*R*,8*S*)-2-(2-phenylethyl)-5,6,7-trihydroxy-5,6,7,8-tetrahydro-8-[2-(2-phenylethyl)-7-methoxychromonyl-6-oxy]chromone (**1**).[4b]

AH_{13} (**3**), colorless needles, $C_{34}H_{30}O_8$, mp 193—194 °C, $[\alpha]_D$ +2° was indicated to be another bi-2-(2-phenylethyl)chromone on the basis of the molecular formula and the IR and UV spectra, which exhibited absorptions analogous to those of **1**. Further, in the ^{1}H-NMR

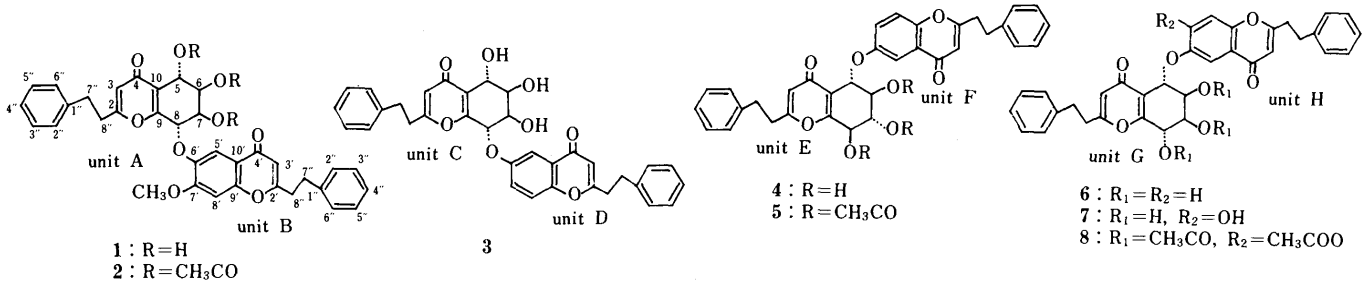

Chart 1

TABLE I. ^{1}H-NMR Spectral Data for AH_{12}, AH_{13}, and AH_{14} (δ in DMSO-d_6)

	AH_{12} (1)		AH_{13} (3)		AH_{14} (4)	
	Unit A	Unit B	Unit C	Unit D	Unit E	Unit F
5-H	4.44 dd (J=7.8, 6.6)	7.70 s	4.44 dd (J=7.9, 6.2)	7.63 d (J=3.2)	5.50 dd (J=7.0, 1.0)	7.78 d (J=2.5)
6-H	3.88 ddd (J=7.8, 5.5, 2.0)		3.88 ddd (J=7.9, 4.0, 2.0)		3.75 ddd (J=9.0, 7.0, 5.0)	
7-H	3.98 ddd (J=3.5, 3.0, 2.0)		4.02 ddd (J=3.5, 3.0, 2.0)	7.43 dd (J=9.3, 3.2)	3.68 ddd (J=9.0, 6.5, 4.5)	7.58 dd (J=9.0, 2.5)
8-H	5.30 d (J=3.0)	7.18 s	5.27 d (J=3.0)	7.59 d (J=9.3)	4.57 ddd (J=6.5, 3.0, 1.0)	7.65 d (J=9.0)
5-OH	6.04 d (J=6.6)		6.04 d (J=6.2)			
6-OH	5.28 d (J=5.5)		5.32 d (J=4.0)		5.70 d (J=5.0)	
7-OH	5.53 d (J=3.5)		5.54 d (J=3.5)		5.40 d (J=4.5)	
8-OH					5.20 d (J=3.0)	
3-H	6.18 s	6.13 s	6.18 s	6.21 s	6.21 s	6.21 s
CH_2CH_2	2.93 m (4H, $C_{7''}$) 2.98 m (4H, $C_{8''}$)		2.78 m (4H, $C_{7''}$) 2.92 m (4H, $C_{8''}$)		2.57 m (2H, $C_{7''}$, unit E) 2.66 m (2H, $C_{8''}$, unit E) 3.01 m (4H, $C_{7''}$,$C_{8''}$, unit F)	
C_6H_5	7.18 m (2H), 7.29 m (8H)		7.21 m (2H), 7.29 m (8H)		6.98 m (2H, $C_{2''}$,$C_{6''}$, unit E) 7.18 m (4H), 7.27 m (4H)	
CH_3O	3.87 s (3H)					

TABLE II. ^{13}C-NMR Spectral Data for AH_{12}, AH_{13}, and AH_{14}[a)]

Carbon	AH_{12} (DMSO-d_6)		AH_{13} (DMSO-d_6)		AH_{14} (C_5D_5N)	
	Unit A	Unit B	Unit C	Unit D	Unit E	Unit F
2	168.3	167.7	168.2	168.0	168.9	168.6
3	112.7	109.0	112.6	108.7	113.7	110.4
4	177.5	175.9	177.2	176.2	180.5	177.5
5	67.8	107.0	67.7	107.5	79.6	109.6
6	70.6	145.7	70.6	155.0	73.5	157.5
7	68.4	154.7	68.4	124.1	74.9	124.7
8	72.2	100.6	72.2	119.5	70.6	119.8
9	165.0	152.1	164.7	150.6	158.9	151.9
10	117.3	116.1	123.5	117.2	122.5	124.7
1''	140.0	139.9	139.7	139.7	140.2	140.4
2'',6''	128.3	128.3	128.1	128.1	128.9	128.9
3'',5''	128.2	128.2	128.1	128.1	128.7	128.7
4''	126.1	126.1	125.9	125.9	126.7	126.7
7''	31.6	32.0	31.6	32.0	32.5	32.9
8''	34.0	34.7	34.0	34.6	35.4	35.8
CH_3O		56.2				

a) The shifts are given in ppm (δ) relative to internal tetramethylsilane (TMS). Assignments were based on the results of ^{1}H–^{13}C-COSY.

spectrum the four methine proton signals of the cyclohexene ring were similar to those of **1** in terms of the chemical shifts and the vicinal coupling systems, as shown in Table I. Three hydroxyl proton signals were confirmed by the saturation transfer method[6)] decreasing the signal of OH protons. The downfield proton signal of OH at δ 6.04 should be ascribed to the 5-OH proton as in the case of **1**, and other protons of the cyclohexene ring were assigned by the double irradiation method based on the assignment of 5-OH. Therefore, one (unit C) of the structural units of **3** was considered to be agarotetrol, and the position of the ether bond to another monomeric unit (unit D) was determined to be C_8, because the doublet signal due to 8-H is shifted to lower field than the other methine proton signals.

The 6-alkoxy-2-(2-phenylethyl)chromone structure of unit D was suggested on the basis of the coupling systems of three aromatic protons at $C_{5'}$, $C_{7'}$ and $C_{8'}$ assigned from the ^{1}H and ^{13}C shift-correlated spectrum (2D-COSY) (Fig. 2 and Table I). The 8,6'-ether bond structure was also confirmed by measuring the NOE difference spectrum; irradiation of 8-H at δ 5.27 gave an appreciable NOE increase of the 5' and 7'-H signals at δ 7.63 and 7.43, respectively.

The above results and the ^{13}C-NMR spectrum support the conclusion that AH_{13} is (5*S*,6*R*,7*R*,8*S*)-2-(2-phenylethyl)-5,6,7-trihydroxy-5,6,7,8-tetrahydro-8-[2-(2-phenylethyl)chromonyl-6-oxy]chromone (**3**).[4b)]

AH_{14} (**4**), a white powder (mp 86—88 °C), $[\alpha]_D$ +64.6° showed a molecular ion at m/z 566 in the field desorption mass spectrum (FD-MS), giving the the molecular formula $C_{34}H_{30}O_8$, and it was also suggested to be a bi-phenylethylchromone derivative by the IR, UV and ^{1}H-NMR spectra. One unit (unit E) of the dimer was considered to be isoagarotetrol[4a)] on the basis of the vicinal coupling systems of four methine proton signals at δ 3.68, 3.75, 4.57 and 5.50 (Table I), which indicated *trans* diaxial substituents on a cyclohexene ring. The double doublet signal of the methine proton at δ 5.50 (J=7.0, 1.0 Hz) can be assigned to 5-H, because of the downfield shift, considered to result from the bonding of the ether at C_5 to another monomeric unit (unit F). The coupling constant, J=1.0 Hz, can be interpreted as a homoallylic coupling between 5-H and 8-H. This was supported by the absence of the proton signal of 5-OH which should be found at lower field than the other three hydroxylic protons at C_6, C_7 and C_8, and the similarity of the ^{13}C-NMR spectrum of **4** to that of isoagarotetrol, except for the C_5 signal, which exhibited a downfield shift by about 8 ppm (Table II).

Acetylation of **4** afforded a triacetate (**5**), colorless nee-

dles and the appearance of three proton signals in the aromatic ABX systems at δ 7.32, 7.43 and 7.87 in the ^{1}H-NMR spectrum was considered to be due to the structure of another phenylethylchromone unit (unit F), characterized as 6-alkoxylate, as in the case of AH_5, AH_{10}, *etc.*[2a,5] The assignments 5′-, 7′- and 8′-H of unit F were supported by ^{1}H–^{13}C COSY (Fig. 3) and the NOE difference spectra, which showed NOE increments of the 5′- and 7′-H signals upon irradiation of 5-H of unit E at 60 °C.

Accordingly, the structure of AH_{14} was elucidated as (5*S*,6*S*,7*S*,8*R*)-2-(2-phenylethyl)-6,7,8-trihydroxy-5,6,7,8-tetrahydro-5-[2-(2-phenylethyl)chromonyl-6-oxy]chromone (**4**).[4b]

AH_{12} (**1**), AH_{13} (**3**), AH_{14} (**4**) and AH_{15} (**7**) were isolated along with AH_{10} (**6**) and AH_{11},[2] and characterized as dimers linked by ether bonds at the 5,6′ or 8,6′-positions between agarotetrol or isoagarotetrol and another 2-(2-phenylethyl)chromone derivative.

The difference in the ^{1}H-NMR spectra between dimers linked at the 5,6′ and 8,6′-positions appeared in a few proton signals of phenylethyl groups, as shown in a partial comparison of the spectra of **3** and **6** (Fig. 1). The assignments of the protons at δ 2.57, 2.64, 6.98 and 7.18 in the spectrum of **6** which showed upfield shifts compared with the chemical shifts of corresponding protons of **3**, were determined from ^{1}H–^{13}C COSY (Figs. 2 and 3) and NOE difference spectra. The proton signals at δ 6.16 and 6.22 was ascribed to 3-H and 3′-H by ^{1}H–^{13}C COSY, and the

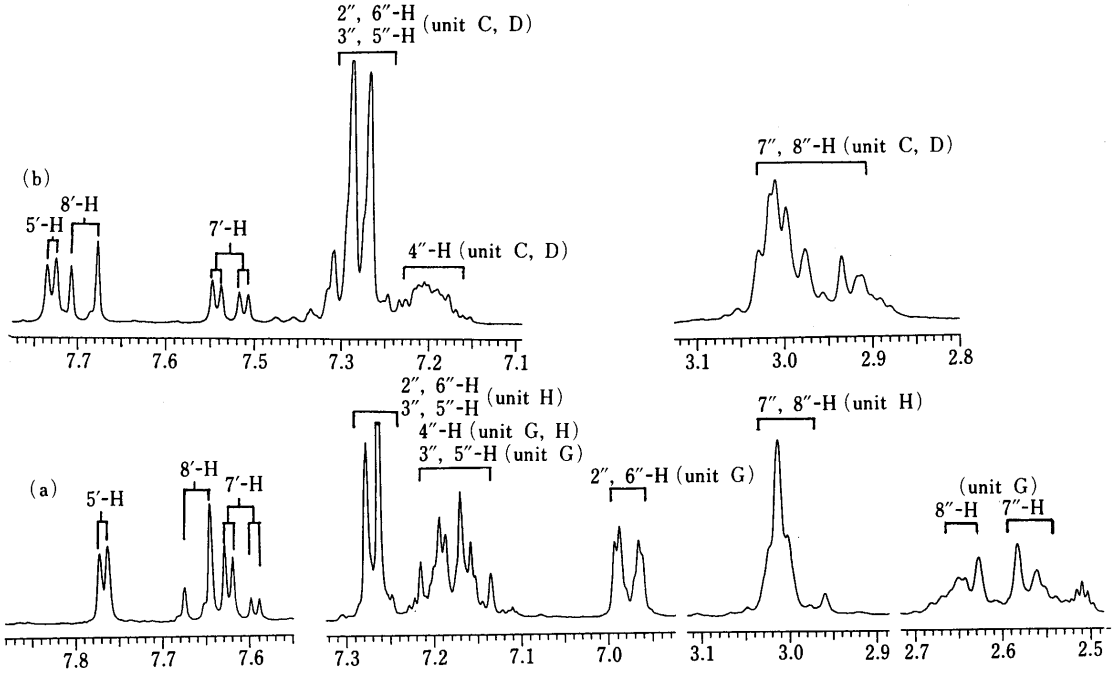

Fig. 1. Partial Comparison of the ^{1}H-NMR Spectra of AH_{10} (a) and AH_{13} (b) (DMSO-d_6, δ ppm)

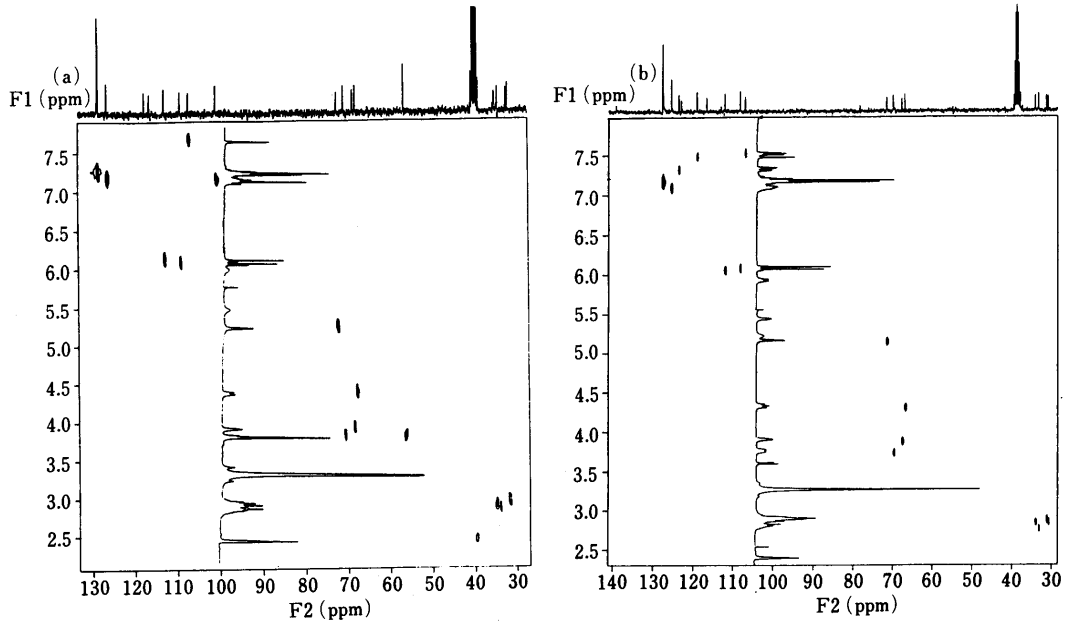

Fig. 2. CH-COSY Spectra of AH_{12} (a) and AH_{13} (b)

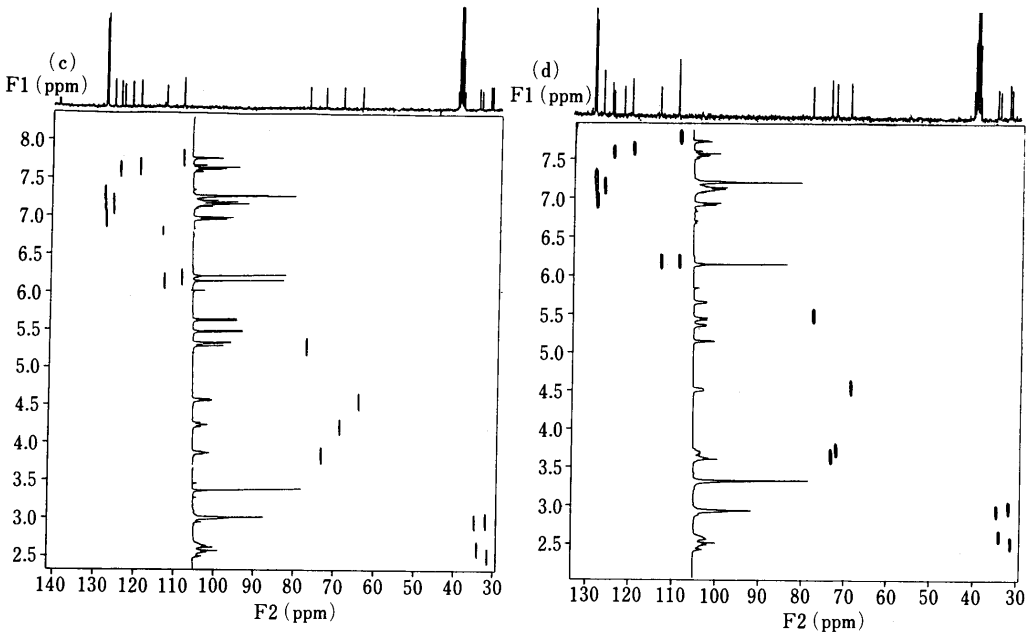

Fig. 3. CH-COSY of AH_{10} (c) and AH_{14} (d)

protons at δ 2.64 and 2.57 were also assigned to the protons at $C_{8''}$ and $C_{7''}$, respectively. Irradiation of the methylene protons at δ 3.02 gave an appreciable NOE increase of the 3′-H signal at δ 6.22, and irradiation of the methylene protons at δ 2.57 caused an increase of the signals at δ 7.18 and 6.98, whereas irradiation at δ2.64 showed a considerable increase only in the signal at δ 6.98. Therefore, the signal at δ 6.98 was assigned to 2″- and 6″-H of agarotetrol (unit G), and the protons at δ 2.64 and 2.57, to 8″- and 7″-CH_2 of unit G, respectively. Further, it was confirmed that the aromatic proton signals at δ7.18 were due to 3″- and 5″-H of unit G together with 4″-H of units G and H. All resuls of ^{1}H-NMR spectra are summarized in Table I (**1**, **3** and **4**) and the experimental section (**6** and **7**).

It can be presumed that the upfield shifts observed in the phenylethyl proton signals of the agarotetrol or isoagarotetrol unit are due to the shielding effects caused by another neighboring chromone ring.

Experimental

Melting points were determined on a micro melting point apparatus (Yanagimoto) and are uncorrected. The UV and circular dichroism (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 (300.0 MHz) and ^{13}C (75.4 MHz) NMR spectra were taken on a Varian XL-300 spectrometer in DMSO-d_6 and $CDCl_3$ solutions. 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).

The ^{1}H–^{13}C COSY[7] experiments on AH_{10}—AH_{15} were performed by using a pulse sequence with 16 phase cycling to provide quadrature detections in both frequency dimensions. The spectra were collected as 128 × 2k or 128 × 1k data points and were processed using double exponential functions (line-broadening: 1 Hz in ^{1}H; 2—3 Hz in ^{13}C) prior to Fourier transformation in both dimensions with zero filling to give 256 × 1 k real data points. Digital resolutions were 7.1—6.4 Hz in ^{13}C and 9.3—7.6 Hz in ^{1}H dimensions.

The ^{1}H–^{1}H NOE experiments in the difference mode[8] were performed at 23 °C. Eight transients were acquired by irradiating the on-resonance position of a spin to saturation and then eight transients were acquired by irradiating at an off-resonance position. This cycle was repeated 6—16 times. The total free induction decay (FID) obtained by off-resonance irradiation was subtracted from the total FID obtained by on-resonance irradiation and the resultant FID was Fourier-transformed. The NOE is the ratio of the intensity (integral values) of a signal to that of the irradiated one in the difference spectrum. The decoupling power (γ $H_2/2\pi$) was 3.4—4.0 Hz. Saturating power was turned off during acquisition so that coupled spectra were obtained. Saturation and acquisition times were 4—5 and 3 s, respectively.

Column chromatographies were performed on kieselgel 60 (70—230 mesh, Merck), Kiesel 60 silanisiert (70—230 mesh, Merck), Sephadex LH-20 (Pharmacia Fine Chemicals) and LiChroprep Rp-8 (40—63 μm) pre-packed column (Merck).

Isolation of AH_{10}, AH_{11}, AH_{12}, AH_{13}, AH_{14} and AH_{15} Twelve derivatives of 2-(2-phenylethyl)chromonyl monomer, tentatively named AH series, were isolated from the ethereal, acetone and pyridine extracts of agalwood from Kalimantan.

A fraction (fr_2, 35.2 g) from the acetone extract was chromatographed on a polyamide column, as described previously.[5] AH_{11} (98 mg) separated as a precipitate from the elute. The filtrate was evaporated to dryness under reduced pressure to yield a residue (18.7 g) which was subjected to the silica gel chromatography ($CHCl_3$–MeOH, 10 : 1 v/v) for isolation of AH_6 and AH_8.[9] Another residue (12.4 g) obtained from eluates of the column chromatography of fr_2 was again column-chromatographed on Sephadex LH-20 (MeOH) to give three fractions (A, 250 mg; B, 599 mg; C, 124 mg). The first fraction A (250 mg) was further subjected to LiChroprep Rp-8 column chromatography (MeOH–H_2O, 7 : 3 v/v) to give AH_{13} (42 mg) and AH_{14} (72 mg). AH_{13} (9.5 mg) was recrystallized as colorless needles from MeOH, and AH_{14} (68 mg) was obtained as a white powder from a solution of AcOEt–MeOH (1 : 1 v/v). The next fraction B (599 mg) was subjected to silica gel chromatography ($CHCl_3$–MeOH, 10 : 1 v/v) to give AH_{12} (13 mg), colorless needles (recrystallized from MeOH), and a crude fraction (521 mg) of AH_{10} were purified by chromatographies on silica gel ($CHCl_3$–MeOH, 20 : 1) and LiChroprep Rp-8 (MeOH–H_2O, 7 : 3 v/v). AH_{10} (153 mg) was deposited as a white powder from AcOEt–MeOH (1 : 1 v/v) solution. The third fraction C (124 mg) was chromatographed over a column of silica gel ($CHCl_3$–MeOH, 15 : 1 v/v) to give a crude fraction (31 mg), from which AH_{15} (10 mg) was obtained as colorless needles after recrystallization from MeOH.

AH_{12} (1) Colorless needles, mp 227 °C, $[\alpha]_D$ +0.7° (c = 14.5, $CHCl_3$–MeOH, 1 : 1 v/v). UV λ_{max}^{MeOH} nm (ε): 209 (51499), 233 (42827), 288 (12783), 315 (10563). IR (KBr, cm^{-1}): 3370 (OH), 1658, 1637, 1615, 1600 (γ-pyrone ring). ^{1}H and ^{13}C-NMR: Table I and II. *Anal.* Calcd for $C_{35}H_{32}O_9 \cdot 1/3H_2O$: C, 69.75; H, 5.46. Found: C, 69.44; H, 5.38.

Acetylation of 1 A mixture of Ac_2O–pyridine (1 : 1 v/v, 2 ml) and **1** (27 mg) was allowed to stand for 2 h at room temperature, and evaporated to dryness under reduced pressure. The residue (32 mg) was purified by column chromatography (hexane–AcOEt, 2 : 3 v/v) to give **2** as colorless prisms (25 mg), recrystallized from MeOH. mp 88—90 °C, $[\alpha]_D$ +6.0°

($c=1.0$, MeOH). UV λ_{max}^{MeOH} nm (ε): 209 (51499), 233 (42827), 288 (12783), 315 (10563). IR ($CHCl_3$, cm^{-1}): 1752 (ester), 1670, 1642, 1605 (γ-pyrone ring). ^{1}H-NMR ($CDCl_3$, 300 MHz, δ): 2.059, 2.091, 2.215 (each 3H, s, CH_3COO), 2.899, 2.974 (8H, m, $CH_2CH_2\times2$), 3.947 (3H, s, CH_3O), 5.508 (1H, d, $J=3.31$ Hz, 8-H), 5.685 (1H, dd, $J=3.39$, 2.33 Hz, 7-H), 5.864 (1H, dd, $J=8.55$, 2.33, 6-H), 6.065, 6.111 (each 1H, s, 3 and 3′-H), 6.161 (1H, d, $J=8.55$, 5-H), 6.849 (1H, s, 8-H), 7.261 (10H, m, aromatic H), 8.009 (1H, s, 5′-H). *Anal.* Calcd for $C_{41}H_{38}O_{12}$: C, 68.13; H. 5.30. Found: C, 67.81; H, 5.38.

AH$_{13}$ (3) Colorless needles, mp 193—194 °C, $[\alpha]_D+2°$ ($c=5.0$, pyridine). UV λ_{max}^{MeOH} nm (ε): 227 (47796), 240 (50437), 250 (34589), 320 (6981). IR (KBr, cm^{-1}): 3410 (OH), 1662, 1651, 1622, 1618, 1600 (γ-pyrone). ^{1}H and ^{13}C-NMR: Table I and II. FD-MS (m/z): 567 (M^++H), 566 (M^+). *Anal.* Calcd for $C_{34}H_{30}O_8\cdot1/3H_2O$: C, 71.32; H, 5.40. Found: C, 71.54; H, 5.28.

AH$_{14}$ (4) A white powder (mp 86—88 °C), $[\alpha]_D+64.4°$ ($c=1.0$, MeOH). UV λ_{max}^{MeOH} nm (ε): 207 (37356), 232 (29375), 250 (20659), 275 (10471), 310 (8037). IR (KBr, cm^{-1}): 3400 (OH), 1655, 1638, 1603, 1578 (γ-pyrone). ^{1}H and ^{13}C-NMR: Table I and II. *Anal.* Calcd for $C_{34}H_{30}O_8$: C, 72.07; H, 5.34. Found: C, 71.90; H, 5.48.

Acetylation of 4 **4** (30 mg) was acetylated in the same manner as described for **2** to give an acetate (**5**, 21 mg), colorless plates, mp 181—182 °C (dec.), $[\alpha]_D+86.7°$ ($c=0.98$, $CHCl_3$). UV λ_{max}^{MeOH} nm (ε): 240 (35119), 250 (25950), 316 (5951). IR ($CHCl_3$, cm^{-1}): 1748 (ester), 1665, 1643, 1635, 1610 (γ-pyrone). ^{1}H-NMR ($CDCl_3$, δ): 2.06 (6H, s, $CH_3COO\times2$), 2.081 (3H, s, CH_3COO), 2.746 (4H, m, CH_2CH_2), 2.952, 3.042 (each 2H, m, CH_2CH_2), 5.370 (1H, d, $J=6.2$, 5-H), 5.373 (1H, dd, $J=7.8$, 5.0, 7-H), 5.572 (1H, dd, $J=7.8$, 6.2, 6-H), 6.171 (1H, d, $J=5.0$, 8-H), 6.125, 6.153 (each 1H, s, 3 and 3′-H), 7.021 (2H, dd, $J=8.0$, 2.0, aromatic H), 7.194 (4H, m, aromatic H), 7.271 (4H, m, aromatic H), 7.321 (1H, dd, $J=9.0$, 3.2, 7′-H), 7.428 (1H, d, $J=9.0$, 8′-H), 7.867 (1H, d, $J=3.17$, 5′-H). ^{13}C-NMR ($CDCl_3$, δ): 20.6 ($\underline{C}H_3COO$), 32.4, 33.0 ($C_{7''}$), 35.1, 36.0 ($C_{8''}$), 65.7 (C_8), 69.300, 69.314 (C_6 and C_7), 74.2 (C_5), 108.8 ($C_{5'}$), 109.4 ($C_{3'}$), 114.0 (C_3), 118.9 ($C_{10'}$), 120.0 ($C_{8'}$), 123.9 ($C_{7'}$), 124.3 (C_{10}), 126.4 ($C_{4''}\times2$), 127.9, 128.1, 128.5 (aromatic carbons), 151.9 ($C_{9'}$), 155.1 ($C_{6'}$), 158.3 (C_9), 167.9, 168.4, 168.9 ($CH_3\underline{C}OO$), 169.2, 169.4 ($C_{2'}$, C_2), 176.2, 177.3 ($C_{4'}$, C_4). *Anal.* Calcd for $C_{40}H_{36}O_{11}$: C, 69.35; H, 5.24. Found: C, 69.83; H, 5.31.

AH$_{10}$ (6) A white powder (mp 110 °C), $[\alpha]_D-127.7°$ ($c=1.12$, MeOH). UV λ_{max}^{EtOH} nm (ε): 206 (41079), 226 (32833), 241 (35818), 319 (5615), IR ($CHCl_3$, cm^{-1}): 3360 (OH), 1662, 1639, 1610, 1582 (γ-pyrone), 1122, 1072, 1028, 695 (mono-substituted benzene). ^{1}H and ^{13}C-NMR[2a]: assignments of phenylethyl and C_3 protons. Unit G; 2.57 (2H, m, 7″-CH_2), 2.64 (2H, m, 8″-CH_2), 6.16 (1H, s, 3-H), 6.98 (2H, dd, $J=8.1$, 1.7, 2″, 6″-H), 7.18 (3H, m, 3″, 4″, 5″-H). Unit F; 3.02 (4H, m, 7″,8″-CH_2), 6.22 (1H, s, 3′-H), 7.18 (1H, m, 4″-H), 7.27 (4H, m, 2″, 3″, 5″, 6″-H). *Anal.* Calcd for $C_{34}H_{30}O_8\cdot1/3H_2O$: C, 71.32; H, 5.40. Found: C, 71.42; H, 5.36.

Acetylation of 6 **6** (25 mg) was acetylated in the same way as described for **2** to yield a white powder (**7**, 22 mg) from hexane–AcOEt (2 : 1 v/v); mp 82—83 °C, $[\alpha]_D$ −43.6° ($c=1.17$, MeOH). UV λ_{max}^{MeOH} nm (ε): 206 (34576), 239 (28774), 316 (4736). ^{1}H-NMR (80 MHz, $CDCl_3$, δ): 2.02, 2.11, 2.12 (each 3H, s, CH_3COO), 2.72 (4H, m, CH_2CH_2), 3.00 (4H, m, CH_2CH_2), 5.40 (1H, d, $J=7.2$, 5-H), 5.56 (1H, dd, $J=4.1$, 2.0, 7-H), 5.64 (1H, dd, $J=7.2$, 2.0, 6-H), 6.08 (1H, d, $J=4.1$, 8-H), 6.13, 6.16 (each 1H, s, 3 and 3′-H), 7.04 (2H, m, aromatic H), 7.24 (8H, m, aromatic H), 7.41 (2H, 7′, 8′-H), 7.95 (1H, d, $J=1.4$, 5′-H). *Anal.* Calcd for $C_{37}H_{36}O_{11}$: C, 69.35; H, 5.24. Found: C, 69.18; H, 5.21.

AH$_{15}$ (8) Colorless needles, mp 244—245 °C, $[\alpha]_D$ +5.8° ($c=0.69$, MeOH). UV λ_{max}^{MeOH} nm (ε): 206 (43499), 244 (36321), 336 (6130). IR (KBr, cm^{-1}): 3370 (OH), 1668, 1625, 1590 (γ-pyrone). ^{1}H and ^{13}C-NMR [2b]: assignments of phenylethyl and C_3 protons. Unit G; 2.51 (4H, m, CH_2CH_2), 6.11 (1H, s, 3-H), 6.96 (2H, dd, $J=7.5$, 2.0, 2″,6″-H), 7.17 (3H, m, 3″,4″,5″-H). Unit F; 2.94 (4H, m, CH_2CH_2), 6.16 (1H, s, 3′-H), 7.17 (1H, m, 4″-H), 7.21 (4H, m, $C_{2''}$, $C_{3''}$, $C_{5''}$, $C_{6''}$-H). FD-MS (m/z): 605 (M^++Na), 582 (M^+), 565 (M^+−OH), 547 (565−H_2O).

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References and Notes

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