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Comparative Studies on the Constituents of Ophiopogonis Tuber and Its Congeners. IV.[1] Studies on the Homoisoflavonoids of the Subterranean Part of *Ophiopogon ohwii* OKUYAMA and *O. jaburan* (KUNTH) LODD.

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Six homoisoflavonoidal compounds, tentatively named NE-I (**1**), NE-II (**2**), NE-III (**3**), NE-IV (**4**), NE-V (**5**) and NE-VI (**6**), were isolated from the ether-soluble fraction of the subterranean part of *Ophiopogon ohwii* OKUYAMA (Liliaceae) and four homoisoflavonoidal compounds, tentatively named JE-I (**7**), JE-II (**8**), JE-III (**9**) and JE-IV (**10**), were isolated from that of *O. jaburan* (KUNTH) LODD. NE-I and NE-II were identified as compound I (**1**) and compound II (**2**), respectively, which had been isolated by Kaneda *et al.* from an Ophiopogonis Tuber imported from China. NE-III, NE-IV and NE-V were identified as methylophiopogonanone A (**3**), methylophiopogonanone B (**4**) and methylophiopogonone A (**5**), respectively.

The structures of NE-VI, JE-I, JE-II, JE-III and JE-IV were elucidated to be 5,7-dihydroxy-6,8-dimethyl-3-(2-hydroxy-3,4-methylenedioxybenzyl)chromone (**6**), 3,5-dihydroxy-7-methoxy-6-methyl-3-(4-hydroxybenzyl)chroman-4-one (**7**), 5-hydroxy-7-methoxy-6-methyl-3-(3,4-dihydroxybenzyl)chromone (**8**), 5,7-dihydroxy-6-methyl-3-(4-hydroxybenzyl)chromone (**9**), and 5,7-dihydroxy-3-(4-hydroxybenzyl)chromone (**10**), respectively.

Keywords——Ophiopogonis Tuber; *Ophiopogon ohwii*; *Ophiopogon jaburan*; Liliaceae; homoisoflavonoid; chemotaxonomy

In the preceding paper,[1] the isolation and structure elucidation of six steroidal glycosides of the subterranean part of *Ophiopogon ohwii* OKUYAMA and another six steroidal glycosides of the subterranean part of *O. jaburan* (KUNTH) LODD. were reported. The present paper deals mainly with the isolation and structure elucidation of homoisoflavonoidal compounds of the subterranean parts of the two Liliaceaous plants reported in the preceding paper.

The subterranean parts of *O. ohwii* OKUYAMA and *O. jaburan* (KUNTH) LODD. were extracted with hot methanol, and both methanol extracts were treated by the method described in the experimental section. Six homoisoflavonoidal compounds, tentatively named NE-I (**1**), NE-II (**2**), NE-III (**3**), NE-IV (**4**), NE-V (**5**) and NE-VI (**6**), were isolated from *O. ohwii* OKUYAMA, and four homoisoflavonoidal compounds, tentatively named JE-I (**7**), JE-II (**8**), JE-III (**9**) and JE-IV (**10**), were isolated from *O. jaburan* (KUNTH) LODD.

NE-V (**5**) was positive in the ferric chloride reaction. The infrared (IR) spectrum of **5** revealed the presence of hydroxyl (3520 cm^{-1}), conjugated ketone (1628 cm^{-1}) and methylenedioxy groups (930 cm^{-1}), and the ultraviolet (UV) spectrum showed two absorption maxima at 265 and 293 nm. The mass spectrum (MS) of **5** showed the molecular ion peak (M^+) at *m/z* 340 and fragment peaks at *m/z* 218 (A_1), 181 (A_2), 160 (B_1), 135 (B_2) and 121 (B_3). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum revealed the presence of two aromatic C-methyl groups at δ 2.12 and 2.21 ppm, a benzylmethylene group at δ 3.68 ppm, a methylenedioxy group at δ 5.94 ppm, three aromatic protons at δ 6.69—

Table I. ^{1}H-NMR Spectral Data for Homoisoflavonoidal Compounds (δ Value, 100 MHz)

Carbon No.	Proton	1[a]	2[a]	3[a]	4[a]	5	6	7[b]	8	9	10
C(2)	$>C<$H	4.25 dd (12, 7)	4.23 dd (12, 7)	4.14 dd (12, 9)	4.09 dd (12, 7)			4.02 d (11)			
	H	4.46 dd (12, 4)	4.46 dd (12, 4)	4.38 dd (12, 4)	4.31 dd (12, 3)			4.15 d (11)			
	$=\overset{\vert}{C}-H$					8.05	8.18		8.00	7.88	7.91
C(3)	$-\overset{\vert}{\underset{\vert}{C}}-H$	2.85 m	2.92 m	2.86 m	2.90 m						
	$-\overset{\vert}{\underset{\vert}{C}}-OH$							4.78			
C(5)	arom-OH	12.98[c]	12.97[c]	12.36	12.34	13.03	12.67	11.84	12.80	13.10	12.84
C(6)	arom-CHO	10.05	10.05								
	arom-CH_3			2.02	2.02	2.12	2.13	1.95	2.03	2.05	
	arom-H										6.24 (2)
C(7)	arom-OH	12.92[c]	12.94[c]				8.82[c]			9.53	
	arom-OCH_3							3.92	3.95		
C(8)	arom-CH_3	2.01	2.01	2.07	2.09	2.21	2.22				
	arom-H							6.18	6.58	6.43	6.35 (2)
C(9)	$-\overset{\vert}{C}H-CH_2-$	2.68 dd (12, 9) 3.20 dd (12, 4)	2.68 dd (12, 9) 3.24 dd (12, 3)	2.66 dd (12, 9) 3.20 d (12)	2.66 dd (12, 9) 3.20 d (12)						
	$-\overset{\vert}{\underset{OH}{C}}-CH_2-$							2.93			
	$=\overset{\vert}{C}-CH_2-$					3.68	3.70		3.64	3.64	3.64
C(2′)	arom-H								6.40 (2)		
	arom-OH						8.62[c]				
C(2′,6′)	arom-H × 2		7.14 d (9)		7.15 d (9)			7.12 d (8)		7.16 d (8)	7.16 d (8)
C(2′,5′,6′)	arom-H × 3	6.60—6.81 m		6.65—6.82 m		6.69—6.81 m					
C(3′)	arom-OH								8.07[c]		
C(3′,5′)	arom-H × 2		6.87 d (9)		6.87 d (9)			6.77 d (8)		6.75 d (8)	6.75 d (8)
C(3′, 4′)	$-O-CH_2-O-$	5.96		5.94		5.94	5.91				
C(4′)	arom-OCH_3		3.80		3.80						
	arom-OH							8.27	8.51[c]	8.14	
C(5′)	arom-H						6.37 d (8)		7.05 d (8)		
C(6′)	arom-H						6.78 d (8)		6.31 dd (8, 2)		

a) These compounds were measured in $CDCl_3$. Figures in parentheses are coupling constants (*J*) in Hz. *b*) This compound was measured in DMSO-d_6 and the others were measured in acetone-d_6. *c*) Assignments may be reversed. d = doublet, m = multiplet; those not cited are singlets.

6.81 ppm, an olefinic proton at δ 8.05 ppm and a chelated hydroxyl group at δ 13.03 ppm. Based on the thin layer chromatographic (TLC) behavior and the IR, UV, MS and ^{1}H-NMR spectra, **5** was suggested to be identical with methylophilopogonone A,[2] and this was confirmed by direct comparison with an authentic sample (TLC behavior and mixed fusion).

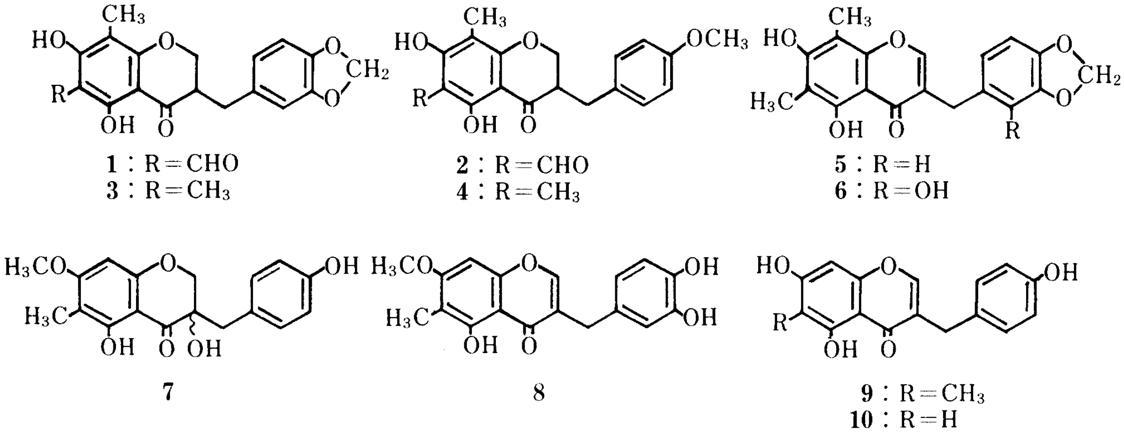
NE-VI (**6**) was positive in the ferric chloride reaction. The IR spectrum of **6** showed the absorption bands due to hydroxyl group, conjugated ketone and methylenedioxy group, while its UV absorption maxima appeared at 263 and 303 nm. The MS of **6** showed the molecular ion peak at *m/z* 356 (M^+) and fragment peaks due to the B-ring moiety at *m/z* 176 and 151, which were higher than those of **5** by 16 mass units each, corresponding to a hydroxyl group. The ^{1}H-NMR spectra of **5** and **6** were nearly superimposable except that the latter spectrum showed two proton signals ($J = 8$ Hz, AB quartet) at δ 6.37 and 6.78 ppm instead of a three-proton multiplet at δ 6.69—6.81 ppm in the former. Based on the color reaction, Liebermann reaction and Gibbs test, and analysis of the ^{1}H-NMR spectrum, the location of the phenolic hydroxyl group of **6** was suggested to be $C_{2'}$ of the B-ring. Consequently, the structure of NE-VI was established to be 2′-hydroxy-methylophiopogonone A (=5,7-dihydroxy-6,8-dimethyl-3-(2-hydroxy-3,4-methylenedioxybenzyl)chromone).

NE-III (**3**) was positive in the ferric chloride reaction and its IR spectrum showed the absorption bands of hydroxyl, ketone and methylenedioxy groups. The MS of **3** showed the same fragment peaks at *m/z* 135 (B_2) and 121 (B_3) as in the case of **5**, but the M^+ ion (*m/z* 342) and the fragment peaks at *m/z* 220 (A_1) and 162 (B_1) were higher than those of NE-V (**5**) by two mass unit each. Consequently, **3** was suggested to be a flavonone-type compound of **5**. This conclusion was supported by the ^{1}H-NMR spectrum of **3**, showing five proton signals at δ 4.14 (C_2-H), 4.38 (C_2-H), 2.86 (C_3-H), 2.66 (C_9-H), and 3.20 (C_9-H). Finally, **3** was identified as methylophiopogonanone A[2] by direct comparison with an authentic sample (TLC behavior and mixed fusion).

NE-IV (**4**) was positive in the ferric chloride reaction and the IR spectrum showed absorption bands due to hydroxyl, ketone and benzylmethylene groups. The MS of **4** showed the same fragment peak at *m/z* 220 (A_1) as that of **3**, but its M^+ ion (*m/z* 328) and B_2-type ion (*m/z* 121) were lower than those of **3** by 14 mass units each. The ^{1}H-NMR spectra of **4** and **3** were similar, but the former showed a methoxyl signal at δ 3.80 ppm and two *ortho*-coupled aromatic proton signals ($J = 7$ Hz) at δ 6.87 and 7.15 ppm in place of methylenedioxy protons at δ 5.94 and three aromatic protons at δ 6.65—6.87 ppm shown in the latter. Finally, **4** was identified as methylophiopogonanone B[2] by direct comparison with an authentic sample (TLC behavior and mixed fusion).

The ^{1}H-NMR spectra of NE-I (**1**) and NE-II (**2**) revealed the presence of an aldehyde group (1H, δ 10.05 ppm) and an aromatic methyl group (δ 2.01 ppm) in both compounds, and the spectra were similar to those of **3** and **4**. Consequently, the structures of **1** and **2** may have an aldehyde group in place of one aromatic methyl group of **3** and **4**, respectively. Finally, **1** and **2** were concluded to be identical with compound I and compound II isolated by Kaneda *et al.*[3] from the commercially available Ophiopogonis Tuber imported from China, based on a direct comparison of their spectra, and mixed fusion.

JE-IV (**10**) was positive in the ferric chloride reaction. The IR spectrum of **10** showed absorption bands due to hydroxyl and conjugated ketone groups, and UV absorption maxima appeared at 259 and 291 nm. Based on the ^{1}H-NMR spectrum of **10**, which showed a benzylmethylene proton signal at δ 3.64 ppm (2H, s) and a vinyl proton signal at δ 7.91 ppm (1H, s), **10** was assumed to have a homoisoflavone skeleton. In addition, it showed two *meta*-coupled aromatic proton signals ($J = 2$ Hz) at δ 6.24 and 6.35 ppm and four proton signals assigned to 1,4-substituted benzene ring protons at δ 6.75 and 7.16 ppm. The MS of **10** showed the molecular ion peak at *m/z* 284 and three fragment peaks at *m/z* 153 (A_2), 132 (B_1) and 107 (B_2). Consequently, the structure of **10** was elucidated as 5,7-dihydroxy-3-(4-hydroxy-



1 : R=CHO
3 : R=CH_3

2 : R=CHO
4 : R=CH_3

5 : R=H
6 : R=OH

7

8

9 : R=CH_3
10 : R=H

Chart 1

benzyl)chromone.

JE-III (**9**) was positive in the ferric chloride reaction. The IR spectrum of **9** showed absorption bands due to hydroxyl and conjugated ketone, while UV absorption maxima appeared at 260 and 295 nm. The MS of **9** showed two fragment ion peaks, m/z 132 (B_1) and 107 (B_2), which are the same as those of **10**, but the M^+ ion (m/z 298) and the fragment ion at m/z 167 (A_2) were higher than those of **10** by 14 mass units each. The ^{1}H-NMR spectrum of **9** showed an aromatic methyl signal at δ 2.05 ppm and an aromatic proton signal at δ 6.43 ppm. Consequently, **9** was deduced to have an aromatic methyl group on the A-ring of **10**. The location of the aromatic methyl group was deduced to be C_6 by comparative analysis of the ^{1}H-NMR spectra of **9** and its triacetate, and the structure of **9** was elucidated to be 5,7-dihydroxy-6-methyl-3-(4-hydroxybenzyl)chromone. Finally, **9** was methylated with diazomethane to afford a dimethyl ether which was identical with the 7-*O*-methyl derivative of ophiopogonone B isolated from the tuber of *Ophiopogon japonicus* KER-GAWLER.[4)]

JE-II (**8**) was positive in the ferric chloride reaction. The IR spectrum of **8** showed absorption bands due to hydroxyl and conjugated ketone, while the UV spectrum showed absorption maxima at 230 and 286 nm. As in the case of **10**, the ^{1}H-NMR spectrum of **8** showed a benzylmethylene proton signal at δ 3.64, a vinyl proton signal at δ 8.00 ppm, an aromatic methyl signal at δ 2.03 ppm, a methoxy methyl signal at δ 3.95 ppm, and three hydroxyl proton signals at δ 8.07, 8.51 and 12.80 ppm which disappeared on addition of deuterium oxide. Consequently, **8** was suggested to be a homoisoflavonoid derivative. The UV spectrum indicated the presence of a 5-hydroxyl group, since a bathochromic shift of 22 nm was observed on the addition of aluminum chloride. The position of the methoxyl group was suggested to be at C_7, because no bathochromic shift was observed on addition of sodium acetate. The ^{1}H-NMR spectrum of the A-ring of **8** was similar to that of the dimethyl ether of **9**, and the methyl group of A-ring of **8** was deduced to be located on C_6. Based on these results, the structure of **8** was concluded to be 5-hydroxy-7-methoxy-6-methyl-3-(3,4-dihydroxybenzyl)chromone.

JE-I (**7**) was positive in the ferric chloride reaction. The IR spectrum of **7** showed absorption bands due to hydroxyl and conjugated ketone, while the UV spectrum showed absorption maxima at 214 and 292 nm. The ^{1}H-NMR spectrum of **7** showed an AB quartet signal at δ 4.02 and 4.15 ppm (each 1H, d, $J = 11$ Hz) and a benzylmethylene signal at δ 2.93 ppm (2H, s) besides aromatic methyl and methoxyl signals. Consequently, **7** was suggested to be a homoisoflavanone derivative carrying a substituent group at C-3. Eucomol has been reported as an example of a homoisoflavanone which has a hydroxyl group at C-3, and the ^{1}H-NMR chemical shifts of the protons on C-2 and C-9 of **7** agreed well with those of eucomol.[5] As in the case of **8**, the MS of **7** showed a fragment peak derived from the A-ring at *m/z* 181 (A_2), and the aromatic methyl group and methoxyl group were suggested to be located on the A-ring. Based on the analysis of the ^{1}H-NMR spectrum and the UV spectral changes using shift reagent, the positions of the methyl and methoxyl groups were concluded to be at C-6 and C-7, respectively. Consequently, the structure of **7** was established to be 3,5-dihydroxy-7-methoxy-6-methyl-3-(4-hydroxybenzyl)chroman-4-one.

In the present paper we have described a study on the homoisoflavonoidal constituents of *Ophiopogon ohwii* OKUYAMA and *O. jaburan* (KUNTH) LODD.; one new compound from the former and four new compounds from the latter have been found. Furthermore, methylophiopogonanones A, B and methylophiopogonone A found in *O. japonicus* KER-GAWLER were also isolated from the former plant. This finding suggests an intimate relationship between these two plants.

Experimental

All melting points were determined on a Yanagimoto micro-melting point apparatus (hot stage type) and are uncorrected. The optical rotations were measured with a JASCO DIP-140 polarimeter. The IR spectra were recorded with a Hitachi EPI-2 and the UV spectra were recorded with a Hitachi 340 spectrophotometer. The ^{1}H-NMR spectra were recorded with a JEOL FX-100 (100 MHz) and the chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. MS were measured with a JEOL JMS-D300 high-resolution mass spectrometer with a direct inlet system, and mass numbers (*m/z*) were determined with perfluorokerosine as an internal standard. TLC was done on precoated Kieselgel 60 F_{254} plates (Merck) and spots were detected by spraying 10% H_2SO_4 followed by heating or by spraying ferric chloride reagent.

Extraction and Isolation of Homoisoflavonoids——i) The fresh subterranean parts of *Ophiopogon ohwii* OKUYAMA (4 kg) cultivated at Kyoto Herbal Garden, Central Research Division, Takeda Chemical Industries, Ltd. were crushed and extracted with hot MeOH (9 l × 4). The extract was combined and evaporated to dryness *in vacuo*. The residue (388 g) was dissolved in water and extracted with ether to afford the ether-soluble fraction (33.5 g). The ether extract was subjected to column chromatography on Sephadex LH-20 with MeOH to afford the crude phenolic fraction (8.2 g), which was subjected to column chromatography on silicic acid with $CHCl_3$ followed with $CHCl_3$–acetone (95 : 5, v/v) to give three fractions (Fr. 1—Fr. 3). Fr. 1 (2.4 g) was subjected to column chromatography on silicic acid with benzene to afford NE-I (**1**, 80 mg) and NE-II (**2**, 19 mg). Fr. 2 (1.3 g) was purified by Sephadex LH-20 column chromatography with ethanol to afford NE-III (**3**, 413 mg) and NE-IV (**4**, 154 mg). Fr. 3 (3.2 g) was separated by column chromatography on silicic acid with benzene–acetone (98 : 2, v/v) to afford NE-V (**5**, 115 mg) and NE-VI (**6**, 42 mg).

ii) The fresh subterranean parts of *O. jaburan* (KUNTH) LODD. (4 kg) cultivated at Yachiyo Farm, Keisei Rose Nursery Inc., were crushed and extracted with hot MeOH (9 l × 4). The extract was combined and evaporated to dryness *in vacuo*. The residue (424 g) was dissolved in water and extracted with ether to afford the ether-soluble fraction (65.5 g). The ether extract was subjected to column chromatography on Sephadex LH-20 with MeOH to afford the crude phenolic fraction (4.3 g), which was subjected to column chromatography on silicic acid with $CHCl_3$ followed with $CHCl_3$–acetone (95 : 5, v/v) to afford three fractions (Fr. 1—Fr. 3). Fr. 1 (1.4 g) was subjected to column chromatography on silicic acid with benzene–acetone (98 : 2, v/v) to afford JE-I (**7**, 14 mg) and JE-II (**8**, 9 mg). Fr. 2 (0.2 g) was purified by silicic acid column chromatography with benzene–acetone (97 : 3, v/v) to afford JE-III (**9**, 18 mg). Fr. 3 (1.7 g) was separated by column chromatography on silicic acid with benzene–acetone (95 : 5, v/v) to afford JE-IV (**10**, 34 mg).

Properties of NE-I—VI and JE-I—IV——NE-I (**1**): Colorless needles from $CHCl_3$–MeOH, mp 175—176 °C, $[\alpha]_D^{21}$ $-11.2°$ ($c=0.41$, $CHCl_3$) (lit.[3] mp 176 °C, $[\alpha]_D$ $-9.9°$ ($CHCl_3$)). MS *m/z*: 356 (M^+), 234, 221, 195, 162, 135. IR ν_{max}^{KBr} cm^{-1}: 3450, 1620, 930. UV $\lambda_{max}^{CHCl_3}$ nm: 276. NE-I was identical with compound I on the basis of mixed fusion and comparisons of the physical data.

NE-II (**2**): Colorless needles from $CHCl_3$–MeOH, mp 141 °C, $[\alpha]_D^{21}$ $-10.4°$ ($c=0.24$, $CHCl_3$), (lit.[3] mp 141 °C, $[\alpha]_D$ $-9.0°$ ($CHCl_3$)). MS *m/z*: 342 (M^+), 234, 221, 195, 148, 121. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1620. UV $\lambda_{max}^{CHCl_3}$ nm: 278. NE-II was identical with compound II on the basis of mixed fusion and comparisons of the physical data.

NE-III (**3**): Colorless needles from CCl_4, mp 165—166 °C, $[\alpha]_D^{22}$ $-80.0°$ ($c=0.20$, $CHCl_3$) (lit.[2] mp 166—167 °C, $[\alpha]_D$ $-72.0°$ ($CHCl_3$)). MS *m/z*: 342 (M^+), 220, 207, 181, 162, 135, 121. IR ν_{max}^{KBr} cm^{-1}: 3280, 1628, 935. UV $\lambda_{max}^{CHCl_3}$ nm: 212, 296. NE-III was identical with authentic methylophiopogonanone A on the basis of mixed fusion and comparisons of the physical data.

NE-IV (**4**): Colorless needles from CCl_4, mp 159—160 °C, $[\alpha]_D^{22}$ $-52.0°$ ($c=0.20$, dioxane) (lit.[2] mp 159—160 °C, $[\alpha]_D$ $-53.0°$ (dioxane)). MS *m/z*: 328 (M^+), 220, 207, 181, 121. IR ν_{max}^{KBr} cm^{-1}: 3430, 1634. UV $\lambda_{max}^{CHCl_3}$ nm: 220, 298.

NE-IV was identical with authentic methylophiopogonanone B on the basis of mixed fusion and comparisons of the physical data.

NE-V (**5**): Pale yellow needles from EtOH, mp 210—211 °C (lit.[2] mp 210—211 °C). MS *m/z*: 340 (M^+), 326, 311, 218, 181, 160, 135, 121. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3520, 1650, 1628, 930. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 265, 293. NE-V was identical with authentic methylophiopogonone A on the basis of mixed fusion and comparisons of the physical data.

NE-VI (**6**): Yellow needles from EtOH, mp 256—257 °C. MS *m/z*: 356 (M^+), 218, 206, 181, 176. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3380, 1645, 1620, 924. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm ($\log\varepsilon$): 263 (4.45), 303 (3.90). UV $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ nm: 316. UV $\lambda_{\max}^{\mathrm{EtOH+NaOAc}}$ nm: 332.

JE-I (**7**): Colorless needles from EtOH, mp 80—81 °C, $[\alpha]_D^{21}$ $-78.2°$ ($c=0.20$, MeOH). MS *m/z*: 330.107 (M^+, Calcd for $C_{18}H_{18}O_6$ 330.110), 312, 218, 206, 181, 107. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400, 1630, 1615, 1570. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm ($\log\varepsilon$): 214 (4.47), 292 (4.26). UV $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ nm: 315.

JE-II (**8**): Pale yellow needles from EtOH, mp 249—250 °C. MS *m/z*: 328.095 (M^+, Calcd for $C_{18}H_{16}O_6$ 328.095), 181, 148, 123. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3300, 1650, 1620, 1565. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm ($\log\varepsilon$): 230 (4.48), 286 (4.19). UV $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ nm: 308.

JE-III (**9**): Pale yellow needles from EtOH, mp 253—255 °C. MS *m/z*: 298.087 (M^+, Calcd for $C_{17}H_{14}O_5$ 298.084), 204, 167, 132, 107. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3280, 1645, 1620, 1585. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm ($\log\varepsilon$): 260 (3.93), 295 (3.70). UV $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ nm: 308. UV $\lambda_{\max}^{\mathrm{EtOH+NaOAc}}$ nm: 332.

JE-IV (**10**): Pale yellow needles from CCl_4–MeOH, mp 218—219 °C. MS *m/z*: 284.071 (M^+, Calcd for $C_{16}H_{12}O_5$ 284.069), 153, 132, 107. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3260, 1650, 1615, 1580. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm ($\log\varepsilon$): 259 (4.49), 291 (3.98). UV $\lambda_{\max}^{\mathrm{EtOH+AlCl_3}}$ nm: 310. UV $\lambda_{\max}^{\mathrm{EtOH+NaOAc}}$ nm: 326.

Acetylation of JE-III——A solution of JE-III (10 mg) in Ac_2O–pyridine (2 ml each) was heated at 80 °C for 30 min and the reaction mixture was treated in the usual way. The product was purified by column chromatography on silicic acid with benzene to afford a triacetate (9 mg), colorless needles from MeOH, mp 175—177 °C. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: OH (nil), 1760 (ester). ^{1}H-NMR ($CDCl_3$) δ: 2.07 (3H, s, 6-CH_3), 2.28, 2.36, 2.48 (3H each, s, OAc), 3.74 (2H, s, 9-H_2), 7.00 (2H, d, $J=8$ Hz, 3′,5′-H), 7.19 (1H, s, 8-H), 7.23 (2H, d, $J=8$ Hz, 2′,6′-H), 7.38 (1H, s, 2-H).

Methylation of JE-III——An excess of ethereal diazomethane was added to a methanolic solution of JE-III (5 mg) and the mixture was allowed to stand for 3 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silicic acid with benzene to afford a dimethyl ether (3 mg), colorless needles from MeOH, mp 151—152 °C. ^{1}H-NMR (acetone-d_6) δ: 2.05 (3H, s, 6-CH_3), 3.76 (2H, s, 9-H_2), 3.76, 3.95 (3H each, s, OCH_3), 6.58 (1H, s, 8-H), 6.84 (1H, d, $J=8$ Hz, 3′,5′-H), 7.26 (2H, d, $J=8$ Hz, 2′,6′-H), 8.02 (1H, s, 2-H), 12.97 (1H, s, 5-OH).

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