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Synthetic Studies of the Flavone Derivatives. VIII.[1,2] Synthesis of Kanzakiflavones and Their Isomers

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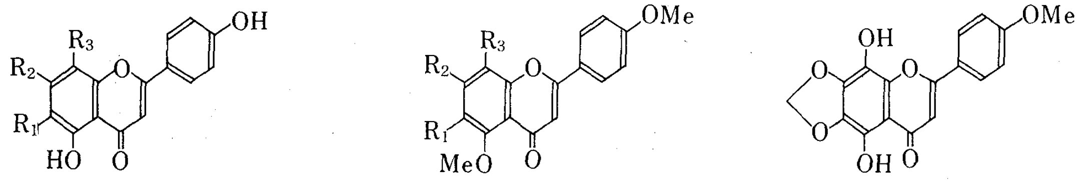
Kanzakiflavone-1 and -2, isolates from *Iris unguicularis*, and their position isomers were synthesized to confirm the structures of the isolates. The differences among these flavones are discussed on the basis of spectral data.

Keywords——kanzakiflavone-1; kanzakiflavone-2; 4′,5-dihydroxy-7,8-methylenedioxyflavone; 6,7-methylenedioxy-4′,5,8-trimethoxyflavone; 7,8-methylenedioxy-4′,5,6-trimethoxyflavone; 3′-acetyl-4′,5-dihydroxy-6,7-methylenedioxyflavone

Two new flavones, kanzakiflavone-2 (I)[3] and kanzakiflavone-1 (V),[4] were isolated from the rhizomes of *Iris unguicularis* Poir together with known isoflavonoids and xanthones, and their structures were determined by chemical and spectral means. To our knowledge, flavonoids substituted with a methylenedioxyl group in ring A have been found in relatively few plants, such as *Spinacia oleracea*,[5] *Helichrysum mundii*,[6] *Gomphrena globosa*,[7] *Melicope indica*,[8] and *Polygonum orientale*.[9] It is generally difficult to clarify the location of a methylenedioxyl group substituted at the 6,7- or 7,8-positions. For the purpose of confirming the structures of kanzakiflavone-1 and -2, flavones containing methylenedioxy in ring A were synthesized (I, II, VI and VII). The syntheses of kanzakiflavone-1 and -2 had already been reported by Bhardwaj *et al.*,[10] but the methods of identification had not been mentioned at all in their paper. In this paper, the syntheses of kanzakiflavone-1 and -2 and their position isomers are described and the characteristics of these flavones are discussed. Kanzakiflavone-2 (4′,5-dihydroxy-6,7-methylenedioxyflavone) (I) and its isomer, 4′,5-dihydroxy-7,8-methylenedioxyflavone (II) were synthesized by methylenation of flavones having the same substitution patterns as I and II, that is, 4′,5,6,7-$[O]_4$flavone, because it is rather difficult to pre-



I: $R_1=R_2=OCH_2O$, $R_3=H$
II: $R_1=H$, $R_2=R_3=OCH_2O$
III: $R_1=R_2=OH$, $R_3=H$
IV: $R_1=H$, $R_2=R_3=OH$
VIII: $R_1=R_2=R_3=OH$

VI: $R_1=R_2=OCH_2O$, $R_3=OMe$
VII: $R_1=OMe$, $R_2=R_3=OCH_2O$

V

Chart 1

pare 2-hydroxy-6-methoxy-4,5-methylenedioxy- and 2-hydroxy-6-methoxy-3,4-methylenedioxyacetophenone as starting materials. 4′,5,6,7-Tetramethoxyflavone (IX)[11] was prepared in the usual way *via* the β-diketone from 2-hydroxy-4,5,6-trimethoxyacetophenone and *p*-anisic acid in three steps, and converted to 4′,5,6,7-tetrahydroxyflavone (scutellarein) (III) by demethylation with $AlCl_3$–NaCl molten mixture in quantitative yield. The Wassely–Moser rearrangement did not occur in the demethylation of IX because further methylation of III gave IX. Compound III was refluxed with methylene bromide and potassium fluoride in dry dimethylformamide (DMF)[12] to afford I in a 40% yield (mp > 300 °C). The synthesis of II was carried out similarly to that of I. 4′,5,7,8-Tetramethoxyflavone (X), which was prepared from 2-hydroxy-3,4,6-trimethoxyacetophenone and *p*-anisic acid, was demethylated to 4′,5,7,8-tetrahydroxyflavone (IV), followed by methylenation to afford II (mp > 300 °C). From a direct comparison (mixed mp, infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR)) of synthesized I and II with natural kanzakiflavone-2, kanzakiflavone-2 was confirmed to be 4′,5-dihydroxy-6,7-methylenedioxyflavone.

Instead of 5,8-dihydroxy-4′-methoxy-6,7-methylenedioxyflavone (V) (the proposed structure for kanzakiflavone-1), 6,7-methylenedioxy-4′,5,8-trimethoxyflavone (VI) was synthesized as the dimethylether of kanzakiflavone-1, because the preparation of 2,3-dihydroxy-6-methoxy-4,5-methylenedioxyacetophenone as an A ring moiety for V is expected to be difficult. As a starting material for VI, 3,6-dimethoxy-2-hydroxy-4,5-methylenedioxyacetophenone (XII) had to be prepared. Lee *et al.*[13] had synthesized 3,6-dimethoxy-2,4,5-trihydroxyacetophenone (XIII) from 2,4-dihydroxy-3,6-dimethoxyacetophenone in three steps (benzylation, the Elbs oxidation and debenzylation) in poor yield. We were able to prepare XIII from 2,4-dihydroxy-3,6-dimethoxyacetophenone directly by the Elbs oxidation in a 53% yield. A partial methylation of XIII gave XII. Based on the usual method of flavone synthesis *via* chalcone, condensation of XII with *p*-anisaldehyde gave 2′-hydroxy-3′,4,6′-trimethoxy-4′,5′-methylenedioxychalcone, and cyclization of the chalcone with H_3PO_4 in ethanol gave 6,7-methylenedioxy-4′,5,8-trimethoxyflavanone (mp 160—161 °C). Oxidation of the flavanone with dichloro-dicyanabenzoquinone (DDQ) in dry dioxane gave VI (mp 212—214 °C). On the other hand, 7,8-methylenedioxy-4′,5,6-trimethoxyflavone (VII) was prepared from tangeritin (ponkanetin) (4′,5,6,7,8-pentamethoxyflavone), isolated from *Citrus reticulata*,[11] as follows; demethylation gave 4′,5,6,7,8-pentahydroxyflavone, and methylenation of this pentahydroxyflavone gave a mixture of two isomers, 6,7-methylenedioxy-4′,5,8-trihydroxyflavone (XIV) and 7,8-methylenedioxy-4′,5,6-trihydroxyflavone (XV) (both flavones, were positive to the alcoholic ferric chloride test). Without separation, methylenation of the mixture gave trimethylethers (XIV′ and XV′). Compound XIV′ coincided with VI and thus XV′ was concluded to be VII. Comparison of the dimethylether of kanzakiflavone-1 with VI and VII indicated that the dimethylether coincided with VI, that is, kanzakiflavone-1 was confirmed to be 5,8-dihydroxy-4′-methoxy-6,7-methylenedioxyflavone.

In the methylenation of III, when the hydroxyl group at C-5 was protected, an improvement of yield would be expected. Therefore, 5-hydroxy-4′,6,7-trimethoxyflavone (salvigenin) was prepared by partial demethylation of X, followed by acetylation to give 5-acetyloxy-4′,6,7-trimethoxyflavone, which was successively demethylated and methylenated in the manner described above to give XI (mp > 300 °C). However, hydrolysis of XI did not give I. The structure of XI was determined to be 3′-acetyl-4′,5-dihydroxy-6, 7-methylenedioxyflavone on the basis of the following spectral data; in the acetate of XI, signals of three acetyl groups were observed and an ABX type pattern was found for ring B protons (2′,5′ and 6′) in the ^{1}H-NMR spectrum, while the fragment m/z 163 derived from the ring B moiety was also found in the mass spectrum (MS). Compound XI was concluded to be produced by the Fries rearrangement during demethylation using $AlCl_3$–NaCl molten mixture.

TABLE I. ^{13}C-NMR Chemical Shifts of I, II, XVI, and XVII

	2	3	4	5	6	7	8	9	10	1′	2′,6′	3′,5′	4′	$\begin{smallmatrix}\mathrm{O}\\\mathrm{O}\end{smallmatrix}\!>$	5-OMe	4′-OMe
I	163.8	106.5	182.1	153.3	129.2	141.2	89.1	152.3	106.5	120.8	127.9	161.0	115.7	102.4	—	—[a]
II	163.1	102.7	181.5	153.3	93.6	138.1	125.8	153.3	103.9	120.6	128.1	161.3	115.9	102.4	—	—[a]
XVI	162.9	103.0	178.5	155.1	135.1	135.1	89.9	154.1	105.7	123.1	128.2	162.7	114.7	102.7	60.9	55.7[b]
XVII	162.1	106.8	176.9	151.9	90.8	141.6	128.2	156.3	109.0	123.2	127.4	159.9	114.2	102.8	56.9	55.3[c]

[a] DMSO-d_6. [b] $CDCl_3+CD_3OD$. [c] $CDCl_3$.

Carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra of I, II and their dimethylethers, 4′,5-dimethoxy-6,7-methylenedioxyflavone (XVI), 4′,5-dimethoxy-7,8-methylenedioxyflavone (XVII), were investigated. The assignment of each carbon of these flavones was made by analogy with the 4′,5,6,7-tetra-oxygenated flavones described in the previous paper.[14] A comparison of I and XVI with II and XVII showed that the differences of substitution pattern were reflected in the chemical shifts of C-9 (at 152 ppm for a 5,6,7-type flavone but at 153 ppm for a 5,7,8-type flavone). There was no difference between the chemical shift of a carbon of methylenedioxy located at 6, 7 and that of methylenedioxy located at 7, 8, but the methoxy carbon at C-5 in XVI, where it is adjacent to the methylenedioxyl group, showed a strong downfield shift to 60.9 ppm due to the steric effect, whereas the methoxy carbon at C-5 in XVII appeared in the usual region (56.9 ppm). This was the most useful factor in determining the position of the methylenedioxyl group. In the case of the isomers, MS and ultraviolet (UV) spectra were also useful, that is, in the MS, the base peak of a flavone possessing the methylenedioxyl group at C-6, 7 (VI) was corresponding to the parent peak, while in the case of a flavone substituted with methylenedioxy at C-7, 8 (VII), the base peak was M^+-15 because of elimination of methyl at C-6 from the parent compound. In the UV spectra, flavones like I and VI had one absorption band at 320—330 nm, whereas flavones like II and VII had two absorption bands at 300—350 nm.

Experimental[15]

4′,5,6,7-Tetrahydroxyflavone (III)——4′,5,6,7-Tetramethoxyflavone (180 mg, 0.5 mmol) was added to a molten mixture of anhyd. $AlCl_3$ (8 g) and NaCl (1.4 g), and the whole was stirred for 5 min at 180 °C. The cooled mixture was poured into 5 N HCl (120 ml) and extracted with AcOEt. The extract was concentrated under reduced pressure. The residue was recrystallized from EtOH to give 130 mg of III. mp >340 °C, a yellow powder. ^{1}H-NMR (dimethyl sulfoxide (DMSO)-d_6) δ: 6.59, 6.71 (2H, each s, H-3, 8), 6.99 (2H, d, $J=9.0$ Hz, H-3′,5′), 7.91 (2H, d, $J=9.0$ Hz, H-2′, 6′). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3300, 1660, 1610, 1580. MS m/z: 286 (M^+).

4′,5-Dihydroxy-6,7-methylenedioxyflavone (I)——A mixture of 500 mg (1.9 mmol) of III, 160 mg of KF and 700 mg of CH_2Br_2 in 20 ml of dry DMF was heated for 1.5 h at 120 °C, then poured into ice water and extracted with AcOEt. The AcOEt was evaporated off, and the residue was purified by column chromatography on silica gel (solvent: $CHCl_3$–MeOH = 10 : 1), yielding 220 mg of I as pale yellow needles. mp >300 °C (MeOH). ^{1}H-NMR (DMSO-d_6) δ: 6.15 (2H, s, $OC\underline{H}_2O$), 6.80, 6.88 (2H, each s, H-3,8), 6.93 (2H, d, $J=9.0$ Hz, H-3′,5′), 7.92 (2H, d, $J=9.0$ Hz, H-2′, 6′). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3300, 1680, 1620, 1610. *Anal.* Calcd for $C_{16}H_{10}O_6$: C, 64.43; H, 3.38. Found: C, 64.46; H, 3.36. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 286, 337. $\lambda^{+\mathrm{AlCl_3}}$: 289 sh, 301, 353. $\lambda^{+\mathrm{AcONa}}$: 286, 337. $\lambda^{+\mathrm{AcONa}+\mathrm{H_3BO_3}}$: 284, 336. MS *m*/*z*: 298 (M^+) (100%), 296, 240, 212, 180, 152, 121.

4′,5-Dimethoxy-6,7-methylenedioxyflavone: Methylation of I by the usual procedure gave the dimethylether as colorless needles. mp 190—191 °C. ^{1}H-NMR (CDCl_3) δ: 3.90, 4.13 (each 3H, each s, $2\times\text{OC}\underline{\text{H}}_3$), 6.10 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 6.77 (2H, s, H-3, 8), 6.98 (2H, d, J=9.0 Hz, H-3′, 5′), 7.82 (2H, d, J=9.0 Hz, H-2′,6′). UV $\lambda_{\max}^{\text{MeOH}}$ nm: 278, 322. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1660, 1650, 1600. MS *m*/*z*: 326 (M^+).

4′,5-Diacetoxy-6,7-methylenedioxyflavone: Acetylation of I in the usual way gave the diacetate of I as colorless needles. mp 236—237 °C (EtOH). ^{1}H-NMR (CDCl_3) δ: 2.23, 2.45 (each 3H, each s, $2\times\text{COC}\underline{\text{H}}_3$), 6.15 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 6.59, 6.90 (2H, each s, H-3, 8), 7.25 (2H, d, J=9.0 Hz, H-3′, 5′), 7.88 (2H, d, J=9.0 Hz, H-2′, 6′). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1760, 1660, 1640, 1620, 1600. MS *m*/*z*: 382, (M^+), 340, 298, 180.

4′,5,7,8-Tetrahydroxyflavone (IV)——4′,5,7,8-Tetramethoxyflavone (200 mg) was demethylated in the same manner as described for III to give 120 mg of IV as a yellow powder. mp >300 °C. ^{1}H-NMR (CDCl_3+DMSO-d_6) δ: 6.22, 6.42 (2H, each s, H-3, 6), 6.95 (2H, d, J=9.0 Hz, H-3′, 5′), 7.95 (2H, d, J=9.0 Hz, H-2′, 6′). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3200, 1600, 1610, 1580. MS *m*/*z*: 286 (M^+).

4′,5-Dihydroxy-7,8-methylenedioxyflavone (II)——Compound IV (500 mg, 1.9 mmol) was methylenated in the same manner as described for I to give 250 mg of II as a yellow powder. mp >300 °C (EtOH). ^{1}H-NMR (DMSO-d_6) δ: 6.19 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 6.50, 6.75 (2H, each s, H-3, 6), 6.93 (2H, d, J=9.0 Hz, H-3′, 5′), 7.81 (2H, d, J=9.0 Hz, H-2′, 6′). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3300, 1670, 1630, 1600, 1580. *Anal.* Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_6$: C, 64.43; H, 3.38. Found: C, 64.58; H, 3.37. MS *m*/*z*: 298 (M^+), 269, 180, 152, 121, 118. UV $\lambda_{\max}^{\text{EtOH}}$ nm: 278, 310, 322 sh. $\lambda^{+\text{AlCl}_3}$: 286, 323, 347.

4′,5-Dimethoxy-7,8-methylenedioxyflavone: mp 204—206 °C (EtOH), colorless needles. ^{1}H-NMR (CDCl_3) δ: 3.85, 3.95 (each 3H, each s, $2\times\text{OC}\underline{\text{H}}_3$), 6.11 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 6.47, 6.52 (2H, each s, H-3, 6), 7.36 (2H, d, J=9.0 Hz, H-3′, 5′), 7.80 (2H, d, J=9.0 Hz, H-2′, 6′). UV $\lambda_{\max}^{\text{EtOH}}$ nm: 276, 301, 347. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1660, 1640, 1660, 1570. MS *m*/*z*: 326 (M^+).

4′,5-Diacetoxy-7,8-methylenedioxyflavone: mp 181—183 °C (EtOH), colorless needles. ^{1}H-NMR (CDCl_3) δ: 2.35, 2.42 (each 3H, each s, $2\times\text{OC}\underline{\text{H}}_3$), 6.21 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 6.54, 6.63 (2H, each s, H-3, 6), 7.25 (2H, d, J=9.0 Hz, H-3′, 5′), 7.56 (2H, d, J=9.0 Hz, H-2′,6′). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1770, 1660, 1640, 1610. MS *m*/*z*: 382 (M^+), 340, 298.

3,6-Dimethoxy-2,4,5-trihydroxyacetophenone (XIII)——A solution of 2,4-dihydroxy-3,6-dimethoxyacetophenone (3.4 g, 16 mmol) in 10% NaOH (32 g) was added dropwise to 250 ml of solution containing 4.5 g of $\text{K}_2\text{S}_2\text{O}_8$ with stirring at 20 °C for 2 h. The mixture was left overnight and acidified to pH 5—6 with conc. HCl. The unreacted acetophenone was removed by extraction with AcOEt, and the aq. solution was further acidified to pH 2 then heated for 2 h after addition of 3 g of Na_2SO_3. The cooled solution was extracted with CHCl_3. The CHCl_3 extract was evaporated under reduced pressure and the residue was chromatographed on silica gel (solvent; C_6H_6–acetone = 8 : 1) to give 2.5 g of XIII as pale greenish needles. mp 137 °C (C_6H_6) (reported[13]) mp 137.5—138.5 °C). ^{1}H-NMR (CDCl_3) δ: 2.58 (3H, s, $\text{COC}\underline{\text{H}}_3$), 3.80, 3.90 (each 3H, each s, $2\times\text{OC}\underline{\text{H}}_3$), 5.90 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 13.86 (1H, O$\underline{\text{H}}$). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1630, 1610.

6,7-Methylenedioxy-4′,5,8-trimethoxyflavanone——A solution of 500 mg (2.1 mmol) of XII and 290 mg (2.2 mmol) of *p*-anisaldehyde in 50 ml of 80% EtOH containing 8.0 g of KOH was stirred at room temperature overnight. The mixture was acidified with HCl, then extracted with AcOEt. The extract was concentrated under reduced pressure and the residue was dissolved in 50 ml of EtOH containing 15 g of 85% H_3PO_4. The solution was boiled for 60 h, then concentrated, and the residue was extracted with water and AcOEt. The extract yielded 320 mg of VI after concentration and purification by column chromatography on silica gel. mp 160—161 °C (dec.) (EtOH), colorless needles. ^{1}H-NMR (CDCl_3) δ: 2.89 (2H, d, J=5.3 Hz, H-3 *cis*), 2.92 (1H, d, J=11.3 Hz, H-3 *trans*), 3.81, 3.89, 3.99 (each 3H, each s, $3\times\text{OC}\underline{\text{H}}_3$), 5.34 (1H, dd, J=5.3, 11.3 Hz, H-2), 5.98 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 6.93 (2H, d, J=9.0 Hz, H-3′, 5′), 7.90 (2H, d, J=9.0 Hz, H-2′,6′). MS *m*/*z*: 358 (M^+). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1670, 1610.

6,7-Methylenedioxy-4′,5,8-trimethoxyflavone (VI)——A solution of 300 mg (2.2 mmol) of the flavone and 650 mg of DDQ in 30 ml of dry dioxane was boiled for 2 h, then cooled. The reduced hydroquinone was removed by filtration, and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography (solvent: CHCl_3) to give 230 mg of VI as colorless needles. mp 212—214 °C (EtOH). ^{1}H-NMR (CDCl_3+DMSO-d_6) δ: 3.87, 4.02, 4.07 (each 3H, each s, $3\times\text{OC}\underline{\text{H}}_3$), 6.02 (2H, s, $\text{OC}\underline{\text{H}}_2\text{O}$), 6.58 (1H, s, H-3), 7.00 (2H, d, J=9.0 Hz, H-3′, 5′), 7.78 (2H, d, J=9.0 Hz, H-2′, 6′). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1640, 1620, 1600. *Anal.* Calcd for $\text{C}_{19}\text{H}_{16}\text{O}_6$: C, 64.04; H, 4.53. Found: C, 63.99; H, 4.55. MS *m*/*z*: 356 (M^+) (100%), 341, 328, 310, 295, 209, 135, 132. UV $\lambda_{\max}^{\text{MeOH}}$ nm: 283, 335.

4′,5,6,7,8-Pentahydroxyflavone——Tangeritin (200 mg) was demethylated in the same manner as described above to give 120 mg of pentahydroxyflavone. mp >330 °C (AcOEt–C_6H_{14}). ^{1}H-NMR (DMSO-d_6) δ: 6.68 (1H, s, H-3), 6.92 (2H, d, J=9.0 Hz, H-3′, 5′), 8.01 (2H, d, J=9.0 Hz, H-2′, 6′). IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3300, 1660, 1610. MS *m*/*z*: 302 (M^+), 184.

7,8-Methylenedioxy-4′,5,6-trimethoxyflavone (VII and XV′)——Pentahydroxyflavone (200 mg) was methylenated in the same manner as described above to give a mixture of two isomers. Without separation, 65 mg of the isomers was methylated, followed by separation with silica gel chromatography to give XIV′ (25 mg) and XV′ (30 mg). XIV′: mp 211—214 °C (MeOH). UV $\lambda_{\max}^{\text{MeOH}}$ nm: 283, 336. XIV′ was shown to be identical with VI by mixed mp and co-thin layer chromatography (TLC). VII and XV′: mp 167—170 °C (EtOH), colorless needles. ^{1}H-NMR (CDCl_3) δ: 3.87, 3.92, 4.02 (each 3H, each s, 3 × $\mathrm{OC\underline{H}_3}$), 6.17 (2H, s, $\mathrm{OC\underline{H}_2O}$), 6.53 (1H, s, H-3), 6.96 (2H, d, J=9.0 Hz, H-3′, 5′), 7.84 (2H, d, J=9.0 Hz, H-2′, 6′). IR $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ cm^{-1}: 1640, 1610. *Anal.* Calcd for $C_{19}H_{16}O_7$: C, 64.04; H, 4.53. Found: C, 64.10; H, 4.51. MS *m*/*z*: 356 (M$^+$), 341 (100%). UV $\lambda_{\mathrm{max}}^{\mathrm{MeOH}}$ nm: 276, 303, 324.

3′-Acetyl-4′,5-dihydroxy-6,7-methylenedioxyflavone (XI)——Demethylation of 200 mg of 5-acetoxy-4′,6,7-trimethoxyflavone, followed by methylenation gave 40 mg of the title flavone. mp >300 °C (MeOH). ^{1}H-NMR (DMSO-d_6) δ: 2.75 (3H, s, $\mathrm{COC\underline{H}_3}$), 6.15 (2H, s, $\mathrm{OC\underline{H}_2O}$), 6.88, 7.00 (2H, each s, H-3, 8), 7.08 (1H, d, J=9.0 Hz, H-5′), 8.0—8.5 (2H, m, H-2′, 6′). IR $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ cm^{-1}: 3400, 1680, 1620, 1580. MS *m*/*z*: 340 (M$^+$) (100%), 180, 163.

3′-Acetyl-4′,5-diacetoxy-6,7-methylenedioxyflavone: ^{1}H-NMR (DMSO-d_6) δ: 2.38, 2.45 (each 3H, each s, 2 × $\mathrm{COC\underline{H}_3}$), 2.61 (3H, s, $\mathrm{COC\underline{H}_3}$), 6.15 (2H, s, $\mathrm{OC\underline{H}_2O}$), 6.60, 6.91 (2H, each s, H-3, 8), 7.28 (1H, d, J=9.0 Hz, H-5′), 8.0—8.5 (2H, m, H-2′, 6′). MS *m*/*z*: 424 (M$^+$), 382, 340 (100%), 163.

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15) Melting points were determined on a Büchi Schmeltzpunktbestimmungsapparat, and are uncorrected. UV spectra were taken on a Hitachi 323 spectrometer and MS were obtained on a JEOL JMS-300 mass spectrometer at 70 eV. ^{1}H-NMR were taken on a Hitachi R-20B instrument at 60 MHz and chemical shifts are given in δ values (ppm) with tetramethylsilane as an internal standard. ^{13}C-NMR spectra were obtained on a JEOL FX-60FT spectrometer operating at 25.15 MHz, spectral width 4000 Hz and 4096 data points. BW-820 MH (Fuji Devison Chemicals, Ltd.) was used for column chromatography.