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Flavonoids Syntheses. III.[1] Syntheses of Flavones Isolated from *Scutellaria rehderiana*

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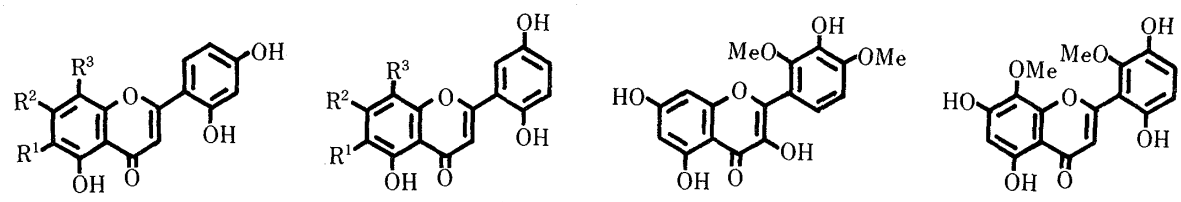
The structures of two new flavones isolated from *Scutellaria rehderiana*, named rehderianin I and viscidulin III, were revised 2′,5,5′-trihydroxy-7,8-dimethoxyflavone and 3′,5,6′,7-tetrahydroxy-2′,8-dimethoxyflavone, respectively, based on a comparison with the synthesized flavones.

Keywords——flavone synthesis; 2′,4′,5-trihydroxy-6,8-dimethoxyflavone; 2′,5,5′-trihydroxy-7,8-dimethoxyflavone; 3,3′,5,7-tetrahydroxy-2′,4′-dimethoxyflavone; 3′,5,6′,7-tetrahydroxy-2′,8-dimethoxyflavone; rehderianin I; viscidulin III

A new flavone, designated as rehderianin I, was isolated from the dried roots of *Scutellaria rehderiana* DIELS (甘肅黃芩) along with several common *Scutellaria* flavones by Liu *et al.*[2] Its structure was deduced to be 2′,4′,5-trihydroxy-6,8-dimethoxyflavone (**1a**) on the basis of the color reaction and spectroscopic analyses. A tetrahydroxy-dimethoxyflavone was also isolated, and was identified as viscidulin III, which had been isolated from *S. viscidula* BUNGE (粘毛黃芩)[3] and proposed to be 3,3′,5,7-tetrahydroxy-2′,4′-dimethoxyflavone (**3**). These two flavones have unprecedented substitutional patterns for *Scutellaria* flavones, in the A and B rings in the case of **1a**, and in the B ring in **3**. A flavone having a 5,6,8-trioxygenated pattern in ring A, 2′,5-dihydroxy-6,8-dimethoxyflavone was isolated from *S. baicalensis* GEORGI (黃芩)[4] and given the name of skullcapflavone I, but afterwards its structure was revised to 2′,5-dihydroxy-7,8-dimethoxyflavone.[5] As regards tetrahydroxy-dimethoxyflavones, 3′,5,6′,7-tetrahydroxy-2′,8-dimethoxyflavone (**4**) has been reported as one of the constituents of *S. baicalensis*. The structure of **4** was elucidated with the aid of color reactions and spectroscopic evidence by Tomimori *et al.*,[6] and supported by an X-ray structure analysis by Kimura *et al.*[7] Finally the structure was confirmed by our synthesis.[1] We describe in this paper the synthesis of **1a**, **3** and related flavones, and the identification of the correct structures for rehderianin I and viscidulin III by direct comparison of the natural products with the synthetic compounds.

In the preparation of **1a**, 2′,4′,5-trihydroxy-6,7-dimethoxy- (**1b**), and 2′,4′,5-trihydroxy-7,8-dimethoxyflavone (**1c**), 2-hydroxy-3,5,6-trimethoxy- (**5**),[5b] 2-hydroxy-4,5,6-trimethoxy-



1 2 3 4

a: $R^1=R^3=OMe$, $R^2=H$
b: $R^1=R^2=OMe$, $R^3=H$
c: $R^2=R^3=OMe$, $R^1=H$

Chart 1

(**6**), and 2-hydroxy-3,4,6-trimethoxyacetophenone (**7**) were esterified with 2,4-diisopropyloxybenzoic acid (**8**) to give the corresponding esters. The resulting esters were subjected to the Baker–Venkataramann rearrangement to afford β-diketone compounds, which were treated with a mixture of acetic acid–sulfuric acid (10:1) to give 2′,4′-diisopropyloxy-5,6,8-trimethoxy- (**9**), 2′,4′-diisopropyloxy-5,6,7-trimethoxy- (**10**), and 2′,4′-diisopropyloxy-5,7,8-trimethoxyflavone (**11**), respectively. The flavones were deisopropylated and partially demethylated with boron trichloride to give the desired flavones **1a** (mp 249—250 °C), **1b** (mp 264—266 °C), and **1c** (mp 288 °C (dec.)). In the proton nuclear magnetic resonance (^{1}H-NMR) spectra of the flavones thus obtained, proton signals due to ring B, which were observed at 6.4 (dd), 6.5 (d), and 7.8 (d) ppm, were completely different from those of rehderianin I (6.90, 7.18 and 7.36 ppm). In the ultraviolet (UV) spectra, the absorption bands based on Band I were observed at *ca.* 350 nm, whereas that of rehderianin I was at 370 nm. By comparison of the spectral data with those for 2′,5′-dimethoxyflavone[8] and 2′,5,5′-trihydroxy-6,7,8-trimethoxyflavone,[6] it was suggested that hydroxygroups of rehderianin I are not located at C-2′ and 4′, but are C-2′ and 5′. To clarify the structure of rehderianin I, two other flavones, 2′,5,5′-trihydroxy-6,7-dimethoxy- (**2b**) and 2′,5,5′-trihydroxy-7,8-dimethoxyflavone (**2c**) were prepared. Esterification of **6** and **7** with 2,5-diisopropyloxybenzoic acid (**12**) gave the respective esters, which were led to **2b** (mp 267—269 °C (dec.)) and **2c** (mp 265 °C) by the same procedures as described above. Comparison of **2b** and **2c** with the natural product by co-thin layer chromatography and spectral comparison[2] showed that **2c** was identical with rehderianin I. Consequently, the structure of rehderianin I should be revised to 2′,5,5′-trihydroxy-7,8-dimethoxyflavone, a new structure for a naturally occurring flavone.

On the other hand, preparation of **3** was carried out as follows; condensation of 2-hydroxy-4,6-diisopropyloxyacetophenone (**13**) with 3-isopropyloxy-2,4-dimethoxybenzaldehyde (**14**) in the presence of potassium hydroxide in methyl cellosolve gave 2′-hydroxy-3,4′,6′-triisopropyloxy-2,4-dimethoxychalcone (**15**) as an orange-yellow oil, which was subjected to the Algar–Flynn–Oyamada reaction (AFO reaction) to afford 3-hydroxy-3′,5,7-triisopropyloxy-2′,4′-dimethoxyflavone (3′,5,7-triisopropyloxy-2′,4′-dimethoxyflavonol) (**16**). The flavone **16** was deisopropylated with boron trichloride to give the flavone **3** (mp 216—218 °C) and a partially demethylated derivative of **3** (mp 272—273 °C) (**17**). The structure of **17** was suggested to be 2′,3,3′,5,7-pentahydroxy-4′-methoxyflavone because the $M^+ - 17$ fragment ion peak appeared clearly in the mass spectrum (MS).[9] The flavones were easily separable by chromatography on silica gel (eluent, benzene–acetone = 3:1). Flavone (**3**) was independently prepared by condensation of 2-hydroxy-4,6-dibenzyloxyacetophenone (**18**) and 3-benzyloxy-2,4-dimethoxybenzaldehyde (**19**), followed by the usual procedures. Based on a comparison **3** with the natural flavone (spectral data),[2] the structure of viscidulin III is not **3**, but **4**. This was further confirmed by comparison with synthetic samples of **4**, as well as 2′,5,6′,7-tetrahydroxy-3′,8-dimethoxy-, and 2′,3′,5,7-tetrahydroxy-6′,8-dimethoxyflavone.[2] Recently Liu *et al.*[10] reported that **4** was also contained in the roots of *S. rehderiana.*

Rehderianin I (**2c**) is the second example of a compound oxygenated at C-2′ and 5′ in *Scutellaria*, the first one being 2′,5,5′-trihydroxy-6,7,8-trimethoxyflavone.[6] Biogenetically, **2c** may be produced by oxidation at C-5′ in skullcapflavone I. From our present study, it has become apparent that 3′,5,6′,7-tetrahydroxy-2′,8-dimethoxyflavone (**4**) is distributed in three *Scutellaria* species.

Experimental[11]

Flavone synthesis by means of the Baker–Venkataramann rearrangement was carried out as described in the

previous paper.[5b])

2′,4′,5-Trihydroxy-6,8-dimethoxyflavone (1a)——Condensation of **5** (2.26 g, 0.01 mol) with **8** (2.38 g, 0.01 mol) yielded 2-(2′,4′-diisopropyloxybenzoyloxy)-3,5,6-trimethoxyacetophenone (3.2 g) as a colorless oil. ^{1}H-NMR (CCl_4) δ: 1.34 (12H, d, J=6 Hz, 2×(CH_3)$_2$CH), 2.37 (3H, s, $COCH_3$), 3.73 (6H, s, 2×OCH_3), 3.80 (3H, s, OCH_3), 4.32—4.83 (2H, m, 2×CH<), 6.39 (1H, d, J=2.4 Hz, H-3′), 6.44 (1H, s, H-4), 6.62 (1H, dd, J=9, 2.4 Hz, H-5′), 7.84 (1H, d, J=9 Hz, H-6′). The above ester (3 g) was dissolved in pyridine (10 ml), and pulverized KOH (5 g) was added to give 2-hydroxy-2′,4′-diisopropyloxy-3,5,6-trimethoxydibenzoylmethane (2.5 g) as a yellow oil after usual work-up. ^{1}H-NMR (CCl_4) δ: 1.35, 1.45 (6H each, d, J=6 Hz, 2×(CH_3)$_2$CH), 6.38—6.71 (3H, m, H-3′,4,5′), 7.91 (1H, d, J=8.8 Hz, H-6′). The resulting β-diketone (2 g) was dissolved in acetic acid (10 ml) and added to a mixture of acetic acid-sulfuric acid (10 : 1) (15 ml). The flavone **9** (1.3 g) was obtained as a colorless oil. ^{1}H-NMR (CCl_4) δ: 1.35, 1.45 (6H each, d, J=6 Hz, 2×(CH_3)$_2$CH), 3.78, 3.88, 3.93 (3H each, s, 3×OCH_3), 4.30—4.78 (2H, m, 2×CH<), 6.41 (1H, d, J=2.2 Hz, H-3′), 6.46 (1H, dd, J=9, 2.2 Hz, H-5′), 6.75, 6.82 (1H each, s, H-3, 7), 7.80 (1H, d, J=9 Hz, H-6′). A solution of **9** (900 mg) in CH_2Cl_2 was cooled to −60 °C and BCl_3 (0.5 ml) was added. The reaction mixture was left at room temperature for 1 h. Usual work-up of the mixture gave **1a** as orange-yellow needles, mp 249—250 °C (AcOEt). ^{1}H-NMR (DMSO-d_6) δ: 3.86, 3.94 (3H each, s, 2×OCH_3), 6.44 (1H, dd, J=9, 2.1 Hz, H-5′), 6.51 (1H, d, J=2.1 Hz, H-3′), 7.08 (1H, s, H-3), 7.19 (1H, s, H-7), 7.76 (1H, d, J=9 Hz, H-6′). MS m/z (rel. int.): 330 [M^+] (77), 315 (100), 181 (60), 153 (21). UV λ_{max}^{MeOH} nm (log ε): 280 sh (4.1), 298 (4.2), 315 sh (4.1), 350 (4.3); $\lambda_{max}^{+AlCl_3}$ nm: 260 sh, 286, 320, 380; $\lambda_{max}^{+AlCl_3+HCl}$ nm: 258 sh, 284, 320 sh, 370; λ_{max}^{+NaOMe} nm: 270 sh, 310, 360 sh, 430; λ_{max}^{+NaOAc} nm: 275 sh, 298, 353; $\lambda_{max}^{+NaOAc+H_3BO_3}$ nm: 280 sh, 297, 351.

2′,4′,5-Trihydroxy-6,7-dimethoxyflavone (1b)——The same procedure as described above was used. 2-(2′,4′-Diisopropylbenzoyloxy)-4,5,6-trimethoxyacetophenone: a colorless oil. ^{1}H-NMR (CCl_4) δ: 2.31 (3H, s, $COCH_3$), 6.29—6.50 (3H, m, H-3,3′,5′), 7.95 (1H, d, J=8.8 Hz, H-6′). 2-Hydroxy-2′,4′-diisopropyloxy-4,5,6-trimethoxydibenzoylmethane; a yellow oil. ^{1}H-NMR (CCl_4) δ: 6.08 (1H, s, H-3), 13.08 (1H, s, OH). **10**: a pale yellow oil. ^{1}H-NMR (CCl_4) δ: 6.40—6.90 (3H, m, H-3′,5′,8), 6.70 (1H, s, H-3), 7.63 (1H, d, J=9 Hz, H-6′). **1b**: mp 264—266 °C (AcOEt), orange-yellow needles. ^{1}H-NMR (DMSO-d_6) δ: 3.76, 3.94 (3H each, s, 2×OCH_3), 6.43 (1H, dd, J=8, 2.1 Hz, H-5′), 6.51 (1H, d, J=2.1 Hz, H-3′), 6.83 (1H, s, H-8), 7.04 (1H, s, H-3), 7.82 (1H, d, J=8 Hz, H-6′). MS m/z (rel. int.): 330 [M^+] (100), 315 (83), 301 (18), 287 (15), 284 (16), 181 (37), 153 (32). UV λ_{max}^{MeOH} nm (log ε): 252 (3.8), 273 (3.9), 350 (4.0); λ_{max}^{+NaOMe} nm: 266, 290 sh, 418; $\lambda_{max}^{+AlCl_3}$ nm: 280 sh, 294, 384; $\lambda_{max}^{+AlCl_3+HCl}$ nm: 280 sh, 290, 370; λ_{max}^{+AcONa} nm: 273, 360, 394 sh; $\lambda_{max}^{+AcONa+H_3BO_3}$ nm: 273, 350.

2′,4′,5-Trihydroxy-7,8-dimethoxyflavone (1c)——The same procedure as described above was used. 2-(2′,4′-Diisopropyloxybenzoyl)-3,4,6-trimethoxyacetophenone: mp 125—126 °C (MeOH), colorless needles. ^{1}H-NMR ($CDCl_3$) δ: 2.43 (3H, s, $COCH_3$), 6.41 (1H, s, H-5), 6.49 (1H, d, J=2.3 Hz, H-3′), 6.50 (1H, dd, J=9, 2.3 Hz, H-5′), 7.98 (1H, d, J=9 Hz, H-6′). 2-Hydroxy-2′,4′-diisopropyloxy-3,4,6-trimethoxydibenzoylmethane; a yellow oil. ^{1}H-NMR (CCl_4) δ: 6.44 (1H, s, H-5), 6.50 (1H, d, J=2.2 Hz, H-3′), 6.51 (1H, dd, J=9, 2.2 Hz, H-5′), 7.95 (1H, d, J=9 Hz, H-6′), 13.59 (1H, s, OH). **11**: mp 56—57 °C (AcOEt–C_6H_{14}), colorless needles. ^{1}H-NMR ($CDCl_3$) δ: 6.41 (1H, s, H-6), 6.51 (1H, d, J=2.2 Hz, H-3′), 6.57 (1H, dd, J=9, 2.2 Hz, H-5′), 6.95 (1H, s, H-3), 7.85 (1H, d, J=9 Hz, H-6′). **1c**: mp 288 °C (dec.) (AcOEt), a yellow powder. ^{1}H-NMR (DMSO-d_6) δ: 3.80, 3.90 (3H each, s, 2×OCH_3), 6.45 (1H, dd, J=9, 2.2 Hz, H-5′), 6.51 (1H, d, J=2.2 Hz, H-3′), 6.52 (1H, s, H-6), 7.02 (1H, s, H-3), 7.76 (1H, d, J=9 Hz, H-6′), 10.10, 10.68 (1H each, s, 2×OH), 12.81 (1H, s, C_5-OH). MS m/z (rel. int.): 330 [M^+] (57), 315 (100), 181 (27), 153 (23), 135 (13). UV λ_{max}^{MeOH} nm (log ε): 255 sh (3.9), 271 (4.0), 291 sh (3.9), 356 (4.0); λ_{max}^{+NaOMe} nm: 265, 293 sh, 424; $\lambda_{max}^{+AlCl_3}$ cm: 278, 303, 360, 406; $\lambda_{max}^{+AlCl_3+HCl}$ nm: 278, 294, 358, 402; λ_{max}^{+AcONa} nm: 270, 290, 365; $\lambda_{max}^{+AcONa+H_3BO_3}$ nm: 270, 290, 360.

2′,5,5′-Trihydroxy-6,7-dimethoxyflavone (2b)——Condensation of **6** (1.3 g, 5.9 mmol) with **12** (1.4 g, 5.9 mmol) gave 2-(2′,5′-diisopropyloxybenzoyl)-4,5,6-trimethoxyacetophenone (2.1 g) as a colorless oil. ^{1}H-NMR (CCl_4) δ: 1.33 (12H, d, J=6 Hz, 2×(CH_3)$_2$CH), 2.48 (3H, s, $COCH_3$), 3.85 (6H, s, 2×OCH_3), 3.93 (3H, s, OCH_3), 4.30—4.70 (2H, m, 2×CH<), 6.53 (1H, s, H-3), 6.95—6.99 (2H, m, H-3′,4′), 7.40—7.45 (1H, m, H-6′). 2-Hydroxy-2′,5′-diisopropyloxy-4,5,6-trimethoxybenzoylmethane: a yellow oil. The ^{1}H-NMR spectrum showed the tautomeric enol derivative, (CCl_4) δ: 4.90 ($COCH_2CO$), 7.53 (1H, s, CHOH), 2′,5′-Diisopropyloxy-5,6,7-trimethoxyflavone: a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 6.75 (1H, s, H-8), 6.90 (1H, s, H-3), 6.95 (2H, s, H-3′,4′), 7.33—7.36 (1H, m, H-6′). **2b**: mp 267—269 °C (dec.) (AcOEt–C_6H_{12}), yellow needles. ^{1}H-NMR (DMSO-d_6) δ: 3.76 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 6.80 (1H, s, H-8), 6.81—6.86 (2H, m, H-3′,4′), 7.14 (1H, s, H-3), 7.28—7.32 (1H, m, H-6′). MS m/z (rel. int.): 330 [M^+] (100), 315 (89), 301 (24), 287 (26), 284 (21), 270 (12), 181 (42), 153 (71). UV λ_{max}^{MeOH} nm (log ε): 272 (4.0), 309 (3.8). 364; λ_{max}^{+NaOMe} nm: 270, 315 sh, 426 (dec.); $\lambda_{max}^{+AlCl_3}$ nm: 280 sh, 298, 334, 396; $\lambda_{max}^{+AlCl_3+HCl}$ nm: 280 sh, 289, 325, 386; λ_{max}^{+NaOAc} nm: 272, 310, 364; $\lambda_{max}^{+NaOAc+H_3BO_3}$ nm: 272, 310, 364.

2′,5,5′-Trihydroxy-7,8-dimethoxyflavone (Rehderianin I) (2c)——Condensation of **7** (1.5 g, 6.6 mmol) with **12** (1.6 g, 6.6 mmol) gave 2-(2′,5′-diisopropyloxybenzoyloxy)-3,4,6-trimethoxyacetophenone (2.5 g) as a colorless oil. ^{1}H-NMR (CCl_4) δ: 2.49 (3H, s, $COCH_3$), 6.41 (1H, s, H-5), 6.98—7.12 (2H, m, H-3′,4′), 7.50 (1H, d, J=2 Hz, H-6′). 2-Hydroxy-2′,5′-diisopropyloxy-3,4,6-trimethoxydibenzoylmethane: a yellow oil, whose ^{1}H-NMR spectrum showed a mixture of β-diketone–enol forms (1 : 5); the following data are for the enol derivative. ^{1}H-NMR ($CDCl_3$) δ: 1.31 (12H, d, J=6 Hz, 2×(CH_3)$_2$CH), 3.62, 3.81, 3.93 (3H each, s, 3×OCH_3), 4.30—4.74 (2H, m, 2×CH<), 6.95—7.01

(2H, m, H-3′,4′), 7.30 (1H, s, H-5), 7.43 (1H, d, J=2 Hz, H-6′), 7.60 (1H, s, CHOH), 2′,5′-Diisopropyloxy-5,7,8-trimethoxyflavone: mp 140 °C (AcOEt–C_6H_{14}), colorless needles. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (12H, d, J=6 Hz, 2×$(CH_3)_2$CH), 3.92, 3.98, 4.00 (3H each, s, 3×OCH_3), 4.41—4.65 (2H, m, 2×CH<), 6.44 (1H, s, H-6), 6.93—7.08 (2H, m, H-3′,4′), 7.50 (1H, d, J=2 Hz, H-6′). **2c**: mp 265 °C (AcOEt–C_6H_{14}), yellow needles (lit.[2] mp 264—267 °C). ^{1}H-NMR (DMSO-d_6) δ: 3.83 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 6.49 (1H, s, H-6), 6.83—6.87 (2H, m, H-3′,4′), 7.11 (1H, s, H-3), 7.30 (1H, d, J=2 Hz, H-6′), 9.09 (1H, s, OH), 12.64 (1H, s, C_5-OH). MS m/z (rel. int.): 330 [M^+] (56), 315 (100), 287 (5), 181 (35), 165 (7), 158 (14), 153 (27), 125 (8). UV λ_{max}^{MeOH} nm (log ε): 274 (3.5), 374 (3.1); λ_{max}^{+NaOMe} nm: 270, 350, 420; $\lambda_{max}^{+AlCl_3}$ nm: 280, 296 sh, 330 sh, 416; $\lambda_{max}^{+AlCl_3+HCl}$ nm: 280, 290 sh, 330 sh, 410; λ_{max}^{+AcONa} nm: 273, 375. $\lambda_{max}^{+AcONa+H_3BO_3}$ nm: 273, 375.

3,3′,5,7-Tetrahydroxy-2′,4′-dimethoxyflavone (3)——According to our previous paper,[1] **13** (2 g), 7.9 mmol) was condensed with **14** (1.8 g, 7.9 mmol) to give 2′-hydroxy-3,4′,6′-triisopropyloxy-2,4-dimethoxychalcone (**15**) (3.2 g) as an orange-yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.30, 1.35, 1.43 (6H each, d, J=6 Hz, 3×$(CH_3)_2$CH), 3.88, 3.91 (3H each, 2×OCH_3), 4.25—4.80 (3H, m, 3×CH<), 5.88, 6.04 (1H each, d, J=2 Hz, H-3′,5′), 6.68, 7.33 (1H each, d, J=9 Hz, H-5,6), 7.98 (2H, s, H-α and β), 14.31 (1H, s, OH). 3-Hydroxy-3′,5,7-triisopropyloxy-2′,4′-dimethoxyflavone (**16**): a pale yellow oil. ^{1}H-NMR (CCl_4) δ: 1.20—1.48 (18H, m, 3×$(CH_3)_2$CH), 3.85, 3.96 (3H each, s, 2×OCH_3), 4.14—4.18 (3H, m, 3×CH<), 6.21, 6.36 (1H each, d, J=2.8 Hz, H-6,8), 6.67, 7.65 (1H each, d, J=9 Hz, H-5′,6′). The resulting flavone (1.2 g) was treated with BCl_3 to give a mixture of **3** and **17**, which were separated by silica gel column chromatography (eluent, C_6H_6–$(CH_3)_2CO$=3:1). **3**: mp 216—218 °C (AcOEt–C_6H_{14}), a pale yellow powder. ^{1}H-NMR (DMSO-d_6) δ: 3.84, 3.96 (3H each, s, 2×OCH_3), 6.17, 6.32 (1H each, d, J=2.3 Hz, H-6,8), 6.32 (1H, d, J=9 Hz, H-5′), 6.92 (1H, d, J=9 Hz, H-6′). MS m/z (rel. int.): 346 [M^+] (100), 315 (39), 303 (22), 300 (26), 192 (70), 165 (30), 164 (39), 153 (98). UV λ_{max}^{MeOH} nm (log ε): 255 (4.4), 300 (4.1), 349 (4.0); λ_{max}^{+NaOMe} nm: 271, 327, 390; $\lambda_{max}^{+AlCl_3}$ nm: 265, 303, 330 sh, 406; $\lambda_{max}^{+AlCl_3+HCl}$ nm: 265, 299, 332 sh, 405; λ_{max}^{+AcONa} nm: 269, 325, 360; $\lambda_{max}^{+AcONa+H_3BO_3}$ nm: 255, 304, 349. Condensation of **18** (2.5 g, 7 mmol) with **19** (2 g, 7 mmol) gave 3,4′,6′-tribenzyloxy-2-hydroxy-2,4-dimethoxychalcone (3.2 g) as a yellow powder, mp 158—159 °C (MeOH). MS m/z (rel. int.): 602 [M^+] (100), 571 (50), 511 (98), 333 (75), 243 (50), 207 (69), 181 (69), 167 (44). 3′,5,7-Tribenzyloxy-3-hydroxy-2′,4′-dimethoxyflavone: a pale yellow oil. MS m/z: 616 [M^+] (98), 526 (82), 497 (100), 435 (63), 407 (32), 399 (20), 331 (38), 315 (35). The above flavone (1.5 g) was debenzylated in AcOEt with 10% Pd–C/H_2 to give **3** (600 mg) as a pale yellow powder.

2′,3,3′,5,7-Pentahydroxy-4′-methoxyflavone (17)——mp 272—273 °C (MeOH–$CHCl_3$), a yelllow powder. ^{1}H-NMR (DMSO-d_6) δ: 3.85 (3H, s, OCH_3), 6.16, 6.29 (1H, each, d, J=2.3 Hz, H-6,8), 6.34 (1H, d, J=9 Hz, H-5′), 6.86 (1H, d, J=9 Hz, H-6′). MS m/z: 332 [M^+] (100), 315 (17), 303 (22), 289 (18), 286 (32), 258 (17), 153 (44). UV λ_{max}^{MeOH} nm (log ε): 258 (4.3), 357 (4.1); λ_{max}^{+NaOMe} nm: 274, 311, 395; $\lambda_{max}^{+AlCl_3}$ nm: 270, 305, 360 sh, 419; $\lambda_{max}^{+AlCl_3+HCl}$ nm: 266, 302, 346 sh, 415; λ_{max}^{+NaOAc} nm: 274, 309, 395; $\lambda_{max}^{+NaOAc+H_3BO_3}$ nm: 260, 300 sh, 325 sh, 368.

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