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Synthetic Studies on Flavone Derivatives. XIV.[1,2] Synthesis of 2′,4′,5′-Trioxygenated Flavones

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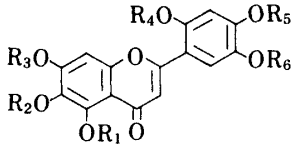
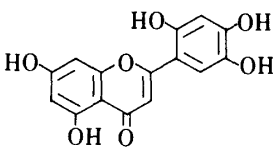
Seven naturally occurring flavones oxygenated at C-2′, C-4′ and C-5′ in ring B were synthesized, together with their isomers, to confirm the proposed structures. The synthesized flavones **1**, **2**, **3a**, **5**, **7** and **8** were identical with the corresponding natural flavones, but **4a** was not. The spectral properties of these flavones are discussed.

Keywords——flavone synthesis; 2′,4′,5,5′,7-pentahydroxyflavone; 2′,4′,5,5′,6,7-hexa-oxygenated flavone; 2′,4′,5,5′,6,7,8-hepta-oxygenated flavone; 2′,4′,5′-tri-oxygenated flavone; UV

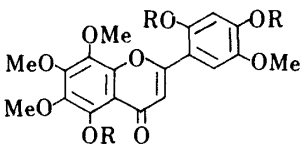
Flavones tri-oxygenated at C-2′, C-4′ and C-5′ in ring B are rarely found in nature in comparison with ones tri-oxygenated at C-3′, C-4′ and C-5′. Up to the present, only seven filavones, to our knowledge, having the former substitutional pattern have been reported; among them, five flavones have been isolated from Compositae,[3] and the others from Meliaceae[4] and Pteridophytes.[5] Some 3-methoxyflavones (flavonols) possessing the same substitutional pattern in ring B have been found in Leguminosae[6] and Geraniaceae.[7] We describe in this paper the syntheses of all these naturally occurring flavones substituted with hydroxyl and/or methoxyl groups at C-2′, C-4′ and C-5′, as well as their isomers, to confirm the proposed structures and to clarify their spectroscopic properties. An improved method using isopropyl instead of benzyl protective groups[8] was developed. The syntheses will be described for convenience in groups based on the number of methoxyl groups in ring B.



2: $R_1=R_3=R_4=R_5=H$, $R_2=R_6=Me$
3a: $R_1=R_4=R_5=H$, $R_2=R_3=R_6=Me$ (arcapillin)
3b: $R_1=R_4=R_6=H$, $R_2=R_3=R_5=Me$
4a: $R_1=R_2=R_5=H$, $R_3=R_4=R_6=Me$ (isoarcapillin)
4b: $R_1=R_3=R_5=H$, $R_2=R_4=R_6=Me$
4c: $R_1=R_3=R_4=H$, $R_2=R_5=R_6=Me$
5: $R_1=R_3=H$, $R_2=R_4=R_5=R_6=Me$ (tabularin)
6a: $R_1=R_2=R_3=R_4=R_5=R_6=Me$
6b: $R_1=H$, $R_2=R_3=R_4=R_5=R_6=Me$



1: isoetin



7: R=Me (agecorynin C)
8: R=H (agecorynin D)

The requisite starting material of the ring B moiety for 2′,4′,5,5′,7-pentahydroxyflavone (**1**) (isoetin; isolated from *Isoetes delilei* and *I. durieui* (Pteridophytes)),[5] 2,4,5-triisopropyloxybenzaldehyde (**9**), was prepared as follows. Diisopropyl ether of protocatechualdehyde

was subjected to the Baeyer–Villiger reaction to give 3,4-diisopropyloxyphenol, and introduction of aldehyde by means of the Vilsmeier reaction of the resulting triisopropyl ether gave **9**. The aldehyde **9** was condensed with 2-hydroxy-4,6-diisopropyloxyacetophenone (**10**) in the presence of potassium hydroxide to yield 2′-hydroxy-2,4,4′,5,6′-pentaisopropyloxychalcone (**11**), which was led to 2′,4′,5,5′,7-pentaisopropyloxyflavone (**12**) by direct dehydrogenative cyclization by the use of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).[9] The flavone **12** was deisopropylated with BCl_3 in dichloromethane[10] to give **1** (mp 305—307 °C). The Baeyer–Villiger reaction of 2,4-diisopropyloxybenzaldehyde, followed by methylation and the Vilsmeier reaction gave 2,4-diisopropyloxy-5-methoxybenzaldehyde (**13**), which is a starting material for the ring B moiety of 2′,4′,5,7-tetrahydroxy-5′,6-dimethoxyflavone (**2**) isolated from *Artemisia ludoviciana var. ludoviciana* (Compositae).[3c] The ring A moiety of **2**, 2-hydroxy-4,6-diisopropyloxy-5-methoxyacetophenone (**14**) was obtained by methylation of 2,5-dihydroxy-4,6-diisopropyloxyacetophenone (**15**), which was derived from **10** by the Elbs oxidation. Condensation of **13** with **14** gave 2′-hydroxy-2,4,4′,6′-tetraisopropyloxy-5,5′-dimethoxychalcone (**16**). After oxidation of the chalcone, the resulting 2′,4′,5,7-tetraisopropyloxy-5′,6-dimethoxyflavone (**17**) was deisopropylated to give **2** (mp 285 °C) (dec.).

The 7-methyl ether of **2**, 2′,4′,5-trihydroxy-5′,6,7-trimethoxyflavone (**3a**), isolated from *Artemisia capillaris* (Compositae),[3a,b] was named arcapillin.[3a] Arcapillin was synthesized as follows, after condensation of **13** with 2-hydroxy-4,5,6-trimethoxyacetophenone (**18**), the resulting 2′-hydroxy-2,4-diisopropyloxy-4′,5,5′,6′-tetramethoxychalcone (**19**) was led to 2′,4′-diisopropyloxy-5,5′,6,7-tetramethoxyflavone (**20**). The isomer of **3a**, 2′,5,5′-trihydroxy-4′,6,7-trimethoxyflavone (**3b**) was also synthesized for comparison with **3a**. The requisite aldehyde for **3b**, 2,5-diisopropyloxy-4-methoxybenzaldehyde (**21**), was prepared from vanillin by the Dakin reaction (1,4-dihydroxy-2-methoxybenzene (**22**)), followed by isopropylation and the Vilsmeier reaction. Condensation of **21** with **18** gave 2′-hydroxy-2,5-diisopropyloxy-4,4′,5′,6′-tetramethoxychalcone (**23**), which was oxidized to give 2′,5′-diisopropyloxy-4′,5,6,7-tetramethoxyflavone (**24**). The flavones (**20** and **24**) were deisopropylated with simultaneous partial demethylation at C-5 to afford **3a** (mp 287—290 °C) and **3b** (mp 285 °C) (dec.).

An isomer of **3a** was also isolated from *Artemisia capillaris*, and the structure was deduced to be 4′,5,6-trihydroxy-2′,5′,7-trimethoxyflavone (**4a**), named isoarcapillin, on the basis of spectral data.[3e] 4-Isopropyloxy-2,5-dimethoxybenzaldehyde (**25**) for the ring B moiety of **4a** was prepared as follows; the Elbs oxidation and subsequent methylation of salicylaldehyde gave 2,5-dimethoxybenzaldehyde (**26**), which was subjected to isopropylation and the Vilsmeier reaction after the Baeyer–Villiger reaction. On the other hand, 2-hydroxy-5-isopropyloxy-4,6-dimethoxyacetophenone (**27**) for the ring A moiety of **4a** was prepared by isopropylation of 2,5-dihydroxy-4,6-dimethoxyacetophenone (used for the preparation of **18**). Further, to investigate the proposed structure for isoarcapillin, 4′,5,7-trihydroxy-2′,5′,6-trimethoxyflavone (**4b**) and 2′,5,7-trihydroxy-4′,5′,6-trimethoxyflavone (**4c**) were also synthesized. As an aldehyde for the ring B moiety of **4c**, 2-isopropyloxy-4,5-dimethoxybenzaldehyde (**28**) was prepared from veratraldehyde in three steps, that is, the Baeyer–Villiger reaction to obtain 3,4-dimethoxyphenol, isopropylation and the Vilsmeier reaction. Condensation of **25** with **27**, **25** with **14**, and **28** with **14** gave 2′-hydroxy-4,5′-diisopropyloxy-2,4′,5,6′-tetramethoxychalcone (**29**), 2′-hydroxy-4,4′,6′-triisopropyloxy-2,5,5′-trimethoxychalcone (**30**) and 2′-hydroxy-2,4′,6′-triisopropyloxy-4,5,5′-trimethoxychalcone (**31**), respectively. After oxidation of the chalcones to the corresponding flavones (in the case of **29**, after conversion to the corresponding flavanone); 4′,6-diisopropyloxy-2′,5,5′,7-tetramethoxy- (**32**), 4′,5,7-triisopropyloxy-2′,5′,6-trimethoxy- (**33**), and 2′,5,7-triisopropyloxy-4′,5′,6-trimethoxyflavone (**34**), they were led to **4a** (mp 246 °C), **4b** (mp 241—242 °C) and **4c** (mp 285—

287 °C) (dec.) by deisopropylation and partial demethylation.

5,7-Dihydroxy-2′,4′,5′,6-tetramethoxyflavone (**5**) isolated from *Chukrasia taburaris* (Meliaceae),[4a] named tabularin and structurally confirmed by synthesis,[4b] was synthesized by our new method. The flavone **5** was prepared as follows; condensation of 2,4,5-trimethoxybenzaldehyde (**35**)[4b] with **14** gave 2′-hydroxy-4′,6′-diisopropyloxy-2,4,5,5′-tetramethoxychalcone (**36**), which was led to 5,7-diisopropyloxy-2′,4′,5′,6-tetramethoxyflavone (**37**) after oxidation and thence to **5** (mp 208—209 °C) by deisopropylation. The flavone (**2**—**5**) thus obtained were methylated to afford the same flavone, 2′,4′,5,5′,6,7-hexamethoxyflavone (**6a**). The flavone **6a** was synthesized as a mother flavone by an independent route using methylated starting materials. 2′-Hydroxy-2,4,4′,5,5′,6′-hexamethoxychalcone (**38**) obtained by condensation of **35** with **18** was oxidized to **6a** (mp 180—181 °C). Partial demethylation of **6a** gave 5-hydroxy-2′,4′,5′,6,7-pentamethoxyflavone (**6b**) (mp 193 °C).

2′,4′,5,5′,6,7,8-Heptamethoxyflavone (**7**) and 2′,4′,5-trihydroxy-5′,6,7,8-tetramethoxyflavone (**8**), isolated from *Ageratum corymbosum* (Compositae),[3d] were named agecorynins C and D, respectively. Syntheses of **7** and **8** were carried out as follows. Condensation of **35** with 2-hydroxy-3,4,5,6-tetramethoxyacetophenone (**39**), obtained from 4′,5,6,7,8-pentamethoxyflavone (tangeritin) by alkaline degradation, and of **13** with **39** gave 2′-hydroxy-2,3′,4,4′,5,5′,6′-heptamethoxychalcone (**40**) and 2′-hydroxy-2,4-diisopropyloxy-3′,4′,5,5′,6′-pentamethoxychalcone (**41**), respectively. These chalcones were oxidized to **7** (mp 155—156 °C) and 2′,4′-diisopropyloxy-5,5′,6,7,8-pentamethoxyflavone (**42**), respectively. The flavone **42** was transformed to **8** (mp 258—260 °C) by treatment with BCl_3.

Among the synthesized flavones, **1**, **2**, **3a**, **7** and **8** were found to be identical with the corresponding natural flavones by direct comparison, and their structures were confirmed to be 2′,4′,5,5′,7-pentahydroxy-, 2′,4′,5,7-tetrahydroxy-5′,6-dimethoxy-, 2′,4′,5-trihydroxy-5′,6,7-trimethoxy-, 2′,4′,5,5′,6,7,8-heptamethoxy-, and 2′,4′,5-trihydroxy-5′,6,7,8-tetramethoxyflavone. However, none of the synthetic flavones **4a**, **4b** and **4c**, was identical with naturally occurring isoarcapillin.

In the proton nuclear magnetic resonance (^{1}H-NMR) spectra of these flavones, the protons H-3′ and H-6′ were each observed as a singlet, the former at high field (6.45—6.72 ppm), and the latter at low field (7.27—7.45 ppm). The proton at C-3 was characteristically observed at lower field than that of general flavones because of the effect of the hydroxyl or methoxyl group at C-2′. In the mass spectra (MS) the flavones substituted at C-2′, C-4′ and C-5′ with hydroxyl and/or methoxyl groups showed fragments based on the ring B moiety, $B_1^{+\cdot}$ (*m/z*: 153, 167, 181, 195) and $B_2^{+\cdot}$ (*m/z*: 150, 164, 178, 192), according to the number and kind of substituents as a result of general fragmentations such as pathways I and II.[11] In the

TABLE I. Bathochromic Shifts of Band I in the UV Spectra of the 2′,4′,5′-Trioxygenated Flavones Induced by Shift Reagents

	Position of hydroxyl groups[a]	+$AlCl_3$	+NaOMe	+NaOAc
4c	2′ (5, 7)	+34	+54	+6
4a	4′ (5, 6)	+35	+37	+10
4b	4′ (5, 7)	+34	+38	+10
2	2′,4′ (5, 7)	+36	+53	+10
3a	2′,4′ (5)	+38	+66	+4
3b	2′,5′ (5)	+38	dec.	+8
1	2′,4′,5′ (5, 7)	+68	+44	+38

a) The numbers in parentheses show the positions of hydroxyl groups in ring A.

case of the flavones having the methoxyl group at C-6, the fragment ($M^+ - 15$) predominantly observed, whereas the flavone (**4a**) lacking a methoxyl group at this position gave the fragment ($M^+ - 18$).

Ultraviolet (UV) spectra of flavones have recently been reviewed by Voirin.[12] In his article, however, the characteristics of flavones possessing a hydroxyl group at C-2′ are not described. The UV spectra of 2′,3′,5′-tri-oxygenated flavones were discussed in our previous paper.[13] The UV spectral results for the present synthesized flavones are summarized in Table I. For flavones having a 2′-hydroxyl group (**4c**, **2** and **3a**), the shift of band I on addition of sodium methoxide is much larger than that of flavones having a 4′-hydroxyl group (**4a** and **4b**). The flavone having a hydroquinone moiety (**3b**) was decomposed by addition of sodium methoxide. These results are generally similar to those for 2′,3′,5′-trioxygenated flavones.

Experimental

Instruments, *etc.*, were as described in the preceding paper.[1]

2,4,5-Triisopropyloxybenzaldehyde (9)——Protocatechualdehyde diisopropyl ether (11.4 g, 0.05 mol) was oxidized with 30% H_2O_2 (6.9 g, 0.06 mol) and 90% HCOOH (55 ml, 1 mol) to give 3,4-diisopropyloxyphenol (6.4 g), which was isopropylated with isopropyl bromide (4.1 g, 33 mmol) and K_2CO_3 (9 g) in *N*, *N*-dimethylformamide (DMF) to afford 1,3,4-triisopropyloxybenzene (6 g). A solution of DMF (48 ml) containing $POCl_3$ (7.2 g, 48 mmol) was added to a solution of the resulting triisopropyl ether (6 g, 24 mmol) in DMF. The mixture was stirred for 5 h, then poured into water and extracted with AcOEt. The extract was evaporated under reduced pressure, and the residue was purified by column chromatography to give **9** (6.2 g) as a brown oil. ^{1}H-NMR ($CDCl_3$) δ: 1.30 (6H, d, J=6 Hz, $(CH_3)_2$), 1.37 (12H, d, J=6 Hz, 2×$(CH_3)_2$), 4.42 (3H, m, 3×C$\underline{H}$<), 6.61 (1H, s, H-3), 7.41 (1H, s, H-6), 10.33 (1H, s, CHO).

2-Hydroxy-4,6-diisopropyloxyacetophenone (10)——Phloroacetophenone (10 g, 60 mmol) was partially isopropylated with isopropyl bromide (14.8 g, 120 mmol) to give 11.5 g of **10** as a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.35, 1.36 (6H, each d, J=6 Hz, $(CH_3)_2$), 2.54 (3H, s, $COCH_3$), 4.64, 4.68 (1H, each hept., C$\underline{H}$<), 5.78 (1H, d, J=2.4 Hz, H-3), 5.90 (1H, d, J=2.4 Hz, H-5), 13.74 (1H, s, OH).

2,4-Diisopropyloxy-5-methoxybenzaldehyde (13)——Resorcinol diisopropyl ether (13.9 g, 0.07 mol) was subjected to the Vilsmeier reaction using a solution of DMF (142 ml) containing $POCl_3$ (21.7 g, 0.14 mol) to give 13.7 g of 2,4-diisopropyloxybenzaldehyde. ^{1}H-NMR ($CDCl_3$) δ: 6.48 (1H, d, J=2.4 Hz, H-3), 6.54 (1H, dd, J=9.0, 2.4 Hz, H-5), 7.80 (1H, d, J=9.0 Hz, H-6), 10.30 (1H, s, CHO). The aldehyde (13.7 g, 62 mmol) was subjected to the Bayer–Villiger reaction with 30% H_2O_2 (8.4 g, 62 mmol) and 90% HCOOH (70 ml, 1.48 mmol) to give 2,4-diisopropyloxyphenol (9.4 g). After methylation, the resulting methyl ether (8 g) was subjected to the Vilsmeier reaction to give 8 g of **13** as a brown oil. ^{1}H-NMR (CCl_4) δ: 1.30 (12H, d, J=6 Hz, 2×$(CH_3)_2$), 3.82 (3H, s, OCH_3), 4.56, 4.66 (1H, each hept., J=6 Hz, C$\underline{H}$<), 6.49 (1H, s, H-3), 7.22 (1H, s, H-6), 10.19 (1H, s, CHO).

2-Hydroxy-4,6-diisopropyloxy-5-methoxyacetophenone (14)——The acetophenone **10** (11.2 g, 44 mmol) was subjected to the Elbs oxidation using $K_2S_2O_8$ (15.2 g, 53 mmol) to give 4.6 g of **15** as yellow needles, mp 37 °C. ^{1}H-NMR ($CDCl_3$) δ: 2.70 (3H, s, $COCH_3$), 5.64 (1H, s, OH), 6.26 (1H, s, H-3), 13.06 (1H, d, OH). Partial methylation of **15** (2.7 g) gave 1.9 g of **14** as a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.27, 1.35 (6H, each d, J=6 Hz, $(CH_3)_2$), 2.68 (3H, s, $COCH_3$), 3.65 (3H, s, OCH_3), 4.71, 4.81 (1H, each hept., J=6 Hz, C$\underline{H}$<), 6.07 (1H, s, H-3), 13.02 (1H, s, OH).

2,5-Diisopropyloxy-4-methoxybenzaldehyde (21)——Vanillin (30.4 g, 0.2 mol) was subjected to the Dakin reaction using 6% H_2O_2 (142 ml, 0.25 mol) to give 16.5 g of **22** as a colorless powder, mp 127—130 °C (C_6H_6). After isopropylation of **22** (16.2 g), the resulting diisopropyl ether (2 g) was subjected to the Vilsmeier reaction to give 2.2 g of **21** as a pale brown oil. ^{1}H-NMR (CCl_4) δ: 1.27, 1.37 (6H, each d, J=6 Hz, $(CH_3)_2$), 3.87 (3H, s, OCH_3), 4.46, 4.50 (1H, each hept., J=6 Hz, C$\underline{H}$<), 6.51 (1H, s, H-3), 7.21 (1H, s, H-6), 10.19 (1H, s, CHO).

4-Isopropyloxy-2,5-dimethoxybenzaldehyde (25)——The Elbs oxidation of salicylaldehyde (6.4 g, 0.05 mol) gave 2.4 g of 2,5-dihydroxybenzaldehyde as yellow needles, mp 91 °C (C_6H_6). After methylation, **26** (5 g, 0.03 mol) was subjected to the Baeyer–Villiger reaction to give 3.6 g of 2,5-dimethoxyphenol as a colorless oil. After isopropylation of the phenol, the resulting isopropyl ether (3.5 g) was converted into **25** by means of the Vilsmeier reaction, yield 3.4 g, mp 76 °C (MeOH), colorless needles. ^{1}H-NMR ($CDCl_3$) δ: 1.41 (6H, d, J=6 Hz, $(CH_3)_2$), 3.86, 3.90 (3H, each s, OCH_3), 4.73 (1H, hept., J=6 Hz, C$\underline{H}$<), 6.54 (1H, s, H-3), 7.35 (1H, s, H-6), 10.78 (1H, s, CHO).

2-Hydroxy-5-isopropyloxy-4,6-dimethoxyacetophenone (27)——2,5-Dihydroxy-4,6-dimethoxyacetophenone (4.2 g, 20 mmol) was partially isopropylated to give 2.2 g of **27** as a brown oil. ^{1}H-NMR ($CDCl_3$) δ: 1.25 (6H, d, J=6 Hz, $(CH_3)_2$), 2.63 (3H, s, $COCH_3$), 3.87, 3.98 (3H, each s, OCH_3), 4.28 (1H, hept., J=6 Hz, C$\underline{H}$<), 6.23 (1H, s, H-3), 13.36 (1H, s, OH).

2-Isopropyloxy-4,5-dimethoxybenzaldehyde (28)——The Baeyer–Villiger reaction of veratraldehyde (7.5 g, 45 mmol) gave 3.1 g of 3,4-dimethoxyphenol. After isopropylation of the phenol, the resulting isopropyl ether (1.5 g,

7.7 mmol) was subjected to the Vilsmeier reaction to give 1.5 g of **28** as colorless needles, mp 61 °C. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (6H, d, J=6 Hz, $(CH_3)_2$), 3.86, 3.96 (3H, each s, OCH_3), 4.65 (1H, hept., J=6 Hz, C<u>H</u><), 6.60 (1H, s, H-3), 7.28 (1H, s, H-6), 10.29 (1H, s, CHO).

2′,4′,5,5′,6,7-Pentahydroxyflavone (1) (Isoetin)——The aldehyde (**9**) (1.12 g, 40 mmol) was condensed with **10** (1.04 g, 40 mmol) to give 1.8 g of **11** as an orange-yellow oil after usual work-up. ^{1}H-NMR ($CDCl_3$) δ: 1.33 (12H, d, J=6 Hz, 2×$(CH_3)_2$), 1.36 (6H, d, J=6 Hz, $(CH_3)_2$), 1.42 (12H, d, J=6 Hz, 2×$(CH_3)_2$), 4.55—4.65 (5H, m, 5×C<u>H</u><), 5.98 (1H, s, J=2.4 Hz, H-3′), 6.08 (1H, d, J=2.4 Hz, H-5′), 6.60 (1H, s, H-3), 7.34 (1H, s, H-6), 7.91 (1H, d, J=15.6 Hz, H-β), 8.32 (1H, d, J=15.6 Hz, H-α), 14.51 (1H, s, OH). A solution of the chalcone (1.8 g, 35 mmol) and DDQ (1.6 g, 70 mmol) in dioxane was heated under reflux for 9 h. Work-up in the same way as described before[9] gave 0.6 g of **12** as a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 6.42 (1H, d, J=3 Hz, H-6), 6.61 (1H, d, J=3 Hz, H-8), 6.67 (1H, s, H-3′), 7.00 (1H, s, H-3), 7.54 (1H, s, H-6′). The flavone **12** (0.5 g, 1 mmol) was deisopropylated in the same manner as reported by Sala *et al.*[10] to give **1** as a greenish-yellow powder (0.2 g), mp 305—307 °C (acetone–C_6H_{14}). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 6.21 (1H, d, J=2.4 Hz, H-6), 6.42 (1H, d, J=2.4 Hz, H-8), 6.60 (1H, s, H-3′), 7.13 (1H, s, H-3), 7.37 (1H, s, H-6′). Infrared (IR) ν_{max}^{KBr} cm^{-1}: 3300, 1650, 1510. UV λ_{max}^{MeOH} nm (log ε): 266 (4.3), 294 (4.1), 376 (4.2). λ^{+AlCl_3}: 271, 444. λ^{+AlCl_3+HCl}: 272, 296, 408. λ^{+NaOMe}: 262, 315, 420. λ^{+NaOAc}: 265, 414. MS m/z (rel. int.): 302 (M^+) (100), 300 (75), 262 (21), 203 (21), 155 (27), 153 (79), 150 (29).

2′,4′,5,7-Tetrahydroxy-5′,6-dimethoxyflavone (2)——Condensation of **14** (1.1 g, 4 mmol) with **13** (1 g, 4 mmol) in the same way as described for **1** gave 1.3 g of **16** as orange-yellow needles, mp 104 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 1.38 (24H, d, J=6 Hz, 4×$(CH_3)_2$), 3.84, 3.91 (3H, each s, OCH_3), 4.65 (4H, hept., J=6 Hz, 4×C<u>H</u><), 6.30 (1H, s, H-3′), 6.64 (1H, s, H-3), 7.26 (1H, s, H-6), 8.00 (1H, d, J=15.6 Hz, H-β), 8.30 (1H, d, J=15.6 Hz, H-α), 13.71 (1H, s, OH). Oxidation of **16** (0.6 g, 1.2 mmol) with DDQ (0.55 g, 2.4 mmol) gave 0.45 g of **17** as a colorless oil. ^{1}H-NMR ($CDCl_3$) δ: 6.66 (1H, s, H-3′), 6.79 (1H, s, H-8), 6.98 (1H, s, H-3), 7.40 (1H, s, H-6′). Deisopropylation of **17** (60 mg, 0.12 mmol) furnished **2** as a pale yellow powder, mp 285 °C (dec.) (acetone–C_6H_{14}), (lit.[3c] mp 291—294 °C (dec.)). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 3.80 (6H, s, 2×OCH_3), 6.45 (1H, s, H-3′), 6.55 (1H, s, H-8), 7.00 (1H, s, H-3), 7.40 (1H, s, H-6′). IR ν_{max}^{KBr} cm^{-1}: 3350, 1640, 1605, 1550. UV λ_{max}^{MeOH} nm (log ε): 266 (4.2), 292 (3.9), 372 (4.3). λ^{+AlCl_3}: 274, 297, 408. λ^{+AlCl_3+HCl}: 268, 296, 402. λ^{+NaOMe}: 274, 316, 425. λ^{+NaOAc}: 270, 295, 382. MS m/z (rel. int.): 346 (M^+) (100), 331 (65), 328 (53), 303 (29), 167 (21), 165 (22), 164 (20).

2′,4′,5-Trihydroxy-5′,6,7-trimethoxyflavone (3a) (Arcapillin)——Condensation of **13** (1.1 g, 4.4 mmol) with **18** (1 g, 4.4 mmol) gave 1.2 g of **19** as red needles, mp 105 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 1.40 (12H, d, J=6 Hz, 2×$(CH_3)_2$), 3.85, 3.92, 3.93, 3.95 (3H, each s, OCH_3), 4.55 (2H, hept., J=6 Hz, 2×C<u>H</u><), 6.32 (1H, s, H-3′), 6.59 (1H, s, H-3), 7.20 (1H, s, H-6), 7.89 (1H, d, J=15.6 Hz, H-β), 8.27 (1H, d, J=15.6 Hz, H-α), 13.85 (1H, s, OH). Oxidation of **19** (0.7 g, 1.5 mmol) with DDQ (0.69 g, 3 mmol) gave 0.28 g of **20** as a brown oil. ^{1}H-NMR ($CDCl_3$) δ: 1.38, 1.40 (6H, each d, J=6 Hz, $(CH_3)_2$), 3.93 (6H, s, 2×OCH_3), 4.02 (6H, s, 2×OCH_3), 4.57 (2H, hept., J=6 Hz, 2×C<u>H</u><), 6.65 (1H, s, H-3′), 6.80 (1H, s, H-8), 7.01 (1H, s, H-3), 7.38 (1H, s, H-6′). Deisopropylation and partial demethylation of **20** (0.28 g, 0.6 mmol) with BCl_3 (0.5 ml) at −70 °C gave 0.12 g of **3a** as a pale yellow powder, mp 287—290 °C (dec.) (acetone–C_6H_{14}), (lit.[3a] mp 272—274 °C). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 3.86, 3.92, 4.02 (3H, each s, OCH_3), 6.64 (1H, s, H-3′), 6.74 (1H, s, H-8), 7.19 (1H, s, H-3), 7.45 (1H, s, H-6′), 13.10 (1H, s, OH). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1650, 1590. UV λ_{max}^{MeOH} nm (log ε): 265 (4.2), 372 (4.3). λ^{+AlCl_3}: 276, 295, 410. λ^{+AlCl_3+HCl}: 276, 295, 400. λ^{+NaOMe}: 268, 438. λ^{+NaOAc}: 268, 376. *Anal.* Calcd for $C_{19}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 59.62; H, 4.49. MS m/z (rel. int.): 360 (M^+) (100), 345 (82), 331 (24), 317 (11), 302 (38), 181 (40), 164 (30), 153 (53).

2,5,5′-Trihydroxy-4′,6,7-trimethoxyflavone (3b)——Condensation of **18** (1 g, 4.4 mmol) with **21** (1.1 g, 4.4 mmol) gave 1.3 g of **23** as red needles, mp 122 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 1.36 (6H, d, J=6 Hz, $(CH_3)_2$), 1.40 (6H, d, J=6 Hz, $(CH_3)_2$), 3.90 (9H, s, 3×OCH_3), 3.96 (3H, s, OCH_3), 4.37, 4.68 (1H, each hept., 2×C<u>H</u><), 6.32 (1H, s, H-3), 6.57 (1H, s, H-3′), 7.26 (1H, s, H-6), 7.88 (1H, d, J=15.6 Hz, H-β), 8.25 (1H, d, J=15.6 Hz, H-α), 13.90 (1H, s, OH). Oxidation of **23** (0.92 g, 2 mmol) with DDQ (0.9 g, 4 mmol) gave 0.28 g of **24** as a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 6.65 (1H, s, H-3′), 6.84 (1H, s, H-8), 7.03 (1H, s, H-3), 7.55 (1H, s, H-6′). Treatment of **24** (0.28 g, 0.61 mmol) with BCl_3 gave 0.15 g of **3b** as a pale yellow powder, mp 285 °C (dec.) (acetone–C_6H_{14}). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 3.81, 3.89, 4.00 (3H, each s, OCH_3), 6.69 (1H, s, H-3′), 6.88 (1H, s, H-8), 7.19 (1H, s, H-3), 7.45 (1H, s, H-6′), 13.03 (1H, s, OH). IR ν_{max}^{KBr} cm^{-1}: 3500, 1650, 1590, 1550. UV λ_{max}^{MeOH} nm (log ε): 265 (4.3), 312 (4.0), 372 (4.3). λ^{+AlCl_3}: 277, 296, 332, 410. λ^{+AlCl_3+HCl}: 276, 295, 328, 405. λ^{+NaOMe}: 270, 372. λ^{+NaOAc}: 267, 380. *Anal.* Calcd for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 59.74; H, 4.45. MS m/z (rel. int.): 360 (M^+) (100), 345 (76), 331 (20), 324 (20), 181 (28), 167 (9), 165 (18), 164 (9), 153 (26).

4′,5,6-Trihydroxy-2′,5′,7-trimethoxyflavone (4a)——Condensation of **25** (1 g, 4.3 mmol) with **27** (1.1 g, 4.3 mmol) gave 1.3 g of **29** as red needles, mp 121—122 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 1.30, 1.40 (6H, each d, J=6 Hz, $(CH_3)_2$), 3.90 (9H, s, 3×OCH_3), 3.96 (3H, s, OCH_3), 4.37, 4.68 (1H, each hept., J=6 Hz, C<u>H</u><), 6.32 (1H, s, H-3), 6.58 (1H, s, H-3′), 7.20 (1H, s, H-6), 7.88 (1H, d, J=15.6 Hz, H-β), 8.24 (1H, d, J=15.6 Hz, H-α), 13.94 (1H, s, OH). A solution of **29** (0.17 g, 1.5 mmol) dissolved in methyl cellosolve containing 10% H_3PO_4 was heated under reflux for 7 h to give 6′-diisopropyloxy-2′,5,5′,7-tetramethoxyflavanone, **4** as pale yellow needles (0.23 g), mp 122—123 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 2.85 (1H, d, J=6 Hz, H-3 *cis*), 2.90 (1H, d, J=10.8 Hz, H-3 *trans*), 5.80 (1H, dd, J=10.8, 6 Hz, H-2). Oxidation of the flavanone (0.23 g, 0.5 mmol) with DDQ (0.15 g, 0.65 mmol) gave 0.12 g of **32** as a

brown oil. ^{1}H-NMR ($CDCl_3$) δ: 1.30, 1.40 (6H, each d, J=6 Hz, $(CH_3)_2$), 3.90 (6H, s, 2×OCH_3), 3.96 (6H, s, 2×OCH_3), 4.52, 4.62 (1H, each hept., J=6 Hz, CH<), 6.64 (1H, s, H-3′), 6.80 (1H, s, H-8), 6.97 (1H, s, H-3), 7.42 (1H, s, H-6′). Treatment of **32** (0.14 g, 0.3 mmol) with BCl_3 gave **4a** as a pale yellow powder (40 mg), mp 246 °C (acetone–C_6H_{14}). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 3.93 (6H, s, 2×OCH_3), 4.00 (3H, s, OCH_3), 6.72 (1H, s, H-3′), 6.82 (1H, s, H-8), 6.93 (1H, s, H-3), 7.45 (1H, s, H-6′). IR ν_{max}^{KBr} cm^{-1}: 3400, 3100, 1650, 1590. UV λ_{max}^{MeOH} nm (log ε): 256 (4.2), 284 (4.3), 365 (4.4). λ^{+AlCl_3}: 277, 296, 332, 410. λ^{+AlCl_3+HCl}: 276, 295, 328, 405. λ^{+NaOMe}: 270, 372. λ^{+NaOAc}: 267, 380. MS m/z (rel. int.): 360 (M^+) (100), 342 (33), 330 (11), 314 (33), 183 (11), 181 (11), 178 (23), 163 (21).

4′,5,7-Trihydroxy-2′,5′,6-Trimethoxyflavone (4b)——Condensation of **25** (0.88 g, 3.9 mmol) with **14** (1.1 g, 3.9 mmol) gave 1.2 g of **30** as red needles, mp 133—134 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 1.27 (6H, d, J=6 Hz, $(CH_3)_2$), 1.40 (12H, d, J=6 Hz, 2×$(CH_3)_2$), 3.82 (3H, s, OCH_3), 3.88 (6H, s, 2×OCH_3), 4.68 (3H, m, 3×CH<), 6.29 (1H, s, H-3′), 6.56 (1H, d, J=15.6 Hz, H-β), 8.28 (1H, d, J=15.6 Hz, H-α), 13.69 (1H, s, OH). Oxidation of **30** (0.5 g, 1 mmol) with DDQ (0.45 g, 2 mmol) gave 0.36 g of **33** as a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.31, 1.37, 1.41 (6H, each d, J=6 Hz, $(CH_3)_2$), 3.76, 3.82, 3.85 (3H, each s, OCH_3), 4.50 (3H, m, 3×CH<), 6.50 (1H, s, H-3′), 6.65 (1H, s, H-8), 6.95 (1H, s, H-3), 7.30 (1H, s, H-6′). Deisopropylation of **33** (0.35 g, 0.72 mmol) with BCl_3 gave **4b** as pale yellow needles (50 mg), mp 241—242 °C (acetone–C_6H_{14}). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 3.75 (3H, s, OCH_3), 3.82 (6H, s, 2×OCH_3), 6.56 (1H, s, H-3′), 6.65 (1H, s, H-8), 6.80 (1H, s, H-3), 7.41 (1H, s, H-6′). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 1640, 1600. UV λ_{max}^{MeOH} nm (log ε): 275 (4.2), 368 (4.3). λ^{+AlCl_3}: 270, 296, 402. λ^{+AlCl_3+HCl}: 265, 295, 394. λ^{+NaOMe}: 275, 416. λ^{+NaOAc}: 265, 295, 378. MS m/z (rel. int.): 360 (M^+) (100), 345 (71), 342 (48), 317 (30), 259 (6), 178 (9), 167 (6), 163 (12), 151 (12).

2′,5,7-Trihydroxy-4′,5′,6-trimethoxyflavone (4c)——Condensation of **28** (0.4 g, 1.8 mmol) with **14** (0.5 g, 1.8 mmol) gave 0.56 g of **31** as an orange-yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 1.33, 1.36, 1.37 (6H, each d, J=6 Hz, $(CH_3)_2$), 3.72 (3H, s, OCH_3), 3.80 (6H, s, 2×OCH_3), 4.46, 4.52, 4.56 (1H, each hept., J=6 Hz, CH<), 6.12 (1H, s, H-3′), 6.44 (1H, s, H-3), 7.11 (1H, s, H-6), 7.79 (1H, d, J=15.6 Hz, H-β), 8.11 (1H, d, J=15.6 Hz, H-α), 13.60 (1H, s, OH). Oxidation of **31** (0.56 g, 1.1 mmol) with DDQ (0.52 g, 2.2 mmol) gave 0.3 g of **34** as a pale yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 6.46 (1H, s, H-3′), 6.67 (1H, s, H-8), 6.98 (1H, s, H-3), 7.24 (1H, s, H-6′). The flavone **34** (0.16 g, 0.33 mmol) was deisopropylated to give **4c** as a yellow powder (20 mg), mp 285—287 °C (acetone–C_6H_{14}). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 3.78 (9H, s, 3×OCH_3), 6.45 (1H, s, H-3′), 6.59 (1H, s, H-8), 7.03 (1H, s, H-3), 7.27 (1H, s, H-6′), 13.04 (1H, s, OH). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 1650, 1610. UV λ_{max}^{MeOH} nm (log ε): 264 (4.3), 288 (4.1), 370 (4.4). λ^{+AlCl_3}: 270, 295, 404. λ^{+AlCl_3+HCl}: 268, 294, 396. λ^{+NaOMe}: 272, 296, 424. λ^{+NaOAc}: 270, 376. *Anal.* Calcd for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 59.74; H, 4.85. MS m/z (rel. int.): 360 (M^+) (100), 345 (73), 342 (42), 327 (15), 317 (21), 179 (12), 178 (12), 171 (11), 167 (9), 164 (17).

5,7-Dihydroxy-2′,4′,5′,6-tetramethoxyflavone (5) (Tabularin)——Condensation of **35** (0.69 g, 3.4 mmol) with **14** (0.97 g, 3.4 mmol) gave 1.5 g of **36** as red needles, mp 132—134 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 1.27, 1.41 (6H, each d, J=6 Hz, $(CH_3)_2$), 3.84 (3H, s, OCH_3), 3.92 (6H, s, 2×OCH_3), 3.97 (3H, s, OCH_3), 4.66, 4.70 (1H, each hept., J=6 Hz, CH<), 6.29 (1H, s, H-3′), 6.58 (1H, s, H-3), 7.24 (1H, s, H-6), 7.93 (1H, d, J=15.6 Hz, H-β), 8.30 (1H, d, J=15.6 Hz, H-α), 13.12 (1H, s, OH). Oxidation of **36** (0.5 g, 1.1 mmol) with DDQ (0.5 g, 2.2 mmol) gave 0.17 g of **37** as a brown oil. ^{1}H-NMR ($CDCl_3$) δ:1.45 (12H, d, J=6 Hz, 2×$(CH_3)_2$), 3.92 (3H, s, OCH_3), 3.96 (6H, s, 2×OCH_3), 4.00 (3H, s, OCH_3), 6.52 (1H, s, H-3′), 6.63 (1H, s, H-8), 7.04 (1H, s, H-3), 7.42 (1H, s, H-6′). Deisopropyloxylation of **37** (0.13 g, 0.28 mmol) gave **5** as pale yellow needles, 70 mg, mp 208—209 °C (acetone–C_6H_{14}) (lit.[4b] mp 210—212 °C). ^{1}H-NMR ($CDCl_3$+DMSO-d_6) δ: 3.85, 3.87, 3.96, 3.97 (3H, each s, OCH_3), 6.56 (1H, s, H-3′), 6.77 (1H, s, H-8), 6.89 (1H, s, H-3), 7.42 (1H, s, H-6′), 13.01 (1H, s, OH). IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 1635, 1600. UV λ_{max}^{MeOH} nm (log ε): 258 (4.3), 272 (4.2), 365 (4.7). λ^{+AlCl_3}: 266, 296, 402. λ^{+AlCl_3+HCl}: 265, 295, 383. λ^{+NaOMe}: 274, 292sh, 382. λ^{+NaOAc}: 272, 375. *Anal.* Calcd for $C_{19}H_{18}O_8$: C, 60.96; H, 4.85. Found: C, 59.77; H, 4.82. MS m/z (rel. int.): 374 (M^+) (100), 359 (70), 331 (35), 192 (11), 178 (18).

2′,4′,5,5′,6,7-Hexamethoxyflavone (6a)——Condensation of **35** (0.65 g, 3.3 mmol) with **18** (0.68 g, 3 mmol) gave 0.8 g of **38** as orange-yellow needles, mp 114 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 3.80 (3H, s, OCH_3), 3.88 (9H, s, 3×OCH_3), 3.90 (6H, s, 2×OCH_3), 6.26 (1H, s, H-3′), 6.50 (1H, s, H-3), 7.10 (1H, s, H-6), 7.80 (1H, d, J=15.6 Hz, H-β), 8.13 (1H, d, J=15.6 Hz, H-α), 13.80 (1H, s, OH). Oxidation of **38** (0.5 g, 2 mmol) with DDQ (0.55 g, 2.4 mmol) gave 0.12 g of **6a** as colorless needles, mp 180—181 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 3.95 (9H, s, 3×OCH_3), 3.99 (3H, s, OCH_3), 4.00 (6H, s, 2×OCH_3), 6.65 (1H, s, H-3′), 6.70 (1H, s, H-8), 7.01 (1H, s, H-3′), 7.42 (1H, s, H-6′). IR ν_{max}^{KBr} cm^{-1}: 2920, 1630, 1600. UV λ_{max}^{MeOH} nm (log ε): 254 (4.3), 305 (4.1), 354 (4.3). *Anal.* Calcd for $C_{21}H_{22}O_8$: C, 62.68; H, 5.51. Found: C, 62.75; H, 5.49. MS m/z (rel. int.): 402 (M^+) (31), 387 (100), 371 (8), 357 (26), 195 (6), 194 (8), 192 (5), 172 (6), 167 (8).

5-Hydroxy-2′,4′,5′,6,7-pentamethoxyflavone (6b)——Partial demethylation of **6a** (50 mg, 0.12 mmol) with BCl_3 gave 40 mg of **6b** as yellow needles, mp 193 °C (MeOH). ^{1}H-NMR ($CDCl_3$) δ: 3.83, 3.88, 3.91 (3H, each s, OCH_3), 3.93 (6H, s, 2×OCH_3), 6.50 (1H, s, H-3′), 6.58 (1H, s, H-8), 6.95 (1H, s, H-3), 7.36 (1H, s, H-6), 12.84 (1H, s, OH). IR ν_{max}^{KBr} cm^{-1}: 3400, 2900, 1645, 1610. UV λ_{max}^{MeOH} nm (log ε): 275 (4.2), 364 (4.3). λ^{+AlCl_3}: 270, 295, 398. λ^{+AlCl_3+HCl}: 265, 294, 398. λ^{+NaOMe}: 288, 350. λ^{+NaOAc}: 275, 365. *Anal.* Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.62; H, 5.14. MS m/z (rel. int.): 388 (M^+) (100), 373 (80), 359 (14), 342 (14).

2′,4′,5,5′,6,7,8-Heptamethoxyflavone (7) (Agecorynin C)——Condensation of **35** (0.13 g, 0.16 mmol) with **39**

(0.16 g, 0.6 mmol) gave 0.16 g of **40** as an orange-yellow oil. ^{1}H-NMR ($CDCl_3$) δ: 3.71 (6H, s, 2 × OCH_3), 3.75 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 3.88 (6H, s, OCH_3), 3.93 (6H, s, 2 × OCH_3), 6.37 (1H, s, H-3), 6.95 (1H, s, H-6), 7.62 (1H, d, J = 15.6 Hz, H-β), 8.03 (1H, d, J = 15.6 Hz, H-α), 13.33 (1H, s, OH). Oxidation of **40** (0.16 g, 0.37 mmol) with DDQ (0.17 g, 0.74 mmol) gave 20 mg of **7** as a colorless powder, mp 155—156 °C (MeOH) lit.[3d] mp 158—160 °C). ^{1}H-NMR ($CDCl_3$) δ: 3.89 (15H, s, 5 × OCH_3), 3.95, 4.05 (3H, each s, OCH_3), 6.56 (1H, s, H-3′), 7.10 (1H, s, H-3), 7.50 (1H, s, H-6′). IR ν_{max}^{KBr} cm^{-1}: 2900, 1630, 1610, 1520. UV λ_{max}^{MeOH} nm (log ε): 256 (4.3), 270 (4.4), 360 (4.3). MS m/z (rel. int.): 432 (M^+) (30), 417 (100), 256 (19), 225 (12), 197 (18), 195 (23). *Anal.* Calcd for $C_{22}H_{24}O_9$: C, 61.10; H, 5.59. Found: C, 60.90; H, 5.59.

2′,4′,5-Trihydroxy-5′,6,7,8-tetramethoxyflavone (8) (Agecorynin D)——Condensation of **39** (0.51 g, 2 mmol) with **13** (0.5 g, 2 mmol) gave 0.35 g of **41** as a red oil. ^{1}H-NMR ($CDCl_3$) δ: 1.34, 1.39 (6H, each d, J = 6 Hz, $(CH_3)_2$), 3.74 (3H, s, OCH_3), 3.76 (6H, s, 2 × OCH_3), 3.78, 3.95 (3H, each s, OCH_3), 4.40 (2H, hept., J = 6 Hz, 2 × C<u>H</u><), 6.38 (1H, s, H-3), 6.99 (1H, s, H-6), 7.68 (1H, d, J = 15.6 Hz, H-β), 8.03 (1H, d, J = 15.6 Hz, H-α), 13.17 (1H, s, OH). Oxidation of **41** (0.32 g, 0.7 mmol) with DDQ (0.3 g, 1.3 mmol) gave 70 mg of **42** as a brown oil. ^{1}H-NMR ($CDCl_3$) δ: 3.80 (9H, s, 3 × OCH_3), 3.88 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 6.44 (1H, s, H-3′), 6.82 (1H, s, H-3), 7.37 (1H, s, H-6′). Deisopropylation of **42** (50 mg) gave 10 mg of **8** as a yellow powder, mp 258—260 °C (AcOEt–C_6H_{14}) (lit.[3d] mp 258—260 °C). ^{1}H-NMR ($CDCl_3$ + DMSO-d_6) δ: 3.78, 3.80, 3.89, 4.00 (3H, each s, OCH_3), 6.53 (1H, s, H-3′), 7.07 (1H, s, H-3). UV λ_{max}^{MeOH} nm (log ε): 275 (4.2), 378 (4.3). λ^{+AlCl_3}: 282, 305, 424. λ^{+AlCl_3+HCl}: 280, 305, 410. λ^{+NaOMe}: 274, 454. λ^{+NaOAc}: 275, 388. MS m/z (rel. int.): 390 (M^+) (75), 375 (100), 211 (29), 183 (19), 165 (9).

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References and Notes

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