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3,5-DIHYDROXY-7,8-DIMETHOXYFLAVONES AND REVISED STRUCTURES FOR SOME NATURAL FLAVONES

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Abstract—Seven 3,5-dihydroxy-7,8-dimethoxyflavones were synthesized from the corresponding 3,5,7,8-tetramethoxyflavones using selective demethylation and protection of 3- or 5- methoxy group, and their properties were clarified by the UV and ^{1}H NMR spectral data. The structures of the four natural flavones were revised as follows: the three flavones, isolated from *Heteromma simplicifolium*, are 5,7-dihydroxy-3,8,3′,4′-tetramethoxyflavone, 5,7-dihydroxy-3,8,3′,4′,5′-pentamethoxyflavone, and 5,7,4′-trihydroxy-3,8,3′-trimethoxyflavone, respectively; the flavone glycoside, isolated from *Rudbeckia bicolor*, is proposed to be 3,5,4′-trihydroxy-6,7-dimethoxyflavone 3-rhamnoside.

INTRODUCTION

General properties of 3,5-dihydroxy-7,8-dimethoxyflavones are not known so far, although the isolation of these flavones from the natural sources is reported [1–3] For example, Bohlmann *et al* [2] have proposed that the structures of three natural flavones, isolated from *Heteromma simplicifolium*, are 3,5-dihydroxy-7,8,3′,4′-tetramethoxyflavone (**1b**), 3,5-dihydroxy-7,8,3′,4′,5′-pentamethoxyflavone (**1c**), and 3,5,4′-trihydroxy-7,8,3′-trimethoxyflavone (**1e**). But the spectral data suggest that the flavones are 5,7-dihydroxy-3,8-dimethoxyflavone derivatives rather than the proposed 3,5-dihydroxyflavones Jauhari *et al.* [3] reported that the glycoside, isolated from *Rudbeckia bicolor*, is 3,5,4′-trihydroxy-7,8-dimethoxyflavone (**1d**) 3-rhamnoside, but the structure of the aglycone is still in doubt. Therefore, we studied the synthesis and characterization of 3,5-dihydroxy-7,8-dimethoxyflavones (**1**) in order to confirm the structures of the natural flavones.

RESULTS AND DISCUSSION

Synthesis and characterization of 3,5-*dihydroxy*-7,8-*dimethoxyflavones* (**1**)

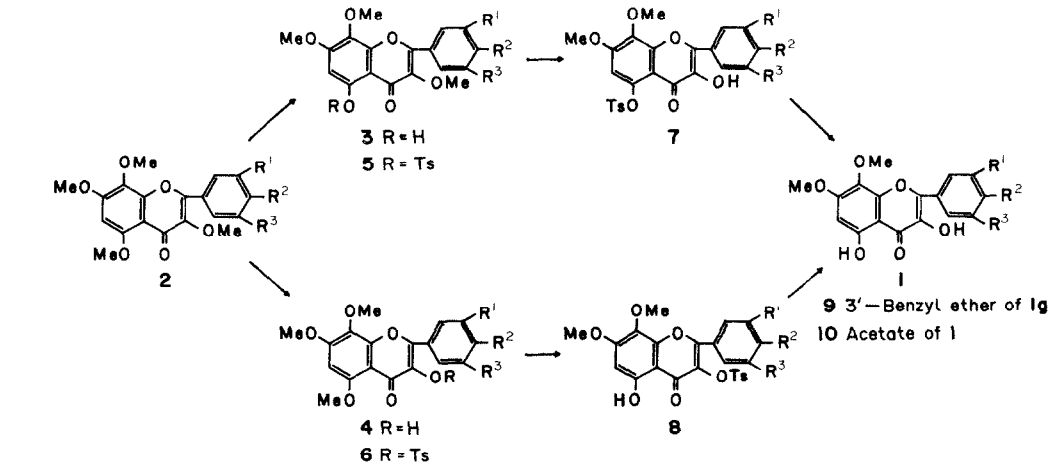
3,5-Dihydroxy-7,8-dimethoxyflavones (**1**) were synthesized from 3,5,7,8-tetramethoxyflavones (**2**) which were easily derived from 7-hydroxy-3,5,8-trimethoxyflavones, according to a similar method described in the previous paper [4] as shown in Scheme 1

In the demethylation of **2** with 5% w/v anhydrous aluminum bromide in acetonitrile at room temperature for one to two hr, the 5- or 3-methoxy group was selectively cleaved to give quantitatively a mixture of the corresponding 5- and 3-hydroxyflavones (**3** and **4**), which were converted into a mixture of the tosylates **5** and **6**. The 3- and 5-methoxy groups in the mixture of tosylates were also cleaved quantitatively under the same demethylating conditions to give a mixture of the corresponding 3- and 5-hydroxyflavones (**7** and **8**). The mixture was easily hydrolysed with anhydrous potassium carbonate in boiling methanol for one to two hr, and the desired 3,5-dihydroxy-7,8-dimethoxyflavones (**1**) were obtained in overall yields of 77–87%. However, the demethylation product from **2k** with two neighbouring benzyloxy groups contained a little of the 3′-benzyl ether (**9**) of **1g** along with **1k**, since the two adjacent benzyloxy groups were cleaved more easily than the others [4].

The benzyloxyflavones (**1h–k**) were debenzylated by the hydrogenolysis with palladium on charcoal to give the desired hydroxyflavones (**1d–g**) in high yields. The synthesized 3,5-dihydroxyflavones (**1a–g**) including five new compounds (**1b–f**) were converted into the corresponding acetates (**10a–g**).

The ^{1}H NMR data for the hydroxyflavones (**1**) (in DMSO-d_6) and their acetates (**10**) (in $CDCl_3$) support well the structures of the corresponding flavones as shown in Table 1. The characteristic signals of the C_6-proton in the 3,5-dihydroxy-7,8-dimethoxyflavones (**1**) and their acetates (**10**) are seen in the range of δ6.50 to 6.54 and 6.61 to 6.67, respectively

In the UV spectra for **1** in ethanol, the clear absorption maxima of Band I are seen at 380 to 388 nm and undergo typical bathochromic shifts (*ca* 60 nm) by the addition of aluminum chloride and their peak intensities are greater than those in ethanol as shown in Table 2 These phenomena are similar to those for 3,5,7-trihydroxy-8-methoxyflavones [4]. On the other hand, in the presence of sodium acetate, the bathochromic shifts of Band II are not observed, but Bands I of all 3,5-dihydroxyflavones (**1**) undergo the typical bathochromic shifts, and the characteristic shift attributed to the 4′-hydroxy group is not observed in the flavones (**1d**, **e**, and **g**). These ^{1}H NMR and UV spectral data are relevant to the structural elucidation of 3,5-dihydroxy-7,8-dimethoxyflavones (**1**).



Scheme 1

Table 1 ^{1}H NMR spectral data for 3,5-dihydroxy-7,8-dimethoxyflavones (**1**) in DMSO-d_6 and their acetates (**10**) in $CDCl_3$*

Compound	Aromatic H					OMe	C_5-OH or OAc
	C_6-H	C_3-H	C_5-H	C_2-H	C_6-H		
1a	6 50 *s*	7 07 *d* (2H)		8 10 *d* (2H)		3 80 *s* (3H) 3 82 *s* (3H) 3 87 *s* (3H)	12 16 *s*
1b	6 52 *s*	—	7 14 *d*	7 76 *d'*	7 83 *dd*	3 83 *s* (9H) 3 90 *s* (3H)	12 17 *s*
1c	6 52 *s*	—	—	7 48 *s* (2H)		3 73 *s* (3H) 3 82 *s* (6H) 3 88 *s* (6H)	12 02 *s*
1d	6 51 *s*	6 94 *d* (2H)		8 05 *d* (2H)		3 80 *s* (3H) 3 89 *s* (3H)	12 24 *s*
1e	6 50 *s*	—	6 96 *d*	7 77 *s*	7 71 *dd*	3 84 *s* (6H) 3 87 *s* (3H)	12 19 *s*
1f	6 52 *s*		7 07 *d*	7 55–7 8 *m* (2H)		3 82 *s* (3H) 3 84 *s* (3H) 3 90 *s* (3H)	12 15 *s*
1g	6 53 *s*	—	6 91 *d*	7 71 *d'*	7 63 *dd*	3 84 *s* (3H) 3 90 *s* (3H)	12 30 *s*
10a	6.64 *s*	6 98 *d* (2H)		7 84 *d* (2H)		3 85 *s* (3H) 3 94 *s* (6H)	2 32 *s* (3H) 2 41 *s* (3H)
10b	6 61 *s*		6 92 *d*	7 41 *d'*	7 49 *dd*	3 90 *s* (3H) 3 92 *s* (9H)	2 32 *s* (3H) 2 40 *s* (3H)
10c	6 63 *s*	—	—	7 11 *s* (2H)		3 86 *s* (6H) 3 89 *s* (3H) 3 93 *s* (6H)	2 33 *s* (3H) 2 41 *s* (3H)
10d	6 64 *s*	7 22 *d* (2H)		7 86 *d* (2H)		3 92 *s* (6H)	2 30 *s* (6H) 2 41 *s* (3H)
10e	6 66 *s*	—	7 13 *d*	7 47 *d'*	7 47 *dd*	3 86 *s* (3H) 3 95 *s* (6H)	2 31 *s* (6H) 2 40 *s* (3H)
10f	6 64 *s*	—	7 07 *d*	7 58 *d'*	7 78 *dd*	3 88 *s* (3H) 3 93 *s* (6H)	2 32 *s* (6H) 2 41 *s* (3H)
10g	6 67 *s*	—	7 32 *d*	7 74 *d'*	7 79 *dd*	3 94 *s* (6H)	2 32 *s* (9H) 2 42 *s* (3H)

*s, Singlet, *d*, doublet (J = 8 5 Hz), *d'*, doublet (J = 2 5 Hz), *dd*, double doublet (J = 8 5, 2 5 Hz), *m*, multiplet

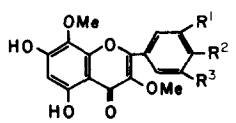
Table 2. UV spectral data for 3,5-dihydroxy-7,8-dimethoxyflavones (**1**)*

Compound		λ_{max}nm (log ε)				
1a	EtOH		273 (4 32)	325 (4 13)	380 (4 25)	
	$EtOH-AlCl_3$		271 (4 30)	354 (4 17)	440 (4 26)	
	EtOH–NaOAc		271 (4 31)	325 (4 00)	388 (4 16)	420 i (4 03)
1b	EtOH	257 (4 37)	275 sh (4 22)	337 (4 08)	384 (4 29)	
	$EtOH-AlCl_3$		267 (4 38)	363 (4 09)	443 (4 34)	
	EtOH–NaOAc	258 (4 36)		335 (3 89)	400 (4 16)	425 i (4 13)
1c	EtOH	256 (4 24)	270 (4 21)	329 (4 07)	382 (4 20)	
	$EtOH-AlCl_3$		272 (4 30)	356 (4 06)	441 (4 27)	
	EtOH–NaOAc	259 (4 29)			393 (4.10)	425 i (3 93)
1d	EtOH		273 (4 27)	329 (4 06)	382 (4.25)	
	$EtOH-AlCl_3$		271 (4 27)	357 (4 10)	441 (4 31)	
	EtOH–NaOAc		273 (4 26)	329 (3 99)	386 (4.19)	420 i (3 87)
1e	EtOH	259 (4.33)	272 i (4 17)		386 (4.25)	
	$EtOH-AlCl_3$		269 (4 36)	367 (4 04)	447 (4 33)	
	EtOH–NaOAc	259 (4 33)		343 sh (3 88)	396 (4 18)	425 i (4 07)
1f	EtOH	258 (4 36)	273 i (4.20)		385 (4 28)	
	$EtOH-AlCl_3$		269 (4 39)	366 (3 99)	445 (4 33)	
	EtOH–NaOAc	259 (4 38)	273 i (4 24)		387 (4 26)	425 i (3 84)
1g	EtOH	260 (4 36)	273 i (4 16)		388 (4 32)	
	$EtOH-AlCl_3$		271 (4 40)	370 (3 95)	449 (4 38)	
	EtOH–NaOAc	260 (4 29)			392 (4 21)	425 i (3 93)

* sh, Shoulder, i, inflection point

Revised structures of some natural flavones

The three natural flavones, isolated from *Heteromma simplicifolium*, have been proposed as **1b**, **1c**, and **1e** on the basis of the spectral data [2] Though the proton signals in ^{1}H NMR data for the three flavones are similar to those for the synthesized **1b**, **1c**, and **1e**, respectively, the chemical shifts of the protons at 2'- and 6'-positions are apparently different from those for synthetic ones, suggesting that the three natural flavones are isomers of **1b**, **1c**, and **1e**, respectively (Table 3) The signals at δ6 79 in ^{1}H NMR data for the natural flavone acetates are also not consistent with those of the C_6-proton in the acetates (**10**) of **1**. These signals, however, are assigned to those of the C_6-proton in the acetates (**12**) of 5,7-dihydroxy-3,8-dimethoxyflavones (**11**) [5], isomers of **1**. Additionally, Bands I in the UV data for the natural flavones are seen at 344 and 355 nm and shift bathochromically into 417 nm by the addition of aluminum chloride These results suggest that the structures of the natural flavones are 5,7-dihydroxy-3,8-dimethoxyflavone derivatives. In the comparison of the natural flavones with **11**, the spectral data for the natural flavones and their acetates are identical with those for the corresponding isomeric flavones (**11**) and their acetates (**12**) [5] as shown in Table 3 Consequently, the structures of the three natural flavones can be revised as 5,7-dihydroxy-3,8,3',4'-tetramethoxy- (**11b**), 5,7-dihydroxy-3,8,3',4',5'-pentamethoxy- (**11c**), and 5,7,4'-trihydroxy-3,8,3'-trimethoxyflavones (**11e**), respectively



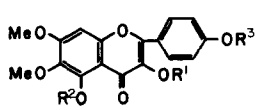
11b, c, and e R = H

12 Acetate of **11**

b $R^1 = R^2 = OMe$, $R^3 = H$

c $R^1 = R^2 = R^3 = OMe$

e $R^1 = OMe$, $R^2 = OH$, $R^3 = H$



13 $R^1 = R^2 = R^3 = H$

14 $R^1 = R^2 = R^3 = Ac$

15 $R^1 = H$, $R^2 = R^3 = Me$

16 $R^1 = R^2 = H$, $R^3 = Me$

The natural flavone glycoside, isolated from *Rudbeckia bicolor*, has been assigned to the structure of 3,5,4'-trihydroxy-7,8-dimethoxyflavone (**1d**) 3-rhamnoside on the basis of the spectral data for the glycoside and its derivatives [3] Although the monomethyl ether of the aglycone, which has been derived from the methyl ether of the glycoside synthesized by the methylation with diazomethane, is identical with tambulin (**1a**) [1, 6], the structure of the aglycone is doubtful. For example, Band I in UV data for the aglycone is seen at 354 nm which is a markedly shorter wavelength than that for **1d**. In the ^{1}H NMR data for the acetate of the aglycone, the signal at δ6 95 is not consistent with that of the C_6-proton in the acetate (**10d**) of **1d**, but those of the C_8-proton in 5,6,7-trioxygenated flavones with a 5-acetoxy and a 7-methoxy groups (δ *ca* 6 9) [7, 8] The results suggest that the structure of the aglycone is 3,5,4'-trihydroxy-6,7-dimethoxyflavone (eupalitin) (**13**) [8], an isomer of **1d**. Actually, the spectral data for the aglycone and its derivatives except for the monomethyl ether are not identical with those for **1d** and its derivatives (**10d** and **4a** [6]), but with those for **13** [8] and its derivatives (**14** [8] and **15** [9]), respectively, as shown in Table 4 Consequently, the structure of the aglycone must be 3,5,4'-trihydroxy-6,7-dimethoxyflavone (eupalitin) (**13**) and that of the glycoside must also be revised to 3-rhamnoside of **13**

EXPERIMENTAL

Mps uncorr ^{1}H NMR spectra were recorded at 60 MHz, using tetramethylsilane as an int standard (chemical shifts in δvalues) Elemental analyses (C, H) were performed with a

Table 3 Comparison of the three natural flavones, isolated from *Heteromma simplicifolium*, with 3,5-dihydroxy-7,8-dimethoxyflavones (**1**) and 5,7-dihydroxy-3,8-dimethoxyflavones (**11**)*

	Derivative	3,5-Dihydroxy-7,8-dimethoxyflavones	Natural flavones	5,7-Dihydroxy-3,8-dimethoxyflavones
		1b		**11b**
Mp (°)		219–219.5	214–215	224–225
^{1}H NMR in $CDCl_3$ (δ)		6.45 *s* 7.03 *d* 7.88 *d'* 7.93 *dd* 3.95 *s*(6H) 3.97 *s* 3.98 *s* 11.57 *s*	6.43 *s* 7.03 *d* 7.77 *d'* 7.81 *dd* 3.90 *s* 3.98 *s* 3.99 *s* 4.03 *s* 12.43 *s*	6.42 *s* 7.02 *d* 7.76 *d'* 7.80 *dd* 3.88 *s* 3.97 *s* 3.98 *s* 4.01 *s* 12.41 *s*
		1c		**11c**
Mp (°)		218–219	Oil	203–204
UV λ_{max} nm		(EtOH) 270 329 382 ($AlCl_3$) 272 356 441	(MeOH) 276 (313) 344 ($AlCl_3$) 285 308 357 417	(EtOH) 280 305 sh 355 sh ($AlCl_3$) 288 313 348 417
^{1}H NMR in $CDCl_3$ (δ)		6.46 *s* 7.60 *s* 3.95 *s* 3.96 *s*(9H) 3.97 *s* 11.50 *s*	6.43 *s* 7.47 *s* 3.91 *s* 3.95 *s*(6H) 3.97 *s* 4.02 *s* 12.35 *s*	6.43 *s* 7.45 *s* 3.89 *s* 3.94 *s*(6H) 3.95 *s* 4.01 *s* 12.34 *s*
	Diacetate	**10c**		**12c**
Mp (°)		150–152	Oil	135–136
^{1}H NMR in $CDCl_3$ (δ)		6.63 *s* 7.11 *s* 3.86 *s*(6H) 3.89 *s* 3.93 *s*(6H) 2.33 *s* 2.41 *s*	6.79 *s* 7.46 *s* 3.85 *s* 3.95 *s*(6H) 3.97 *s* 4.03 *s* 2.39 *s* 2.42 *s*	6.77 *s* 7.43 *s* 3.83 *s* 3.91 *s* 3.93 *s*(6H) 4.00 *s* 2.36 *s* 2.43 *s*
		1e		**11e**
Mp (°)		225–225.5	Oil	215–217
UV λ_{max} nm		(EtOH) 259 272 sh 386 ($AlCl_3$) 269 367 447	(MeOH) 257 273 355 ($AlCl_3$) 283 304 363 417	(EtOH) 257 276 338 sh 367 ($AlCl_3$) 267 285 360 417
^{1}H NMR in $CDCl_3$ (δ)		6.45 *s* 7.07 *d* 7.89 *d'* 7.87 *dd* 3.95 *s*(6H) 4.00 *s* 11.57 *s*	6.43 *s* 7.07 *d* 7.77 *d'* 7.73 *dd* 3.88 *s* 3.99 *s* 4.01 *s* 12.41 *s*	6.42 *s* 7.07 *d* 7.76 *d'* 7.73 *dd* 3.88 *s* 4.00 *s* 4.01 *s* 12.42 *s*
	Triacetate	**10e**		**12e**
Mp (°)		195–197	Oil	138–139
^{1}H NMR in $CDCl_3$ (δ)		6.66 *s* 7.13 *d* 7.47 *d'* 7.47 *dd* 3.86 *s* 3.95 *s*(6H) 2.31 *s*(6H) 2.40 *s*	6.79 *s* 7.18 *d* 7.80 *d'* 7.75 *dd* 3.83 *s* 3.90 *s* 3.98 *s* 2.35 *s* 2.37 *s* 2.45 *s*	6.77 *s* 7.16 *d* 7.79 *d'* 7.74 *dd* 3.82 *s* 3.89 *s* 3.97 *s* 2.33 *s* 2.36 *s* 2.44 *s*

*^{1}H NMR spectra of the hydroxyflavones (**1** and **11**) were measured with a Varian XL-200 spectrometer

Table 4 Comparison of the aglycone of the natural flavone glycoside, isolated from *Rudbeckia bicolar*, with 3,5,4'-trihydroxy-7,8-dimethoxyflavone (**1d**) and 3,5,4'-trihydroxy-6,7-dimethoxyflavone (**13**)

	Derivatives	3,5,4'-Trihydroxy-7,8-dimethoxyflavone	Aglycone of natural flavone glycoside	3,5,4'-Trihydroxy-6,7-dimethoxyflavone
		1d		**13** [8]
Mp (°)		244–246	262	291–292
UV λ_{max} nm		(EtOH) 273 329 382	(MeOH) 272 354	(MeOH) 270 365
	Triacetate	**10d**		**14** [8]
Mp (°)		185–187	200	210–211
^{1}H NMR in $CDCl_3$ (δ)		6.64 *s* 7.21 *d* 7.86 *d* 3.92 *s*(6H) 2.30 *s*(6H) 2.41 *s*	6.95 *s* 7.2 *d* 7.8 *d* 3.84 *s* 3.97 *s* 2.29 *s* 2.32 *s* 2.45 *s*	6.91 *s* 7.27 *d* 7.88 *d* 3.87 *s* 3.97 *s* 2.32 *s*(6H) 2.48 *s*
	5,4'-Dimethyl ether	**4a** [6]		**15** [9]
Mp (°)		198–200	108	136–138
UV λ_{max} nm		(EtOH) 269 312 373 ($AlCl_3$) 263 344 433	(MeOH) 260 352 ($AlCl_3$) 414	(MeOH) 259 352
	4'-Methyl ether	**1a**		**16** [9]
Mp (°)		206–207	205	212–214
UV λ_{max} nm		(EtOH) 273 325 380 ($AlCl_3$) 271 312 sh 354 440	(MeOH) 272 326 380 ($AlCl_3$) 270 315 350 438	(MeOH) 256 271 339 sh 361

Yanaco CHN corder Model MT-2 and the values of all compounds in this paper were within 0.3% of the theoretical values.

3,5,7,8-*Tetramethoxyflavones* (**2**). Flavones **2** were quantitatively synthesized from 7-hydroxy-3,5,8-trimethoxyflavones [4, 5] by the methylation with Me_2SO_4 and dry K_2CO_3 in boiling Me_2CO **2a**, mp 158–160° (lit. [10] 156–158°), **2b**, mp 167–168° (lit. [11] 168–169°), **2c**, mp 189–190° (lit [12] 192–193°), **2h**, mp 148–150° (lit. [13] 146–148°), **2i**, mp 134–136° and 154–155°

(from EtOAc or MeOH); **2j**, mp 165–167° (lit [13, 14] 170–173°, 165–167°); **2k**, mp 120–121° (lit. [15] 132–133°)

General method for synthesizing 3,5-*dihydroxy*-7,8-*dimethoxyflavones* (**1**) *from* 3,5,7,8-*tetramethoxyflavones* (**2**) Flavone **2** (1 mmol) was dissolved in 5% w/v dry $AlBr_3$ in MeCN (3 5–5 5 mmol; 20–30 ml) and the solution is allowed to stand at room temp (*ca* 25°) for 2 hr The reaction time in the demethylation of the flavones (**1h–k**) with benzyloxy groups on B ring was reduced to 1 hr. The solution was poured into *ca* 2% HCl (40–60 ml) and heated at 70–80° for 15–20 min. After the solvent was evapd under red. pressure, the yellow crystal separated was collected, washed with H_2O, and then dried to give a mixture of **3** and **4**.

The mixture was refluxed with *p*-toluenesulphonyl chloride (1 5 mmol; 290 mg) and dry K_2CO_3 (10–14 mmol, 1.4–2.0 g) in Me_2CO (40–50 ml) with stirring till the hydroxyflavones disappeared (4–6 hr). The mixture was poured into dil HCl and the solvent was evapd under red. pressure. The ppt was collected, washed with H_2O, and dried to give a mixture of **5** and **6**

The mixture was demethylated with 5% w/v dry $AlBr_3$ in MeCN under the same conditions as described above. The demethylated products were collected by filtration or extraction with EtOAc to give a mixture of **7** and **8**.

To the mixture, MeOH (40–50 ml) and dry K_2CO_3 (10–14 mmol; 1 4–2 0 g) were added, then the mixture was refluxed with stirring under N_2 atmosphere for 1–2 hr and poured into dil. HCl After the solvent was evapd under red pressure, the yellow crystals separated were collected and recrystallized to give **1** as yellow needles. The 3′-benzyl ether (**9**) of **1g** was obtained from the mother liquor of the recrystallization of **1k** by CC on silica gel (Merck, Kieselgel 60) with $CHCl_3$. **1a** [6], mp 206–207° (from $CHCl_3$–MeOH) (lit. [1] mp 205°), yield 81%. **1b**, mp 219–219.5° (from $CHCl_3$–MeOH); yield 85% **1c**, mp 218–219° (from EtOAc–MeOH); yield 80%. **1h**, mp 215–216° (from EtOAc–MeOH); yield 80%; UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 274 (4 32), 327 (4.17), 380 (4.28); ^{1}H NMR (DMSO-d_6). 3 81, 3.89 (each 3H, *s*, OMe), 5 18 (2H, *s*, OCH_2Ph), 6 52 (1H, *s*, C_6-H), 7.18 (2H, *d*, J=8.5 Hz, $C_{3',5'}$-H), 8.13 (2H, *d*, J=8.5 Hz, $C_{2',6'}$-H), 12.21 (1H, *s*, C_5-OH). **1i**, mp 216–217° (from $CHCl_3$–MeOH); yield 82%, UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 258 (4.38), 271i (4 23), 340 (4 09), 385 (4 29), ^{1}H NMR (DMSO-d_6): 3.83 (6H, *s*, 2 × OMe), 3 92 (3H, *s*, OMe), 5.18 (2H, *s*, OCH_2Ph), 6 54 (1H, *s*, C_6-H), 7.23 (1H, *d*, J = 8.5 Hz, C_5-H), 7 78 (1H, *d*, J = 2 5 Hz, $C_{2'}$-H), 7.82 (1H, *dd*, J = 8.5, 2.5 Hz, $C_{6'}$-H), 12.17 (1H, *s*, C_5-OH). **1j**, mp 208–210° (from $CHCl_3$–MeOH), yield 87%; UV λ_{max}^{EtOH} nm ($\log\varepsilon$) 258 (4.38), 273 sh (4 21) 337 (4 07), 384 (4 29); ^{1}H NMR (DMSO-d_6): 3.77, 3.83, 3.86 (each 3H, *s*, OMe), 5.12 (2H, *s*, OCH_2Ph), 6.52 (1H, *s*, C_6-H), 7.15 (1H, *d*, J=8.5 Hz, C_5-H), 7.65–8.0 (2H, *m*, $C_{2',6'}$-H), 12.15 (1H, *s*, C_5-OH) **1k** [6], mp 208–209° (from EtOAc); yield 77%. **9** as a byproduct of **1k**, mp 195–197° (from $CHCl_3$); yield 1 7%; UV λ_{max}^{EtOH} nm ($\log\varepsilon$): 258 (4.35), 273 i (4 16), 340 sh (4.03), 385 (4.25), ^{1}H NMR (DMSO-d_6): 3.80, 3.89 (each 3H, *s*, OMe), 5 18 (2H, *s*, OCH_2Ph), 6.51 (1H, *s*, C_6-H), 7 69 (1H, *s*, $C_{2'}$-H), 7 77 (1H, *dd*, J=8.5, 2.5 Hz, $C_{6'}$-H), 12.15 (1H, *s*, C_5-OH)

3,5-*Dihydroxy*-7,8-*dimethoxyflavones* (**1d–g**) *with hydroxy groups on B ring.* Benzyloxyflavone (**1h, i, j,** or **k**) (200 mg) was hydrogenated over Pd-C (10%; 100 mg) in EtOAc–MeOH (1 . 2; 300–500 ml) till the uptake of H_2 ceased. After the catalyst was filtered off, the filtrate was evapd and the residue was recrystallized to give **1** as yellow needles: **1d**, mp 244–246° (from MeOH), yield 96%, **1e**, mp 225–225.5° (from EtOAc–MeOH), yield 95%; **1f**, mp 247–249° (MeCOEt), yield 94%; **1g** [6], mp 280–282° (from EtOAc–MeOH), yield 82%

3,5-*Diacetoxy*-7,8-*dimethoxyflavones* (**10**) Flavone (**1**) (30–40 mg) was dissolved in Ac_2O–pyridine (10 1, 0 5 ml) and the soln was allowed to stand at room temp. for 1 day The mixture was treated with H_2O and the product was recrystallized to give **10** as colourless needles. **10a**, mp 163–164° (from aq MeOH) (lit. [1] mp 160–161°), **10b**, mp 173–174° (from MeOH), **10c**, mp 150–152° (from MeOH); **10d**, mp 185–187° (from MeOH), **10e**, mp 195–197° (from MeOH); **10f**, mp 168–170° (from Et_2O–MeOH), **10g**, mp 175–177° (from MeOH)

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