A NEW FLAVONOL FROM *MURRAYA PANICULATA* VAR. *OMPHALOCARPA* : ^{13}C-NMR AS A USEFUL TOOL FOR STRUCTURE ELUCIDATION OF POLYOXYFLAVONES

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Abstract—A highly oxygenated flavone was isolated from the leaves of *Murraya paniculata* var. *omphalocarpa* (Rutaceae). The spectroscopic analysis of this compound revealed the presence of an unusual *para*-diphenol moiety in the A ring and its structure was finally elucidated as 3',4',6,7-tetramethoxy-3,5,8-trihydroxyflavone (**1**). The assignment of ^{13}C resonances of nineteen polyoxyflavones was also made by use of 2D correlation spectroscopy and the usefulness of ^{13}C NMR for identifying polyoxyflavones was discussed.

Murraya paniculata var. *omphalocarpa* (Hayata) Tanaka is a rutaceous shrub indigenous to Lan Yu (Botel Tobago), Taiwan, and one of three occurring varieties of *M. paniculata.* Though the mother species has found wide medicinal value in tropical and subtropical Asia, this plant is not considered to be medicinal. However, it has been extensively investigated by Wu *et al.*, and the presence of alkaloids, coumarins and flavones in the fruits,[1] flowers,[2] leaves[3,4] and root bark[5,6] was indicated. The author undertook chemical investigation of this plant mainly from a chemosystematic interest and reported the isolation of coumarin derivatives earlier.[7,8] Further detailed chemical investigation of the same plant led to the isolation of a new polyoxyflavone (**1**), and this paper describes its structure elucidation.The assignment of ^{13}C resonances of various polyoxyflavones was also attempted with the aim at quick identification of highly oxygenated flavones.

Compound (**1**) was isolated as yellow fine needles of mp 243-246°C, and showed a positive $FeCl_3$ test. Its IR and UV spectra suggested that it is a highly oxygenated flavone. Though the addition of shift reagents such as MeONa and $AlCl_3$ in the UV spectrum produced complex bathochromic shifts, these findings did not furnish any useful structural information leading to the structure assignment of **1**. Permethylation of this compound with diazomethane gave rise to a heptamethoxyflavone, which was identified with a known compound 3,3',4',5,6,7,8-heptamethoxyflavone by comparing its mp and spectroscopic data with those reported in the literature.[9] The ^{1}H-NMR spectrum revealed the presence of three hydroxyls, four methoxyls and an ABX aromatic proton system in the molecule. One hydroxyl signal was observed in the low field (δ 11.90) as a very sharp singlet, and was assignable to a chelated hydroxyl group at the 5-position in **1**. The ^{1}H-NMR spectrum was not of further help in elucidating the structure of **1**. On the other hand, the ^{13}C-NMR spectrum was more informative with respect to the location of methoxyls. Four

methoxyl carbons of **1** were observed at δ 55.6 (2 x C), 60.5 and 61.1, respectively, in its ^{13}C-NMR spectrum. Stothers *et al.* reported that methoxyl carbon signals of *ortho*-disubstituted anisoles move downfield by *ca.* 5 ppm as compared to those of *ortho*-mono- or non-substituted anisoles where methoxyl signals generally appear at *ca.* 55 ppm.[10] Therefore, two methoxyls observed at δ 55.6 (2 x C) should be assigned to 3'- and 4'-positions in the B-ring since one of the positions *ortho* to each methoxyl is unsubstituted, whereas the other two methoxyls were located at either 3-, 6-, 7- or 8-positions of the fully substituted A- and C- rings. Compound (**1**) was then subjected to the long range ^{13}C-^{1}H COSY spectral analysis since three hydroxyl protons occurring in this compound were observed as relatively sharp singlets and thus the observation of correlation between these protons and corresponding ^{13}C resonances was expected. The carbon signals showing ^{2}J or ^{3}J correlation peaks with 5-OH were those at δ 105.7, 135.4 and 143.6 (Figure 1). A carbon signal at δ 135.4 also showed a ^{3}J correlation with a methoxyl signal at δ 3.83. Therefore, the carbon signal at δ 135.4 was assigned to C-6 and a methoxyl group was found to occur at the 6-position. The one carbon signal at δ 105.7 was characteristic of C-10 in the flavone skeleton, and the other at δ 143.6 was thus assigned to C-5. A singlet hydroxyl signal at δ 9.63 showed a cross peak with a qurternaly carbon signal at δ 147.0 which was assigned to C-2. The presence of a hydroxyl group at the 3-position was apparent since C-2 was also correlated with 2'-H (δ 7.87). Cross peaks were observed among the following ^{13}C-^{1}H pairs: δ 147.7/δ 3.94, δ 147.7/δ 9.24 and δ 140.8/δ 9.24. However, the substitution patern at 7- and 8-positions could not be determined unequivocally from these correlations unless the assignments of carbon signals at 7-, 8- and 9-positions were confirmed. Apart from the assignments of these three carbons, it is possible to spectroscopically distinguish 5,8-dihydroxy-6,7-dimethoxyl substitution from 5,7-dihydroxy-6,8-dimethoxyl substitution in the A-ring. The 5,8-dihydroxy-6,7-dimethoxy substitution pattern for the A-ring of **1** was finally confirmed by an irradiation experiment in which a small but substantial 2.6% NOE on a methoxyl signal at δ 3.94 on irradiation of the methoxyl at δ 3.83. This also confirmed the assignment of a quarternary carbon signal at δ 147.7 to C-7. The assignment of 5,8-dihydroxy-6,7-dimethoxyl substitution for the A-ring of **1** was further substantiated by a good agreement of its A-ring ^{13}C resonances with those of a synthetic flavone **4**. From the above discussion the structure for **1** was unequivocally elucidated as 3',4',6,7-tetramethoxy-3,5,8-trihydroxyflavone. Flavones possessing a *para*-diphenol group in the A-ring are quite rare. This is, to the author's knowledge, the first report of isolation of this type of flavone from Rutaceae.

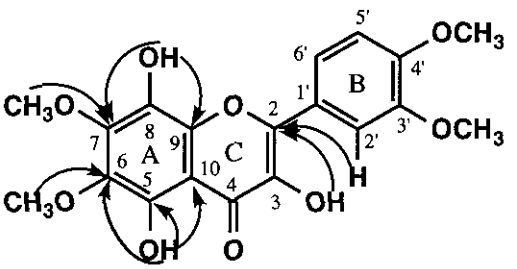

Figure 1 ^{2}J and ^{3}J Interactions obtained from Long Range ^{13}C-^{1}H COSY of **1**

The identification and structure elucidation of polyoxyflavones is not as easy as generally conceived with their relatively simple structures. The ^{1}H-NMR is not particularly helpful since it provides only limited structural informations due to the simplicity of ^{1}H resonances. The ^{13}C-NMR would be more helpful since it provides informations related to carbon backbones of the molecules. However, it is rather difficult to make assignments of ^{13}C resonances in these compounds that are mostly constructed with

quarternary sp^2 carbons. If there had been sufficient data on ^{13}C resonances of polyoxyflavones, the difficulty of structure elucidation of the above new compound and identification of known compounds with those reported earlier would have been much reduced. There were several reports attempting to assign ^{13}C resonances of polyoxyflavones,[11,12] but the earlier works were based on either theoretical calculations or empirical additivity principles of substituent effects. In the case of highly oxygenated flavones the assignments were mainly deduced from the cumulative application of substituent effects from simple substituent systems to complex systems. One can easily imagine that the introduction of a methoxyl *ortho* to an existing methoxyl, where steric hindrance is expected, would give rather modified substituent effects as compared to those established for simple aromatics. Hence the inaccuracies inherent in data obtained from simple substituent systems and applied to complex systems are also cumulative implying more overall errors. Nowadays high resolution NMR hardwares using a superconducting magnet have become common worldwide, and most of magnetic resonance data are provided with such superconducting NMR spectroscopy. However, as mentioned before, information on ^{13}C resonances of polyoxyflavones is still too little to be utilized for their structure elucidation. Fortunately the author has accumulated a sufficient number of pure polyoxyflavones, and thus attempted to make complete assignment of ^{13}C resonances of polyoxyflavones, some of which have the A-ring fully substituted with methoxyls or hydroxyls. The procedure of assignments are shown below.

The polyoxyflavone library used for this study is shown in Table I. Among those listed in this Table, ^{13}C resonances of compounds (**10**-**13**) and (**15**-**19**) were completely assigned by use of 2D spectrometry. As for compounds (**1**) and (**8**) the assignments of ^{13}C resonances were partially completed with C-8 and C-9 for the former and C-7 and C-8 for the latter unassigned. Since compound (**8**) can be nominally regarded as a methoxyl being introduced into C-8 of compound (**12**), it is possible to calculate the approximate chemical shifts of corresponding carbons using the substituent effect of a methoxyl to the aromatic ring. According to Levy and Nelson,[13] the introduction of a methoxyl to a simple aromatic system causes a downfield shift of 31.4 ppm at a junction carbon, upfield shifts of 14.4 ppm and 7.7 ppm at *ortho*- and *para*- positions respectively, and a slight downfield shift of 1.0 ppm at a *meta*-position. However, as mentioned above, it is not appropriate to apply these values obtained from a simple system (benzene) to a complex system (pentasubstituted aromatic ring) since large steric hindrances between neighboring methoxyls and the presence of a strong electron withdrawing functional group would be expected to modify the substitution effect. Since all ^{13}C resonances of both compounds (**15**) and (**18**) were unequivocally assigned, it would be rather better to use the approximate values extrapolated from **15** and **18** for estimating chemical shifts of unassigned carbons of **8**. These values of the substituent effect are shown in Figure 2. However, in conclusion, the real value of the substituent effect at a junction carbon of a methoxyl in compound (**8**) was much larger than the one extrapolated from **15** and **18**, indicating that the ^{13}C assignment of polyoxyflavones based on empirical additivity rules was unreliable. Two unassigned ^{13}C resonances of **8** were thus determined as shown in Table II. In order to make the assignment of the A-ring carbons of 5,6,7,8,3',4',5'-heptamethoxyflavone (**9**) the methylation effect of a hydrogen-bonded hydroxyl was calculated from compounds (**12**) and (**13**). Significant downfield shifts were observed at C-6 and C-10 by 7.6 ppm and 6.6 ppm respectively, and at C-8 by 5.4 ppm, while the influence of

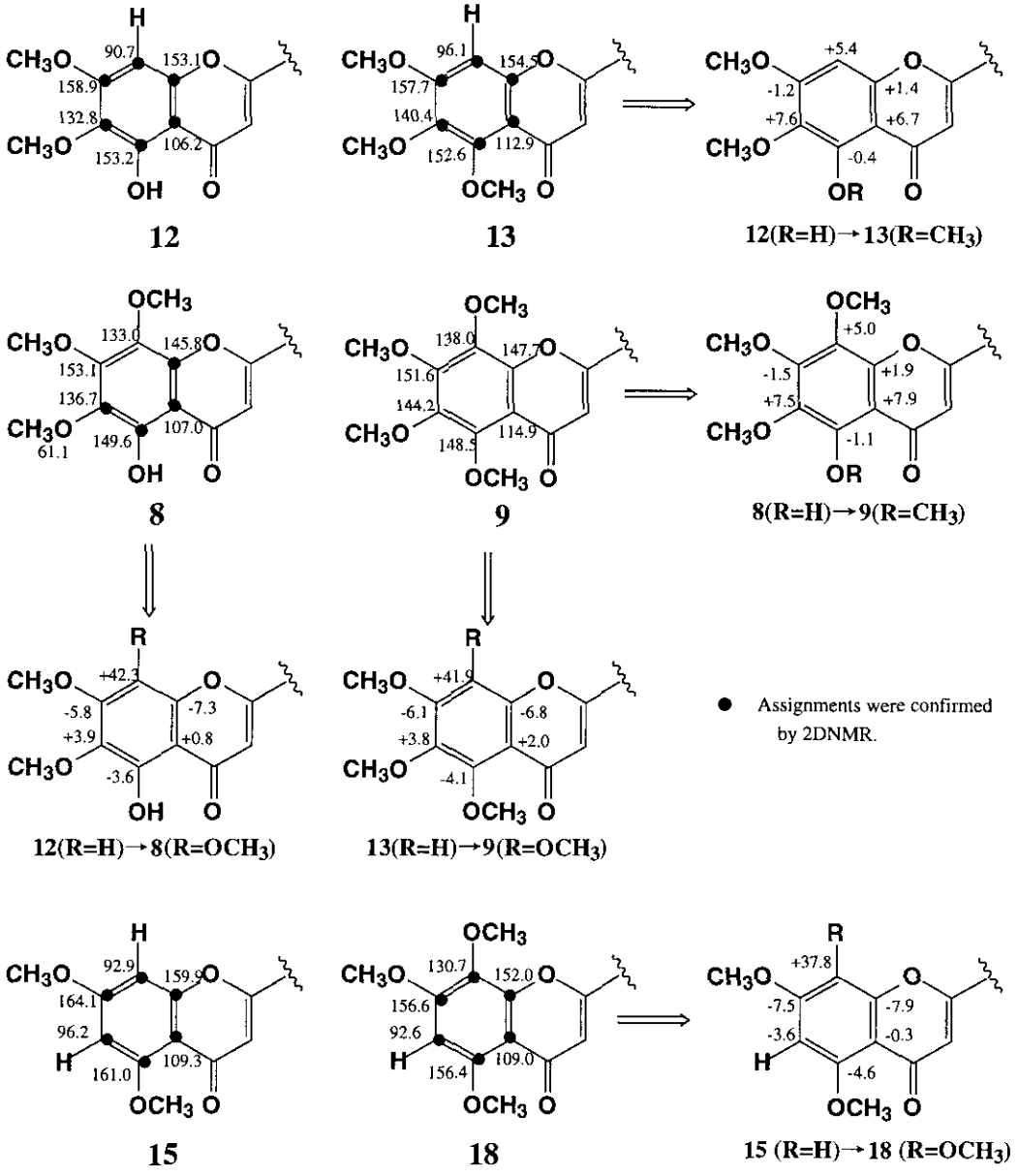

Figure 2 Chemical Shift Differences by Introducing Methoxyl or Methyl into Corresponding Carbons or Hydroxyl group

methylation of 5-OH was slight at C-7 and C-9. Applying these values to **8** accomplished the assignment of the fully substituted A-ring carbons of **9**. The results were also in good agreement with those estimated from the substitution effect of a methoxyl group at C-8 of **13**. In this case the difference of chemical shifts between C-5 and C-9 is very small, but these two carbons were easily distibguished since only C-5 has a ^{3}J correlation with a methoxyl in the long range ^{13}C-^{1}H COSY spectrum. Carbons at 8- and 9-positions of 3',4',6,7-tetramethoxy-3,5,8-trihydroxyflavone (**1**) were also assigned by use of the methylation effect of a hydroxyl in the similar way described above. The differentiation between

Table I. List of Various Polyoxyflavonoids

Compd.	*Numbering of Carbons in Flavone									Names	Ref.
	3	5	6	7	8	2'	3'	4'	5'		
1	OH	OH	OCH_3	OCH_3	OH	H	OCH_3	OCH_3	H	-	-
2	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3	H	OCH_3	OCH_3	H	-	-
3	OCH_3	OCH_3	OCH_3	OCH_3	OCH_3	H	OCH_3	OCH_3	OCH_3	exoticin	14
4	H	OH	OCH_3	OCH_3	OH	OH	H	H	H	synthetic	15
5	H	OH	OCH_3	OH	OCH_3	H	H	OCH_3	H	nebadensin	15
6	H	OH	OCH_3	OCH_3	OCH_3	H	OH	OCH_3	OH	gardenin E	16
7	H	OH	OCH_3	OCH_3	OCH_3	H	OH	OCH_3	OCH_3	gardenin C	16
8	H	OH	OCH_3	OCH_3	OCH_3	H	OCH_3	OCH_3	OCH_3	gardenin A	16
9	H	OCH_3	OCH_3	OCH_3	OCH_3	H	OCH_3	OCH_3	OCH_3	-	16
10	H	OH	OCH_3	OCH_3	H	H	OH	OCH_3	OH	-	16
11	H	OH	OCH_3	OCH_3	H	H	OH	OCH_3	OCH_3	-	16
12	H	OH	OCH_3	OCH_3	H	H	OCH_3	OCH_3	OCH_3	-	16
13	H	OCH_3	OCH_3	OCH_3	H	H	OCH_3	OCH_3	OCH_3	-	16
14	OCH_3	OCH_3	OCH_3	OCH_3	H	H	OCH_3	OCH_3	OCH_3	-	17
15	H	OCH_3	H	OCH_3	H	H	OCH_3	OCH_3	OCH_3	-	18
16	OH	OCH_3	H	OCH_3	H	H	OCH_3	OCH_3	OCH_3	-	18
17	OCH_3	OCH_3	H	OCH_3	H	H	OCH_3	OCH_3	OCH_3	-	18
18	H	OCH_3	H	OCH_3	OCH_3	H	OCH_3	OCH_3	OCH_3	-	18
19	OCH_3	OCH_3	H	OCH_3	OCH_3	H	OCH_3	OCH_3	OCH_3	-	18

*See Figure 1.

Table II. The ^{13}C Assignments of Various Polyoxyflavones[§]

C	1[¶]	2	3	4	5	6	7	8	9	10[†]	11	12	13	14	15	16	17	18	19
2	147.0	146.7	152.7	161.6	163.2	165.0	163.7	163.6	160.8	164.7	163.6	163.8	160.9	152.5	160.5	139.7	152.3	160.2	151.9
3	136.2	140.8	140.3	108.6	103.1	105.0	104.9	104.8	107.7	105.1	105.3	105.4	108.2	140.2	108.9	138.1	140.1	108.0	140.1
4	176.7	173.9	173.9	183.1	182.3	183.9	183.0	182.9	177.3	183.0	182.7	182.6	177.0	173.6	177.5	172.0	174.0	177.7	174.2
5	143.6	148.8	148.2	144.6	148.4	150.3	149.5	149.6	148.5	153.5	153.1	153.2	152.6	153.1	161.0	160.7	161.1	156.4	156.4
6	135.4	143.9	143.9	136.1	131.6	137.4	136.7	136.7	144.2	133.0	132.8	132.8	140.4	140.2	96.2	95.8	95.8	92.6	92.4
7	147.7	151.3	151.5	148.2	151.0	154.1	153.1	153.1	151.6	159.3	158.9	158.9	157.7	157.8	164.1	164.6	164.0	156.6	156.4
8	130.4	137.9	137.8	130.6	128.0	134.1	133.0	133.0	138.0	91.2	90.7	90.7	96.1	96.0	92.9	92.5	92.5	130.7	130.5
9	140.8	148.2	146.7	141.7	145.4	146.6	145.8	145.8	147.7	153.4	153.3	153.1	154.5	153.5	159.9	158.9	158.8	152.0	150.9
10	105.7	115.1	115.1	106.4	103.0	107.6	107.1	107.0	114.9	106.4	106.3	106.2	112.9	113.2	109.3	106.2	109.5	109.0	109.4
1'	123.4	123.5	126.0	117.2*	123.0	127.4	126.8	126.3	126.7	127.3	126.9	126.5	126.8	125.9	126.8	126.4	126.0	126.7	126.2
2'	111.5	111.0	105.8	156.9	128.2	106.9	106.8	103.8	103.4	107.0	106.8	103.9	103.5	106.0	103.5	105.1	105.9	103.3	105.7
3'	148.3	151.1	153.2	117.1*	114.8	152.0	149.8	153.7	153.6	152.8	149.7	153.7	153.5	153.1	153.6	153.3	153.1	153.6	153.1
4'	150.6	153.1	141.2	133.1	162.4	139.8	138.8	141.7	141.1	140.5	138.6	141.6	141.0	141.2	140.9	141.7	141.6	140.9	141.3
5'	111.2	111.1	153.2	119.5	114.8	152.0	152.6	153.7	153.6	152.8	152.6	153.7	153.5	153.1	153.6	153.3	153.1	153.6	153.1
6'	121.9	121.9	105.8	128.8	128.2	106.9	102.4	103.8	103.4	107.0	102.4	103.9	103.5	106.0	103.5	105.1	105.9	103.3	105.7
3-OCH_3	-	59.9	60.0	-	-	-	-	-	-	-	-	-	-	60.1	-	-	60.1	-	60.0
5-OCH_3	-	62.3	62.3	-	-	-	-	-	62.3	-	-	-	62.1	62.2	56.4	56.4	56.4	56.6*	56.6*
6-OCH_3	60.5	61.8	61.8	60.5	60.2*	60.8*	61.1*	61.0*	61.8	60.2*	60.9	60.9	61.5	61.6	-	-	-	-	-
7-OCH_3	61.1	61.7	61.7	61.2	-	62.0	61.7	61.7	61.7	56.3	56.4*	56.4	56.3	56.4	55.8	55.9	55.8	56.3*	56.4*
8-OCH_3	-	62.0	61.9	-	60.3*	62.4	62.1	62.0	62.0	-	-	-	-	-	-	-	-	61.4	61.4
3'-OCH_3	55.6	55.9*	56.2	-	-	-	-	56.3	56.3	-	-	56.4	56.4	56.4	56.4	56.4	56.4	56.2	56.1
4'-OCH_3	55.6	60.0*	61.0	-	55.6	61.0*	61.2*	61.1*	61.0	60.5*	61.2	61.0	61.0	61.0	61.0	61.0	61.0	61.0	61.0
5'-OCH_3	-	-	56.2	-	-	-	56.0	56.3	56.3	-	56.2*	56.4	56.4	56.4	56.4	56.4	56.4	56.2	56.1

[§] measured at 100 MHz in $CDCl_3$ with TMS as internal standard (δ ppm).
[†] measured in pyridine-d_5.
[¶] measured in DMSO-d_6.
*,** Assingments in the same column may be interchangeable.

5,7-dihydroxy-6,8-dimethoxyflavones and 5,8-dihydroxy-6,7-dimethoxyflavones is very difficult by conventional methods. However, the results summarized in Table II indicats that these two substitution patterns can be easily distinguished by ^{13}C-NMR. It should be noted that most of ^{13}C resonance data of polyoxyflavones reported so far require more or less revision. These data would be a useful aid for structure elucidation and identification of highly oxygenated flavones.

EXPERIMENTAL

Melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. Spectral data were obtained using the following apparatus: proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra with a JEOL JNM GSX-400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer with tetramethylsilane (TMS) as an internal standard; MS spectra with a JEOL JMS-SX-102A mass spectrometer; IR spectra with a JASCO FT/IR-8000 infrared spectrophotometer; UV spectra with a Shimadzu UV-240 spectrophotometer.

Plant Material The leaves of *M. paniculata* var. *omphalocarpa* were collected in 1988 in Lan Yu, Taiwan. A voucher specimen is on deposit at the Herbarium of Taiwan Forestry Research Institute, Heng-Chun, Taiwan and Medicinal Plants Research Station, Faculty of Pharmaceutical Sciences, Teikyo University.

Extraction and Isolation Extraxtion of the dried leaves (2 Kg) of *M. paniculata* var. *omphalocarpa* and procedure for fractionation of the extracts (127.4 g) were already described in the previous papers.[7,8] Yellow precipitates deposited in Fr. XV was collected and recrystalised from acetone to give compound 3',4',6,7-tetramethoxy-3,5,8-trihydroxyflavone (68 mg).

3',4',6,7-Tetramethoxy-3,5,8-trihydroxyflavone (1) Yellow fine needles from acetone, mp 243-246°C. IR ν_{max}^{KBr} cm^{-1}: 3461, 1653, 1601, 1572, 1480. UV λ_{max}^{MeOH} nm (log ε): 260 (4.47), 282 (4.39), 345 (4.35), 385 (4.22); $\lambda_{max}^{MeOH+AcONa}$ nm: 260, 282, 345, 385; $\lambda_{max}^{MeOH+MeONa}$ nm: 272, 380, 500 (br); $\lambda_{max}^{MeOH+AlCl3}$ nm: 273, 385, 445. ^{1}H-NMR (DMSO-d_6) δ: 11.90 (1H, s, 5-OH, disappeared by the addition of D_2O), 9.63 (1H, s, 3-OH, disappeared by the addition of D_2O), 9.24 (1H, s, 8-OH, disappeared by the addition of D_2O), 7.93 (1H, dd, *J*=2.1 Hz, 8.7 Hz, 6'-H), 7.87 (1H, d, *J*=2.1 Hz, 2'-H), 7.17 (1H, d, *J*=8.7 Hz, 5'-H), 3.94 (3H, s, 7-OCH_3), 3.86 (3H, s, 3'-OCH_3), 3.84 (3H, s, 4'-OCH_3), 3.83 (3H, s, 6-OCH_3). ^{13}C-Nmr (DMSO-d_6) δ: see Table II. EI-MS *m/z* (rel. int., %): 390 (M^+, 100), 375 (M^+-CH_3, 19), 347 (M^+-CH_3-CO, 38). HR-MS: Found 390.0951; $C_{19}H_{18}O_9$ requires 390.0951.

Methylation of 3',4',6,7-Tetramethoxy-3,5,8-trihydroxyflavone To a MeOH solution of 3',4',6,7-tetramethoxy-3,5,8-trihydroxyflavone (15 mg) was added an exess amount of etheral doazomethane, and the mixture was kept at 0° for 24 h. Excess diazomethane was decomposed by adding formic acid, and then the solvent was removed. The residue was recrystallized from MeOH-H_2O to furnish 3,3',4', 5,6,7,8-heptamethoxyflavone (**2**) (12 mg). mp 129-131° (lit.,[9] 128.5-130°). UV λ_{max}^{MeOH} nm: 252, 270sh, 342. ^{1}H NMR ($CDCl_3$): 7.85 (1H, dd, *J*=8.5 Hz, 2.1 Hz, 6'-H), 7.81 (1H, d, *J*=2.1 Hz, 2'-H), 7.02 (1H, d, *J*=8.5 Hz, 5'-H), 4.10, 4.01, 3.98, 3.98, 3.97, 3.95, 3.89 (3H each, s, OCH_3). ^{13}C NMR ($CDCl_3$): see Table II.

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