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Highly Oxygenated Flavonoids from *Polygonum orientale*

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Nine highly oxygenated flavonoids, having eight oxygen functional groups at C-3, 3′, 4′, 5, 5′, 6, 7 and 8, were isolated from *Polygonum orientale*. Of these compounds, seven (**1**, **2**, **3a**, **4**, **5a**, **6** and **7a**) are new compounds and the structures were determined on the basis of spectral evidence as 3,3′,5,6,7,8-hexamethoxy-4′,5′-methylenedioxy-(**1**), 5-hydroxy-3,3′,6,7,8-pentamethoxy-4′,5′-methylenedioxy-(**2a**), 3′-hydroxy-3,4′,5,5′,6,7,8-heptamethoxy-(**3a**), 3,3′,5,8-tetramethoxy-4′,5′,6,7-bis(methylenedioxy)-(**4**), 3′-hydroxy-3,4′,5,5′,8-pentamethoxy-6,7-methylenedioxy-(**5a**), 3,3′,4′,5,5′,8-hexamethoxy-6,7-methylenedioxy-(**6**) and 3′,5-dihydroxy-3,4′,5′,8-tetramethoxy-6,7-methylenedioxyflavone (**7a**).

Keywords——*Polygonum orientale*; Polygonaceae; highly oxygenated flavonoids; solvent shift in ^{1}H-NMR; MS

Polygonum orientale L. (Japanese name "Ohoketade") (Polygonaceae) originated in East Asia, but is now widely distributed and is one of the largest *Polygonum* plants in Japan. The isolation of C-glycosides, *i.e.*, orientin, homoorientin and vitexin, from the plant has been reported.[1] This paper deals with the isolation and structural elucidation of highly oxygenated flavonoids from the plant.

From the methanol (MeOH) extract of the dried aerial part of the plant, nine highly oxygenated flavonoids, **1**, **2a**, **3a**, **4**, **5a**, **6**, **7a**, digicitrin (**8a**) and exoticin (**9**), and quercitrin (**10**) were isolated, of which **1**, **2a**, **3a**, **4**, **5a**, **6** and **7a** are new compounds.

Compound **1** was obtained as pale yellow needles, $C_{22}H_{22}O_{10}$, mp 149—151°C. The infrared (IR) and ultraviolet (UV) spectra suggested the presence of a flavone skeleton. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** showed the presence of six methoxyl groups, one methylenedioxy group and two aromatic protons meta-coupled to each other (J=2.0 Hz). From the chemical shifts (δ 7.28 and 7.43) of the aromatic protons, their positions were suggested to be C-2′ and C-6′. Thus the substitution pattern of the B-ring was revealed to be 3′-methoxy-4′,5′-methylenedioxy and the other five methoxy groups were accomondated at C-3, C-5, C-6, C-7 and C-8. These conclusions indicated that the structure of **1** is 3,3′,5,6,7,8-hexamethoxy-4′,5-methylenedioxyflavone.

Compound **2a** was obtained as yellow needles, mp 187—188°C, $C_{21}H_{20}O_{10}$. IR and UV spectra suggested that **2a** is also a flavone derivative. The presence of a hydroxyl group was not confirmed by the IR spectrum, but the presence of hydrogen-bonded hydroxyl group at C-5 of the flavone ring was confirmed by the ^{1}H-NMR spectrum (δ 12.4)[3] and formation of a monoacetate (**2b**), mp 162—163°C, $C_{23}H_{22}O_{10}$, upon acetylation. The ^{1}H-NMR spectrum of **2a** showed the presence of five methoxy groups, one methylenedioxy group and two aromatic protons, whose chemical shift and coupling pattern are the same as those of **1** having a 3-methoxy-4,5-methylenedioxyphenyl B ring (type A in Fig. 1, Table I). These results indicated that the structure of **2a** is 5-hydroxy-3,3′,6,7,8-pentamethoxy-4′,5′-methylenedioxyflavone, which was also supported by the spectral data of **2b**.

Compound **3a** was obtained as pale yellow needles, mp 137—138°C, $C_{22}H_{24}O_{10}$. The IR and UV spectra suggested that **3a** is a flavone derivative. The ^{1}H-NMR spectrum indicated the presence of seven methoxyl groups, one hydroxyl group (δ 6.20) and two meta-coupled aromatic protons (type B in Fig. 1) as in the case of **8a** (*vide infra*), having a 3,4-dimethoxy-5-hydroxyphenyl group. Compound **3a** gave a monoacetate (**3b**), mp 141—142°C, $C_{24}H_{26}O_{11}$.

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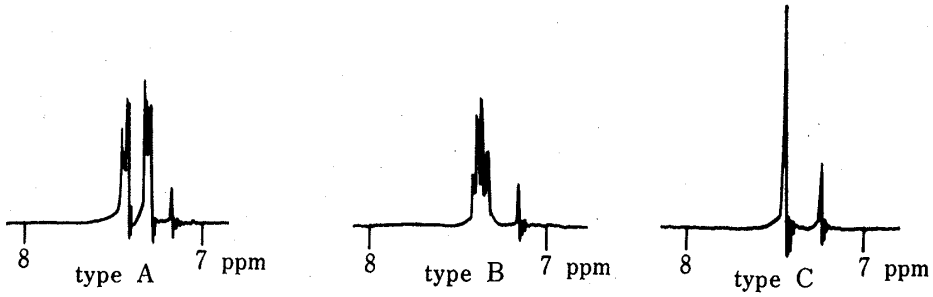

Fig. 1. Variation of the ^{1}H-NMR Patterns of the Aromatic Protons on the B Ring According to the Substitution Patterns

Table I. ^{1}H-NMR Data of the Flavonoids and Their Acetyl Derivatives in $CDCl_3$ and C_6D_6

Compd.	Solvent	OMe	OCH_2O	OH	OAc	Arom. H
1	$CDCl_3$	3.85, 3.90, 3.93(6H), 3.95, 4.04	5.98			7.29, 7.41
	C_6D_6	3.58, 3.64, 3.73, 3.78(6H), 3.97	5.40			7.47(s)
2a	$CDCl_3$	3.67, 3.90 (6H), 3.92, 4.05	5.99	12.35		7.28, 7.40
	C_6D_6	3.52, 3.61, 3.68, 3.80, 3.82	5.30	12.91		7.40(s)
2b	$CDCl_3$	3.67, 3.72, 3.91, 3.96, 4.02	5.98		2.45	7.25, 7.37
	C_6D_6	3.49 (6H), 3.64, 3.86(6H)	5.24		2.33	7.34(s)
3a	$CDCl_3$	3.88, 3.92(6H), 3.95(6H), 3.99, 4.06		6.20		7.32, 7.41
	C_6D_6	3.42, 3.60(6H), 3.69, 3.71, 3.77, 3.94		6.60		7.29, 7.65
3b	$CDCl_3$	3.87, 3.90, 3.92(6H), 3.94(6H), 4.05			2.35	7.47, 7.66
	C_6D_6	3.39, 3.62, 3.70, 3.72, 3.78, 3.80, 3.97			1.87	7.59, 7.78
4[a]	$CDCl_3$	3.85, 3.39, 4.00, 4.02	6.00(4H)			7.28, 7.42
5a[a]	$CDCl_3$	3.87, 3.90, 3.95, 4.01(6H)	6.01	6.25		7.33, 7.38
5b	$CDCl_3$	3.87(6H), 3.90, 4.00(6H)	6.00		2.35	7.44, 7.64
	C_6D_6	3.38, 3.65, 3.88(6H), 3.96	5.04		1.85	7.54, 7.70
6	$CDCl_3$	3.86, 3.88(9H), 4.02(6H)	6.00			7.39(s)
	C_6D_6	3.52(6H), 3.70, 3.82(6H), 3.96	5.18			7.43(s)
7a[a]	$CDCl_3$	3.85, 3.89, 3.97(6H)	6.02	5.90, 12.07		7.29, 7.33
7b	$CDCl_3$	3.79, 3.87, 3.89, 4.04	6.02	2.34, 2.42		7.40, 7.69
	C_6D_6	3.39, 3.63, 3.70, 3.80	5.06	1.85, 2.27		7.51, 7.68
8a[a]	$CDCl_3$	3.85, 3.91(9H), 3.96, 4.06		6.12, 12.26		7.30, 7.36
8b	$CDCl_3$	3.85, 3.86, 3.90(9H), 4.04		12.27	2.36	7.44, 7.61
	C_6D_6	3.40, 3.63, 3.67, 3.79(9H)		12.86	1.89	7.49, 7.69
8c	$CDCl_3$	3.79, 3.83, 3.88, 3.90, 3.97, 4.04		2.33, 2.46		7.44, 7.60
	C_6D_6	3.45, 3.59, 3.71(9H), 3.80		1.92, 2.36		7.47, 7.64
9	$CDCl_3$	3.87, 3.89(15H), 3.98, 4.05				7.39(s)
	C_6D_6	3.55(6H), 3.63, 3.70, 3.74, 3.80(6H), 3.95				7.42(s)

a) The spectra of **4**, **5a**, **7a** and **8a** were not recorded in C_6D_6 because the compounds were insoluble.

These results indicated that the structure of **3a** is 3′-hydroxy-3,4′,5,5′,6,7,8-heptamethoxyflavone. The spectral data of **3b** also supported this structure.

Compound **4** was obtained as pale yellow needles, mp 222—225°C, $C_{21}H_{18}O_{10}$. The IR and UV spectra indicated flavone character. The ^{1}H-NMR spectrum of **4** indicated the presence of four methoxyl groups, two methylenedioxy groups and two aromatic protons, which are meta-coupled to each other and whose signal pattern is superimposable on that of **1** and **2a** (type A) having a 3-methoxy-4,5-methylenedioxyphenyl group. These result indicated that the structure of **4** is 3,3′,5,8-tetramethoxy-4′,5′,6,7-bis(methylenedioxy)flavone or a position isomer of the methylenedioxy group on the A ring, such as at C-5,6 or C-7,8. The position of the methylenedioxy group will be discussed later.

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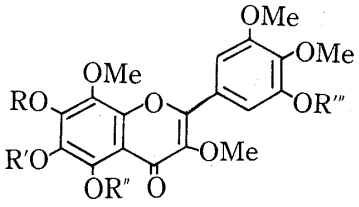
Compound **5a** was obtained as pale yellow needles, mp 183—185°C, $C_{21}H_{20}O_{10}$. The IR and UV spectra of **5a** indicated flavone character and the presence of a hydroxy group. Compound **5a** gave a monoacetate (**5b**), mp 150—151°C, $C_{23}H_{22}O_{10}$. The ^{1}H-NMR spectrum of **5a** indicated the presence of five methoxyl groups, one hydroxyl group (δ 6.25), one methylenedioxy group and two aromatic protons which are meta-coupled to each other as in **3a** and **8a** (type B). Thus, the substitution pattern of the B ring is 3′-hydroxy-4′,5′-dimethoxy, which was supported by the ^{1}H-NMR spectrum of **5b**. These results indicated that the structure of **5a** is 3′-hydroxy-3,4′,5,5′,8-pentamethoxy-6,7-methylenedioxyflavone or a position isomer as in the case of **4**.

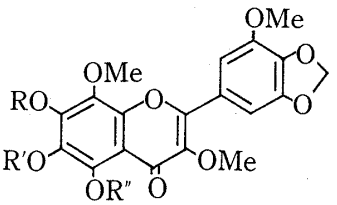
Compound **6** was obtained as pale yellow needles, mp 169—170°C, $C_{22}H_{22}O_{10}$. The IR and UV spectra of **6** indicated flavone character. The ^{1}H-NMR spectrum of **6** indicated the presence of six methoxyl groups, one methylenedioxy group and two aromatic protons as in **1**, except that the aromatic protons appear as a singlet. Thus, the B ring is symmetrical (such as 3,4,5-trimethoxyphenyl)and accordingly the methylenedioxy group exists on the A ring. These results indicated that the structure of **6** is 3,3′,4′,5,5′,8-hexamethoxy-6,7-methylenedioxyflavone or a position isomer as in the case of **4** and **5**.

Compound **7a** was obtained as yellow needles, mp 207—208°C, $C_{20}H_{18}O_{10}$. The IR and UV spectra indicated flavone character and the presence of a hydroxy group (3470 cm^{-1}). Compound **7a** gave a diacetate (**7b**), mp 197—200°C, $C_{24}H_{22}O_{12}$. The ^{1}H-NMR spectrum of **7a** indicated the presence of four methoxyl groups, two hydroxy groups, one methylenedioxy group and two aromatic protons. One of the hydroxyl groups exists at C-5 (δ 12.1) and the aromatic protons appear as a meta-coupled signal, as in **3a** and **5a** (type B) having a 3-hydroxy-4,5-methylenedioxyphenyl group. These results indicated that the structure of **7a** is 3′,5-dihydroxy-3,4′,5′,8-tetramethoxy-6,7-methylenedioxyflavone or a position isomer having the methylenedioxy group at C-7,8. This was supported by the spectral data of **7b**.

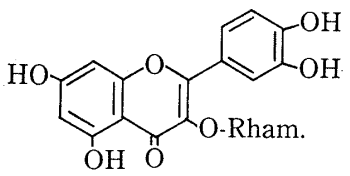
In the mass spectra (MS) of 6-methoxyflavone derivatives it is well known that a demethyl fragment from the molecular ion appears as a large fragment due to the formation of a cation



3a: R=R′=R″=Me, R‴=H
3b: R=R′=R″=Me, R‴=Ac
5a: R,R′=-CH_2-, R″=Me, R‴=H
5b: R,R′=-CH_2-, R″=Me, R‴=Ac
7a: R,R′=-CH_2-, R″=R‴=H
7b: R,R′=-CH_2-, R″=R‴=Ac
8a: R=R′=Me, R″=R‴=H
8b: R=R′=Me, R″=H, R‴=Ac
8c: R=R′=Me, R″=R‴=Ac



1 : R=R′=R″=Me
2a: R=R′=Me, R″=H
2b: R=R′=Me, R″=Ac
4 : R,R′=-CH_2-, R″=Me



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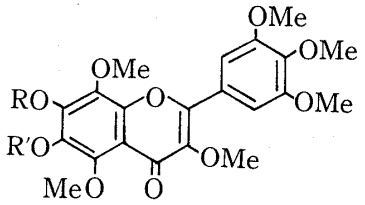

6: R,R′=-CH_2-
9: R=R′=Me

Chart 1

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Table II. Intensity of Parent Peaks (M^+) and Demethyl Fragments (M^+-Me) of the Flavonoids

Compound	No. of MeO	M^+	M^+-Me
1	6	70%	100%
2a	5	71	100
3a	7	54	100
8a	6	70	100
9	8	42	100
4	4	100	50
5a	5	100	78
6	6	100	93
7a	4	100	92

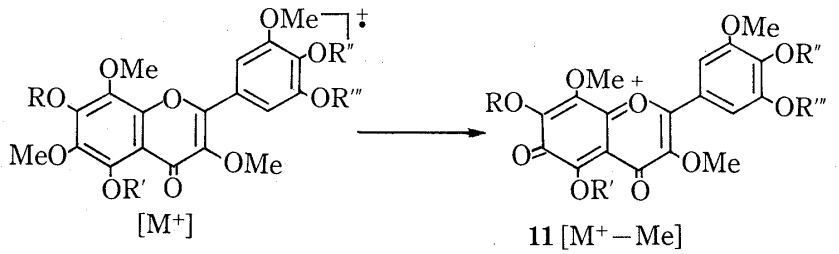

Chart 2

such as **11**.[4] The five compounds, **1**, **2a**, **3a**, **8a** and **9**, having a methoxyl group at C-6, gave the demethyl fragment ion (M^+-15) as the base peak (Table II), but **4**, **5a**, **6** and **7a** gave the molecular ion as the base peak (Table II). The MS data indicated that **4**, **5a**, **6** and **7a** have no methoxyl group at C-6. Thus, the structure of **7a** was proved to be 3′,5-dihydroxy-3,4′,5′,8-tetramethoxy-6,7-methylenedioxyflavone, and **4**, **5a** and **6** were each proved to be one of two isomers having the methylenedioxy group either at C-6,7 or at C-5,6.

In the ^{1}H-NMR spectra in C_6D_6, **1**, **3a**, **3b** and **9**, having a methoxyl group at C-5, showed the lowest methoxyl signal at the range of δ 3.94—3.97, and **2a**, **2b**, **7a**, **8b** and **8c**, having no methoxyl group at C-5, showed the lowest methoxyl signal at the range of δ 3.79—3.86 (Table I). In the case of **5b** and **6**, having a methylenedioxy group on the A ring, the lowest methoxyl group appeared at δ 3.96 (Table I). These results indicated that **5a** and **6** must bear a methoxyl group at C-5. In the ^{1}H-NMR spectra of **4**, **5a** and **6** in $CDCl_3$, two methoxyl groups appeared at relatively lower field compared with other methoxyl groups (Table I). This suggested that **4** has the same substitution pattern of the A ring as **5a** and **6**. The solvent shift of a methoxyl group at C-5 suffers a drastic change in magnitude from a relatively large positive value in the absence of a methoxyl group at C-6 to a small or negative value in the presence of the group at C-6.[5] The characteristic solvent shift has proved to be useful in the structure elucidation of zapotin.[6] From the solvent shift, the signal of **5b** and **6** at δ 3.96 is assignable to the methoxyl group at C-5. These observations indicated that **4**, **5a** and **6** have the methylenedioxy group at the C-6,7 position.

In addition, digicitrin (**8a**), a component of *Digitalis purpurea*,[7] and exoticin (**9**), a component of *Murraya exotica*,[8] were obtained from the extract. Their structures were confirmed by the spectral data of **8a**, **8b** and **8c**, and **9**.

Many highly oxygenated flavonoids have been reported,[9] but flavonoids having eight oxygen functional groups (at C-3, 3′, 4′, 5, 5′, 6, 7 and 8) are relatively rare.[10] The isolation of so many highly oxygenated flavonoids from the same source is very interesting, and it is the first time that such compounds have been isolated from Polygonaceae.

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Experimental

Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IRA-2 instrument and UV spectra were recorded on a Hitachi model 200-10 spectrometer. ^{1}H-NMR spectra were recorded on a Hitachi R-24B (60 MHz) instrument with tetramethylsilane as an internal standard (δ value). MS were recorded on a JEOL JMS 01SG-2 instrument. Column chromatography was carried out on silica gel (Merck, type 60). Preparative thin-layer chromatography (PLC) was carried out using Kieselgel 60F_{254} (Merck).

Isolation of the Constituents——Dried and chipped aerial parts of *P. orientale* (2 kg), collected at Shizuoka city, were extracted with boiling MeOH. The MeOH extract was suspended in water and extracted with AcOEt to give AcOEt extract (50 g) and aqueous layer. The aqueous layer was extracted with *n*-butanol to give *n*-butanol extract and aqueous layer. The AcOEt extract showed many spots on TLC compared with the *n*-butanol extract. The AcOEt extract was chromatographed on a silica gel column using a $CHCl_3$–MeOH gradient solvent system followed by rechromatography on a silica gel column using a benzene–AcOEt gradient solvent system to give ten fractions, fractions A-J. Fraction B was purified by PLC to give a crystalline compound, which was recrystallized from AcOEt to give **2a** (80 mg). Fraction D gave yellow crystals (400 mg), which showed one spot in TLC, but which appeared to be a mixture of two compounds on the basis of the ^{1}H-NMR spectrum. The yellow crystals (300 mg) were acetylated to give a pale yellow crystalline compound, which has recrystallized from MeOH to give a diacetate (**7b**) (120 mg) of **7a**. The mother liquor was purified by PLC to give pale yellow crystals, which were recrystallized from MeOH to give a diacetate (**8c**) (180 mg) of **8a**. The diacetates, **7b** and **8c**, were hydrolyzed with 1% KOH–MeOH to give **7a** and **8a**, which were recrystallized from benzene and $CHCl_3$, respectively, to give **7a** (70 mg) and **8a** (100 mg). Fraction E gave a pale yellow crystalline compound, which was recrystallized from acetone to give **1** (450 mg). Fraction F gave a pale yellow crystalline compound, which was recrystallized from $CHCl_3$–MeOH to give **4** (110 mg). Fraction G was chromatographed on a silica gel column to give **1** (70 mg) and a pale yellow crystalline compound, which was recrystallized from MeOH to give **9** (130 mg). Fraction H was subjected to silica gel column chromatography and PLC successively to give a pale yellow powder, which was recrystallized from benzene–hexane to give **3a** (80 mg). Fraction I was sabjected to silica gel column chromatography and PLC successively to give two kinds of crystalline compounds, which were recrystallized from hexane and MeOH respectively to give **5a** (70 mg) and **6** (140 mg). Fraction J was chromatographed on a silica gel column to give a pale yellow powder, which was recrystallized from MeOH to give quercitrin (**10**).

3,3′,5,6,7,8-Hexamethoxy-4′,5′-methylenedioxyflavone (**1**)——Pale yellow needles, mp 149—151°C, UV λ_{max}^{MeOH} nm (log ε): 344 (4.26), 273 sh (3.97), 252 (4.94). IR ν_{max}^{KBr} cm^{-1}: 1640, 1615, 1587, 1502, 1460, 1375, 1215, 1150, 1050. MS *m/e*: 446 (M$^+$) (100%). *Anal.* Calcd for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.97. Found: C, 59.19; H, 4.97.

5-Hydroxy-3,3′,6,7,8-pentamethoxy-4′,5′-methylenedioxyflavone (**2a**)——Yellow needles, mp 187—188 °C, UV λ_{max}^{MeOH} nm (log ε): 454 sh (4.19), 344 (4.20), 280 (4.13), 223 (4.35). IR ν_{max}^{KBr} cm^{-1}: 1648, 1629, 1600, 1585, 1510, 1480, 1465, 1450, 1410, 1374, 1388, 1282, 1215. MS *m/e*: 432 (M$^+$) (71%), 417 (100%). *Anal.* Calcd for $C_{21}H_{20}O_{10}$: C, 58.33; H, 4.66. Found: C, 58.15; H, 4.67.

Acetate (**2b**) **of 2a**——**2a** (40 mg) gave a monoacetate (**2b**) upon acetylation with Ac_2O–pyridine, and this was recrystallized from MeOH to give pale yellow needles (30 mg), mp 162—163°C, IR ν_{max}^{KBr} cm^{-1}: 1755, 1630, 1608, 1460, 1380, 1220, 1200, 1146, 1095, 1041. MS *m/e*: 474 (M$^+$) (10%), 432 (87%), 417 (100%). *Anal.* Calcd for $C_{23}H_{22}O_{11}$: C, 58.23; H, 4.67. Found: C, 58.23; H, 4.65.

3′-Hydroxy-3,4′,5,5′,6,7,8-heptamethoxyflavone (**3a**)——Pale yellow powdery crystals, mp 137—138°C, UV λ_{max}^{MeOH} nm (log ε): 331 (4.30), 268 (4.11), 254 (4.18). IR ν_{max}^{KBr} cm^{-1}: 3490, 1644, 1598, 1510, 1468, 1416, 1380, 1370, 1296, 1210, 1119, 1060. MS *m/e*: 448 (M$^+$) (54%), 447 (18%), 433 (100%). *Anal.* Calcd for $C_{22}H_{24}O_{10}$: C, 58.92; H, 5.40. Found: C, 59.12; H, 5.36.

Acetate (**3b**) **of 3a**——**3a** (50 mg) was acetylated with Ac_2O–pyridine to give an acetate (**3b**), which was recrystallized from MeOH to give colorless needles (30 mg), mp 141—142°C, IR ν_{max}^{KBr} cm^{-1}: 1759, 1635, 1614, 1585, 1459, 1464, 1406, 1358, 1210, 1095, 1055. MS *m/e*: 490 (M$^+$) (52%), 475 (100%). *Anal.* Calcd for $C_{24}H_{26}O_{11}$: C, 68.77; H, 5.34. Found: C, 58.62; H, 5.29.

3,3′,5,8-Tetramethoxy-4′,5′,6,7-bis(methylenedioxy)flavone (**4**)——Pale yellow needles, mp 222—225°C, UV λ_{max}^{MeOH} nm (log ε): 340 (4.28), 276 (4.03), 245 (4.20), 221 (4.48). IR ν_{max}^{KBr} cm^{-1}: 1620, 1585, 1428, 1380, 1272, 1203, 1035. MS *m/e*: 430 (M$^+$) (100%), 429 (58%), 415 (50%). *Anal.* Calcd for $C_{21}H_{18}O_{10}$: C, 58.61; H, 4.22. Found: C, 58.67; H, 4.22.

3′-Hydroxy-3,4′,5,5′,8-pentamethoxy-6,7-methylenedioxyflavone (**5a**)——Pale yellow needles, mp 183—185°C, UV λ_{max}^{MeOH} nm (log ε): 328 (4.28), 276 (4.14), 223 (4.34). IR ν_{max}^{KBr} cm^{-1}: 3330, 1622, 1575, 1507, 1490, 1434, 1375, 1280, 1222, 1117, 1075, 1036. MS *m/e*: 432 (M$^+$) (100%), 431 (44%), 417 (78%). *Anal.* Calcd for $C_{21}H_{20}O_{10}$: C, 58.33; H, 4.66. Found: C, 58.45; H, 4.64.

Acetate (**5b**) **of 5a**——**5a** (50 mg) was acetylated with Ac_2O–pyridine to give an acetate (**5b**), which was recrystallized from MeOH to give colorless needles (35 mg), mp 150—151°C, IR ν_{max}^{KBr} cm^{-1}: 1761, 1622, 1495, 1426, 1368, 1275, 1231, 1210, 1200, 1096, 1070. MS *m/e*: 474 (M$^+$) (83%), 459 (45%), 431 (100%), 417 (77%).

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Anal. Calcd for $C_{23}H_{22}O_{11}$: C, 58.23; H, 4.67. Found: C, 58.31; H, 4.66.

3,3′,4′,5,5′,8-Hexamethoxy-6,7-methylenedioxyflavone (6)——Pale yellow needles, mp 169—170°C, UV λ_{max}^{MeOH} nm (log ε): 330 (4.43), 278 (4.29), 224 (4.51). IR ν_{max}^{KBr} cm^{-1} 1623, 1596, 1575, 1500, 1485, 1465, 1440, 1430, 1361, 1327, 1272, 1220, 1114. MS *m/e*: 446 (M$^+$) (100%), 445 (34%), 431 (95%). *Anal.* Calcd for $C_{22}H_{22}O_{10}$: C, 59.19; H, 4.97. Found: C, 59.33; H, 4.96.

3′,5-Dihydroxy-3,4′,5′,8-tetramethoxy-6,7-methylenedioxyflavone (7a)——Yellow needles, mp 207—208°C, UV λ_{max}^{MeOH} nm (log ε): 341 (4.34), 287 (4.24). IR ν_{max}^{KBr} cm^{-1}: 3470, 1674, 1590, 1580, 1499, 1450, 1370, 1216, 1120, 1207. MS *m/e*: 418 (M$^+$) (100%), 403 (92%). *Anal.* Calcd for $C_{20}H_{18}O_{10}$: C, 57.42; H, 4.34. Found: C, 57.11; H, 4.36.

Acetate (7b) of 7*a*——**7a** (40 mg) was acetylated with Ac_2O–pyridine to give a diacetate (**7b**), which was recrystallized from MeOH to give pale yellow needles (25 mg), mp 197—200°C, IR ν_{max}^{KBr} cm^{-1}: 1765, 1628, 1587, 1490, 1438, 1367, 1210, 1200, 1090. MS *m/e*: 502 (M$^+$) (8%), 460 (100%), 445 (29%). *Anal.* Calcd for $C_{24}H_{22}O_{12}$: C, 57.37; H, 4.41. Found: C, 57.16; H, 4.40.

Digicitrin (8a)——Yellow needles, mp 182—184°C, UV λ_{max}^{MeOH} nm (log ε): 334 (4.24), 282 (4.26). IR ν_{max}^{KBr} cm^{-1}: 3390, 1634, 1586, 1460, 1420, 1366, 1275, 1205, 1155, 1108, 1045. MS *m/e*: 434 (M$^+$) (76%), 419 (100%). *Anal.* Calcd for $C_{21}H_{22}O_{10}$: C, 58.06; H, 5.11. Found: C, 58.03; H, 5.05.

Monoacetate (8b) and Diacetate (8c) of 8a——**8a** (60 mg) was treated with Ac_2O–pyridine at room temperature overnight to give a mixture of **8b** and **8c**, which were separated by PLC and recrystallized from MeOH to give **8b** as yellow needles (20 mg) and **8c** as pale yellow needles (30 mg). **8b**, mp 123—125°C, IR ν_{max}^{KBr} cm^{-1}: 1752, 1645, 1591, 1480, 1460, 1420, 1280, 1250, 1220, 1100, 1050. MS *m/e*: 476 (M$^+$) (100%), 461 (99%), 418 (44%) *Anal.* Calcd for $C_{23}H_{24}O_{11}$: C, 57.98; H, 5.08. Found: C, 57.82; H, 5.20. **8c**, mp 151—153°C, IR ν_{max}^{KBr} cm^{-1}: 1758, 1628, 1595, 1556, 1458, 1405, 1364, 1280, 1220, 1195, 1095. MS *m/e*: 518 (M$^+$) (9%), 476 (100%), 461 (79%), 433 (11%), 419 (24%). *Anal.* Calcd for $C_{25}H_{26}O_{12}$: C, 57.91; H, 5.05. Found: C, 57.68; H, 4.99.

Exoticin (9)——Pale yellow needles, mp 131—132°C, UV λ_{max}^{MeOH} nm (log ε): 328 (4.31), 271 (4.21), 266 (4.22), 250 (4.23), 224 (4.38). IR ν_{max}^{KBr} cm^{-1}: 1640, 1592, 1505, 1481, 1465, 1435, 1412, 1363, 1335, 1290, 1242, 1219, 1134, 1060. MS *m/e*: 462 (M$^+$) (42%), 447 (100%). *Anal.* Calcd for $C_{23}H_{26}O_{10}$: C, 59.73; H, 5.67. Found: C, 58.67; H, 4.22.

Quercitrin (10)——Pale yellow powder, mp 179—182°C, IR ν_{max}^{KBr} cm^{-1}: 3350 (br), 1660, 1600, 1566, 1503, 1448, 1300, 1200, 1150, 1060. ^{1}H-NMR (CD_3OD, δ): 0.98 (3H, d, J=5.5 Hz, CH_3 on rhamnosyl group), 3.72 (1H, m, CH of rhamnosyl group), 4.23 (1H, dd, J=1.5, 4.0 Hz, CH of rhamnosyl group), 5.34 (1H, d, J=1.5 Hz, anomeric H of rhamnosyl group), 6.16 (1H, d, J=2.5 Hz, at C-8), 6.32 (1H, d, J=2.5 Hz, at C-6), 6.87 (1H, d, J=9.0 Hz, at C-5′), 7.27 (1H, dd, J=9.0, 2.0 Hz, at 6′), 7.32 (1H, d, J=2.0 Hz, at C-2′).

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