Novel Flavonoids from *Chrysosplenium grayanum* MAXIM. (Saxifragaceae)

Munehisa ARISAWA,*[,a] Hua BAI,[b] Miwa SHIOJIMA,[a] Toshimitsu HAYASHI,[a] Yasuhiro TEZUKA,[c] Tooru TAGA,[d] Yoshihisa MIWA,[d] Yusuke ITO,[b] Tohru KIKUCHI,[c] and Naokata MORITA[a]

Department of Medicinal Resources, Faculty of Pharmaceutical Sciences,[a] Department of Anesthesiology, Faculty of Medicine,[b] and Research Institute for WAKAN-YAKU (Oriental Medicines),[c] Toyama Medical & Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan, and Faculty of Pharmaceutical Sciences, Kyoto University,[d] Yoshida-shimoadachi-cho, Sakyo-ku, Kyoto 606, Japan. Received September 9, 1992

Three novel flavonoids, chrysograyanone (1), chrysoquinone A (2), and chrysosplenoside H (3), have been isolated from fresh whole plants of *Chrysosplenium grayanum* MAXIM. (Saxifragaceae) and their structures were determined to be 5-hydroxy-2-(1,*trans*-5-dihydroxy-4-methoxy-5-methoxycarbonyl-2-oxo-cyclopent-3-enyl)-3,7-dimethoxychromone (1), 2′,5′-dihydro-5-hydroxy-3,7,4′,6′-tetramethoxyflavone-2′,5′-dione (2), and 5,2′-dihydroxy-3,6,7,4′,5′-pentamethoxyflavone (brickellin)-2′-*O*-β-D-glucopyranoside (3) on the basis of spectroscopic evidence and X-ray analysis.

Keywords cyclopentenyl chromone; benzoquinonyl chromone; *Chrysosplenium grayanum*; chrysograyanone; chrysoquinone A; chrysosplenoside H

Introduction

We previously reported[1,2] the isolation of two new flavonols[1] and a cytotoxic principle[2] from the MeOH extract of the fresh whole plant of *Chrysosplenium grayanum* MAXIM. (Saxifragaceae) and the cytotoxic activities and antitumor effects. More recently, we reported a novel flavonoid called chrysograyanone (**1**) which is the first example of a chromone having a cyclopentenyl group at the C-2 position.[3]

In a continuing investigation, we have isolated two more novel flavonoids, called chrysoquinone A (**2**) and chrysosplenoside H (**3**). This paper deals with the structure elucidation of **2** and **3** together with **1**.

Results and Discussion

The 1—2% MeOH/$CHCl_3$ eluate from the column chromatography of the 95% MeOH extract[1-3] was further chromatographed on a silica gel column and elution with EtOAc/*n*-hexane mixture gave **1** and **2**; **3** was obtained from the 10—20% MeOH/$CHCl_3$ eluate of the column chromatography.

Chrysograyanone (**1**) showed a positive $FeCl_3$ reaction and a positive flavone reaction.[4] The UV spectrum of **1** in MeOH exhibited absorptions at 247, 296 and 330 nm (sh), and on addition of $AlCl_3$/HCl a significant bathochromic shift was observed, though no shift was observed with the addition of NaOAc. The data indicated the presence of hydroxyl group at C-5 and the absence of this group at the C-7.[5] The IR spectrum of **1** showed absorption bands at 3460 (OH), 3340 (OH), 1730 (ester CO), 1710 (ketone CO), 1660 (α,β-unsaturated CO), 1620 (double bond), 1600 (benzene ring), and 1230 cm^{-1} (ester). The electron impact (EI)-MS of **1** exhibited the molecular ion (M^+) peak at *m/z* 422 together with strong fragment peaks at *m/z* 363 (M−COOMe) and 167 ($C_8H_7O_4^+$) which may have been formed by retro-Diels–Alder fragmentation combined with a hydrogen transfer. The molecular formula was determined to be $C_{19}H_{18}O_{11}$ by high resolution (HR) EI-MS analysis. Acetylation of **1** with Ac_2O and pyridine gave a monoacetate (**1a**), mp 230 °C, EI-MS *m/z* 464 (M^+). The ^{1}H-NMR spectrum of **1** in dimethyl sulfoxide (DMSO-d_6) showed signals due to three hydroxyl protons at δ 12.44 (5-OH), 6.99, and 6.78 ppm, a pair of *meta*-coupled aromatic protons (d, J=1.7 Hz) at δ 6.56 and 6.37 ppm, an isolated olefinic proton at δ 5.38 ppm, and four methoxyls at δ 3.91, 3.87, 3.71 and 3.61 ppm (Table I). The ^{13}C-NMR spectrum of **1** exhibited nineteen signals including four methoxyls at δ 52.3 (q, 4′-OMe), 56.0 (q, 7-OMe), 59.2 (q, 3-OMe), and 59.9 ppm (q, 6′-OMe) and three carbonyls at δ 177.9 (s, C-4), 182.6 (s, C-6′), and 196.3 ppm (s, C-2′). The ^{13}C-signals at δ 92.2 (d), 97.9 (d), 105.5 (s), 139.3 (s), 156.4 (s), 156.8 (s), 160.9 (s), and 165.1 ppm (s) were attributed to C-8, C-6, C-10, C-3, C-2, C-9, C-5, and C-7 on the chromone skeleton,[6] respectively, and were indicative that **1** has a 5-hydroxy-3,7-dimethoxychromone skeleton.[6] The other ^{1}H- and ^{13}C-signals were analyzed with the aid of long range C–H (LRCH) shift correlation spectroscopy (COSY), long range

TABLE I. NMR Data of Chrysograyanone (**1**)

Position	Chemical shifts		Observed correlated carbons		
	^{1}H	^{13}C	HMBC	LRCH (J=10 Hz)	LSPD
2		156.4 (s)			
3		139.3 (s)			
4		177.9 (s)			
5		160.9 (s)			
6	6.37 (1H, d)	97.9 (d)	5, 7, 8, 10	5, 7, 8, 10	5, 8, 10
7		165.1 (s)			
8	6.56 (1H, d)	92.2 (d)	6, 7, 9, 10	6, 7, 9, 10	6, 9, 10
9		156.8 (s)			
10		105.5 (s)			
1′		84.1 (s)			
2′		196.3 (s)			
3′	5.38 (1H, s)	104.8 (d)	1′, 2′, 5′	1′, 2′[a], 5′	1′, 5′
4′		169.2 (s)			
5′		84.3 (s)			
6′		182.6 (s)			
5-OH	12.44 (1H, s)		5, 6, 10	5, 6, 10	5, 6, 10
1′-OH	6.99 (1H, s)		2, 1′, 2′	1′	1′, 5′
5′-OH	6.78 (1H, s)		4′, 5′, 6′	4′, 5′,[a] 6′	1′, 4′, 5′, 6′
3-OMe	3.61 (3H, s)	59.2 (q)	3	3	3
7-OMe	3.87 (3H, s)	56.0 (q)	7	7	7
4′-OMe	3.71 (3H, s)	52.3 (q)	4′	4′	4′
6′-OMe	3.91 (3H, s)	59.9 (q)	6′	6′	6′

a) Observed at J=6 Hz.

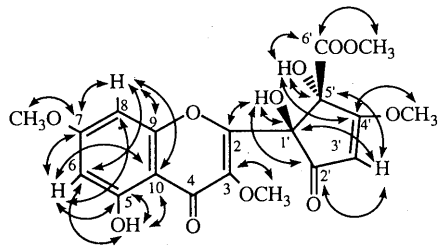

Fig. 1. Significant Multiple-Bond Connections Observed in the HMBC Spectrum of **1**

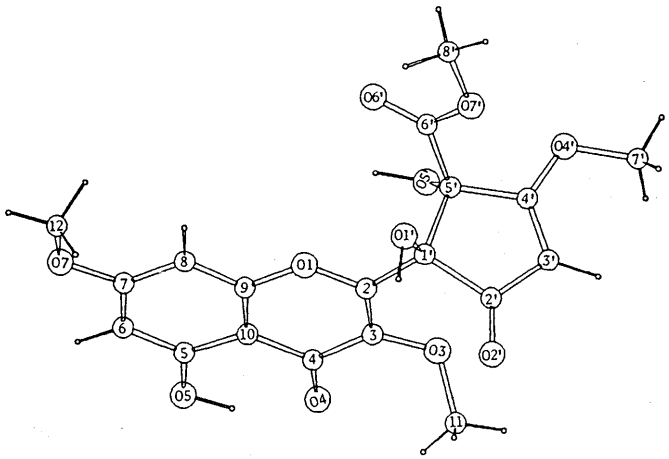

Fig. 2. Molecular Structure of Chrysograyanone (**1**)

selective proton decoupling (LSPD), and heteronuclear multiple bond connectivity (HMBC) (Table I).

In the HMBC spectrum of **1**, the ^{1}H-signal at δ 6.99 ppm (1′-OH) showed significant long-range correlations with the ^{13}C-signals at δ 84.1 (C-1′), 156.4 (C-2), and 196.3 ppm (C-2′), while the ^{1}H-signal at δ 6.78 ppm (5′-OH) showed correlations with the signals at δ 84.3 (C-5′), 169.2 (C-4′), and 182.6 (C-6′), ppm. On the other hand, the ^{1}H-signal at δ 5.38 ppm (3′-H) showed correlations with the signals at δ 84.3, 84.1, and 196.3 ppm.

The signal at δ 6.78 ppm also showed significant long-range correlation with the ^{13}C-signal at δ 84.1 ppm in an LSPD experiment. The significant multiple-bond correlations observed in the HMBC spectrum are shown by arrows in Fig. 1, and those observed in LRCH COSY and LSPD spectra are shown in Table I. From the foregoing evidence, the planar structure of **1** was established to be 5-hydroxy-2-(1,5-dihydroxy-4-methoxy-5-methoxycarbonyl-2-oxo-cyclopent-3-enyl)-3,7-dimethoxychromone (**1**). In order to clarify the stereochemistry of 1′- and 5′-positions, we made a single crystal X-ray analysis of **1**. The analysis showed the same planar structure as established by the two dimensional (2D)-NMR method, and simultaneously showed the hydroxyl group at the C-1′ position to be in β-configuration, and the methoxycarbonyl group at the C-5′ position to be in β-configurations. The molecular structure of **1** is illustrated in Fig. 2, and the atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms of **1** are listed in Table II.[7]

Thus, the relative structure of chrysograyanone (**1**) was determined to be 5-hydroxy-2-(1,*trans*-5-dihydroxy-4-methoxy-5-methoxycarbonyl-2-oxo-cyclopent-3-enyl)-3,7-dimethoxychromone (**1**). Our present result provide the first example of a chromone having a cyclopentenyl group at the C-2 position, which is a unique structural feature.

TABLE II. Atomic Coordinates and Equivalent Isotropic Temperature Factors for Non-hydrogen Atoms of Chrysograyanone (**1**)

Atom	x	y	z	U_{eq}
C-2	0.0431 (2)	0.0116 (3)	0.1530 (1)	0.035 (1)
C-3	0.1054 (2)	−0.0588 (3)	0.1739 (1)	0.037 (1)
C-4	0.0978 (2)	−0.1950 (3)	0.1803 (2)	0.041 (1)
C-5	0.0017 (2)	−0.3763 (3)	0.1675 (2)	0.046 (1)
C-6	−0.0751 (2)	−0.4206 (3)	0.1533 (2)	0.049 (1)
C-7	−0.1352 (2)	−0.3385 (3)	0.1353 (2)	0.045 (1)
C-8	−0.1203 (2)	−0.2075 (3)	0.1295 (2)	0.042 (1)
C-9	−0.0432 (2)	−0.1654 (3)	0.1446 (1)	0.038 (1)
C-10	0.0190 (2)	−0.2451 (3)	0.1649 (2)	0.039 (1)
C-11	0.2112 (2)	−0.0065 (4)	0.2461 (2)	0.051 (1)
C-12	−0.2757 (2)	−0.3062 (4)	0.1147 (2)	0.062 (1)
O-1	−0.0307 (1)	−0.0383 (2)	0.1384 (1)	0.039 (1)
O-3	0.1795 (1)	−0.0027 (2)	0.1819 (1)	0.041 (1)
O-4	0.1561 (1)	−0.2629 (2)	0.1965 (1)	0.058 (1)
O-5	0.0599 (2)	−0.4586 (2)	0.1845 (1)	0.062 (1)
O-7	−0.2088 (1)	−0.3888 (2)	0.1233 (1)	0.055 (1)
C-1′	0.0455 (2)	0.1515 (3)	0.1390 (1)	0.034 (1)
C-2′	0.1058 (2)	0.2267 (3)	0.1804 (1)	0.037 (1)
C-3′	0.1597 (2)	0.2973 (3)	0.1406 (2)	0.040 (1)
C-4′	0.1415 (2)	0.2754 (3)	0.0802 (1)	0.035 (1)
C-5′	0.0757 (2)	0.1783 (3)	0.0693 (1)	0.033 (1)
C-6′	0.0039 (2)	0.2214 (3)	0.0288 (1)	0.034 (1)
C-7′	0.2406 (2)	0.4119 (4)	0.0383 (2)	0.054 (1)
C-8′	−0.0813 (2)	0.3894 (3)	0.0001 (2)	0.051 (1)
O-1′	−0.0322 (1)	0.2057 (2)	0.1465 (1)	0.039 (1)
O-2′	0.1007 (1)	0.2311 (2)	0.2379 (1)	0.049 (1)
O-4′	0.1747 (1)	0.3238 (2)	0.0275 (1)	0.044 (1)
O-5′	0.1123 (1)	0.0732 (2)	0.0402 (1)	0.036 (1)
O-6′	−0.0366 (1)	0.1478 (2)	−0.0008 (1)	0.047 (1)
O-7′	−0.0089 (1)	0.3439 (2)	0.0313 (1)	0.042 (1)

$U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \boldsymbol{a}_j$.

Chrysoquinone A (**2**) showed a positive $FeCl_3$ reaction and a positive flavone reaction.[4] The UV spectrum of **2** in MeOH exhibited absorptions at 252, 292, and 340 nm (sh). The spectra obtained when $AlCl_3$/HCl and NaOAc were added indicated the presence of hydroxyl group at the C-5 and the absence of hydroxyl group at the C-7.[5] The IR spectrum of **2** exhibited absorption bands at 3450 (OH), 1700, 1650 (α,β-unsaturated CO) and 1600 cm^{-1} (benzene ring). The EI-MS of **2** exhibited a molecular ion (M^+) peak at m/z 388 and prominent peaks at m/z 373 (M−Me), 357 (M−OMe), 345 (M−Me−CO), and 167 ($C_8H_7O_4^+$) which may be formed by retro-Diels–Alder fragmentation combined with a hydrogen transfer. The molecular formula was determined to be $C_{19}H_{16}O_9$ by HREI-MS analysis. The ^{1}H-NMR spectrum of **2** in $CDCl_3$ showed the presence of hydroxyl group at δ 12.40 (5-OH), a pair of *meta*-coupled aromatic protons at δ 6.37 and 6.38 ppm (each, d, J= 2.0 Hz), an isolated olefinic proton at δ 5.99 ppm, and four methoxyl groups at δ 3.85, 3.87 (×2), and 4.00 ppm. The ^{13}C-NMR spectrum of **2** in $CDCl_3$ exhibited nineteen signals including four methoxyls at δ 55.8, 56.7, 60.5, and 60.6 ppm, and three carbonyls at δ 177.2, 178.1 (C-4), and 183.8 ppm. The ^{13}C-signals at δ 92.5 (d), 98.3 (d), 106.8 (s), 141.7 (s), 149.2 (s), 157.3 (s), 162.3 (s), and 165.7 ppm (s) were attributed to C-8, C-6, C-10, C-3, C-2, C-9, C-5, and C-7 on the chromone skelton,[6] respectively, and indicate the presence of a 5-hydroxy-3,7-dimethoxychromone skeleton.[6] The signals at δ 183.8 and 177.2 ppm suggested

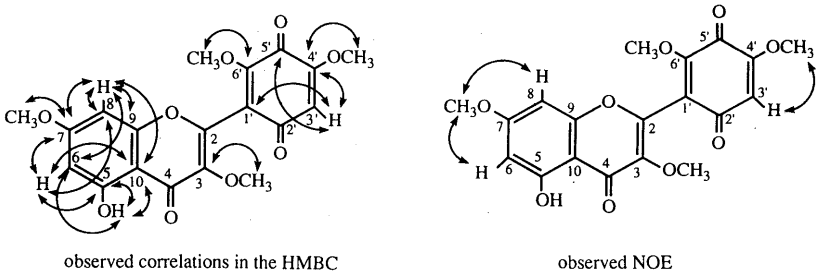

Fig. 3. Significant Correlations Observed in the HMBC and NOE Spectra of **2**

TABLE III. Assignments of ^{1}H- and ^{13}C-Signals of **2** in 5% C_5D_5N/$CDCl_3$

Position	^{1}H	^{13}C	Position	^{1}H	^{13}C
2		149.1 (s)	1′		116.0 (s)
3		141.5 (s)	2′		183.5 (s)
4		178.0 (s)	3′	5.98 (1H, s)	107.1 (d)
5		162.2 (s)	4′		157.3 (s)
6	6.36 (1H, d)	98.1 (d)	5′		176.9 (s)
7		165.5 (s)	6′		155.3 (s)
8	6.38 (1H, d)	92.3 (d)	3-OMe	3.88 (3H, s)	60.5 (q)[a]
9		157.1 (s)	7-OMe	3.83 (3H, s)	56.5 (q)
10		106.6 (s)	4′-OMe	3.85 (3H, s)	56.6 (q)
			6′-OMe	4.00 (3H, s)	60.3 (q)[a]

a) Assignments may be interchanged.

the presence of 2,5-benzoquinonyl grouping, while the signals at δ 60.5 and 60.6 ppm indicate the presence of two *ortho*-disubstituted aromatic methoxyl groups,[6] that is, at the C-3 and C-6′ positions. The other ^{1}H- and ^{13}C-signals on B-ring were analyzed with the aid of the HMBC method. In the HMBC spectrum of **2**, a ^{1}H-signal at δ 5.99 ppm (3′-H) showed significant long-range correlations with the ^{13}C-signals at δ 116.0 (C-1′), 157.4 (C-4′), 177.2 (C-5′), and 183.8 ppm (C-2′). To further clarify the structure of **2**, we measured the HMBC and difference nuclear Overhauser effect (NOE) spectra in 5% $C_5D_5N/CDCl_3$. The assignments of the ^{1}H- and ^{13}C-signals are shown in Table III.

In the difference NOE spectra of **2**, positive NOE were mutually observed between a signal at δ 5.98 ppm and a separated signal at δ 3.85 ppm. The significant multiple-bond correlations observed in HMBC and NOE are illustrated by arrows in Fig. 3.

From the foregoing evidence, the structure of chrysoquinone A (**2**) was established to be 2′,5′-dihydro-5-hydroxy-3,7,4′,6′-tetramethoxyflavone-2′,5′-dione (**2**).

Chrysosplenoside H (**3**) showed a positive $FeCl_3$ reaction and a positive flavone reaction.[4] The UV spectrum of **3** in MeOH exhibited absorptions at 254, 300 (sh), and 332 nm. The spectra obtained on addition of $AlCl_3$/HCl and NaOAc indicated the presence of hydroxyl group at the C-5 position and the absence of hydroxyl group at the C-7.[5] The IR spectrum of **3** exhibited absorption bands at 3470 (OH), 1660 (α,β-unsaturated CO), 1610 (double bond), and 1600 cm^{-1} (benzene ring). The EI-MS of **3** exhibited the M^+ peak at *m/z* 566 together with fragment peaks at *m/z* 565 (M−H) and 403 ($M-C_6H_{11}O_5$). The ^{1}H-NMR spectrum of **3** in DMSO-d_6 showed the presence of hydroxyl group at δ 12.67 ppm (5-OH), three aromatic protons at δ 7.04 ppm overlapping two signals of 3′-H and 6′-H and at

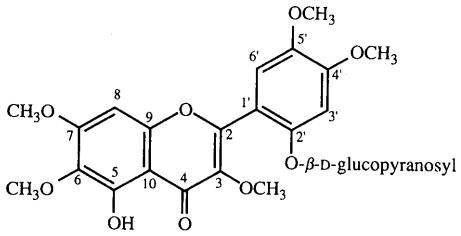

Fig. 4. Structure of Chrysosplenoside H (**3**)

δ 6.76 ppm (8-H), and four methoxyl groups at δ 3.89, 3.85, 3.753, and 3.746 ppm (×2). A signal at δ 4.82 ppm (d, J=7.7 Hz) was attributed to an anomeric proton of β-D-glucopyranosyl moiety. The ^{13}C-NMR spectrum of **3** in DMSO-d_6 exhibited twenty-five signals including an overlapping signal at δ 60.0 ppm (×2). The spectrum showed five methoxyl groups at δ 55.6, 56.2, 56.3 and 60.0 ppm (×2), and a β-D-glucopyranosyl moiety at δ 61.0 (G.C-6), 70.1 (G.C-4), 73.1 (G.C-2), 76.7 (G.C-3), 77.3 (G.C-5) and 102.0 ppm (G.C-1). The methoxyl signals at δ 60.0 ppm (×2) thus indicate the presence of two *ortho*-disubstituted aromatic methoxyl groups[6] at the C-3 and C-6 positions. The ^{13}C-signals for chromone moiety of flavonoid skeleton appeared at δ 91.3 (C-8), 106.2 (C-10), 131.1 (C-6), 139.2 (C-3), 150.2 (C-5), 151.8 (C-9), 156.1 (C-2), 158.5 (C-7) and 178.5 ppm (C-4) and indicate a 5-hydroxy-3,6,7-trimethoxyflavone skeleton.[6] The signals on B-ring of the skeleton at δ 101.6 (d), 110.8 (s), 113.1 (d), 143.3 (s), 151.5 (s), and 152.5 ppm (s) are attributed to C-3′, C-1′, C-6′, C-2′, C-4′ and C-5′, respectively. Hydrolysis of **3** with 10% H_2SO_4 afforded brickellin[8,9] (5,2′-dihydroxy-3,6,7,4′,5′-pentamethoxyflavone) and D-glucose.

From the foregoing evidence the structure of **3** was established to be 5,2′-dihydroxy-3,6,7,4′,5′-pentamethoxyflavone (brickellin)-2′-*O*-β-D-glucopyranoside.

Our present result for chrysoquinone A (**2**) provides the first example of chromone having a benzoquinonyl group at the C-2 position, which is a unique structural feature. Chrysoquinone A (**2**) and chrysograyanone (**1**) could be biosynthetically concerned with the oxidative pathway.

Experimental

General Procedures All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectrum was recorded on a Hitachi 260-10 IR spectrometer with polystyrene calibration at 1601 cm^{-1}, Specific optical rotation was determined on a JASCO DIP-400 digital polarimeter. ^{1}H- and ^{13}C-NMR spectra were taken on a JEOL JNM-GX 270 or 400 spectrometer at 270 or 400 and 67.9 or 100 MHz, respectively, with tetramethylsilane as an internal standard. The chemical shifts are recorded in δ (ppm) values. Multiplicity of the ^{13}C-NMR data was determined by distortionless

enhancement by polarization transfer (DEPT) method. 2D-NMR spectra were taken on a JNM-CX 400 spectrometer. EI-MS and HREI-MS were obtained on a JEOL JMS-D-200 mass spectrometer operating at 70 eV.

Plant Materials The collection and identification of *Chrysosplenium grayanum* (Saxifragaceae) were described previously.[1,2]

Extraction and Isolation The $CHCl_3$-soluble fraction of MeOH extract, which was prepared from fresh whole plants of *C. grayanum*, was previously partitioned between 95% MeOH and *n*-hexane.[1,2] The elution of the column chromatograph of the 95% MeOH extract was divided into 6 fractions eluting with $CHCl_3$, 1—2% MeOH/$CHCl_3$, 10% MeOH/$CHCl_3$, 10—20% MeOH/$CHCl_3$, 25—50% MeOH/$CHCl_3$, and MeOH. The 1—2% MeOH/$CHCl_3$ eluent was subdivided on another silica gel column by elution with an EtOAc/*n*-hexane mixture. The 25% EtOAc/*n*-hexane eluent afforded reddish brown fine needles (**2**), 15 mg (3.57×10^{-4} % from fresh material) and 50% EtOAc/*n*-hexane eluent afforded colorless prisms (**1**), 20 mg (4.76×10^{-4} %). The 10—20% MeOH/$CHCl_3$ eluate of the column of the 95% MeOH extract afforded pale yellow fine needles (**3**), 30 mg (7.14×10^{-4} %).

Chrysograyanone (1) Colorless prisms, mp 231—232 °C. Purplish brown with $FeCl_3$, yellow with Mg + HCl. UV λ_{max}^{MeOH} nm (log ε): 247 (4.34), 296 (3.92), 330 (sh) (3.82), $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 268, 314, 380, $\lambda_{max}^{MeOH+NaOAc}$ nm: similar to λ_{max}^{MeOH} nm. IR ν_{max}^{KBr} cm^{-1}: 3460, 3340, 1730, 1710, 1660, 1620, 1600, 1230. EI-MS *m/z*: 422 (M^+), 363, 167. HREI-MS *m/z*: 422.0890, Calcd for $C_{19}H_{18}O_{11}$, 422.0848. ^{1}H- and ^{13}C-NMR see Table I.

Acetylation of 1 Compound **1** was reacted with Ac_2O in pyridine at room temperature overnight. The reaction mixture was treated in the usual way to afford monoacetate (**1a**), colorless prisms, mp 230 °C. EI-MS *m/z*: 464 (M^+), 422, 405, 390, 377, 363, 345, 314, 249, 167. ^{1}H-NMR (DMSO-d_6) δ: 2.42 (3H, s, OAc), 3.84 (3H, s, OMe), 3.87 (3H, s, OMe), 3.88 (3H, s, OMe), 3.98 (3H, s, OMe), 5.78 (1H, s, 3′-H), 6.57 (1H, d, J = 2.3 Hz, 6-H), 6.69 (1H, d, J = 2.3 Hz, 8-H). ^{13}C-NMR (DMSO-d_6) δ: 196.4 (C-2′), 182.4 (C-6′), 171.8 (C-4), 169.4 (C-4′), 168.8 ($\underline{O}\underline{C}OCH_3$), 162.9 (C-7), 157.6 (C-2), 154.2 (C-9), 149.8 (C-5), 140.9 (C-3), 110.5 (C-10), 108.3 (C-6), 105.0 (C-3′), 98.9 (C-8), 84.2 (C-1′), 83.3 (C-5′), 59.3 (OMe-6′), 58.9 (OMe-3), 56.4 (OMe-7), 52.5 (OMe-4′), 20.9 ($OCO\underline{C}H_3$).

Crystallographic Analysis of 1 Crystal data: $C_{19}H_{18}O_{11}$, M_r = 422.34, orthorhombic, P_{bcn}; a = 16.485 (4), b = 10.589 (2), c = 21.11 (1) Å, V = 3685 (1) Å^3, Z = 8, D_{calcd} = 1.522 g/cm^3. Intensity data were collected within $2\theta < 120°$ by using graphaite monochromated CuK_α radiation (λ = 1.54178 Å) at T = 295 K on a Rigaku AFC5-RU. Absorption correction was not applied [crystal size: 0.3 × 0.2 × 0.2 mm, μ(CuK_α) = 10.5 cm^{-1}]. The structure was solved by direct methods and refined by block-diagonal least-squares methods to R = 0.052, wR = 0.066 for 2253 independent reflections [$F_o > 3\sigma(F_o)$], using KPPXRAY software in the Data Processing Center of Kyoto University. For the fractional atomic coordinates and the equivalent temperature factors for non-hydrogen atoms of **1** see Table II.[7]

Chrysoquinone A (2) Reddish brown micro needles, mp 185—187 °C. Purplish brown with $FeCl_3$, yellow with Mg + HCl. UV λ_{max}^{MeOH} nm (log ε): 252 (4.28), 292 (3.88), 340 (sh, 3.45), $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 266, 312, 380, $\lambda_{max}^{MeOH+NaOAc}$ nm: similar to λ_{max}^{MeOH}. IR ν_{max}^{KBr} cm^{-1}: 3450, 1700, 1650, 1600. EI-MS *m/z*: 388 (M^+), 373, 357, 345, 167. HREI-MS *m/z*: 388.0773, Calcd for $C_{19}H_{16}O_9$, 388.0793. ^{1}H- and ^{13}C-NMR (C_5D_5N) see Table III. ^{1}H-NMR ($CDCl_3$) δ: 12.40 (1H, s, 5-OH), 6.38 (1H, d, J = 2.0 Hz, 6-H), 6.37 (1H, d, J = 2.0 Hz, 8-H), 5.99 (1H, s, 3′-H), 4.00 (3H, s, OMe), 3.87 (6H, s, OMe × 2), 3.85 (3H, s, OMe). ^{13}C-NMR ($CDCl_3$) δ: 183.8 (s, C-2′), 178.1 (s, C-4), 177.2 (s, C-5′), 165.7 (s, C-7), 162.3 (s, C-5), 157.4 (s, C-4′), 157.3 (s, C-9), 155.4 (s, C-6′), 149.2 (s, C-2), 141.7 (s, C-3), 116.0 (s, C-1′), 107.4 (d, C-3′), 106.8 (s, C-10), 98.3 (d, C-6), 92.5 (d, C-8), 60.6 (q, OMe-3 or 6′), 60.5 (q, OMe-6′ or 3), 56.7 (q, OMe-7 or 4′), 55.8 (q, OMe-4′ or 7).

Chrysosplenoside H (3) Pale yellow micro needles, mp 257—258 °C. Purplish brown with $FeCl_3$, yellow with Mg + HCl. UV λ_{max}^{MeOH} nm (log ε): 254 (4.56), 300 (sh) (3.88), 332 (4.22), $\lambda_{max}^{MeOH+AlCl_3}$ nm: 271, 321, 379, $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 269, 321 (sh), 351, 380 (sh), $\lambda_{max}^{MeOH+NaOMe}$ nm: 255, 274, 365 (sh), $\lambda_{max}^{MeOH+NaOAc}$ and $\lambda_{max}^{MeOH+NaOAc+H_3BO_3}$ nm: similar to λ_{max}^{MeOH}. IR ν_{max}^{KBr} cm^{-1}: 3470, 1660, 1610, 1600. EI-MS *m/z*: 566 (M^+), 565, 404, 403, 390, 388, 374, 373, 359, 343, 208, 193, 181, 179. HREI-MS *m/z*: 566.1619, Calcd for $C_{26}H_{30}O_{14}$, 566.1633. ^{1}H-NMR (DMSO-d_6) δ: 12.67 (1H, s, 5-OH), 7.04 (2H, s, 3′- and 6′-H), 6.76 (1H, s, 8-H), 4.82 (1H, d, J = 7.7 Hz, anomeric H), 3.89 (3H, s, OMe), 3.85 (3H, s, OMe), 3.753 (3H, s, OMe), 3.756 (6H, s, OMe × 2). ^{13}C-NMR (DMSO-d_6) δ: 178.5 (s, C-4), 158.5 (s, C-7), 156.1 (s, C-2), 152.5 (s, C-5′), 151.8 (s, C-9), 151.5 (s, C-4′), 150.2 (s, C-5), 143.3 (s, C-2′), 139.2 (s, C-3), 131.1 (s, C-6), 113.1 (d, C-6′), 110.8 (s, C-1′), 106.2 (s, C-10), 102.0 (d, G.-1), 101.6 (d, C-3′), 91.3 (d, C-8), 77.3 (d, G.-5), 76.7 (d, G.-3), 73.1 (d, G.-2), 70.1 (d, G.-4), 61.0 (t, G.-6), 60.0 (q, OCH_3 × 2), 56.3 (q, OCH_3), 56.1 (q, OCH_3), 55.6 (q, OCH_3).

Hydrolysis of 3 Compound **3** was reacted with 10% H_2SO_4 on a water bath for 1 h. The reaction mixture was treated in the usual way to afford an aglycone and D-glucose. The aglycone, pale yellow needles, mp 190—193 °C, was identified as brickellin (5,2′-dihydroxy-3,6,7,4′,5′-hexamethoxyflavone)[8] by direct comparison with an authentic sample.[9]

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References and Notes

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