Studies on the Constituents of *Scutellaria* Species (XXII).[1] Constituents of the Roots of *Scutellaria amabilis* HARA

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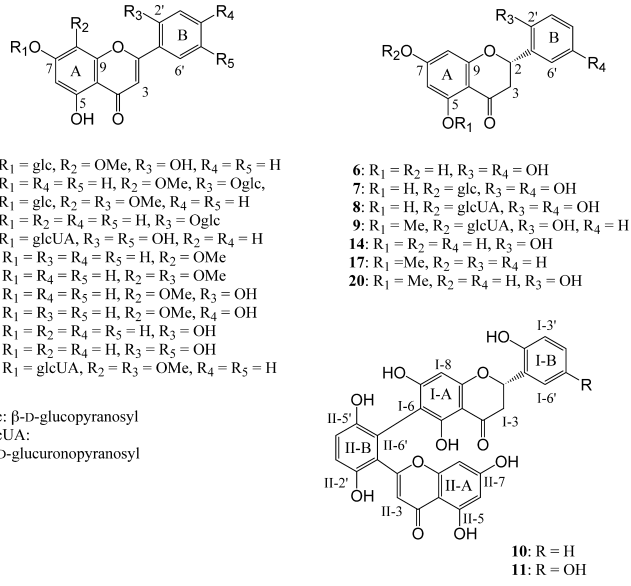
From the roots of *Scutellaria amabilis* HARA, eleven new flavonoids, 5,7,2′-trihydroxy-8-methoxyflavone 7-*O*-*β*-D-glucopyranoside, 5,7,2′-trihydroxy-8-methoxyflavone 2′-*O*-*β*-D-glucopyranoside, 5,7-dihydroxy-8,2′-dimethoxyflavone 7-*O*-*β*-D-glucopyranoside, 5,7,2′-trihydroxyflavone 2′-*O*-*β*-D-glucopyranoside, 5,7,2′,5′-tetrahydroxyflavone 7-*O*-*β*-D-glucuronopyranoside, (2*S*)-5,7,2′,5′-tetrahydroxyflavanone, (2*S*)-5,7,2′,5′-tetrahydroxyflavanone 7-*O*-*β*-D-glucopyranoside, (2*S*)-5,7,2′,5′-tetrahydroxyflavanone 7-*O*-*β*-D-glucuronopyranoside, (2*S*)-7,2′-dihydroxy-5-methoxyflavanone 7-*O*-*β*-D-glucuronopyranoside, (I-2*S*)-I-5,II-5,I-7,II-7,I-2′,II-2′,II-5′-heptahydroxy-[I-6,II-6′]-flavanonylflavone and (I-2*S*)-I-5,II-5,I-7,II-7,I-2′,II-2′,I-5′,II-5′-octahydroxy-[I-6,II-6′]-flavanonylflavone, were isolated, together with ten known flavonoids, wogonin (5,7-dihydroxy-8-methoxyflavone), 5,7-dihydroxy-8,2′-dimethoxyflavone, (2*S*)-5,7,2′-trihydroxyflavanone, scutevulin (5,7,2′-trihydroxy-8-methoxyflavone), 5,7,4′-trihydroxy-8-methoxyflavone, alpinetin ((2*S*)-7-hydroxy-5-methoxyflavanone), 5,7,2′-trihydroxyflavone, 5,7,2′,5′-tetrahydroxyflavone, (2*S*)-7,2′-dihydroxy-5-methoxyflavanone and 5,7-dihydroxy-8,2′-dimethoxyflavone 7-*O*-*β*-D-glucuronopyranoside. The structures were determined on the basis of chemical and spectral data.

Key words *Scutellaria amabilis*; flavonoid; biflavonoid; Labiatae; structure elucidation

Scutellaria amabilis HARA (Yamaji-tatsunamisou in Japanese) is a perennial herb of the family Labiatae, which is found throughout Japan.[2] No work has been reported regarding the constituents of this plant. In our studies of the constituents of *Scutellaria* species,[1] we isolated five new natural flavone glycosides (**1**—**5**), a flavanone (**6**), three flavanone glycosides (**7**—**9**) and two biflavonoids (**10**, **11**), together with ten known flavonoids (**12**—**21**) from the MeOH extract of the roots of this plant. This paper deals with identification of their structures.

The structures of the known flavonoids were identified as wogonin (5,7-dihydroxy-8-methoxyflavone) (**12**),[3] 5,7-dihydroxy-8,2′-dimethoxyflavone (**13**),[3] (2*S*)-5,7,2′-trihydroxyflavanone (**14**),[3] scutevulin (5,7,2′-trihydroxy-8-methoxyflavone) (**15**),[3] 5,7,4′-trihydroxy-8-methoxyflavone (**16**),[3] alpinetin ((2*S*)-7-hydroxy-5-methoxyflavanone) (**17**),[3] 5,7,2′-trihydroxyflavone (**18**),[4] 5,7,2′,5′-tetrahydroxyflavone (**19**),[5] (2*S*)-7,2′-dihydroxy-5-methoxyflavanone (**20**)[6] and 5,7-dihydroxy-8,2′-dimethoxyflavone 7-*O*-*β*-D-glucuronopyranoside (**21**),[3] respectively, by direct comparison with the respective authentic samples.



1: R_1 = glc, R_2 = OMe, R_3 = OH, R_4 = R_5 = H
2: R_1 = R_4 = R_5 = H, R_2 = OMe, R_3 = Oglc,
3: R_1 = glc, R_2 = R_3 = OMe, R_4 = R_5 = H
4: R_1 = R_2 = R_4 = R_5 = H, R_3 = Oglc
5: R_1 = glcUA, R_3 = R_5 = OH, R_2 = R_4 = H
12: R_1 = R_3 = R_4 = R_5 = H, R_2 = OMe
13: R_1 = R_4 = R_5 = H, R_2 = R_3 = OMe
15: R_1 = R_4 = R_5 = H, R_2 = OMe, R_3 = OH
16: R_1 = R_3 = R_5 = H, R_2 = OMe, R_4 = OH
18: R_1 = R_2 = R_4 = R_5 = H, R_3 = OH
19: R_1 = R_2 = R_4 = H, R_3 = R_5 = OH
21: R_1 = glcUA, R_2 = R_3 = OMe, R_4 = R_5 = H

glc: β-D-glucopyranosyl
glcUA:
β-D-glucuronopyranosyl

6: R_1 = R_2 = H, R_3 = R_4 = OH
7: R_1 = H, R_2 = glc, R_3 = R_4 = OH
8: R_1 = H, R_2 = glcUA, R_3 = R_4 = OH
9: R_1 = Me, R_2 = glcUA, R_3 = OH, R_4 = H
14: R_1 = R_2 = R_4 = H, R_3 = OH
17: R_1 =Me, R_2 = R_3 = R_4 = H
20: R_1 = Me, R_2 = R_4 = H, R_3 = OH

10: R = H
11: R = OH

Chart 1

Compounds **1**—**9** gave yellow-orange coloration with a dil. H_2SO_4 reagent on TLC, and showed positive color reactions to Mg–HCl. They had absorption bands assignable to hydroxyl, conjugated carbonyl groups and aromatic rings in the IR spectra. The UV spectra of **1**—**5** and **6**—**9** were characteristic of flavone and flavanone series, respectively, and those of **1**—**8** showed bathochromic shifts by the addition of $AlCl_3$/HCl, indicating the presence of a chelated hydroxyl at the C-5 position.[7] Of the new compounds **1**—**11**, ^{1}H- and ^{13}C-NMR spectra suggested **1**—**5** and **7**—**9** to be monoglycosides.

Flavone glycosides **1** and **2** were obtained as yellow needles, mp 263—264 °C (dec.), $[\alpha]_D^{25}$ −77.5°, and yellow needles, mp 266—267 °C (dec.), $[\alpha]_D^{25}$ −51.3°, respectively. Both of their molecular formulae were determined to be $C_{22}H_{22}O_{11}$ by high resolution (HR)-MS and ^{13}C-NMR spectral data. In the ^{1}H- and ^{13}C-NMR spectra of **1** and **2**, an anomeric proton signal at δ 5.07 (d, J=7.6 Hz) and δ 5.14 (d, J=7.6 Hz) and a set of carbon signals due to the sugar moiety including an anomeric carbon signal at δ 100.3 and δ 100.1, respectively, indicated the presence of a β-glucopyranosyl unit in **1** and **2**.[8]

On enzymatic hydrolysis with β-glucosidase, **1** and **2** gave scutevulin (5,7,2′-trihydroxy-8-methoxyflavone) (**15**)[3] as a common aglycone, and a sugar portion, which was shown to consist of D-glucose as described in the experimental section. In the ^{13}C-NMR spectra of **1** and **2**, the ppm values of the B-ring carbon signals of **1** and the A-ring carbon signals of **2** agreed well with those of **15**, respectively, indicating that **1** and **2** are a 7-*O*-glucoside of **15** and a 2′-*O*-glucoside of **15**, respectively.

From these results, the structures of **1** and **2** were deter-

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Table 1. ^{1}H-Chemical Shifts of Flavones **1**—**5**, **13**, **15**, and **18**—**19**, δ (ppm) in DMSO-d_6 (J/Hz in Parentheses)

H	1	2	3	4	5	13	15	18	19
3	7.13 s	7.02 s	6.91 s	7.01 s	7.14 s	6.83 s	7.06 s	7.06 s	7.08 s
6	6.66 s	6.31 s	6.68 s	6.21 d (2.0)	6.44 d (2.2)	6.30 s	6.29 s	6.22 d (1.7)	6.20 d (2.0)
8				6.47 d (2.0)	6.78 d (2.2)			6.49 d (1.7)	6.42 d (2.0)
3′	7.08 br d (8.0)	7.37 br d (8.0)	7.28 br d (8.0)	7.35 br d (8.0)	6.90 d (8.8)	7.25 br d (7.8)	7.07 br d (8.0)	7.07 br d (8.0)	6.89 d (9.0)
4′	7.43 ddd (2.0, 8.0, 8.0)	7.57 ddd (2.0, 8.0 8.0)	7.61 br dd (8.0, 8.0)	7.55 ddd (2.0, 8.0, 8.0)	6.85 dd (2.4, 8.8)	7.58 ddd (1.8, 7.8, 7.8)	7.41 ddd (2.0, 8.0, 8.0)	7.41 ddd (2.0, 8.0, 8.0)	6.84 dd (2.6, 9.0)
5′	7.05 br dd (8.0, 8.0)	7.25 br dd (8.0, 8.0)	7.19 br dd (8.0, 8.0)	7.21 br dd (8.0, 8.0)		7.17 br dd (7.8, 7.8)	7.04 br dd (8.0, 8.0)	7.04 br dd (8.0, 8.0)	
6′	7.89 dd (2.0, 8.0)	7.88 dd (2.0, 8.0)	7.88 br d (8.0)	7.88 dd (2.0, 8.0)	7.28 d (2.4)	7.58 dd (1.8, 7.8)	7.87 dd (2.0, 8.0)	7.87 dd (2.0, 8.0)	7.25 d (2.6)
1″	5.07 d (7.6)	5.14 d (7.6)	5.08 d (7.6)	5.07 d (7.6)	5.18 d (7.4)				
2″	3.18—3.35 m	3.18—3.35 m	3.18—3.40 m	3.18—3.40 m	3.16—3.50 m				
3″	3.18—3.35 m	3.18—3.35 m	3.18—3.40 m	3.18—3.40 m	3.16—3.50 m				
4″	3.18—3.35 m	3.18—3.35 m	3.18—3.40 m	3.18—3.40 m	3.16—3.50 m				
5″	3.42 m	3.40 m	3.45 m	3.40 m	3.80 d (9.0)				
6″	3.84 m, 3.71 dd (5.8, 11.0)	3.48 td (6.0, 12.0), 3.71 br d (12.0)	3.48 m, 3.71 m	3.47 td (6.0, 12.0), 3.69 br d (12.0)					
8-OMe	3.87 s	3.82 s	3.85 s			3.81 s	3.83 s		
2′-OMe			3.94 s			3.93 s			
5-OH	12.59 s	12.58 s	12.53 s	12.90 s	12.91 s	12.50 s	12.56 s	12.90 s	12.91 s
7-OH		10.79 s		10.88 s		10.76 s	10.83 s	10.88 s	10.85 s
2′-OH	10.91 s				10.22 s		10.74 s	10.74 s	10.12 s
5′-OH					9.24 s				9.16 s
6″-OH	4.61 t (5.8)	4.60 t (6.0)	4.62 t (5.8)	4.58 t (6.0)					
2″,3″, 4″-OH	5.06 d (5.0), 5.14 d (4.5), 5.40 d (5.0)	5.08 d (5.0), 5.11 d (4.0), 5.33 d (4.4)	5.08 br s, 5.14 br s, 5.41 br s	5.08 br s, 5.13 br s, 5.23 br s					
2″, 3″-OH					5.31 d (4.0), 5.48 d (5.2)				

mined to be 5,7,2′-trihydroxy-8-methoxyflavone 7-*O*-β-D-glucopyranoside and 5,7,2′-trihydroxy-8-methoxyflavone 2′-*O*-β-D-glucopyranoside, respectively.

Flavone glycosides **3** and **4** were obtained as yellow needles, mp 248—249 °C (dec.), $[\alpha]_D^{25}$ −25.3°, and yellow needles, mp 252—253 °C (dec.), $[\alpha]_D^{25}$ −67.6°, respectively. The molecular formulae were determined to be $C_{23}H_{24}O_{11}$ (**3**) and $C_{21}H_{20}O_{10}$ (**4**) by HR-MS and ^{13}C-NMR spectral data. The diagnostic shift in the UV spectrum caused by the addition of NaOAc suggested the presence of a free hydroxyl group at the C-7 position in **4**, and the absence of such in **3**.[7]

On enzymatic hydrolysis with β-glucosidase, **3** and **4** gave 5,7-dihydroxy-8,2′-dimethoxyflavone (**13**)[3] and 5,7,2′-trihydroxyflavone (**18**),[4] respectively, together with D-glucose as a common sugar component. In the ^{1}H-NMR spectra of **3** and **4**, an anomeric proton signal was observed at δ 5.08 and δ 5.07 (each 1H, d, J=7.6 Hz), respectively, and the J value indicated that their glycosidic linkages were of β-configuration. In the ^{13}C-NMR spectra of **3** and **4**, the ppm values of the A-ring carbon signals of **3** and the B-ring carbon signals of **4** agreed well with those of **1** and **2**, respectively, indicating that **3** and **4** are a 7-*O*-glucoside of **13** and a 2′-*O*-glucoside of **18**, respectively.

Based on these results, the structures of **3** and **4** were determined to be 5,7-dihydroxy-8,2′-dimethoxyflavone 7-*O*-β-D-glucopyranoside and 5,7,2′-trihydroxyflavone 2′-*O*-β-D-glucopyranoside, respectively.

Flavone glycoside **5** was obtained as yellow needles, mp 226—227 °C (dec.), $[\alpha]_D^{25}$ −69.1°, $C_{21}H_{18}O_{12}$. In the ^{1}H- and ^{13}C-NMR spectra of **5**, an anomeric proton signal at δ 5.18 (d, J=7.4 Hz) and a set of carbon signals due to the sugar moiety, including anomeric and carbonyl carbon signals at δ 99.5 and δ 170.6, indicated the presence of a β-glucuronopyranosyl unit in **5**.[8]

On acid hydrolysis, **5** gave 5,7,2′,5′-tetrahydroxyflavone (**19**)[5] and D-glucuronic acid. In the ^{13}C-NMR spectrum of **5**, the signal pattern of the A-ring and the B-ring were almost identical with those of apigenin 7-*O*-β-D-glucuronopyranoside (**22**)[9] and **19**, respectively. Therefore, **5** was concluded to be 5,7,2′,5′-tetrahydroxyflavone 7-*O*-β-D-glucuronopyranoside.

Flavanone **6** was obtained as colorless needles, mp 266—267 °C (dec.), $C_{15}H_{12}O_6$. The ^{1}H-NMR spectrum of **6** showed the presence of four hydroxyls (δ 8.84, 9.09, 10.82, 12.12) and an AMX-type grouping due to the C-2 (δ 5.63) and C-3 protons (δ 2.72, 3.11). In the aromatic region of the spectrum, the remaining five protons occurred as a set of *meta* coupled doublets at δ 5.90 and 5.93 for the A-ring protons, and a double doublet (δ 6.59, 1H, J=2.8, 8.4 Hz) and two doublets (δ 6.69, 1H, J=8.4 Hz; δ 6.84, 1H, J=2.8 Hz) for the B-ring protons.

These data indicated that the substitution pattern of the A-ring was 5,7-dihydroxy, and the latter three signals were assigned to the C-3′, C-4′ and C-6′ protons, respectively, from their chemical shifts and coupling patterns. These assignments were further supported by the ^{13}C-NMR spectrum of **6**, in which the signal patterns of the A-ring and of the B-ring were almost identical with those of (2*S*)-5,7,2′-trihydroxyflavanone (**14**)[3] and (2*S*)-5,7,2′,5′-tetrahydroxy-6-methoxyflavanone (**23**),[10] respectively. The CD curve of **6** exhibited positive and negative maxima at 330 and 288 nm, which established the (2*S*)-configuration.[11] Thus, **6** was determined to

Table 2. ^{1}H-Chemical Shifts of Flavanones **6**—**9** and **20**, δ (ppm) in DMSO-d_6 (J/Hz in Parentheses)

H	6	7	8	9	20
2	5.63 dd (3.0, 12.6)	5.69 dd (3.0, 13.0)	5.70 dd (3.0, 12.5)	5.69 dd (3.0, 12.8)	5.62 dd (3.0, 12.6)
3	2.72 dd (3.3, 17.2), 3.11 dd (12.6, 17.2)	2.75 dd (3.0, 17.2), 3.20 dd (13.0, 17.2)	2.76 dd (3.0, 17.2), 3.20 dd (12.5, 17.2)	2.61 dd (3.0, 16.2), 3.01 dd (12.8, 16.2)	2.57 dd (3.0, 12.6), 2.91 dd (12.6, 16.0)
6	5.90 d (2.0)	6.15 d (2.2)	6.16 d (2.2)	6.26 d (2.0)	6.00 d (2.0)
8	5.93 d (2.0)	6.18 d (2.2)	6.20 d (2.2)	6.34 d (2.0)	6.08 d (2.0)
3′	6.69 d (8.4)	6.69 d (8.8)	6.69 d (8.5)	6.87 d (8.0)	6.86 br d (7.6)
4′	6.59 dd (2.8, 8.4)	6.60 dd (3.0, 8.8)	6.60 dd (3.0, 8.5)	7.18 ddd (1.8, 8.0, 8.0)	7.17 ddd (1.8, 7.6, 7.6)
5′				6.86 dd (8.0, 8.0)	6.85 br dd (7.6, 7.6)
6′	6.84 d (2.8)	6.84 d (3.0)	6.84 d (3.0)	7.42 dd (1.8, 8.0)	7.40 dd (1.8, 7.6)
1″		4.97 d (7.6)	5.16 d (7.4)	5.21 d (7.6)	
2″		3.24—3.41 m	3.27 m	3.24—3.40 m	
3″		3.24—3.41 m	3.27 m	3.24—3.40 m	
4″		3.24—3.41 m	3.38 dd (9.0, 9.0)	3.24—3.40 m	
5″		3.24—3.41 m	3.97 d (9.0)	3.99 d (9.8)	
6″		3.44 m, 3.67 ddd (2.0, 5.8, 11.0)			
5-OMe				3.78 s	3.74 s
5-OH	12.12 s	12.03 s	12.03 s		
7-OH	10.82 s				10.54 s
2′-OH	9.09 s	9.11 s	9.11 s	9.79 s	9.76 s
5′-OH	8.84 s	8.84 s	8.85 s		
6″-OH		4.56 t (5.8)			
2″,3″,4″-OH		5.03 d (5.4), 5.09 d (4.5), 5.35 d (5.0)			
2″,3″-OH			5.24 d (4.6), 5.48 d (5.0)	5.24 br d (4.0), 5.46 br d (4.0)	

Table 3. ^{13}C-Chemical Shifts of Compounds **1**—**9**, **13**, **15**, **18**—**20** and **22**—**24**, δ (ppm) in DMSO-d_6

C	1	2	3	4	5	6	7	8	9	13	15	18	19	20	22	23	24
2	161.7	160.7	161.7	160.7	161.0	74.0	74.2	74.2	73.8	161.2	161.2	161.6	161.2	73.5	164.3	74.2	78.7
3	109.0	110.3	109.6	110.2	109.2	41.2	41.3	41.3	43.6	109.5	108.9	109.2	109.1	43.8	103.0	41.3	42.0
4	182.4	182.1	182.3	181.9	182.1	196.3	197.1	197.1	188.2	181.9	182.1	182.1	181.9	187.8	181.9	197.2	197.2
5	156.0	156.2	156.0	157.6	161.8	163.5	163.0	162.9	161.6	156.2	156.1	161.6	161.5	162.2	161.5	155.4	162.9
6	98.6	98.9	98.7	98.8	99.4	95.9	96.5	96.3	94.1	99.0	98.9	98.8	98.8	93.3	99.2	129.2	96.5
7	156.3	157.2	156.4	164.3	162.9	166.6	165.3	164.8	162.7	157.3	157.1	164.5	164.3	164.3	162.5	159.7	165.2
8	129.1	127.7	129.1	93.9	94.4	95.0	95.4	95.2	95.5	127.7	127.6	94.0	93.8	95.6	94.6	95.1	95.4
9	149.1	149.9	149.3	161.4	157.1	163.1	162.9	162.9	164.3	149.8	149.6	157.7	157.5	164.5	156.9	158.4	162.8
10	104.9	103.6	105.0	103.8	105.4	101.7	103.2	103.3	106.1	103.5	103.5	103.9	103.8	104.3	105.4	101.9	103.3
1′	117.2	120.4	119.4	120.2	116.9	125.4	125.0	125.0	124.9	119.6	117.4	117.4	117.1	125.2	120.9	125.6	128.8
2′	157.0	155.5	157.9	155.4	149.7	146.4	146.5	146.5	154.2	157.8	156.8	156.8	149.6	154.1	128.5	146.6	128.5
3′	117.2	115.5	112.7	115.4	118.0	116.3	116.3	116.3	115.4	112.6	117.1	117.1	118.0	115.4	116.0	116.4	115.2
4′	133.1	132.9	133.4	132.8	120.5	115.8	115.9	115.9	129.2	133.2	132.8	132.9	120.3	129.1	161.1	115.9	157.8
5′	119.6	122.1	120.9	121.9	149.9	149.9	149.9	149.9	119.0	120.9	119.6	119.6	150.0	119.1	116.0	150.1	115.2
6′	128.3	128.9	129.1	129.1	113.4	113.1	113.3	113.2	126.8	128.9	128.2	128.7	113.4	126.7	128.5	113.2	128.5
1″	100.3	100.1	100.3	100.1	99.5		99.6	98.9	98.9						99.4		99.5
2″	73.2	73.3	73.2	73.3	73.0		73.0	72.7	72.7						72.8		73.1
3″	76.6	76.7	76.6	76.7	75.2		76.3	75.2	75.2						75.6		76.3
4″	69.6	69.6	69.6	69.6	71.4		69.5	71.2	71.2						71.3		69.5
5″	77.2	77.2	77.2	77.2	76.0		77.1	75.6	75.6						75.3		77.1
6″	60.6	60.6	60.6	60.6	170.6		60.6	170.0	170.0						170.2		60.6
5-OMe									55.9					55.6			
6-OMe																60.1	
8-OMe	61.3	61.1	61.3							61.0	61.0						
2′-OMe			56.0							55.9							

be (2*S*)-5,7,2′,5′-tetrahydroxyflavanone.

Flavanone glycosides **7** and **8** were obtained as colorless needles, mp 194—195 °C (dec.), $[\alpha]_D^{25}$ −151.0°, and colorless needles, mp 179—180 °C (dec.), $[\alpha]_D^{25}$ −129.8°, respectively. The molecular formulae were determined to be $C_{21}H_{22}O_{11}$ (**7**) and $C_{21}H_{20}O_{12}$ (**8**) by HR-MS and ^{13}C-NMR spectral data. On enzymatic hydrolysis of **7** with β-glucosidase and acid hydrolysis of **8**, **7** and **8** gave D-glucose and D-glucuronic acid, respectively, together with **6** and the racemate of **6**. ^{1}H- and ^{13}C-NMR spectra of **7** and **8** suggested that their glycosidic linkages were of β-configuration. In the ^{13}C-NMR spectra of **7** and **8**, the signal patterns of the A-ring and the B-ring were almost identical with those of naringenin 7-*O*-β-D-glucopyranoside (**24**)[12] and **6**, respectively. The (2*S*)-configuration of **7** and **8** were confirmed in the same way as in the case of **6**.[11]

Table 4. ^{1}H-Chemical Shifts of Compounds **10** and **11** δ (ppm) in DMSO-d_6 (J/Hz in Parentheses)

H	**10**		**11**	
	10a	**10b**	**11a**	**11b**
I-2	5.59 dd (3.0, 13.0)	5.70 dd (3.0, 13.0)	5.51 dd (3.0, 12.8)	5.59 dd (3.0, 12.8)
I-3	2.68 dd (3.0, 17.4), 3.21 dd (13.0, 17.4)	2.72 dd (3.0, 17.4), 3.17 dd (13.0, 17.4)	2.63 dd (3.0, 17.0), 3.10 br dd (12.8, 17.0)	2.67 dd (3.0, 17.0), 3.10 br dd (12.8, 17.0)
I-8	5.92 s	5.95 s	5.93 s	5.94 s
I-3′	6.87 br d (7.8)	6.87 br d (7.8)	6.68 d (8.8)	6.68 d (8.8)
I-4′	7.19 ddd (1.8, 7.8, 7.8)	7.17 ddd (1.8, 7.8, 7.8)	6.59 dd (2.8, 8.8)	6.60 dd (2.8, 8.8)
I-5′	6.79 br dd (7.8, 7.8)	6.86 br dd (7.8, 7.8)		
I-6′	7.41 dd (1.8, 7.8)	7.35 dd (1.8, 7.8)	6.85 d (2.8)	6.83 d (2.8)
II-3	6.04 s	5.99 s	6.04 s	6.01 s
II-6	6.14 d (1.8)	6.15 d (1.8)	6.13 d (1.8)	6.13 d (1.8)
II-8	6.15 d (1.8)	6.15 d (1.8)	6.15 d (1.8)	6.15 d (1.8)
II-3′	6.82 d (8.8)	6.82 d (8.8)	6.88 d (8.8)	6.89 d (8.8)
II-4′	6.87 d (8.8)	6.88 d (8.8)	6.82 d (8.8)	6.82 d (8.8)
I-5-OH	12.30 s	12.28 s	12.30 s	12.29 s
I-7-OH	10.61 br s	10.64 br s	10.61 br s	10.61 br s
I-2′-OH	9.84 br s	9.84 br s	9.07 br s	9.07 br s
I-5′-OH			8.84 s	8.81 s
II-5-OH	12.77 s	12.77 s	12.76 s	12.76 s
II-7-OH	10.80 br s	10.80 br s	10.79 br s	10.79 br s
II-2′-OH	9.28 s	9.26 s	8.65 br s	8.67 br s
II-5′-OH	8.66 s	8.69 s	9.27 s	9.25 s

From these results, the structures of **7** and **8** were determined to be (2*S*)-5,7,2′,5′-tetrahydroxyflavanone 7-*O*-β-D-glucopyranoside and (2*S*)-5,7,2′,5′-tetrahydroxyflavanone 7-*O*-β-D-glucuronopyranoside, respectively.

Flavanone glycoside **9** was obtained as colorless needles, mp 190—191 °C (dec.), $[\alpha]_D^{25}$ −116.8°, $C_{22}H_{22}O_{11}$. The UV spectrum and the diagnostic shifts suggested the absence of hydroxyls at the C-5 and C-7 positions in the flavanone nucleus.[7] ^{1}H-NMR spectrum of **9** showed the presence of a methoxyl (δ 3.78), a non-chelated hydroxyl (δ 9.79) and an AMX-type grouping due to the C-2 (δ 5.69) and C-3 protons (δ 2.61, 3.01).

On acid hydrolysis, **9** gave 7,2′-dihydroxy-5-methoxyflavanone (**20**)[6] as a racemate, 2,2′,4′-trihydroxy-6′-methoxychalcone (**25**)[6] and D-glucuronic acid. In the ^{13}C-NMR spectrum of **9**, the signal patterns of the B-ring were almost identical with those of **20**. ^{1}H- and ^{13}C-NMR spectra of **9** suggested that the glycosidic linkage was of β-configuration. The absolute configuration at C-2 in **9** was confirmed as *S* from the CD spectrum.[11] Hence, **9** was determined to be (2*S*)-7,2′-dihydroxy-5-methoxyflavanone 7-*O*-β-D-glucuronopyranoside.

Compounds **10** and **11** gave orange coloration with a dil. H_2SO_4 reagent on TLC, and showed positive color reactions to Mg–HCl. They had absorption bands assignable to hydroxyl, conjugated carbonyl groups and aromatic rings in the IR spectra. Both of their UV spectra suggested the presence of flavone and flavanone moieties in **10** and **11**.[7]

Compound **10** was obtained as yellow needles, mp 217—218 °C (dec.). HR-MS and the ^{13}C-NMR spectrum of **10** gave the molecular formula $C_{30}H_{20}O_{11}$. **10** was shown to exist as equimolecular equilibrium mixtures of **10a** and **10b** by its ^{1}H- and ^{13}C-NMR spectra in DMSO-d_6.

The ^{1}H-NMR spectra of **10a** and **10b** closely resembled each other, and the mixture of the spectra showed the presence of ten non-chelated hydroxyls (δ 8.66, 8.69, 9.26, 9.28, 9.84(×2), 10.61, 10.64, 10.80(×2)), four chelated hydroxyls (δ 12.28, 12.30, 12.77(×2)), and two AMX type signals for the C-2 (δ 5.59, 5.70) and C-3 (δ 2.68, 2.72, 3.17, 3.21) protons due to the flavanone nucleus. In the aromatic region of the spectrum, twenty proton signals occurred as singlets (δ

Table 5. ^{13}C-Chemical Shifts of Compounds **10** and **11**, δ (ppm) in DMSO-d_6

C	**10**		**11**	
	10a	**10b**	**11a**	**11b**
I-2	73.76	73.92	73.96	74.08
I-3	41.02	41.02	41.24	41.38
I-4	196.30	196.30	196.27	196.52
I-5	161.18	161.21	161.21	161.27
I-6	104.62	104.62	104.67	104.70
I-7	164.30	164.30	164.29	164.29
I-8	94.17	94.28	94.17	94.32
I-9	161.88	161.97	161.84	162.03
I-10	101.25	101.34	101.25	101.31
I-1′	124.69	124.69	125.29	125.33
I-2′	154.23	154.36	146.47	164.47
I-3′	115.42	115.53	116.24	116.30
I-4′	129.38	129.45	115.82	115.82
I-5′	119.06	119.10	149.91	150.00
I-6′	126.87	127.13	113.18	113.18
II-2	164.39	164.44	164.36	164.41
II-3	110.17	110.27	110.21	110.29
II-4	181.41	181.41	181.44	181.44
II-5	161.34	161.37	161.36	161.36
II-6	98.68	98.68	98.68	98.68
II-7	164.11	164.11	164.11	164.11
II-8	93.49	93.53	93.50	93.50
II-9	158.00	158.03	158.00	158.03
II-10	103.66	103.66	103.66	103.69
II-1′	121.19	121.39	120.11	120.14
II-2′	147.90	147.93	148.37	148.44
II-3′	116.02	116.05	118.42	118.45
II-4′	118.37	118.43	116.07	116.07
II-5′	148.35	148.42	147.94	147.94
II-6′	120.11	120.14	121.20	121.38

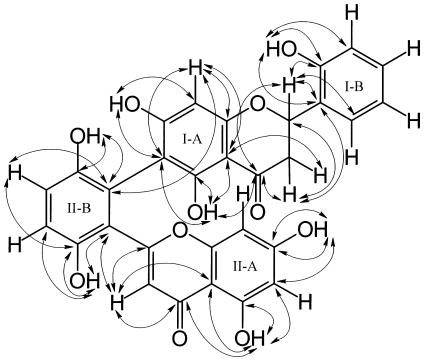
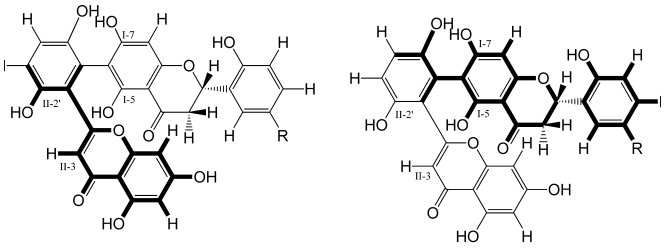


Fig. 1. Significant Correlations in the ^{1}H–^{13}C Long-Range COSY Spectrum of **10**



10a: R = H
11a: R = OH

10b: R = H
11b: R = OH

Chart 2

5.92, 5.95, 5.99, 6.04) and *meta* coupled doublets (δ 6.14, 6.15(×3)) for the C-3 protons of the flavone nucleus and A-ring protons, and *ortho* coupled doublets (δ 6.82(×2), 6.87, 6.88), *ortho–meta* coupled double doublets (δ 7.35, 7.41) and a broad doublet (δ 6.87(×2)), and *ortho–ortho–meta* coupled double double doublets (δ 7.17, 7.19) and broad double doublets (δ 6.79, 6.86) for the B-ring protons, deducing from their chemical shifts. These findings indicated that **10** is a biflavonoid consisting of a flavone and a flavanone having a 1,2,3,5-tetrasubstituted benzene and a 1,2,3,4,5-pentasubstituted benzene as A-rings, and a 1,2-disubstituted benzene and a 1,2,3,4-tetrasubstituted benzene as B-rings. In the ^{13}C-NMR spectra of **10a** and **10b**, the carbon signals due to the benzoyl moiety of the flavones and the dihydrocinnnamoyl moiety of the flavanones were almost identical with those of **19** and **14**, respectively. The linkage of these partial structures and the remaining hydroxyls were clarified based on the ^{1}H–^{13}C long-range COSY spectrum, as shown in Fig. 1. The absolute configuration at C-2 in **10** was confirmed to be *S* from the CD spectrum.[11)]

From these results, both of the structures of **10a** and **10b** were determined to be (I-2*S*)-I-5,II-5,I-7,II-7,I-2′,II-2′,II-5′-heptahydroxy-[I-6,II-6′]-flavanonylflavone.

In the difference NOE spectra of **10a** and **10b**, irradiation of the H-II-3 signal enhanced the C-I-5 and II-2′-OH, but no enhancement of the C-I-7-OH signal was observed. In the ^{1}H-NMR spectrum of **10a**, the C-I-2 proton signal of **10a** was observed to have a shielding effect of 0.11 ppm by II-A-ring current compared with that of **10b**. From these facts, **10** was concluded to be a mixture of conformational isomers having two stable conformations (**10a**, **10b**), as shown in Chart 2.

Compound **11** was obtained as yellow needles, mp 229—230 °C (dec.), $C_{30}H_{20}O_{12}$, which was confirmed to be an equilibrium mixture of conformational isomers **11a** and **11b** in the same way as in the case of **10**.

In the ^{1}H- and ^{13}C-NMR spectra of **11**, the proton and carbon signals were almost identical with those of **10** except for the I-B-ring, and the I-B-ring signals were observed to be almost superimposable on those of **6**. The absolute configuration at C-I-2 in **11** was confirmed to be *S* from the CD spectrum.[11)]

Hence **11** was determined to be (I-2*S*)-I-5,II-5,I-7,II-7,I-2′,II-2′,I-5′,II-5′-octahydroxy-[I-6,II-6′]-flavanonylflavone.

[I-6,II-6′]-Biflavonoids have already been isolated from *Dicranoloma robustum*.[13)]

Experimental

General Procedures All melting points were determined on a Yanagimoto micromelting point apparatus and were uncorrected. NMR spectra were taken in DMSO-d_6 on a JEOL GSX-400 spectrometer (^{1}H-NMR at 400 MHz and ^{13}C-NMR at 100 MHz), using TMS as an internal standard. MS were recorded on a JEOL JMS-SX-102A mass spectrometer. UV spectra were taken on a Shimadzu dual-wavelength/double beam recording spectrophotometer. Samples for IR spectra were prepared as a KBr disk, and the spectra were taken on a Hitachi 270-30 infrared spectrophotometer. Optical rotation was measured by a JASCO DIP-370 digital polarimeter. For column chromatography, silica gel (Wako-gel C-300) and ODS (Cosmosil 140 C_{18}-OPN) were used. HPLC analysis of sugar was carried out in these conditions: column, YMC-Pack Polyamine-II (250 mm×4.6 mm i.d.); solv., $CH_3CN : H_2O : H_3PO_4 = 86 : 14 : 0.05$ (HPLC-1), $= 70 : 30 : 0.05$ (HPLC-2); detector, Shimadzu RID-2A refractive index detector and JASCO OR-990 optical rotation detector; temperature, 50 °C.

Plant Material The plant material was collected in Ishikawa Prefecture and cultivated in the botanical garden of the Faculty of Pharmaceutical Sciences, Hokuriku University, Kanazawa, Japan for two years, and harvested in July. A voucher specimen is deposited at the Herbarium of this university.

Extraction and Separation The dried roots (850 g) of *S. amabilis* were extracted four times with MeOH under reflux. The MeOH extract was concentrated to dryness under reduced pressure, and the resulting residue (125 g) was suspended in water and then extracted successively with ether and *n*-BuOH.

The ether soluble fraction (25 g) was partitioned between *n*-hexane and MeOH/H_2O (trace), and the latter fraction was concentrated. The residue (9 g) was chromatographed on silica gel (1 kg) and eluted with a gradient of *n*-hexane–acetone (4 : 1→1 : 2) to give eight fractions (frs. 1—8), in order of elution. Fractions 1—3, 5, 7 and 8 were recrystallized from MeOH to give **12** (30 mg), **13** (277 mg), **14** (163 mg), **6** (45 mg), **10** (44 mg) and **11** (43 mg). Fractions 4 and 6 were subjected to silica gel column chromatography using benzene–EtOAc (10 : 1→1 : 1) to give **15** (12 mg), **16** (14 mg), **17** (6 mg) and **18** (5 mg), and **19** (150 mg) and **20** (104 mg), respectively.

The *n*-BuOH-soluble fraction (30 g) was chromatographed on silica gel (2 kg) and eluted with a gradient of $CHCl_3$–MeOH–H_2O (8 : 1 : 0.05→3 : 1 : 0.05) to give six fractions (frs. 9—14), in order of elution. Fractions 9—13 were recrystallized from MeOH to give **21** (40 mg), **1** (5 mg), **2** (21 mg), **3** (23 mg) and **4** (4 mg), respectively. Fraction 14 was chromatographed on a silica gel column using EtOAc–MeOH (10 : 1→1 : 1) to give fraction 15 and **7** (8 mg). Fraction 15 was chromatographed on an ODS column and eluted with a gradient of H_2O–MeOH (7 : 1→1 : 2) to give **5** (9 mg), **8** (42 mg) and **9** (44 mg).

Compound **1**: Yellow needles (MeOH), mp 263—264 °C (dec.), $C_{22}H_{22}O_{11}$. $[\alpha]_D^{25}$ −77.5° (c=0.035, MeOH). HR-FAB-MS *m/z*: 463.1231, Calcd for $C_{22}H_{23}O_{11}$ $[M+H]^+$ 463.1240; 485.1054, Calcd for $C_{22}H_{22}O_{11}Na$ $[M+Na]^+$ 485.1060. EI-MS *m/z* (%): 300 (45), 285 (76), 270 (100), 257 (25). FAB-MS *m/z* (%): 463 $[M+H]^+$ (2.5), 485 $[M+Na]^+$ (2). IR ν_{max} (KBr) cm^{-1}: 3404 (OH), 1654 (conjugated CO), 1616, 1574 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 246 (3.60), 254 (3.82), 260 (4.14), 272 (4.40), 337 (4.06); λ_{max} (NaOMe) nm (log ε): 230 (4.30), 246 (3.86), 254 (4.00), 260 (4.18), 269 (4.32), 310 (3.79), 410 (4.13); λ_{max} ($AlCl_3$) nm (log ε): 253 (3.66), 260 (3.84), 281 (4.37), 294sh (4.34), 346 (4.12), 400 (3.94); λ_{max} ($AlCl_3$–HCl) nm (log ε): 253 (3.70), 260 (3.86), 281 (4.40), 293 (4.36), 350 (4.16), 400 (3.90); λ_{max} (NaOAc) nm (log ε): 246 (3.79), 253 (3.90), 260 (4.16), 270 (4.35), 338 (3.93), 410 (3.79); λ_{max} (NaOAc–H_3BO_4) nm (log ε): 249 (3.70), 254 (3.85), 261 (4.08), 272 (4.41), 340 (4.07). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 3.

Enzymatic Hydrolysis of 1 A solution of **1** (2 mg) in H_2O (2 ml) and β-

glucosidase (Sweet Almonds, P-L Biochemicals, Inc.) (0.5 mg, pH 7.0) was incubated at 37 °C for 3 d. The reaction mixture was extracted with EtOAc, which was chromatographed on silica gel using $CHCl_3$–MeOH (10 : 1) as an eluent to give yellow needles (0.7 mg). This product was identical with scutevulin (**15**) by direct comparison (NMR and mixed fusion). The H_2O layer was concentrated to dryness and the residue was extracted with MeOH. The MeOH-soluble portion showed a peak of D-glucose (t_R 16.9 min, α_D+) on HPLC-1 analysis.

Compound **2**: Yellow needles (MeOH), mp 266—267 °C (dec.), $C_{22}H_{22}O_{11}$. $[\alpha]_D^{25}$ −51.3° (c=0.048, pyridine). HR-MS *m/z*: 462.1154, Calcd for $C_{22}H_{22}O_{11}$ [M]$^+$ 462.1162. EI-MS *m/z* (%): 462 (9), 300 (88), 285 (100), 257 (30). FAB-MS *m/z* (%): 463 [M+H]$^+$ (8), 485 [M+Na]$^+$ (3). IR ν_{max} (KBr) cm^{-1}: 3484 (OH), 1662 (conjugated CO), 1614, 1576 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 225 (4.33), 273 (4.35), 318 (4.03), 343 (3.84); λ_{max} (NaOMe) nm (log ε): 233 (4.31), 260 (4.31), 280 (4.50), 318 (3.83), 343 (3.83); λ_{max} ($AlCl_3$) nm (log ε): 225 (4.40), 250 (4.04), 282 (4.47), 295 (4.36), 335 (4.13), 343 (4.10), 400 (4.30); λ_{max} ($AlCl_3$–HCl) nm (log ε): 225 (4.41), 245 (4.11), 282 (4.78), 292 (4.44), 333 (4.12), 343 (4.03), 400 (3.03); λ_{max} (NaOAc) nm (log ε): 262 (4.30), 280 (4.49), 343 (3.78), 375 (3.64); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 273 (4.45), 319 (3.90), 343 (3.76). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 3.

Enzymatic Hydrolysis of 2 A solution of **2** (5 mg) in H_2O was hydrolyzed with β-glucosidase and worked up in the same way as **1** to give scutevulin (**15**) (1.5 mg) and a sugar fraction, which was shown to contain D-glucose by HPLC-1.

Compound **3**: Yellow needles (MeOH), mp 248—249 °C (dec.), $C_{23}H_{24}O_{11}$. $[\alpha]_D^{25}$ −252.5° (c=0.075, pyridine). HR-FAB-MS *m/z*: 477.1400, Calcd for $C_{23}H_{25}O_{11}$ [M+H]$^+$ 477.1397. EI-MS *m/z* (%): 314 (56), 299 (100), 284 (30), 269 (48). FAB-MS *m/z* (%): 477 [M+H]$^+$ (1.5). IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1660 (conjugated CO), 1612, 1580 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 278 (5.42), 330 (4.95), 348 (4.92); λ_{max} (NaOMe) nm (log ε): 274 (5.41), 318 (4.96), 343 (4.69); λ_{max} ($AlCl_3$) nm (log ε): 282 (5.39), 295sh (5.34), 338 (5.03), 343 (5.02), 400 (4.63); λ_{max} ($AlCl_3$–HCl) nm (log ε): 282 (5.41), 295 (5.35), 335 (5.03), 343 (5.00), 400 (4.56); λ_{max} (NaOAc) nm (log ε): 272 (5.42), 326 (4.96), 343 (4.89); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 272 (5.42), 326 (4.95), 343 (4.90). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 3.

Enzymatic Hydrolysis of 3 A solution of **3** (5 mg) in H_2O was hydrolyzed with β-glucosidase and worked up in the same way as **1** to give compound **13** (1.6 mg) and a sugar fraction, which was shown to contain D-glucose by HPLC-1.

Compound **4**: Yellow needles (MeOH), mp 252—253 °C (dec.), $C_{21}H_{20}O_{10}$. $[\alpha]_D^{25}$ −67.6° (c=0.042, MeOH). HR-FAB-MS *m/z*: 433.1053, Calcd for $C_{21}H_{21}O_{10}$ [M+H]$^+$ 433.1135. EI-MS *m/z* (%): 300 (60), 285 (100), 270 (75). FAB-MS *m/z* (%): 433 [M+H]$^+$ (5), 457 [M+Na]$^+$ (4). IR ν_{max} (KBr) cm^{-1}: 3464 (OH), 1656 (conjugated CO), 1622, 1576 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 254 (4.07), 260 (4.27), 268 (4.40), 325 (4.09); λ_{max} (NaOMe) nm (log ε): 247 (4.04), 254 (4.14), 260 (4.29), 272 (4.43), 370 (4.04); λ_{max} ($AlCl_3$) nm (log ε): 247 (4.00), 254 (3.95), 260 (4.06), 278 (4.42), 338 (4.16); λ_{max} ($AlCl_3$–HCl) nm (log ε): 240 (4.11), 247 (4.02), 254 (3.96), 260 (4.07), 278 (4.45), 333 (4.16); λ_{max} (NaOAc) nm (log ε): 254 (4.12), 260 (4.29), 272 (4.44), 355 (4.02); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 254 (4.10), 260 (4.30), 268 (4.42), 325 (4.10). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 3.

Enzymatic Hydrolysis of 4 A solution of **4** (2 mg) in H_2O was hydrolyzed with β-glucosidase and worked up in the same way as **1** to give compound **18** (0.6 mg) and a sugar fraction, which was shown to contain D-glucose by HPLC-1.

Compound **5**: Yellow needles (MeOH), mp 226—227 °C (dec.), $C_{21}H_{18}O_{12}$. $[\alpha]_D^{25}$ −69.1° (c=0.039, MeOH). HR-FAB-MS *m/z*: 463.0871, Calcd for $C_{21}H_{19}O_{12}$ [M+H]$^+$ 463.0877. EI-MS *m/z* (%): 286 (100). FAB-MS *m/z* (%): 463 [M+H]$^+$ (2.5). IR ν_{max} (KBr) cm^{-1}: 3432 (OH), 1744 (conjugated CO), 1654, 1618 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 247 (4.01), 254 (415), 260 (4.26), 267 (4.37), 300 (4.00), 362 (4.03); λ_{max} (NaOMe) nm (log ε): 240 (4.19), 246 (4.14), 253 (4.14), 260 (4.20), 268 (4.25); λ_{max} ($AlCl_3$) nm (log ε): 246 (3.76), 254 (3.87), 273 (4.42), 290 (4.27), 316 (4.03), 400 (4.15); λ_{max} ($AlCl_3$–HCl) nm (log ε): 246 (3.83), 254 (3.93), 260 (4.19), 273 (4.42), 290 (4.30), 316 (4.02), 395 (4.15); λ_{max} (NaOAc) nm (log ε): 246 (4.06), 254 (4.17), 260 (4.27), 267 (4.34), 300 (4.01), 365 (4.01); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 246 (4.07), 254 (4.17), 260 (4.27), 267 (4.34), 300 (4.03), 365 (4.03). ^{1}H-NMR: Table 1. ^{13}C-NMR: Table 3.

Acid Hydrolysis of 5 A solution of **5** (5 mg) in 2 N H_2SO_4 (3 ml) was heated at 90 °C for 3 h. After cooling, the reaction mixture was neutralized with Ag_2CO_3 and extracted with EtOAc. The EtOAc extract was chromatographed on silica gel using $CHCl_3$–MeOH (20 : 3) as an eluent to give yellow needles (1.3 mg). This product was identical with compound **19** by direct comparison (NMR and mixed fusion). The H_2O layer was concentrated to dryness and extracted with MeOH. The MeOH-soluble portion showed the peak of D-glucuronic acid (t_R 13.2 min, α_D+) on HPLC-2 analysis.

Compound **6**: Colorless needles (MeOH), mp 266—267 °C (dec.), $C_{15}H_{12}O_6$. HR-MS *m/z*: 288.0627, Calcd for $C_{15}H_{12}O_6$ [M]$^+$ 288.0634. EI-MS *m/z* (%): 288 (72), 270 (100), 153 (75). IR ν_{max} (KBr) cm^{-1}: 3346 (OH), 1642 (conjugated CO), 1604 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 288 (4.11), 289 (4.11), 328 (3.57); λ_{max} (NaOMe) nm (log ε): 244 (5.91), 319 (6.35); λ_{max} ($AlCl_3$) nm (log ε): 222 (4.28), 308 (4.23), 375 (3.47); λ_{max} ($AlCl_3$–HCl) nm (log ε): 222 (4.29), 306 (4.21), 375 (3.46); λ_{max} (NaOAc) nm (log ε): 245 (3.90), 323 (4.50); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 290 (5.15), 325 (3.93). CD (c=1.81×10^{-4}, MeOH) [θ]^{31} (nm): −607.2 (247.0) (negative maximum), −51130 (287.6) (negative maximum), −6806 (313.1) (negative maximum), +9910 (329.9) (positive maximum). ^{1}H-NMR: Table 2. ^{13}C-NMR: Table 3.

Compound **7**: Colorless needles (MeOH), mp 194—195 °C (dec.), $C_{21}H_{22}O_{11}$. $[\alpha]_D^{25}$ −151.0° (c=0.045, MeOH). HR-FAB-MS *m/z*: 451.1245, Calcd for $C_{21}H_{23}O_{11}$ [M+H]$^+$ 451.1240; 473.1056, Calcd for $C_{21}H_{22}O_{11}Na$ [M+Na]$^+$ 473.1060. EI-MS *m/z* (%): 288 (73), 270 (100), 269 (58), 153 (67). FAB-MS *m/z* (%): 451 [M+H]$^+$ (10), 473 [M+Na]$^+$ (8). IR ν_{max} (KBr) cm^{-1}: 3400 (OH), 1646 (conjugated CO), 1580 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 225 (4.08), 285 (3.97); λ_{max} (NaOMe) nm (log ε): 242 (3.89), 285 (3.90), 319 (3.70); λ_{max} ($AlCl_3$) nm (log ε): 223 (4.24), 308 (4.10), 365 (3.48); λ_{max} ($AlCl_3$–HCl) nm (log ε): 223 (4.10), 305 (4.09), 365 (3.52); λ_{max} (NaOAc) nm (log ε): 284 (4.40), 335 (3.75); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 285 (4.12), 335 (3.49). CD (c=1.24×10^{-4}, MeOH) [θ]^{31} (nm): −294 (244.4) (negative maximum), −49500 (283.2) (negative maximum), +3937 (307.0) (positive maximum), +7890 (336.2) (positive maximum). ^{1}H-NMR: Table 2. ^{13}C-NMR: Table 3.

Enzymatic Hydrolysis of 7 A solution of **7** (3 mg) in H_2O was hydrolyzed with β-glucosidase and worked up in the same way as **1** to give compound **6** (1.1 mg) and a sugar fraction, which was shown to contain D-glucose by HPLC-1.

Compound **8**: Colorless needles (MeOH), mp 179—180 °C (dec.), $C_{21}H_{20}O_{12}$. $[\alpha]_D^{25}$ −129.8° (c=0.045, MeOH). HR-FAB-MS *m/z*: 465.1045, Calcd for $C_{21}H_{21}O_{11}$ [M+H]$^+$ 465.1033. EI-MS *m/z* (%): 342 (10), 324 (10), 288 (55), 270 (100), 269 (55). FAB-MS *m/z* (%): 465 [M+H]$^+$ (5), 503 [M+Na]$^+$ (4). IR ν_{max} (KBr) cm^{-1}: 3436 (OH), 1753 (conjugated CO), 1644, 1584 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 225 (4.29), 285 (4.15); λ_{max} (NaOMe) nm (log ε): 244 (4.10), 283 (4.06), 320 (3.87); λ_{max} ($AlCl_3$) nm (log ε): 223 (4.30), 286 (3.97), 304 (3.99); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 223 (4.28), 286 (4.00), 300 (4.05); λ_{max} (NaOAc) nm (log ε): 284 (4.24), 333 (3.61); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 285 (4.17), 333 (3.52). CD (c=9.91×10^{-5}, MeOH) [θ]^{31} (nm): −488.2 (244.7) (negative maximum), −44000 (284.1) (negative maximum), +2863 (307.1) (positive maximum), +6170 (336.1) (positive maximum). ^{1}H-NMR: Table 2. ^{13}C-NMR: Table 3.

Acid Hydrolysis of 8 A solution of **8** (3 mg) was hydrolyzed with 2 N H_2SO_4 and worked up in the same way as **5** to give compound **6** (1.0 mg) as a racemate and a sugar fraction, which was shown to contain D-glucuronic acid by HPLC-2.

Compound **9**: Colorless needles (MeOH), mp 190—191 °C (dec.), $C_{22}H_{22}O_{11}$. $[\alpha]_D^{25}$ −116.8° (c=0.052, MeOH). HR-FAB-MS *m/z*: 463.1202, Calcd for $C_{22}H_{23}O_{11}$ [M+H]$^+$ 463.1240; 485.1082, Calcd for $C_{22}H_{22}O_{11}Na$ [M+Na]$^+$ 485.1060. EI-MS *m/z* (%): 286 (20), 268 (100), 267 (40), 167 (50). FAB-MS *m/z* (%): 463 [M+H]$^+$ (5), 507 [M+Na]$^+$ (4). IR ν_{max} (KBr) cm^{-1}: 3384 (OH), 1746 (conjugated CO), 1648, 1616, 1657 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 280 (4.05), 315 (3.46); λ_{max} (NaOMe) nm (log ε): 280 (4.03), 300 (3.68), 332 (3.38); λ_{max} ($AlCl_3$) nm (log ε): 222 (4.35), 278 (4.13), 318 (3.64), 363 (3.27); λ_{max} ($AlCl_3$–HCl) nm (log ε): 222 (4.35), 278 (4.16), 318 (3.67), 363 (3.31); λ_{max} (NaOAc) nm (log ε): 273 (4.28), 279 (4.32), 319 (3.74); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 273 (4.26), 279 (4.29), 319 (3.70). CD (c=866×10^{-5}, MeOH) [θ]^{31} (nm): +192.9 (243.2) (positive maximum), −35790 (274.1) (negative maximum), −13780 (292.7) (negative maximum), −12800 (309.2) (negative maximum), +10930 (339.2) (positive maximum). ^{1}H-NMR: Table 2. ^{13}C-NMR: Table 3.

Acid Hydrolysis of 9 A solution of **9** (20 mg) was hydrolyzed with 2 N H_2SO_4 and worked up in the same way as **5** to give compound **6** (8.0 mg) as a racemate, 2,2′,4′-trihydroxy-6′-methoxychalcone[6] (2.5 mg) and a sugar fraction, which was shown to contain D-glucuronic acid by HPLC-2.

Compound **10**: Yellow needles (MeOH), mp 217—218 °C (dec.), $C_{30}H_{20}O_{11}$. HR-MS *m/z*: 556.0999, Calcd for $C_{30}H_{22}O_{11}$ $[M]^+$ 556.1006. EI-MS *m/z* (%): 556 (100), 521 (25), 520 (25), 326 (70), 298 (63), 284 (35). IR ν_{max} (KBr) cm^{-1}: 3404 (OH), 1645 (conjugated CO), 1626, 1600 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 255 (3.75), 294 (3.69), 331 (3.49); λ_{max} (NaOMe) nm (log ε): 266 (3.86), 319 (3.88), 328 (3.85); λ_{max} ($AlCl_3$) nm (log ε): 220 (4.10), 266 (3.88), 310 (3.82), 373 (3.56); λ_{max} ($AlCl_3$–HCl) nm (log ε): 220 (4.10), 266 (3.88), 310 (3.82), 373 (3.56); λ_{max} (NaOAc) nm (log ε): 262 (4.72), 322 (4.72); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 257 (4.05), 300 (3.90), 344 (3.71). CD (c=0.97×10^{-4}, MeOH) $[\theta]^{31}$ (nm): −28210 (290.0) (negative maximum), +5121 (315.2) (positive maximum), +8206 (332.0) (positive maximum). ^{1}H-NMR: Table 4. ^{13}C-NMR: Table 5.

Compound **11**: Yellow needles (MeOH), mp 229—230 °C (dec.), $C_{30}H_{20}O_{12}$. HR-MS *m/z*: 572.0947, Calcd for $C_{30}H_{20}O_{12}$ $[M]^+$ 572.0956. EI-MS *m/z* (%): 572 (10), 326 (100), 298 (73). IR ν_{max} (KBr) cm^{-1}: 3404 (OH), 1648 (conjugated CO), 1626, 1600 (arom. C=C). UV λ_{max} (MeOH) nm (log ε): 254 (4.10), 295 (4.10), 331 (3.83); λ_{max} (NaOMe) nm (log ε): 266 (4.19), 319 (4.25), 326 (4.23); λ_{max} ($AlCl_3$) nm (log ε): 268 (4.56), 306 (4.54), 372 (4.18); λ_{max} ($AlCl_3$–HCl) nm (log ε): 263 (4.56), 306 (4.54), 372 (4.18); λ_{max} (NaOAc) nm (log ε): 263 (4.53), 322 (4.56); λ_{max} (NaOAc–H_3BO_3) nm (log ε): 255 (4.48), 300 (4.39), 343 (4.16). CD (c=1.50×10^{-4}, MeOH) $[\theta]^{31}$ (nm): −31230 (289.4) (negative maximum), +4859 (317.4) (positive maximum), +9132 (332.5) (positive maximum). ^{1}H-NMR: Table 4. ^{13}C-NMR: Table 5.

Identification of 12—21 Compounds **12—21** were identified as wogonin (5,7-dihydroxy-8-methoxyflavone),[3] 5,7-dihydroxy-8,2′-dimethoxyflavone,[3] (2*S*)-5,7,2′-trihydroxyflavanone,[3] scutevulin (5,7,2′-trihydroxy-8-methoxyflavone),[3] 5,7,4′-trihydroxy-8-methoxyflavone,[3] alpinetin ((2*S*)-7-hydroxy-5-methoxyflavanone),[3] 5,7,2′-trihydroxyflavone,[4] 5,7,2′,5′-tetrahydroxyflavone,[5] (2*S*)-7,2′-dihydroxy-5-methoxyflavanone[6] and 5,7-dihydroxy-8,2′-dimethoxyflavone 7-*O*-β-glucuronopyranoside,[3] respectively, by direct comparison with the respective authentic samples (UV, IR, CD, ^{1}H- and ^{13}C-NMR and mixed fusion).

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References and Notes

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