Studies on the Constituents of *Viburnum* Species. On Phenolic Glycosides from the Leaves of *Viburnum wrightii* MIQ.

Koichi MACHIDA and Masao KIKUCHI*

Tohoku College of Pharmacy, 4–1 Komatsushima 4-chome, Aobaku, Sendai, Miyagi 981, Japan.
Received June 8, 1992

Four new phenolic glycosides, umbelliferone 6-*O*-*trans*-caffeoyl-β-D-glucopyranoside, *p*-hydroxyphenyl 4-*O*-*trans*-caffeoyl-β-D-glucopyranoside, *p*-hydroxyphenyl 2-*O*-*cis*-*p*-coumaroyl-β-D-glucopyranoside and *p*-hydroxyphenyl 6-*O*-*cis*-*p*-coumaroyl-β-D-glucopyranoside, and five known compounds were isolated from the leaves of *Viburnum wrightii* MIQ.

Keywords *Viburnum wrightii*; *cis-trans* isomer; phenolic glycoside; Caprifoliaceae

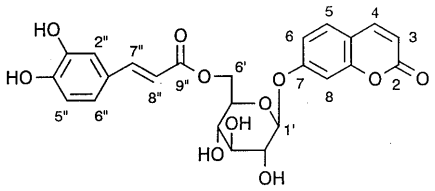
In continuation of our studies of the glycosides in *Viburnum* species,[1-5] we have now investigated *V. wrightii* MIQ. The deciduous shrub *V. wrightii* is widely distributed in Japan and China.[6] In chemical studies on the constituents of this plant, Iwagawa *et al.*[7] reported the isolation of a phenolic alloside together with seven known compounds from leaves. We now describe the isolation and structure determination of four new phenolic glycosides and five known compounds from the leaves of this plant.

The isolation and purification of the compounds are described in detail in the Experimental section.

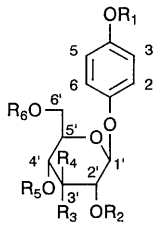
Compound **1** was obtained as an amorphous powder. The ultraviolet (UV) spectrum showed absorption maxima at 213 (4.14), 247 (3.81), 290 sh (4.01) and 319 (4.11) nm (log ε). The fast atom bombardment mass spectrometry (FAB-MS) afforded $[M+Na]^+$ at *m/z* 509. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **1** showed the presence of the coumarin moiety [δ 6.21 (d, J=9.5, H-3), 7.75 (d, J=9.5, H-4)], a *trans* caffeoyl moiety [an ABX signal due to aromatic protons, δ 6.77 (d, J=8.1, H-5″), 6.91 (dd, J=8.1, 1.8, H-6″), 6.99 (d, J=1.8, H-2″) and a pair of *trans*-olefinic signals, δ 6.28 (d, J=15.8, H-8″), 7.48 (d, J=15.8, H-7″)] and a glucosyl moiety. An ABX signal, δ 7.04 (dd, J=9.2, 2.5), 7.05 (d, J=2.5) and 7.47 (d, J=9.2), showed that mono substituent was at C-6 or C-7 in the coumarin unit of the B-ring. In a nuclear Overhauser effect (NOE) experiment, irradiation at δ 5.06 (H-1′ of the β-glucopyranosyl moiety) enhanced the intensity of the signals at δ 7.04 and 7.05. The determination of the location of the glucosyl moiety was made by examining the ^{13}C–^{1}H shift correlation spectroscopy (^{13}C–^{1}H COSY) and ^{1}H-detected multiple-bond connectivity (HMBC) spectra. In the HMBC spectrum, the cross peak between the proton signal at δ 7.47 (d, J=9.2) in the coumarin unit of the B-ring and the carbon signal at δ 145.4 (C-4) suggested the proton at δ 7.47 should be assigned to the H-5 position. This indicated that the glucosyl moiety was attached to the C-7 hydroxyl group. The cross peaks between H-6′ (δ 4.34, 4.54) of glucosyl moiety and the carbonyl carbon (δ 169.0) of caffeoyl moiety, on the other hand, suggested the location of the caffeoyl moiety at the C-6′ hydroxyl group. From these data, the structure of **1** was determined to be umbelliferone 6-*O*-*trans*-caffeoyl-β-D-glucopyranoside.

Compound **2** was obtained as an amorphous. The ^{1}H-NMR spectrum of **2** showed signals of an anomeric proton at δ 4.80 (1H, d, J=7.7), two *trans* olefinic protons at δ 6.31 and 7.60 (each 1H, d, J=16.0), *p*-substituted phenyl protons at δ 6.70 and 6.99 (each 2H, d, J=9.0) and 3,4-disubstituted phenyl protons. The ^{13}C-NMR spectrum of **2** suggested the presence of *p*-hydroxyphenyl, *trans*-caffeoyl and glucosyl groups. The chemical shifts were compared with those of *p*-hydroxyphenyl β-D-glucopyranoside (arbutin), especially in the sugar carbon region. In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum, the signal due to C-4′ of glucopyranoside was shifted downfield, whereas the neighboring C-3′ and C-5′ signals were shifted upfield, suggesting the *trans*-caffeoyl group was located at the C-4′ hydroxyl group (Table I). On acetylation, **2** afforded a hexaacetate **2a**. The HMBC spectrum showed a cross peak between H-4′ (δ 5.30) of the glucosyl moiety and the carbonyl carbon (δ 164.9) of *trans*-caffeoyl moiety. From these data, the structure of **2** was determined to be *p*-hydroxyphenyl 4-*O*-*trans*-caffeoyl-β-D-glucopyranoside.

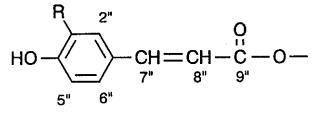
Compounds **3**—**6** and **8** are known phenolic glycosides, which were identified as *p*-hydroxyphenyl 6-*O*-*trans*-caffeoyl-β-D-glucopyranoside, *p*-hydroxyphenyl 6-*O*-*trans*-caffeoyl-β-D-allopyranoside, 2-*O*-acetylarbutin, *p*-hydroxyphenyl 2-*O*-*trans*-*p*-coumaroyl-β-D-glucopyranoside and



1



2 : R_1=R_2=R_3=R_6=H, R_4=OH, R_5= *trans* -caffeoyl
2a: R_1=R_2=R_6=Ac, R_3=H, R_4=OAc, R_5= *trans* -caffeoyl(Ac)
3 : R_1=R_2=R_3=R_5=H, R_4=OH, R_6= *trans* -caffeoyl
4 : R_1=R_2=R_4=R_5=H, R_3=OH, R_6= *trans* -caffeoyl
5 : R_1=R_3=R_5=R_6=H, R_2=Ac, R_4=OH
6 : R_1=R_3=R_5=R_6=H, R_2= *trans* - *p* -coumaroyl, R_4=OH
7 : R_1=R_3=R_5=R_6=H, R_2= *cis* - *p* -coumaroyl, R_4=OH
8 : R_1=R_2=R_3=R_5=H, R_4=OH, R_6= *trans* - *p* -coumaroyl
9 : R_1=R_2=R_3=R_5=H, R_4=OH, R_6= *cis* - *p* -coumaroyl



caffeoyl: R=OH
p -coumaroyl: R=H

Chart 1

TABLE I. ^{13}C-NMR Chemical Shifts (100 MHz, CD_3OD)

Carbon	Arbutin	2	2a[a]	3	4	5	6	7	6-*O*-Acetyl-arbutin	8	9
1	153.8	153.9	154.5	153.9	153.7	154.2	154.1	154.1	154.3	154.0	154.0
2	119.3	119.5	122.6	119.6	119.5	119.3	119.5	119.3	119.6	119.7	119.8
3	116.6	116.7	118.0	116.7	116.7	116.8	116.8[b]	115.9[c]	116.6	116.7[d]	115.9[e]
4	152.4	152.4	146.3	152.3	152.4	152.2	152.3	152.2	152.3	152.4	152.3
5	116.6	116.7	118.0	116.7	116.7	116.8	116.8[b]	115.9[c]	116.6	116.7[d]	115.9[e]
6	119.3	119.5	122.6	119.6	119.5	119.3	119.5	119.3	119.6	119.7	119.8
1′	103.6	103.7	99.6	103.7	101.4	101.8	102.2	101.8	103.7	103.8	103.9
2′	75.0	75.2	71.2	74.9	72.0	75.3	75.2	74.9	74.9	75.0	75.0
3′	78.0	76.3	72.5	77.9	72.9	76.1	76.2	76.1	77.9	78.0	78.0
4′	71.3	72.3	68.7	71.8	69.1	71.5	71.6	71.6	71.7	71.9	71.8
5′	78.0	75.3	72.2	75.5	73.1	78.3	78.3	78.3	75.3	75.6	75.5
6′	62.5	62.3	62.2	64.7	65.2	62.5	62.6	62.5	64.8	64.7	64.4
1″		127.7	132.7	127.7	127.7		127.2	127.7		127.2	127.6
2″		114.8	123.0	115.1	115.1		131.3	133.7		131.3	133.8
3″		149.8	143.9	149.6	149.6		116.9[b]	116.8[c]		117.0[d]	116.7[e]
4″		146.9	142.5	146.8	146.7		161.3	160.1		161.5	160.2
5″		116.6	124.1	116.6	116.6		116.9[b]	116.8[c]		117.0[d]	116.7[e]
6″		123.1	126.7	123.2	123.2		131.3	133.7		131.3	133.8
7″		147.7	144.9	147.2	147.2		147.1	145.2		146.9	145.4
8″		114.8	117.4	114.9	114.9		115.1	116.6		115.0	116.3
9″		168.6	164.9	169.1	169.2		168.5	167.4		169.0	168.1
$\underline{C}H_3COO$			21.1			21.0			20.8		
			20.7								
			20.6								
$CH_3\underline{C}OO$			170.5			171.9			172.7		
			170.2								
			169.7								
			169.3								
			168.0								
			167.9								

a) Measured in $CDCl_3$. *b*—*e*) Assignments may be interchanged within each column.

p-hydroxyphenyl 6-*O*-*trans*-*p*-coumaroyl-*β*-D-glucopyranoside, respectivey, by direct comparison with authentic samples[4] and various diagnostic data with reported values.[8,9]

Compound **7** was obtained as a yellow amorphous powder, mp 143—145 °C. The UV spectrum showed absorption maxima at 222 (4.11), 297 (4.00) and 308 (4.01) nm (log ε). The FAB-MS exhibited ions at *m/z* 419[M+H]$^+$ and 441[M+Na]$^+$. Its ^{1}H-NMR spectrum closely resembled that of **6**, except that the olefin proton signals at *δ* 5.82 and 6.89 (each 1H, d) shifted upfield and their coupling constant (J=12.5) was smaller than that of **6**. This indicates that the configuration of the olefin in the *p*-coumaroyl moiety of **7** is in the *cis*-form. The ^{13}C-NMR spectrum confirmed that **7** is the *cis*-isomer of **6**. On the basis of the above data, the structure of **7** was determined to be *p*-hydroxyphenyl 2-*O*-*cis*-*p*-coumaroyl-*β*-D-glucopyranoside.

Compound **9** was obtained as a yellow amorphous powder, mp 108—113 °C. The UV spectrum showed absorption maxima at 222 (4.08), 297 (4.00) and 308 (4.01) nm (log ε). The FAB-MS exhibited ions at *m/z* 419[M+H]$^+$ and 441[M+Na]$^+$. The ^{1}H- and ^{13}C-NMR spectra closely resembled that of **8**, except for the signals due to *p*-coumaroyl moiety. In the ^{1}H-NMR spectrum of **9**, the olefin proton signals were observed at *δ* 5.79, 6.89 (each 1H, d, J=12.9), showing upfield shifts (by 0.56, 0.75 ppm) and a small coupling constant compared with those of **8**. From these data, the structure of **9** was determined to be *p*-hydroxyphenyl 6-*O*-*cis*-*p*-coumaroyl-*β*-D-glucopyranoside.

Compound **3** seemes to be an artifact, since treatment of **2** with MeOH at room temperature resulted in transfer of the *trans*-caffeoyl group to give **3**.[10,11]

Manju *et al.* have reported the isolation of compounds **6** and **8** from the leaves of *Grevillea robusta*,[8] although the NMR data of the native forms were not described.

Compounds **6**, **7**, **8** and **9** were very difficult to isolate despite the use of several forms of chromatography because these two pairs of compounds (**6** and **7** or **8** and **9**) are isomers (they readily interchange in the daylight).[12—14] Thereafter, purification and instrumental analyses were done avoiding the daylight. In order to examine *cis–trans* isomerization in the light, the following experiments were carried out: under two conditions (irradiation with a fluorescent lamp [*ca.* 800 lux] and irradiation by daylight through a window [*ca.* 3000 lux]), we measured the quantity of *cis–trans* isomerization of each compound by high-performance liquid chromatography (HPLC). Each was dissolved in the mobile phase, and these solutions were placed in individual transparent glass tube.

Despite irradiation of compound **6** with the fluorescent lamp for over 6 h, isomerization of the *trans* to the *cis* isomer did not take place. In contrast, when irradiated by daylight through the window, compound **6** was isomerized to the *cis* isomer (**7**) (detected at 35.2 min and shown in Fig. 1, left). Isomerization of the *trans* (**6**) to the *cis* isomer (**7**) came to equilibrium by irradiation with daylight through the window for 8 h. The ratio of each isomer was roughly calculated from the peak areas to be 66 : 34 for **6** and **7**.

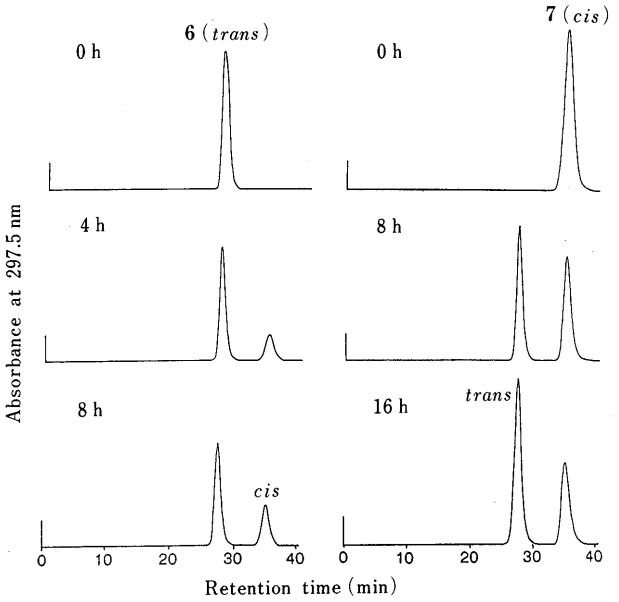


Fig. 1. Relationship of *cis–trans* Isomerization and the Passage of Time

HPLC conditions: column, TSK gel 80TM (6 mm i.d. × 15 cm); solvent, MeOH–H_2O (2 : 3); flow rate, 0.6 ml/min; detector, UV (297.5 nm).

Isomerization of the *cis* to the *trans* was not influenced by irradiation with the fluorescent lamp, whereas under irradiation with daylight through the window compound **7** was rapidly isomerized to the *trans* isomer (**6**). The ratio of the peak area for **7** to **6** was 50 : 50 during irradiation for 8 h (Fig. 1, right). After 8 h, isomerization of the *cis* (**7**) to the *trans* (**6**) isomer reached equilibrium by irradiation with daylight through the window. The ratio of the peak areas for **7** to **6** was 36 : 64.

The *cis–trans* isomerization reaction of compounds **8** and **9** resembles that of compounds **6** and **7**; that is, *cis–trans* isomerization reactions did not occur by irradiation with the fluorescent lamp, whereas compounds **8** and **9** came to equilibrium by irradiation with daylight through the window for 8 and 10 h, respectively. The ratio of each isomer was roughly calculated from the peak areas to be 65 : 35 for *trans* and *cis* isomer.

From these data, *cis–trans* isomerization reactions of these compounds occurred by irradiation with daylight, while they did not with irradiation with the fluorescent lamp. In short, even if the mixture of *cis–trans* isomers is irradiated with the fluorescent lamp, it is possible to isolate each compound unless the daylight is irradiated. In addition, the *cis* isomers (**7** and **9**) are not artifacts from their *trans* isomers (**6** and **8**) during extraction and isolation. The time necessary to reach equilibrium state and the ratios of each *cis–trans* isomer may vary due to the conditions (the quantity of UV irradiation, solvent, *etc.*).

Experimental

Melting points were determined on a Yanagimoto MP-S3 micro-melting point apparatus and are uncorrected. Optical rotations were determined with a JASCO DIP-360 digital polarimeter. Infrared (IR) spectra were recorded with a Perkin-Elmer 1725X FT-IR instrument and UV spectra with a Beckman DU-64 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL JNM-GSX 400 (400 and 100 MHz, respectively) spectrometer. Chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; dd, double doublet; ddd, double double doublet; m, multiplet). MS were recorded on a JEOL JMS-DX 300 mass spectrometer. Column chromatography was carried out on Kieselgel 60 (Merck; 70—230 and 230—400 mesh) and Sephadex LH-20 (Pharmacia Fine Chemicals). Thin layer chromatography (TLC) was carried out with precoated Kieselgel 60 plates (Merck) and detection was achieved by spraying 50% H_2SO_4 followed by heating. Preparative HPLC was carried out on a Tosoh HPLC system (pump, CCPM; detector, UV-8000) using TSK gel ODS-120A and ODS-80TM (Tosoh) column. Illumination intensity was measured with a ANA-500S (SIBATA).

Isolation Fresh leaves of *V. wrightii* (2.0 kg) collected in August 1989 in Sendai, Japan, were extracted with MeOH at room temperature for two months. The MeOH extract was concentrated under reduced pressure and the residue was suspended in a small excess of water. This suspension was successively extracted with $CHCl_3$, Et_2O, AcOEt and *n*-BuOH. The AcOEt soluble fraction was concentrated under reduced pressure to produce a residue (8.0 g). This residue was chromatographed on a silica gel column using $CHCl_3$–MeOH–H_2O (30 : 10 : 1) and the eluate was separated into twelve fractions (fr. 1—12). Fraction 8 was subjected to HPLC (MeOH–H_2O, 2 : 3) to give compounds **1** (10 mg), **5** (10 mg), **6** (25 mg), **7** (15 mg), **8** (8 mg) and **9** (5 mg). For compounds **6**—**9**, purification and instrumental analysis were carried out to avoid the daylight. Fraction 9 was rechromatographed on a Sephadex LH-20 column using MeOH–H_2O (1 : 1) and the eluate was separated into four fractions. Fraction 9-2 was subjected to HPLC (MeOH–H_2O, 1 : 1) to give compounds **2** (4 mg), **3** (50 mg) and **4** (3 mg).

Umbelliferone 6-*O*-*trans*-Caffeoyl-*β*-D-glucopyranoside (1) An amorphous powder, mp 168—171 °C, $[\alpha]_D$ −62.5° (c=0.1, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3398, 1689, 1615, 1283, 847. UV λ_{max}^{MeOH} nm (log ε): 213 (4.14), 247 (3.81), 290 sh (4.01), 319 (4.11). FAB-MS m/z: 487 $(M+H)^+$, 509 $(M+Na)^+$. ^{1}H-NMR (400 MHz, CD_3OD) δ: 3.41 (1H, dd, J=9.5, 8.8 Hz, 4′-H), 3.52 (2H, m, 2′-H and 3′-H), 3.81 (1H, ddd, J=9.5, 7.3, 2.5 Hz, 5′-H), 4.34 (1H, dd, J=11.9, 7.3 Hz, 6′-H_A), 4.54 (1H, dd, J=11.9, 2.5 Hz, 6′-H_B), 5.06 (1H, d, J=7.7 Hz, 1′-H), 6.21 (1H, d, J=9.5 Hz, 3-H), 6.28 (1H, d, J=15.8 Hz, 8″-H), 6.77 (1H, d, J=8.1 Hz, 5″-H), 6.91 (1H, dd, J=8.1, 1.8 Hz, 6″-H), 6.99 (1H, d, J=1.8 Hz, 2″-H), 7.04 (1H, dd, J=9.2, 2.5 Hz, 6-H), 7.05 (1H, d, J=2.5 Hz, 8-H), 7.47 (1H, d, J=9.2 Hz, 5-H), 7.48 (1H, d, J=15.8 Hz, 7″-H), 7.75 (1H, d, J=9.5 Hz, 4-H). ^{13}C-NMR (100 MHz, CD_3OD) δ: 64.7 (C-6′), 72.0 (C-4′), 74.7 (C-2′), 75.7 (C-5′), 77.9 (C-3′), 101.6 (C-1′), 104.9 (C-8), 114.3 (C-3), 114.8 (C-8″), 115.2 (C-2″), 115.3 (C-10), 115.4 (C-6), 116.7 (C-5″), 123.0 (C-6″), 127.6 (C-1″), 130.4 (C-5), 145.4 (C-4), 146.8 (C-4″), 147.3 (C-7″), 149.7 (C-3″), 156.9 (C-9), 161.9 (C-7), 163.2 (C-2), 169.0 (C-9″).

***p*-Hydroxyphenyl 4-*O*-*trans*-Caffeoyl-*β*-D-glucopyranoside (2)** An amorphous. FAB-MS m/z: 435 $(M+H)^+$, 457 $(M+Na)^+$. ^{1}H-NMR (400 MHz, CD_3OD) δ: 3.50—3.76 (4H, m, 2′,3′,5′ and 6′-H), 4.80 (1H, d, J=7.7 Hz, 1′-H), 4.92 (1H, t, J=9.5 Hz, 4′-H), 6.31 (1H, d, J=16.0 Hz, 8″-H), 6.70 (2H, d, J=9.0 Hz, 3,5-H), 6.78 (1H, d, J=8.1 Hz, 5″-H), 6.96 (1H, dd, J=8.1, 1.8 Hz, 6″-H), 6.99 (2H, d, J=9.0 Hz, 2, 6-H), 7.05 (1H, d, J=1.8 Hz, 2″-H), 7.60 (1H, d, J=16.0 Hz, 7″-H). ^{13}C-NMR (100 MHz, CD_3OD): Table I.

Treatment of **2** (4 mg) with MeOH (5 ml) at room temperature overnight resulted in transfer of the *trans*-caffeoyl group to give **3** (the ratio of the peak areas for **2** to **3** was 68 : 32 by HPLC analyses).

Acetylation of 2 Compound **2** (3 mg) was acetylated with Ac_2O–pyridine in the usual manner to give the **2a** (2 mg). An amorphous, $[\alpha]_D$ −72.2° (c=0.17, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1757, 1639, 1602, 1504, 1232. UV λ_{max}^{MeOH} nm (log ε): 208 (4.30), 217 (4.33), 278 (4.27). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 2.05, 2.06, 2.07 (each 3H, s, CH_3COO), 2.29, 2.30, 2.31 (each 3H, s, CH_3COO), 3.82 (1H, m, 5′-H), 4.21 (1H, dd, J=12.0, 2.9 Hz, 6′-H_A), 4.27 (1H, dd, J=12.0, 5.3 Hz, 6′-H_B), 5.07 (1H, d, J=7.3 Hz, 1′-H), 5.30 (1H, dd, J=9.8, 7.6 Hz, 4′-H), 5.40 (2H, m, 2′, 3′-H), 6.32 (1H, d, J=16.0 Hz, 8″-H), 7.02 (4H, s, 2,3,5 and 6-H), 7.24 (1H, d, J=8.5 Hz, 5″-H), 7.37 (1H, d, J=2.0 Hz, 2″-H), 7.41 (1H, dd, J=8.5, 2.0 Hz, 6″-H), 7.64 (1H, d, J=16.0 Hz, 7″-H). ^{13}C-NMR (100 MHz, $CDCl_3$): Table I.

***p*-Hydroxyphenyl 6-*O*-*trans*-Caffeoyl-*β*-D-glucopyranoside (3)** An amorphous powder, mp 142—144 °C, $[\alpha]_D$ −52.4° (c=1.1, MeOH). This was identical to an authentic sample.[4]

***p*-Hydroxyphenyl 6-*O*-*trans*-Caffeoyl-*β*-D-allopyranoside (4)** An amorphous powder, mp 127—128 °C, $[\alpha]_D$ −67.3° (c=0.5, MeOH). This was identical to an authentic sample.[4]

2-*O*-Acetylarbutin (5) An amorphous powder, $[\alpha]_D$ −21.2° (c=0.9, MeOH). ^{1}H-NMR (400 MHz, CD_3OD) δ: 2.10 (3H, s, CH_3COO), 3.45 (2H, m, 4′,5′-H), 3.56 (1H, t, J=8.3 Hz, 3′-H), 3.71 (1H, dd, J=12.0, 5.3 Hz, 6′-H_A), 3.91 (1H, dd, J=12.0, 2.0 Hz, 6′-H_B), 4.90 (1H, d, J=7.6 Hz, 1′-H), 4.92 (1H, dd, J=7.6, 8.3 Hz, 2′-H), 6.68 (2H, d, J=8.9 Hz, 3,5-H), 6.87 (2H, d, J=8.9 Hz, 2,6-H). ^{13}C-NMR (100 MHz, CD_3OD): Table I.

***p*-Hydroxyphenyl 2-*O*-*trans*-*p*-Coumaroyl-β-D-glucopyranoside (6)** A yellow amorphous powder, mp 172—174 °C, $[\alpha]_D$ −7.2° (c=1.0, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3392, 1698, 1631, 1605, 1511. UV λ_{max}^{MeOH} nm (log ε): 223 (4.10), 298 sh (4.15), 312 (4.19). FAB-MS m/z: 419 $(M+H)^+$, 441 $(M+Na)^+$. ^{1}H-NMR (400 MHz, CD_3OD) δ: 3.46 (1H, m, 5′-H), 3.50 (1H, t, J=9.2 Hz, 4′-H), 3.68 (1H, t, J=9.2 Hz, 3′-H), 3.75 (1H, dd, J=12.0, 5.0 Hz, 6′-H_A), 3.93 (1H, dd, J=2.0, 12.0 Hz, 6′-H_B), 4.95 (1H, d, J=7.9 Hz, 1′-H), 5.05 (1H, dd, J=9.2, 7.9 Hz, 2′-H), 6.39 (1H, d, J=16.0 Hz, 8″-H), 6.66 (2H, d, J=8.9 Hz, 3,5-H), 6.80 (2H, d, J=8.6 Hz, 3″,5″-H), 6.86 (2H, d, J=8.9 Hz, 2,6-H), 7.46 (2H, d, J=8.6 Hz, 2″,6″-H), 7.68 (1H, d, J=16.0 Hz, 7″-H). ^{13}C-NMR (100 Hz, CD_3OD): Table I.

***p*-Hydroxyphenyl 2-*O*-*cis*-*p*-Coumaroyl-β-D-glucopyranoside (7)** A yellow amorphous powder, mp 143—145 °C, $[\alpha]_D$ +99.9° (c=0.3, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3370, 1711, 1602, 1511. UV λ_{max}^{MeOH} nm (log ε): 222 (4.11), 297 (4.00), 308 (4.01). FAB-MS m/z: 419 $(M+H)^+$, 441 $(M+Na)^+$. ^{1}H-NMR (400 MHz, CD_3OD) δ: 3.40 (1H, m, 5′-H), 3.47 (1H, t, J=9.2 Hz, 4′-H), 3.60 (1H, t, J=9.2 Hz, 3′-H), 3.71 (1H, dd, J=12.0, 5.3 Hz, 6′-H_A), 3.91 (1H, dd, J=12.0, 2.0 Hz, 6′-H_B), 4.89 (1H, d, J=8.3 Hz, 1′-H), 5.02 (1H, dd, J=9.2, 8.3 Hz, 2′-H), 5.82 (1H, d, J=12.5 Hz, 8″-H), 6.672 (2H, d, J=8.9 Hz, 3,5-H), 6.674 (2H, d, J=8.6 Hz, 3″,5″-H), 6.86 (2H, d, J=8.9 Hz, 2,6-H), 6.89 (1H, d, J=12.5 Hz, 7″-H), 7.61 (2H, d, J=8.6 Hz, 2″,6″-H). ^{13}C-NMR (100 MHz, CD_3OD): Table I.

***p*-Hydroxyphenyl 6-*O*-*trans*-*p*-Coumaroyl-β-D-glucopyranoside (8)** A yellow amorphous powder, mp 138—140 °C, $[\alpha]_D$ −58.0° (c=0.5, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3387, 1688, 1606, 1511. UV λ_{max}^{MeOH} nm (log ε): 223 (4.08), 298 (4.12), 311 (4.16). FAB-MS m/z: 441 $(M+Na)^+$. ^{1}H-NMR (400 MHz, CD_3OD) δ: 3.42 (3H, m, 2′,3′,4′-H), 3.64 (1H, m, 5′-H), 4.34 (1H, dd, J=11.9, 6.6 Hz, 6′-H_A), 4.53 (1H, dd, J=11.9, 2.3 Hz, 6′-H_B), 4.73 (1H, d, J=7.3 Hz, 1′-H), 6.35 (1H, d, J=15.8 Hz, 8″-H), 6.65 (2H, d, J=9.2 Hz, 3,5-H), 6.82 (2H, d, J=8.6 Hz, 3″,5″-H), 6.95 (2H, d, J=9.2 Hz, 2,6-H), 7.46 (2H, d, J=8.6 Hz, 2″,6″-H), 7.64 (1H, d, J=15.8 Hz, 7″-H). ^{13}C-NMR (100 MHz, CD_3OD): Table I.

***p*-Hydroxyphenyl 6-*O*-*cis*-*p*-coumaroyl-β-D-glucopyranoside (9)** A yellow amorphous powder, mp 108—113 °C, $[\alpha]_D$ −53.3° (c=0.3, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3385, 1680, 1609, 1514. UV λ_{max}^{MeOH} nm (log ε): 222 (4.08), 297 (4.00), 308 (4.01). FAB-MS m/z: 419 $(M+H)^+$, 441 $(M+Na)^+$. ^{1}H-NMR (400 MHz, CD_3OD) δ: 3.40 (3H, m, 2′,3′,4′-H), 3.58 (1H, ddd, J=9.5, 6.6, 2.3 Hz, 5′-H), 4.30 (1H, dd, J=11.9, 6.6 Hz, 6′-H_A), 4.48 (1H, dd, J=11.9, 2.3 Hz, 6′-H_B), 4.68 (1H, d, J=7.6 Hz, 1′-H), 5.79 (1H, d, J=12.9 Hz, 8″-H), 6.65 (2H, d, J=9.2 Hz, 3,5-H), 6.72 (2H, d, J=8.6 Hz, 3″,5″-H), 6.89 (1H, d, J=12.9 Hz, 7″-H), 6.92 (2H, d, J=9.2 Hz, 2,6-H), 7.62 (2H, d, J=8.6 Hz, 2″,6″-H). ^{13}C-NMR (100 MHz, CD_3OD): Table I.

Acknowledgement The authors are grateful to Dr. S. Suzuki and Dr. K. Hisamichi of their college for measurements of the FAB-MS and NMR spectra, respectively.

References

1) T. Kurihara and M. Kikuchi, *Yakugaku Zasshi*, **95**, 1098 (1975).
2) T. Kurihara and M. Kikuchi, *Tohoku Yakka Daigaku Kenkyu Nempo*, **24**, 123 (1977).
3) K. Machida and M. Kikuchi, *Tohoku Yakka Daigaku Kenkyu Nempo*, **37**, 57 (1990).
4) K. Machida, Y. Nakano and M. Kikuchi, *Phytochemistry*, **30**, 2013 (1991).
5) K. Machida and M. Kikuchi, *Phytochemistry*, **31**, 3654 (1992).
6) Y. Hayashi, K. Furusato and T. Nakamura, "Illustrated Tree in Colour," The Hokuryukan Co., Ltd., Tokyo, 1985, p. 705.
7) T. Iwagawa, H. Takahashi, K. Munesada and T. Hase, *Phytochemistry*, **23**, 468 (1984).
8) M. Manju, R. S. Varma and M. R. Parthasarathy, *Phytochemistry*, **16**, 793 (1977).
9) A. Askari and L. R. Worthen, *Phytochemistry*, **11**, 1509 (1972).
10) K. Yoshimoto and Y. Tsuda, Abstracts of Papers, the 101th Annual Meeting of the Pharmaceutical Society of Japan, Kumamoto, April 1981, p. 481.
11) M. Sasahara, Y. Tamayama, S. Nishibe, T. Kawamura, M. Noro and T. Tanaka, Abstracts of Papers, the 111th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, March 1991, II-144.
12) H. Sasaki, H. Nishimura, M. Chin and H. Mitsuhashi, *Phytochemistry*, **28**, 875 (1989).
13) M. Sugiyama and M. Kikuchi, *Chem. Pharm. Bull.*, **38**, 2953 (1990).
14) H. Nishimura, H. Sasaki, N. Inagaki, M. Chin and H. Mitsuhashi, *Phytochemistry*, **30**, 965 (1991).