HETEROCYCLES, Vol. 83, No. 11, 2011, pp. 2615 - 2625. © 2011 The Japan Institute of Heterocyclic Chemistry
Received, 8th August, 2011, Accepted, 16th September, 2011, Published online, 30th September, 2011
DOI: 10.3987/COM-11-12330

NEW FLAVONOL GLYCOSIDES FROM *CARDAMINE KOMAROVII*

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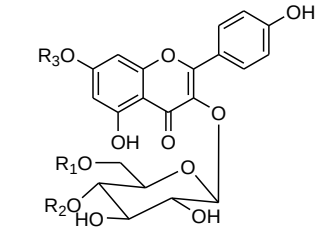
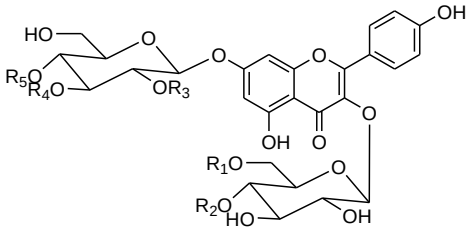
Abstract – Seven new kaempferol glycosides (**1 - 7**), together with three known kaempferol glycosides (**8 - 10**), were isolated from a MeOH extract of *Cardamine komarovii* NAKAI (Cruciferae). The chemical structures of the new compounds (**1 - 7**) were determined on the basis of their MS, ^{1}H-NMR, ^{13}C-NMR, COSY, HMBC, NOESY and TOCSY data, and results of hydrolysis.

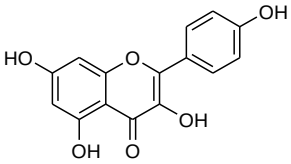
The genus *Cardamine* includes a group of 10 species.[1] Previous phytochemical studies on the *Cardamine* species indicated that flavonoid glycosides and glycerides were isolated from aerial parts of *Cardamine impatiens*[2,3] and some kaempferol glycosides from the whole herbs of *Cardamine leucantha*.[4] In our search for bioactive constituents from Korean medicinal plants, we investigated the methanol extract of *Cardamine komarovii* NAKAI (Cruciferae). *C. komarovii* is widely distributed in the northern parts of Korea.[1] This indigenous herb is used in Chinese medicine for the treatment of hemostasis, depressed blood pressure.[5] We have recently reported the isolation of megastigmane derivatives from this plant.[6] In continuing research on this source, 7 new kaempferol glycosides (**1 - 7**) and three known kaempferol glycosides (**8 - 10**) were further isolated from the MeOH extract. The structures of the known compounds (**8 - 10**) were identified as kaempferol 3-*O*-*β*-D-glucopyranoside (**8**),[7] kaempferol 3-*O*-rutinoside (**9**),[8] and kaempferol 3-*O*-rutinopyranosyl-7-*O*-*β*-D-glucopyranoside (**10**)[9] by comparing their spectroscopic data with data in the literature. Compounds (**8 - 10**) were known but, to the best of our knowledge, this is the first report of their being isolated from this source. The structures of these new compounds were elucidated on the basis of 1D and 2D NMR spectroscopic data analysis (^{1}H-, ^{13}C-NMR, COSY, HMQC, HMBC, TOCSY and, NOESY), as well as chemical means.



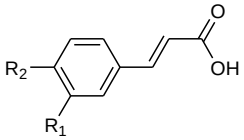
2 : R_1=Rha, R_2=Glc, R_3=H
8 : R_1=R_2=H
9 : R_1=Rha, R_2=R_3=H
10 : R_1=Rha, R_2=H, R_3=Glc



1 : R_1=R_2=R_3=R_4=H, R_5=Glc
3 : R_1=Rha, R_2=Glc, R_3=R_4=R_5=H
4 : R_1=Rha, R_2=Glc, R_3=(*E*)-caffeoyl, R_4=R_5=H
5 : R_1=Rha, R_2=Glc, R_3=(*E*)-feruloyl, R_4=R_5=H
6 : R_1=Rha, R_2=Glc, R_3=(*E*)-*p*-coumaroyl, R_4=R_5=H
7 : R_1=Rha, R_2=Glc, R_3=H, R_4=(*E*)-feruloyl, R_5=H



2a



4a : R_1=R_2=OH
5a : R_1=OMe, R_2=OH
6a : R_1=H, R_2=OH

Figure 1. Structures of isolated compounds (**1 - 10**) from *C. komarovii*.

Compound **1**, was obtained as a yellowish gum, and its molecular formula $C_{33}H_{40}O_{21}$ was inferred from the negative ion HRFABMS *m/z* 771.1984 $[M-H]^-$ (calcd. for 771.1984). The kaempferol skeleton was evident from the ^{1}H-NMR spectral signals at δ_H 8.03 (2H, d, J = 8.8, H-2', H-6'), 6.88 (2H, d, J = 8.8 Hz, H-3', H-5'), 6.77 (1H, d, J = 2.0 Hz, H-8), 6.42 (1H, d, J = 2.0 Hz, H-6) and ^{13}C-NMR spectral signals of the B-ring at δ_C 160.8 (C-4'), 131.7 (C-2', C-6'), 121.4 (C-1'), 115.9 (C-3', C-5') as well as other signals of the A- and C-rings shown in Table 1.[10] The ^{1}H- and ^{13}C-NMR spectra of **1** also showed three anomeric proton signals at δ_H 5.50 (1H, d, J = 7.6 Hz), 5.06 (1H, d, J = 7.6 Hz), and 4.29 (1H, d, J = 7.6 Hz) and anomeric carbon resonances at δ_C 103.8, 101.2 and 100.5, respectively. The anomeric configurations for the sugar moieties were defined as β for glucose from coupling constant of 7.6 Hz. Enzyme hydrolysis of **1** **1** with β-glucosidase (emulsin) yielded compound **8**, and D-glucose ($[\alpha]_D^{25}$: +50.4° (*c* 0.05 in H_2O). The sugar sequence was determined on the basis of both 1D- and 2D-NMR, especially HMBC and NOESY experiments. The positions of attachment of glucoses with the aglycone were confirmed by HMBC correlations; δ_H 5.50 (1H, d, J = 7.6 Hz, H-1'') of glucose-I to δ_C 134.1 (C-3); δ_H 5.06 (1H, d, J = 7.6 Hz, H-1''') of glucose-II to δ_C 163.6 (C-7); δ_H 4.29 (1H, d, J = 7.6, H-1'''') of glucose-III to δ_C 80.8 (C-4''') of glucose-II. The position of attachment of Glc-II was further confirmed through NOESY correlation between H-1''' (δ 5.06) and H-6/8 (δ 6.42/6.77). These data indicated the structure of **1** to be kaempferol 3-*O*-β-D-glucopyranosyl-7-*O*-β-D-glucopyranosyl(1→3)-β-D-glucopyranoside.

Compound **2**, was obtained as a yellowish gum, and its molecular formula $C_{33}H_{40}O_{20}$ was inferred from the negative ion HRFABMS *m/z* 755.2051 $[M - H]^-$ (calcd. for 755.2035). The NMR spectral data were very similar to those of compound **9**, which was isolated from *Lathyrus davidii*.[8] The main differences were the additional glucose signals in the ^{13}C-NMR spectrum of **2**; δ_C 104.2, 77.5, 77.2, 73.7, 70.7, 61.8. The units with an anomeric proton signals at δ_H 5.33 (1H, d, J = 7.8 Hz), 4.13 (1H, d, J = 7.8 Hz), 4.40 (1H, s) and a methyl group at δ_H 0.92 (3H, d, J = 6.8 Hz), was identified as D-glucopyranosyl and L-rhamnophyranosyl moiety. The position of attachment of glucose was confirmed by the HMBC correlations; δ_H 4.13 (1H, d, J = 7.8 Hz, H-1''') of glucose-II to δ_C 80.9 (C-4'') of glucose-I. These data indicated the structure of **2** to be kaempferol 3-*O*-*β*-D-glucopyranosyl(1→4)-[*α*-L-rhamnopyranosyl-(1→6)]-*β*-D-glucopyranoside. Acid hydrolysis of **2** with 1M HCl yielded kaempferol and, L-rhamnose and D-glucose as the residues, which were identified by GC analysis of their corresponding trimethylsilylated L-cysteine adducts.[11]

Compound **3**, was obtained as a yellowish gum, and its molecular formula $C_{39}H_{50}O_{25}$ was inferred from the negative ion HRFABMS *m/z* 917.2554 $[M - H]^-$ (calcd. for 917.2563). The NMR spectra of **3** were very similar to those of compound **2**; The differences in the ^{1}H-NMR spectrum of **3** showed that two *meta*-coupled aromatic proton signals at δ_H 6.39 (1H, d, J = 2.0 Hz, H-8) and 6.19 (1H, d, J = 2.0 Hz, H-6) in **2** were shifted downfield to δ_H 6.74 (1H, d, J = 2.0 Hz, H-8) and 6.44 (1H, d, J = 2.0 Hz, H-6) in **3**, implying that **3** was also glucosylated at C-7. Enzyme hydrolysis of **3** with *β*-glucosidase (emulsin) yielded compound **2** and D-glucose. The position of attachment of **2** with the aglycone were confirmed by the HMBC correlations; δ_H 5.06 (1H, d, J = 7.6 Hz, H-1'''') of glucose-III to δ_C 163.4 (C-7). The anomeric configurations for the sugar moieties were defined as *β* for glucose from coupling constant of 7.6 Hz. These data indicated the structure of **3** to be kaempferol 3-*O*-*β*-D-glucopyranosyl(1→4)-[*α*-L-rhamnopyranosyl(1→6)]-*β*-D-glucopyranoside-7-*O*-*β*-D-glucopyranoside.

Compound **4**, was obtained as a yellowish gum, and its molecular formula $C_{48}H_{56}O_{28}$ was inferred from the negative ion HRFABMS *m/z* 1079.2881 $[M - H]^-$ (calcd. for 1079.2880). The NMR spectra of **4** were very similar to those of compound **3**. The major differences in the NMR spectra of **4** were the additional presence of the (*E*)-caffeoyl group[12]; ^{1}H-NMR spectrum, δ_H 7.48 (1H, d, J = 15.6 Hz), 7.00 (1H, d, J = 2.0 Hz), 6.97 (1H, dd, J = 8.8, 2.0 Hz), 6.73 (1H, d, J = 8.8 Hz), 6.25 (1H, d, J = 15.6 Hz); ^{13}C-NMR spectrum: δ_C 166.2, 149.2, 146.3, 146.3, 126.1, 122.1, 116.5, 115.5, 114.4. Its linkage to C-2'''' of glucose-III was corroborated by the long range coupling of the ester carbonyl carbon (δ_C 166.2) with δ_H 4.91 (1H, d, J = 8.8 Hz, H-2'''') of glucose-III in the HMBC spectrum. Alkaline hydrolysis of **4** afforded a compound **3** and (*E*)-caffeic acid.[12] These data indicated the structure of **4** to be kaempferol 3-*O*-*β*-D-glucopyranosyl(1→4)-[*α*-L-rhamnopyranosyl(1→6)]-*β*-D-glucopyranoside-7-*O*-[2-*O*-(*E*)-caffeoyl]-*β*-D-

glucopyranoside.

Compound **5**, was obtained as a yellowish gum, and its molecular formula $C_{48}H_{56}O_{28}$ was inferred from the negative ion HRFABMS *m/z* 1093.3064 $[M-H]^-$ (calcd. for 1093.3036). Comparison of the NMR data of **5** with **4** showed that the two compounds were identical except for the nature of the side chain attached at glucose-III. The ^{1}H and ^{13}C-NMR spectra of **5** indicated the presence of a *trans*-ferulic acid moiety[13]; ^{1}H-NMR spectrum, δ_H 7.56 (1H, dd, J = 15.6 Hz), 7.26 (1H, d, J = 2.0 Hz), 7.07 (1H, dd, J = 8.8, 2.0 Hz), 6.75 (1H, d, J = 8.8 Hz), 6.44 (1H, d, J = 15.6 Hz), 3.77 (3H, s); ^{13}C-NMR spectrum, δ_C 166.3, 150.1, 148.6, 146.1, 126.2, 124.0, 116.2, 115.0, 111.8, 56.4. Its linkage to C-2"" of glucose-III was corroborated by the long range coupling of the ester carbonyl carbon (δ_C 166.3) with δ_H 4.92 (1H, d, J = 8.8 Hz, H-2"") of glucose-III in the HMBC spectrum. Alkaline hydrolysis of **5** afforded a compound **3** and (*E*)-ferulic acid.[13] These data indicated the structure of **5** to be kaempferol 3-*O*-*β*-D-glucopyranosyl(1→4)-[*α*-L-rhamnopyranosyl(1→6)]-*β*-D-glucopyranoside-7-*O*-[2-*O*-*(E)*-feruloyl]-*β*-D-glucopyranoside.

Compound **6**, was obtained as a yellowish gum, and its molecular formula $C_{48}H_{56}O_{27}$ was inferred from the negative ion HRFABMS *m/z* 1063.2939 $[M-H]^-$ (calcd. for 1063.2931). The NMR spectra of **6** were very similar to those of **4** and **5**. The presence of a *trans*-coumaroyl moiety[14]; ^{1}H-NMR spectrum, δ_H 7.61 (2H, d, J = 8.8 Hz), 7.56 (1H, d, J = 15.8 Hz), 6.72 (2H, d, J = 8.8 Hz), 6.35 (1H, d, J = 15.8 Hz); ^{13}C-NMR spectrum, δ_C 165.7, 156.7, 146.1, 133.2, 133.2, 126.0, 115.6, 115.6, 114.8. Its linkage to C-2"" of glucose-III was corroborated by the long range coupling of the ester carbonyl carbon (δ_C 165.7) with δ_H 4.91 (1H, d, J = 8.8 Hz, H-2"") of glucose-III in the HMBC spectrum. The position of the (*E*)-*p*-coumaroyl group was also determined by an HMBC experiment. Alkaline hydrolysis of **6** afforded a compound **3** and (*E*)-*p*-coumaric acid.[14] These data indicated the structure of **6** to be kaempferol 3-*O*-*β*-D-glucopyranosyl(1→4)-[*α*-L-rhamnopyranosyl(1→6)]-*β*-D-glucopyranoside-7-*O*-[2-*O*-(*E*)-*p*-coumaroyl]-*β*-D-glucopyranoside.

Compound **7**, was obtained as a yellowish gum, and its molecular formula $C_{49}H_{58}O_{27}$ was inferred from the negative ion HRFABMS *m/z* 1093.3064 $[M-H]^-$ (calcd. for 1093.3036). The NMR spectra of **7** were very similar to those of compound **5**. The linkage to C-3"" of glucose-III of the *trans*-ferulic acid moiety was corroborated by the long range coupling of the ester carbonyl carbon (δ_C 166.9) with δ_H 5.05 (1H, t, J = 8.7 Hz, H-3"") of glucose-III in the HMBC spectrum and also by significant downfield shifts of H-3"" at δ_H 5.05 (1H, t, J = 8.7 Hz) and H-4"" at δ_H 3.47 (1H, m) of the glucose-III, as well as downfield shifts of the adjacent carbon C-1"" at δ_C 100.1 and C-3"" at 77.9 that were observed. Alkaline hydrolysis of **7** afforded a compound **3** and (*E*)-ferulic acid.[13] These data indicated the structure of **7** to be kaempferol 3-*O*-*β*-D-glucopyranosyl(1→4)-[*α*-L-rhamnopyranosyl(1→6)]-*β*-D-glucopyranoside-7-*O*-[3-*O*-(*E*)-coumaroyl]-*β*-D-glucopyranoside.

EXPERIMENTAL

General and Plant material. See previous paper.[6]

Extraction and isolation. The aerial parts of *C. komarovii* NAKAI (1.7 kg) were extracted with 80% MeOH three times at room temperature. The resultant MeOH extracts (120 g) were suspended in distilled water (800 mL × 3) and then successively partitioned with hexane, $CHCl_3$, EtOAc and *n*-BuOH, yielding residues weighing 12 g, 13 g, 3 g and 26 g, respectively. The *n*-BuOH-soluble fraction (26 g) was chromatographed on a Diaion HP-20 column eluting with a gradient solvent system consisting of 100% H_2O and 100% MeOH. This yielded two subfractions A and B. Fraction B (9.7 g) was purified using a silica gel (230 - 400 mesh, 100 g) column eluted with $CHCl_3$ - MeOH - H_2O (10 : 4 : 0.5) to yield fractions B1 - B14. Fraction B9 (300 mg) was loaded on a Sephadex LH-20 column and eluted with 80% MeOH to yield sub-fractions B91 - 93. Fraction B93 (25 mg) was subjected to preparative reverse-phase HPLC using 60% MeOH as the eluant to give **9** (11 mg). Fraction B10 (700 mg) was loaded on a Sephadex LH-20 column eluted with 80% MeOH to yield sub-fractions B101 - 106. Fraction B103 (50 mg) was loaded on a preparative reverse-phase HPLC using 50% MeOH as eluant to give **8** (15 mg). Fraction B11 (2.0 g) was chromatographed on a Sephadex LH-20 column and eluted with 80% MeOH to yield sub-fractions B111 - B113. Fraction B113 (30 mg) was purified by preparative reverse-phase HPLC using 20% MeCN as eluant to give **2** (11 mg). Fraction B12 (1.3 g) was purified on a Sephadex LH-20 column eluted with 80% MeOH to yield sub-fractions B121 - B124. Fraction B121 (110 mg) was chromatographed on an LiChroprep Lobar-A RP-18 column (using 35% MeOH as eluant) and then reverse-phase HPLC using 20% MeCN as eluant to yield compounds **10** (20 mg) and **5** (26 mg). Fraction B123 (250 mg) was purified by reverse-phase HPLC using 25% MeCN as eluant to yield compound **7** (50 mg). Fraction B13 (600 mg) was chromatographed on an RP-C18 silica gel (230 - 400 mesh, 100 g) column eluted with 50% MeOH to give sub-fractions B131 - B134. Fraction B131 (370 mg) was subjected to a Sephadex LH-20 (using 70% MeOH as eluant) and preparative reverse-phase HPLC using 50% MeOH as eluant to yield compound **6** (14 mg). Fraction B133 (25 mg) was separated by reverse-phase HPLC using 30% MeOH as eluant to yield compound **1** (5 mg). Fraction B14 (700 mg) was subjected to a Sephadex LH-20 column eluted with 70% MeOH to yield sub-fractions B141 - B142. Fractions B141 and B142 were separated by reverse-phase HPLC using 40% MeOH and 20% MeCN as eluants, respectively, to yield compounds **3** (660 mg) and **4** (35 mg).

Compound (**1**): yellowish gum; IR (KBr) ν_{max} 3380, 2947, 2833, 1659, 1451, 1032, 669 cm^{-1}; UV (MeOH) λ_{max} (log ε) 345 (3.9), 265 (3.7) nm; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 2; FABMS *m/z* 771 $[M - H]^-$; HRFABMS *m/z* 771.1984 $[M - H]^-$; (calcd for $C_{33}H_{39}O_{21}$, 771.1984).

Compound (**2**): yellowish gum; IR (KBr) ν_{max} 3355, 2943, 2832, 1658, 1451, 1032, 669 cm^{-1}; UV (MeOH) λ_{max} (log ε) 349 (4.3), 265 (4.5) nm; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 2; FABMS *m/z* 755 $[M-H]^-$; HRFABMS *m/z* 755.2051 $[M-H]^-$; (calcd for $C_{33}H_{39}O_{20}$, 755.2035).

Compound (**3**): yellowish gum; IR (KBr) ν_{max} 3355, 2945, 2832, 1451, 1032, 796, 670 cm^{-1}; UV (MeOH) λ_{max} (log ε) 348 (4.1), 256 (4.3) nm; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 2; FABMS *m/z* 917 $[M-H]^-$; HRFABMS *m/z* 917.2554 $[M-H]^-$ (calcd for $C_{39}H_{49}O_{25}$, 917.2563).

Compound (**4**): yellowish gum; IR (KBr) ν_{max} 3358, 2942, 2832, 1655, 1600, 1450, 1286, 1209, 1180, 1031, 670 cm^{-1}; UV (MeOH) λ_{max} (log ε) 315 (4.5), 266 (4.3) nm; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 2; FABMS *m/z* 1079 [M - H]-; HRFABMS *m/z* 1079.2881 $[M-H]^-$ (calcd for $C_{48}H_{55}O_{28}$, 1079.2880).

Compound (**5**): yellowish gum; IR (KBr) ν_{max} 3374, 2922, 1710, 1655, 1600, 1514, 1491, 1450, 1348, 1209, 1180, 1073, 1024, 670 cm^{-1}; UV (MeOH) λ_{max} (log ε) 325 (4.0), 267 (3.8) nm; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 2; FABMS *m/z* 1093 $[M-H]^-$; HRFABMS *m/z* 1093.3064 $[M-H]^-$ (calcd for $C_{49}H_{57}O_{28}$, 1093.3036).

Compound (**6**): yellowish gum; IR (KBr) ν_{max} 3356, 2943, 2832, 1657, 1601, 1451, 1032, 670 cm^{-1}; UV (MeOH) λ_{max} (log ε) 320 (4.3), 267 (4.0) nm; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 2; FABMS *m/z* 1063 $[M-H]^-$; HRFABMS *m/z* 1063.2939 $[M-H]^-$ (calcd for $C_{48}H_{55}O_{27}$, 1063.2931).

Compound (**7**): yellowish gum; IR (KBr) ν_{max} 3361, 2941, 2831, 1658, 1601, 1450, 1285, 1165, 1031, 824, 670 cm^{-1}; UV (MeOH) λ_{max} (log ε) 323 (4.0), 267 (3.8) nm; ^{1}H-NMR data, see Table 1; ^{13}C-NMR data, see Table 2; FABMS *m/z* 1093 $[M-H]^-$; HRFABMS *m/z* 1093.3064 $[M-H]^-$ (calcd for $C_{49}H_{57}O_{28}$, 1093.3036).

Enzymatic hydrolysis of 1 and 3. Compound **1** (5 mg) along with 2 mL of H_2O and 5 mg of *β*-glucosidase (Emulsin) was shaken for 6 h at 37 °C.[15] The aqueous solution was then extracted with EtOAc three times, and the EtOAc extract was evaporated in *vacuo*. The EtOAc extract was purified using HPLC [Optimapak ODS-A, 250 × 4.6 mm; mobile phase: 40 % MeOH; Detector: RI; flow rate: 2.0 ml/min] to yield compound **8** (2.0 mg). The water layer was evaporated in *vacuo*. The water layer was purified using HPLC [Phenomenex Luna 5*μ* silica, 250 × 10 mm; EtOAc : MeOH : H_2O = 9 : 3 : 1; Detector: RI; flow rate: 2.0 ml/min]to yield sugar (2 mg), and sugar in the water layer was identified as D-glucose by co-TLC (EtOAc : MeOH : H_2O = 9 : 3 : 1, R_f value : 0.2) with a D-glucose standard (Aldrich

Co., USA). Compound **3** (10 mg) was treated in the same way to give compound **2** (4.0 mg) and D-glucose (4.0 mg).

Acid hydrolysis of 2. Compound **2** (10 mg) was shaken with 2 mL of 1M HCl for 1 h at 90 °C.[11] The hydrolysate was extracted with EtOAc, and the EtOAc extract was evaporated in *vacuo*. The EtOAc extract was purified using HPLC [Optimapak ODS-A, 250 × 4.6 mm; mobile phase: 55% MeOH; Detector: RI; flow rate: 2.0 ml/min] to yield kaempferol (3 mg).

Alkaline hydrolysis of 4. A solution of compound **4** (5 mg) in 0.05M KOH (2 mL) was stirred at room temperature for 2 h.[16] The reaction mixture was neutralized with Dowex HCR W2 (H^+ form) and the resin was removed by filtration. A portion of the reaction product was purified by HPLC [Optimapak ODS-A, 250 × 4.6 mm; mobile phase: 45% MeOH; Detector: RI; flow rate: 2.0 mL/min] to yield compound **4** (2.0 mg) and (*E*)-caffeic acid (1.0 mg).

Alkaline hydrolysis of 5 and 7. A solution of compound **5** (10 mg) in 0.05M KOH (3 mL) was stirred at room temperature for 7 h.[16] The reaction mixture was neutralized with Dowex HCR W2 (H^+ form) and the resin was removed by filtration. A portion of the reaction product was purified by HPLC [Optimapak ODS-A, 250 × 4.6 mm; mobile phase: 45% MeOH; Detector: RI; flow rate: 2.0 mL/min] to yield compound **3** (5.0 mg) and (*E*)-ferulic acid (2.0 mg). Compound **7** (11 mg) was treated using the same method to give compound **3** (7.0 mg) and (*E*)-ferulic acid (2.0 mg).

Alkaline hydrolysis of 6. A solution of compound **6** (5 mg) in 0.05M KOH (2 mL) was stirred at room temperature for 5 h.[16] The reaction mixture was neutralized with Dowex HCR W2 (H^+ form) and the resin was removed by filtration. A part of the reaction product was subjected to HPLC [Optimapak ODS-A, 250 × 4.6 mm; mobile phase: 45% MeOH; Detector: RI; flow rate: 2.0 mL/min] to yield compound **3** (2.0 mg) and (*E*)-*p*-coumaric acid (1.0 mg).

Determination of the sugar of compound 2. The sugar (3.0 mg) obtained from the hydrolysis of **2** was dissolved in anhydrous pyridine (0.1 mL) and L-cysteine methyl ester hydrochloride (2.0 mg) was added. The mixture was stirred at 60 °C for 1.5 h.[11] After the reaction mixture was dried in *vacuo*, the residue was trimethylsilylated with 1-trimethylsilylimidazole (0.1 mL) for 2 h. The mixture was partitioned between hexane and H_2O (0.3 mL, each), and the organic layer (1 μL) was analyzed by GC.[11] Identification of D-glucose and L-rhamnose for **2** were detected in each case by co-injection of the hydrolysate with standard silylated samples, giving single peaks at D-glucose (10.11 min) and L-rhamnose (5.58 min) of **2**, respectively.

Table 1. ^{1}H NMR Data of Compounds **1** - **7** (DMSO-d_6, 500 MHz, δ in ppm, J in Hz)[a]

H	1			2			3			4			5		
Flavonol															
6	6.42	d	(2.0)	6.19	d	(2.0)	6.44	d	(2.0)	6.35	d	(2.0)	6.35	d	(2.0)
8	6.77	d	(2.0)	6.39	d	(2.0)	6.74	d	(2.0)	3.72	d	(2.0)	6.72	d	(2.0)
2'	8.03	d	(8.8)	7.93	d	(8.8)	7.99	d	(8.8)	7.96	d	(8.8)	7.96	d	(8.8)
3'	6.88	d	(8.8)	6.86	d	(8.8)	6.89	d	(8.8)	6.87	d	(8.8)	6.87	d	(8.8)
5'	6.88	d	(8.8)	6.86	d	(8.8)	6.89	d	(8.8)	6.87	d	(8.8)	6.87	d	(8.8)
6'	8.03	d	(8.8)	7.93	d	(8.8)	7.99	d	(8.8)	7.96	d	(8.8)	7.96	d	(8.8)
Glc-I															
1"	5.50	d	(7.6)	5.33	d	(7.8)	5.37	d	(7.6)	5.38	d	(7.8)	5.35	d	(7.8)
2	3.25	m		3.20	m		3.24	m		3.22	m		3.24	m	
3	3.29	m		3.36	m		3.38	m		3.39	m		3.36	m	
4	3.18	m		3.30	m		3.35	m		3.32	m		3.34	m	
5	3.44	m		3.41	m		3.43	m		3.43	m		3.41	m	
6	3.68	m		3.73	m		3.76	m		3.75	m		3.74	m	
	3.48	m		3.44	m		3.44	m		3.46	m		3.50	m	
Glc-II															
1'''	5.06	d	(7.6)	4.13	d	(7.8)	4.16	d	(7.6)	4.14	d	(7.8)	4.13	d	(7.8)
2	3.25	m		2.95	m		2.96	t	(8.8)	2.95	t	(8.7)	2.95	t	(8.7)
3	3.40	m		3.12	m		3.13	m		3.12	m		3.13	m	
4	3.38	m		3.05	m		3.06	m		3.03	m		3.05	m	
5	3.27	m		3.18	m		3.18	m		3.18	m		3.18	m	
6	3.70			3.67	m		3.70	m		3.69	m		3.70	m	
	3.48			3.39	m		3.45	m		3.41	m		3.40	m	
Glc-III															
1''''	4.29	d	(7.6)				5.06	d	(7.6)	5.42	d	(7.8)	5.40	d	(7.8)
2	2.99	m					3.25	m		4.91	d	(8.8)	4.92	d	(8.8)
3	3.20	m					3.28	m		3.58	dd	(9.8, 8.8)	3.58	dd	(9.8, 8.8)
4	3.07	m					3.17	m		3.30	m		3.30	m	
5	3.19	m					3.43	m		3.56	m		3.57	m	
6	3.70	m					3.68	m		3.72	m		3.72	m	
	3.42	m					3.44	m		3.52	m		3.54	m	
Rha-I															
1'''''				4.40	s		4.43	s		4.41	d	(2.0)	4.40	d	(2.0)
2				3.43	m		3.45			3.43	m		3.41	m	
3				3.29	m		3.32			3.29	m		3.30	m	
4				3.08	m		3.07			3.05	m		3.06	m	
5				3.25	m		3.28			3.25	m		3.25	m	
6				0.92	d	(6.8)	0.93	d	(6.0)	0.92	d	(5.8)	0.90	d	(6.0)
Acyl															
2'''''										7.00	d	(2.0)	7.26	d	(2.0)
3															
5										6.73	d	(8.8)	6.75	d	(8.8)
6										6.97	dd	(8.8, 2.0)	7.07	dd	(8.8, 2.0)
α										6.25	d	(15.6)	6.44	d	(15.6)
β										7.48	d	(15.6)	7.56	d	(15.6)
-OMe													3.77	s	

[a] 500 MHz, DMSO-d_6; chemical shifts in ppm relative to TMS; coupling constants (J) in Hz.

Table 1. (Continued)

H	6			7			H	6			7		
Flavonol							Glc-III						
6	6.34	d	(2.0)	6.48	d	(2.0)	1""	5.39	d	(7.8)	5.25	d	(7.8)
8	6.71	d	(2.0)	6.78	d	(2.0)	2	4.91	d	(8.8)	3.49	m	
2'	7.98	d	(8.8)	7.98	d	(8.8)	3	3.55	dd	(9.8, 8.8)	5.05	t	(8.7)
3'	6.87	d	(8.8)	6.89	d	(8.8)	4	3.29	m		3.47	m	
5'	6.87	d	(8.8)	6.89	d	(8.8)	5	3.54	m		3.62	m	
6'	7.98	d	(8.8)	7.98	d	(8.8)	6	3.71	m		3.70	m	
Glc-I								3.52	m		3.54	m	
1"	5.37	d	(7.8)	5.38	d	(7.8)	Rha-I						
2	3.22	m		3.26	m		1""	4.40	d	(2.0)	4.42	d	(2.0)
3	3.37	m		3.40	m		2	3.42	m		3.50	m	
4	3.33	m		3.33	m		3	3.27	m		3.30	m	
5	3.42	m		3.44	m		4	3.08	m		3.09	m	
6	3.75	m		3.78	m		5	3.26	m		3.27	m	
	3.48	m		3.48	m		6	0.96	d	(5.8)	0.93	d	(6.4)
Glc-II							Acyl						
1""	4.15	d	(7.8)	4.14	d	(7.8)	2""	7.61	d	(8.8)	7.31	d	(2.0)
2	2.95	t	(8.7)	2.98	t	(8.7)	3	6.72	d	(8.8)			
3	3.12	m		3.12	m		5	6.72	d	(8.8)	6.79	d	(8.8)
4	3.06	m		3.08	m		6	7.61	d	(8.8)	7.11	dd	(8.8, 2.0)
5	3.19	m		3.21	m		α	6.35	d	(15.8)	6.48	d	(15.8)
6	3.70	m		3.72	m		β	7.56	d	(15.8)	7.56	d	(15.8)
	3.41	m		3.43	m		-OMe				3.81	s	(2.0)
-OMe				3.81	s								

[a] 500 MHz, DMSO-d_6; chemical shifts in ppm relative to TMS; coupling constants (J) in Hz.

Table 2. ^{13}C NMR Data of Compounds **1** - **7** (DMSO-d_6, 125 MHz, δ in ppm)[b]

C	1	2	3	4	5	6	7
Flavonol							
2	157.6	157.6	156.8	156.7	156.7	158.1	158.2
3	134.1	133.8	134.1	134.2	134.2	134.2	134.1
4	178.3	177.9	178.2	178.2	178.2	178.2	178.2
5	161.5	161.9	161.6	161.6	161.6	161.7	161.6
6	100.1	99.5	100.1	99.9	99.9	99.9	100.2
7	163.6	165.1	163.4	162.8	162.9	162.8	163.3
8	95.2	94.5	95.4	95.4	95.4	95.4	95.4
9	156.7	157.2	158.2	158.1	158.1	159.6	156.8
10	106.3	104.6	106.5	106.6	106.6	106.6	106.5
1'	121.4	121.5	121.7	121.3	121.3	121.2	121.3
2'	131.7	131.5	131.6	131.6	131.6	131.6	131.6
3'	115.9	115.9	115.9	115.9	115.9	115.9	115.9
4'	160.8	160.8	160.9	160.1	160.8	160.9	160.8
5'	115.9	115.9	115.9	115.9	115.9	115.9	115.9
6'	131.7	131.5	131.6	131.6	131.6	131.6	131.6
Glc-I							
1"	101.2	101.8	101.6	101.6	101.6	101.6	101.6
2	74.6	74.7	74.7	74.5	74.6	74.6	74.6
3	77.1	75.3	75.3	75.3	75.3	75.3	75.3
4	70.3	80.9	80.9	80.9	80.9	80.9	80.9
5	77.9	74.4	74.5	74.5	74.5	74.5	74.5
6	60.9	66.7	66.7	66.7	66.7	66.7	66.8

Glc-II							
1'''	100.5	104.2	104.2	104.2	104.2	104.1	104.2
2	73.8	73.7	73.9	73.8	73.8	73.7	73.8
3	75.4	77.2	77.1	77.1	77.1	76.9	77.2
4	80.8	70.7	70.7	70.7	70.7	70.6	70.7
5	76.1	77.5	77.5	77.5	77.5	77.5	77.5
6	61.3	61.8	61.8	61.8	61.8	61.8	61.8
Glc-III							
1''''	103.8		100.6	98.2	98.2	98.2	100.1
2	74.0		73.8	73.8	73.8	73.8	72.1
3	77.5		77.1	74.6	74.6	74.5	77.9
4	70.7		70.3	70.4	70.5	70.3	68.2
5	77.5		77.8	78.1	78.1	77.9	77.6
6	61.7		61.3	61.2	61.2	61.1	61.0
Rha-I							
1'''''		101.3	101.3	101.2	101.2	101.4	101.3
2		71.1	71.1	71.1	71.1	71.1	71.1
3		71.4	71.4	71.3	71.4	71.4	71.4
4		72.5	72.5	72.5	72.5	72.3	72.5
5		68.9	68.9	68.9	68.9	68.9	68.9
6		18.4	18.4	18.4	18.4	18.4	18.4
Acyl							
1''''''				126.1	126.2	126.0	126.4
2				115.5	111.8	133.2	111.8
3				146.3	148.6	115.6	148.7
4				149.2	150.1	156.7	149.9
5				116.5	116.2	115.6	116.2
6				122.1	124.0	133.2	123.7
α				114.4	115.0	114.8	115.8
β				146.3	146.1	146.1	145.5
C=O				166.2	166.3	165.7	166.9
-OMe					56.4		56.4

[b] 500 MHz, DMSO-d_6; chemical shifts in ppm relative to TMS.

ACKNOWLEDGEMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (20100029358). We thank Drs. E. J. Bang, S. G. Kim, and J. J. Seo at the Korea Basic Science Institute for their aid in obtaining the NMR and mass spectra.

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