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A New Flavonol Glycoside from *Hylomecon vernalis*

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Purification of a MeOH extract from the aerial parts of *Hylomecon vernalis* Maxim. (Papaveraceae) using column chromatography furnished a new acetylated flavonol glycoside (**1**), together with twenty known phenolic compounds (**2-21**). Structural elucidation of **1** was based on 1D- and 2D-NMR spectroscopy data analysis to be quercetin 3-*O*-[4'''-*O*-acetyl-α-L-arabinopyranosyl]-(1'''→6'')-β-D-galactopyranoside (**1**). The structures of compounds **2-21** were elucidated by spectroscopy and confirmed by comparison with reported data; quercetin 3-*O*-[2'''-*O*-acetyl-α-L-arabinopyranosyl]-(1'''→6'')-β-D-galactopyranoside (**2**), quercetin 3-*O*-α-L-arabinopyranosyl-(1'''→6'')-β-D-galactopyranoside (**3**), quercetin 3-*O*-β-D-galactopyranoside (**4**), kaempferol 3,7-*O*-α-L-dirhamnopyranoside (**5**), diosmetin 7-*O*-β-D-glucopyranoside (**6**), diosmetin 7-*O*-β-D-xylopyranosyl-(1'''→6'')-β-D-glucopyranoside (**7**), *p*-hydroxybenzoic acid (**8**), protocatechuic acid (**9**), caffeic acid (**10**), 6-hydroxy-3,4-dihydro-1-oxo-β-carboline (**11**), (*Z*)-3-hexenyl-β-D-glucopyranoside (**12**), (*E*)-2-hexenyl-β-D-glucopyranoside (**13**), (*Z*)-3-hexenyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**14**), oct-1-en-3-yl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**15**), benzyl-β-D-apiofuranosyl-(1''→6')-β-D-glucopyranoside (**16**), benzyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**17**), benzyl-β-D-xylopyranosyl-(1''→6')-β-D-glucopyranoside (**18**), 2-phenylethyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**19**), 2-phenylethyl-β-D-apiofuranosyl-(1''→6')-β-D-glucopyranoside (**20**), and aryl-β-D-glucopyranoside (**21**). Compounds **2-21** were isolated for the first time from this plant. The isolated compounds were tested for cytotoxicity against four human tumor cell lines *in vitro* using a Sulforhodamin B bioassay.

Key words: *Hylomecon vernalis*, Papaveraceae, Acetylated flavonol glycoside

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INTRODUCTION

Hylomecon vernalis Maxim. is an east Asian herbaceous medicinal plant belonging to the Papaveraceae. *H. vernalis* is widely distributed in the mountainous regions of Korea and China (Lee, 1996). *H. vernalis* has been used in Chinese folk medicine for the treatment of arthritis, neuralgia, and eczema (Kim et al., 2003). Previous phytochemical and pharmacological studies on this plant reported the isolation of several alkaloids and reported to have anti-inflammatory, antispasmodic, antimicrobial, and anti-tumoral activities (Kang et al., 2003). We have investigated constituents from the aerial parts of *H. vernalis* as part of our continuing study on the constituents of Korean medicinal plant sources. Column chromatography separation of constituents in the MeOH extract of *H. vernalis* resulted in the isolation of twenty one compounds, including a new acetylated flavonol glycoside (**1**). Their structures were determined by spectroscopic methods. Compound **1** was newly isolated from natural sources, and compounds **2-21** were isolated for the first time from this particular plant. The isolated compounds were tested for cytotoxicity against four human tumor cells *in vitro* using a Sulforhodamin B bioassay.

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MATERIALS AND METHODS

General experimental procedure

Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. Optical rotations were measured on a JASCO P-1020 Polarimeter. IR spectra were recorded on a Bruker IFS-66/S FT-IR spectrometer. UV spectra were recorded with a Shimadzu UV-1601 UV-Visible spectrophotometer. NMR spectra were recorded on a Varian UNITY INOVA 500 NMR spectrometer. ESI and HR-ESI mass spectra were obtained on a VG BIOTECH platform LC-mass spectrometer. Preparative HPLC was performed using a Gilson 306 pump with a Shodex refractive index detector and an Apollo Silica 5 μ column (250 × 22 mm) or an Econosil® RP-18 10 μ column (250 × 22 mm). Silica gel 60 (Merck, 70~230 mesh and 230~400 mesh) was used for column chromatography. TLC was performed using Merck precoated Silica gel F_{254} plates and RP-18 F_{254s} plates. The packing material for molecular sieve column chromatography was Sephadex LH-20 (Pharmacia Co.). Low-pressure liquid chromatography was performed over Merck LiChroprep Lobar®-A Si 60 (240 × 10 mm) or LiChroprep Lobar®-A RP-18 (240 × 10 mm) columns with a FMI QSY-0 pump (ISCO).

Plant materials

The aerial parts of *Hylomecon vernalis* Maxim. were collected at Taebaek mountain in Ganawon-Do province, Korea in May 2009. A voucher specimen (SKKU-2009-002) was deposited at the School of Pharmacy in Sungkyunkwan University.

Extraction and isolation

The half dried aerial parts of *H. vernalis* (2.6 kg) were extracted at room temperature with 80% MeOH and evaporated under reduced pressure to give a residue (240 g), that was dissolved in water (800 mL three times) and then partitioned into a series of other solvents. These solvents, and the residues found in each were as follows; *n*-hexane (40 g), CH_2Cl_2 (1 g), EtOAc (3 g), and *n*-BuOH (30 g). The EtOAc fraction (3 g) was separated over a silica gel column with a solvent system of (*n*-hexane-$CHCl_3$-MeOH = 10:5:1 – $CHCl_3$-MeOH = 1:1) as the eluant to give fifteen fractions (E1-E15). Fraction E3 was purified with a silica gel prep HPLC ($CHCl_3$-MeOH = 12:1) to yield compound **8** (5 mg, R_t = 12 min). Fraction E6 was subjected to Sephadex LH-20 column chromatography (80% MeOH) as the eluant to give three subfractions (E61-E63). Subfraction E63 (60 mg) was purified with a silica gel prep HPLC ($CHCl_3$-MeOH = 12:1) to yield compound **9** (4 mg, R_t = 13 min), **10** (4 mg, R_t = 15 min) and **11** (5 mg, R_t = 16 min). Fraction E8 was subjected to Sephadex LH-20 column chromatography (80% MeOH) as the eluant to give five subfractions (E81-E85). Subfraction E82 (40 mg) was purified with an RP-C_{18} prep HPLC (50% MeOH) to yield compound **4** (17 mg, R_t = 12 min). Subfraction E83 (40 mg) was purified with an RP-C_{18} prep HPLC (55% MeOH) to yield compound **5** (17 mg, R_t = 11 min). Subfraction E84 (40 mg) was purified with an RP-C_{18} prep HPLC (50% MeOH) to yield compound **1** (15 mg, R_t = 11 min) and **6** (12 mg, R_t = 15 min). Fraction E13 was separated over a RP-C_{18} Lobar A®-column with a solvent system of 40% MeOH as the eluant to give four subfractions (E131-E134). Subfraction E133 (20 mg) was purified with an RP-C_{18} prep HPLC (50% MeOH) to yield compound **3** (9 mg, R_t = 12 min). The n-BuOH soluble fraction (30 g) was chromatographed on a diaion HP-20, and eluted using a gradient solvent system that varied from 100% water to 100% MeOH. This gave two subfraction. Fraction B (8 g) was separated over a silica gel column with a solvent system of ($CHCl_3$-MeOH-Water = 10:5:1 – 6:4:1) as the eluant to give thirteen fractions (B1-B13). Fraction B3 was separated over an RP-C_{18} Lobar A®-column with a solvent system of 40% MeOH as the eluant to give three subfractions (B31-B33). Subfraction B32 (80 mg) was purified with an RP-C_{18} prep HPLC (50% MeOH) to yield compound **12** (8 mg, R_t = 15 min) and **13** (5 mg, R_t = 16 min). Fraction B4 was separated over an RP-C_{18} Lobar A®-column with a solvent system of 45% MeOH as the eluant to give four subfractions (B41-B44). Subfraction B44 (17 mg) was purified with a silica gel prep HPLC (CH_2Cl_2-MeOH = 5:1) to yield compound **21** (5 mg, R_t = 12 min). Fraction B5 was separated over an RP-C_{18} Lobar A®-column with a solvent system of 45% MeOH as the eluant to give five subfractions (B51-B55). Subfraction B53 (50 mg) was purified with an RP-C_{18} prep HPLC (45% MeOH) to yield compound **20** (10 mg, R_t = 17 min). Subfraction B55 (15 mg) was purified with a RP-C_{18} prep HPLC (50% MeOH) to yield compound **15** (5 mg, R_t = 15 min). Fraction B6 was was separated over an RP-C_{18} silica gel column with a solvent system of 45% MeOH as the eluant to give three subfractions (B61-B63). Subfraction B61 (60 mg) was purified with a silica gel prep HPLC ($CHCl_3$-MeOH-H_2O = 9:4:0.5) to yield compounds **16** (5 mg, R_t = 13 min), **17** (5 mg, R_t = 14 min), and **18** (8 mg, R_t = 16 min). Subfraction B62 (30 mg) was purified with an RP-C_{18} prep HPLC (50% MeOH) to yield compound **19** (13 mg, R_t = 13 min). Subfraction B63 (35 mg) was purified with an RP-C_{18} prep HPLC (50% MeOH) to yield compound **14** (12 mg, R_t =

15 min). Fraction B7 was was separated over an RP-C_{18} silica gel column with a solvent system of 50% MeOH as the eluant to give four subfractions (B71-B74). Subfraction B71 (35 mg) was purified with an RP-C_{18} prep HPLC (30% MeCN) to yield compound **7** (15 mg, R_t = 11 min). Fraction B8 was separated over an RP-C_{18} Lobar A®-column with a solvent system of 35% MeOH as the eluant to give four subfractions (B81-B84). Subfraction B84 (100 mg) was subjected to Sephadex LH-20 column chromatography (90% MeOH) as the eluant to give fractions purified with an RP-C_{18} prep HPLC (20% MeCN) to yield compound **2** (15 mg, R_t = 15 min).

Quercetin 3-*O*-[4'''-*O*-acetyl-α-L-arabinopyranosyl]-(1'''→6'')-β-D-galactopyranoside (1)

Yellow gum, $[\alpha]_D^{25}$ –80° (*c* 0.08, MeOH); IR (KBr) ν_{max} cm^{-1}: 3401, 1646, 1528, 1366, 1021, 672; UV [MeOH) nm (log ε): 258 (4.91), 362 (4.84); HR-ESI-MS *m/z* (rel. int.): 661.1375 $[M + Na]^+$ (calcd for: 661.1375); ^{1}H-NMR (500 MHz, DMSO-d_6): 12.61 (C_5-OH), 7.77 (1H, dd, *J* = 8.8, 2.3 Hz, H-6'), 7.62 (1H, d, *J* = 2.3 Hz, H-2'), 6.83 (1H, d, *J* = 8.8 Hz, H-5'), 6.42 (1H, s, H-8), 6.20 (1H, s, H-6), 5.26 (1H, d, *J* = 7.6 Hz, H-1''), 4.06 (1H, *J* = 6.4 Hz, H-1'''), 1.98 (3H, s, $COCH_3$) and ^{13}C-NMR (125 MHz, DMSO-d_6): 178.1 (C-4), 170.6 (C=O), 164.3 (C-7), 161.9 (C-5), 157.0 (C-2, 9), 149.2 (C-4'), 145.5 (C-3'), 134.2 (C-3), 122.78 (C-6'), 121.7 (C-1'), 116.6 (C-5'), 115.9 (C-2'), 104.6 (C-10), 103.5 (C-1'''), 102.6 (C-1''), 99.4 (C-6), 94.2 (C-8), 75.0 (C-5''), 73.7 (C-3''), 71.7 (C-2'''), 71.5 (C-4'''), 71.4 (C-2''), 71.2 (C-3'''), 68.9 (C-4''), 67.6 (C-6''), 63.4 (C-5'''), 21.6($COCH_3$).

Quercetin 3-*O*-[2'''-*O*-acetyl-α-L-arabinopyranosyl]-(1'''→6'')-β-D-galactopyranoside (2)

Yellow gum; FAB-MS m/z: 639 $[M+H]^+$; ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 12.65 (1H, brs, 5-OH), 7.77 (1H, dd, *J* = 8.5, 2.5 Hz, H-6'), 7.63 (1H, d, *J* = 2.5 Hz, H-2'), 6.83 (1H, d, *J* = 8.5 Hz, H-5'), 6.42 (1H, brs, H-8), 6.20 (1H, brs, H-6), 5.26 (1H, d, *J* = 7.5 Hz, H-1''), 4.06 (1H, d, *J* = 8.0 Hz, H-1'''), 1.65 (3H, s, $CO\underline{CH_3}$); ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 177.9 (C-4), 169.7 ($\underline{C}$=O), 164.8 (C-7), 161.7 (C-5), 156.8 (C-9), 156.6 (C-2), 149.1 (C-4'), 145.4 (C-3'), 134.0 (C-3), 122.5 (C-6'), 121.4 (C-1'), 116.3 (C-5'), 115.7 (C-2'), 104.4 (C-10), 102.5 (C-1''), 100.9 (C-1'''), 99.2 (C-6), 94.1 (C-8), 76.1 (C-5''), 73.2 (C-3''), 72.5 (C-2'''), 71.4 (C-2''), 70.8 (C-3'''), 69.2 (C-4''), 68.4 (C-4'''), 67.4 (C-6''), 66.1 (C-5'''), 20.7 (CH_3).

Quercetin 3-*O*-α-L-arabinopyranosyl-(1'''→6'')-β-D-galactopyranoside (3)

Yellow solid; mp 252-253°C; $[\alpha]_D^{25}$ –87° (*c* 0.44 in MeOH); FAB-MS m/z: 597 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.67 (1H, dd, *J* = 8.2, 2.3 Hz, H-6'), 7.57 (1H, d, *J* = 2.3 Hz, H-2'), 6.86 (1H, d, *J* = 8.2 Hz, H-5'), 6.37 (1H, brs, H-8), 6.17 (1H, brs, H-6), 5.30 (1H, d, *J* = 7.6 Hz, H-1''), 3.99 (1H, d, *J* = 6.4 Hz, H-1'''); ^{13}C-NMR (CD_3OD, 125 MHz): δ 178.1 (C-4), 164.9 (C-7), 161.9 (C-5), 157.0 (C-2, 9), 149.2 (C-4'), 145.5 (C-3'), 134.2 (C-3), 122.7 (C-6'), 121.8 (C-1'), 116.6 (C-5'), 115.9 (C-2'), 104.6 (C-10), 103.3 (C-1'''), 102.5 (C-1''), 99.4 (C-6), 94.2 (C-8), 75.0 (C-5''), 73.7 (C-3''), 73.1 (C-3'''), 71.1 (C-2''), 71.1 (C-2'''), 68.9 (C-4''), 68.0 (C-4'''), 67.2 (C-6''), 65.6 (C-5''').

Quercetin 3-*O*-β-D-galactopyranoside (Hyperin) (4)

Yellow powder; mp 253-254°C; FAB-MS m/z: 465 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.68 (1H, dd, *J* = 8.2, 2.3 Hz, H-6'), 7.57 (1H, d, *J* = 2.3 Hz, H-2'), 6.93 (1H, d, *J* = 8.2 Hz, H-5'), 6.40 (1H, brs, H-8), 6.20 (1H, brs, H-6), 5.37 (1H, d, *J* = 7.6 Hz, H-1''); ^{13}C-NMR (CD_3OD, 125 MHz): δ 178.2 (C-4), 164.9 (C-7), 161.9 (C-5), 156.9 (C-2, 9), 149.2 (C-4'), 145.5 (C-3'), 134.2 (C-3), 122.7 (C-6'), 121.8 (C-1'), 116.6 (C-5'), 115.9 (C-2'), 104.6 (C-10), 102.5 (C-1''), 99.4 (C-6), 94.2 (C-8), 76.5 (C-5''), 73.9 (C-3''), 71.9 (C-2''), 68.6 (C-4''), 60.8 (C-6'').

Kaempferol 3,7-*O*-α-L-dirhamnopyranoside (5)

Yellow powder; mp 209-213°C; FAB-MS m/z: 579 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.79 (2H, d, *J* = 8.5 Hz, H-2', 6'), 6.94 (2H, d, *J* = 8.0 Hz, H-3', 5'), 6.72 (1H, brs, H-8), 6.46 (1H, brs, H-6), 5.57 (1H, d, *J* = 1.5 Hz, H-1'''), 5.40 (1H, d, *J* = 1.5 Hz, H-1''), 1.26 (1H, d, *J* = 6.0 Hz, H-6'''), 0.93 (1H, d, *J* = 6.0 Hz, H-6''); ^{13}C-NMR (CD_3OD, 125 MHz): δ 178.6 (C-4), 162.3 (C-7), 161.8 (C-5), 160.6 (C-4'), 158.6 (C-2), 156.9 (C-9), 135.3 (C-3), 130.8 (C-2', 6'), 121.2 (C-1'), 115.4 (C-3', 5'), 106.4 (C-10), 102.3 (C-1''), 99.4 (C-1'''), 98.7 (C-6), 94.4 (C-8), 72.4 (C-4''), 72.0 (C-4'''), 70.9 (C-3''), 70.8 (C-3'''), 70.5 (C-2'''), 70.4 (C-2''), 70.1 (C-5''), 70.0 (C-5'''), 16.8 (C-6'''), 16.5 (C-6'').

Diosmetin-7-*O*-β-D-glucopyranoside (6)

Yellow solid; FAB-MS m/z: 463 $[M+H]^+$; ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 12.94 (1H, brs, 5-OH), 7.58 (1H, dd, *J* = 8.2, 2.3 Hz, H-6'), 7.46 (1H, d, *J* = 2.3 Hz, H-2'), 7.11 (1H, d, *J* = 8.2 Hz, H-5'), 6.83 (1H, s, H-3), 6.82 (1H, d, *J* = 2.3 Hz, H-8), 6.45 (1H, d, *J* = 2.3 Hz, H-6), 5.08 (1H, d, *J* = 7.6 Hz, H-1''), 3.88 (1H, s, -OCH_3); ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 182.6 (C-4), 164.8 (C-7), 163.7 (C-2), 161.8 (C-5), 157.7 (C-9), 152.0 (C-4'), 147.5 (C-3'), 123.6 (C-1'), 119.6 (C-6'), 113.9 (C-2'), 112.9 (C-5'), 106.1 (C-3), 104.5 (C-10), 100.6 (C-1''),

100.2 (C-8), 95.5 (C-6), 77.8 (C-5''), 77.1 (C-3''), 73.8 (C-2''), 70.3 (C-4''), 61.3 (C-6''), 56.6 (O<u>C</u>H$_3$).

Diosmetin-7-*O*-β-D-xylopyranosyl-(1'''→6'')-β-D-glucopyranoside (7)
Yellow solid; mp 262-264°C; FAB-MS m/z: 595 $[M+H]^+$; ^{1}H-NMR (DMSO-d_6, 500 MHz): δ 12.94 (1H, brs, 5-OH), 7.60 (1H, dd, *J* = 8.2, 2.3 Hz, H-6'), 7.53 (1H, d, *J* = 2.3 Hz, H-2'), 7.15 (1H, d, *J* = 8.2 Hz, H-5'), 6.82 (1H, s, H-3), 6.81 (1H, d, *J* = 2.3 Hz, H-8), 6.48 (1H, d, *J* = 2.3 Hz, H-6), 5.05 (1H, d, *J* = 7.0 Hz, H-1''), 4.17 (1H, d, *J* = 7.6 Hz, H-1'''), 3.88 (1H, s, -OCH$_3$); ^{13}C-NMR (DMSO-d_6, 125 MHz): δ 182.6 (C-4), 164.9 (C-7), 163.7 (C-2), 161.8 (C-5), 157.7 (C-9), 152.0 (C-4'), 147.5 (C-3'), 123.6 (C-1'), 119.6 (C-6'), 113.9 (C-2'), 112.9 (C-5'), 106.1 (C-3), 104.8 (C-10), 104.5 (C-1'''), 100.6 (C-1''), 100.4 (C-8), 95.5 (C-6), 77.2 (C-5''), 76.9 (C-3''), 76.3 (C-3'''), 74.1 (C-2'''), 73.8 (C-2''), 70.2 (C-4''), 70.1 (C-4'''), 69.1 (C-6''), 66.3 (C-5'''), 56.6 (O<u>C</u>H$_3$).

***p*-Hydroxybenzoic acid (8)**
White amorphous powder; mp 211-212°C; EI-MS m/z: 138 $[M]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.87 (2H, d, *J* = 8.8 Hz, H-2, 6), 6.82 (2H, d, *J* = 8.8 Hz, H-3, 5); ^{13}C-NMR (CD_3OD, 125 MHz): δ 170.1 (C=O), 162.1 (C-4), 131.8 (C-2, 6), 122.9 (C-1), 5), 115.6 (C-3, 5).

Protocatechuic acid (9)
White amorphous powder; mp 211-212°C; EI-MS m/z: 154 $[M]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.43 (1H, d, *J* = 1.8 Hz, H-2), 7.40 (1H, dd, *J* = 8.0, 1.8 Hz, H-6), 6.79 (1H, d, *J* = 8.0 Hz, H-5); ^{13}C-NMR (CD_3OD, 125 MHz): δ 169.1 (C=O), 150.3 (C-4), 144.9 (C-3), 122.7 (C-6), 122.1 (C-1), 116.6 (C-2), 114.6 (C-5).

Caffeic acid (10)
White amorphous powder; mp 193-194°C; EI-MS m/z: 180 $[M]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.52 (1H, d, *J* = 15.8 Hz, H-7), 7.03 (1H, d, *J* = 2.3 Hz, H-2), 6.93 (1H, dd, *J* = 8.2, 2.3 Hz, H-6), 6.78 (1H, d, *J* = 8.2 Hz, H-5), 6.23 (1H, d, *J* = 15.8 Hz, H-8); ^{13}C-NMR (CD_3OD, 125 MHz): δ 169.8 (C-9), 148.2 (C-4), 145.6 (C-7), 145.6 (C-3), 126.7 (C-1), 121.6 (C-6), 115.3 (C-5), 114.5 (C-8), 113.9 (C-2).

6-Hydroxy-3,4-dihydro-1-oxo-β-carboline (11)
Colorless gum; mp 182-184°C; FAB-MS m/z: 203 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.27 (1H, d, *J* = 9.0 Hz, H-8), 6.90 (1H, d, *J* = 2.5 Hz, H-5), 6.84 (1H, d, *J* = 9.0, 2.5 Hz, H-7), 3.61 (1H, t, *J* = 7.0 Hz, H-3), 2.94 (1H, t, *J* = 7.0 Hz, H-4); ^{13}C-NMR (CD_3OD, 125 MHz): δ 163.9 (C-1), 151.0 (C-6), 133.1 (C-8a) 126.8 (C-9a), 125.9 (C-4b), 119.1 (C-4a), 115.7 (C-7), 112.9 (C-8), 103.1 (C-5), 41.6 (C-3), 20.4 (C-4).

(*Z*)-3-Hexenyl-β-D-glucopyranoisde (12)
Colorless amorphous solid; $[\alpha]_D^{25}$ −38.0° (c 0.48 in EtOH); FAB-MS m/z: 261 $[M-H]^-$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 5.45 (1H, m, H-4), 5.37 (1H, m, H-3), 4.26 (1H, d, *J* = 7.5 Hz, H-1'), 2.38 (1H, q, *J* = 7.0 Hz, H-2), 2.08 (1H, quintet, *J* = 7.0 Hz, H-5), 0.97 (1H, t, *J* = 7.6 Hz, H-6); ^{13}C-NMR (CD_3OD, 125 MHz): δ 133.3 (C-3), 124.7 (C-4), 103.2 (C-1'), 76.9 (C-5'), 76.8 (C-3'), 73.9 (C-2'), 70.5 (C-4'), 69.3 (C-1), 61.6 (C-6'), 27.6 (C-2), 20.3 (C-5), 13.4 (C-6).

(*E*)-3-Hexenyl-β-D-glucopyranoisde (13)
Colorless amorphous solid; $[\alpha]_D^{25}$ −28.3° (c 0.48 in EtOH); FAB-MS m/z: 261 $[M-H]^-$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 5.75 (1H, m, H-4), 5.60 (1H, m, H-3), 4.29 (1H, d, *J* = 7.5 Hz, H-1'), 2.04 (1H, q, *J* = 7.0 Hz, H-2), 1.42 (1H, quintet, *J* = 7.0 Hz, H-5), 0.92 (1H, t, *J* = 7.6 Hz, H-6); ^{13}C-NMR (CD_3OD, 125 MHz): δ 134.7 (C-3), 126.2 (C-4), 101.8 (C-1'), 76.9 (C-5'), 76.8 (C-3'), 73.9 (C-2'), 70.5 (C-4'), 69.3 (C-1), 61.6 (C-6'), 34.3 (C-2), 22.2 (C-5), 12.8 (C-6).

(*Z*)-3-Hexenyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoisde (14)
Colorless amorphous solid; $[\alpha]_D^{25}$ −38.0° (c 0.48 in EtOH); FAB-MS m/z: 395 $[M-H]^-$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 5.45 (1H, m, H-4), 5.37 (1H, m, H-3), 4.31 (1H, d, *J* = 7.0 Hz, H-1''), 4.26 (1H, d, *J* = 7.6 Hz, H-1'), 2.38 (1H, q, *J* = 7.0 Hz, H-2), 2.08 (1H, quintet, *J* = 7.0 Hz, H-5), 0.97 (1H, t, *J* = 7.6 Hz, H-6); ^{13}C-NMR (CD_3OD, 125 MHz): δ 133.3 (C-3), 124.7 (C-4), 103.9 (C-1''), 103.2 (C-1'), 76.7 (C-5'), 75.7 (C-3'), 73.9 (C-2'), 73.0 (C-3''), 71.2 (C-2''), 70.4 (C-4'), 69.4 (C-1), 68.2 (C-6', 4''), 65.5 (C-5''), 27.6 (C-2), 20.3 (C-5), 13.4 (C-6).

Oct-1-en-3-yl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoisde (15)
Colorless gum; $[\alpha]_D^{25}$ −27.0° (c 0.3 in MeOH); FAB-MS m/z: 445 $[M+Na]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 5.86 (1H, m, H-2), 5.22 (1H, brd, *J* = 17.6 Hz, H-1a), 5.10 (1H, d, *J* = 10.5 Hz, H-1b), 4.33 (1H, d, *J* = 6.4 Hz, H-1''), 4.32 (1H, d, *J* = 8.2 Hz, H-1'), 4.12 (1H, q, *J* = 7.0 Hz, H-3), 1.66 (1H, m, H-4), 1.52 (1H, m, H-4), 1.30-1.40 (3H, m, H-5, 6, 7); ^{13}C-NMR (CD_3OD, 125 MHz): δ 139.7 (C-2), 114.9 (C-1), 103.7 (C-1''), 102.2 (C-1'), 76.7 (C-3'), 75.7 (C-5'), 74.1 (C-2'), 73.0 (C-3''), 71.2 (C-2''), 70.4 (C-4'), 68.1 (C-6'), 68.0 (C-6', 4''), 65.2 (C-5'')

Benzyl-β-D-apiofuranosyl-(1''→6')-β-D-glucopyranoside (16)
Colorless gum; FAB-MS m/z: 425 $[M+Na]^+$; ^{1}H-NMR

(CD_3OD, 500 MHz): δ 7.25-7.43 (5H, m, phenyl), 5.05 (1H, d, *J* = 2.3 Hz, H-1''), 4.88 (1H, d, *J* = 11.7 Hz, H-7a), 4.65 (1H, d, *J* = 11.7 Hz, H-7b), 4.32 (1H, d, *J* = 8.2 Hz, H-1'); ^{13}C-NMR (CD_3OD, 125 MHz): δ 137.8, 128.1, 128.0, 127.5 (phenyl), 109.9 (C-1''), 102.0 (C-1), 79.4 (C-3''), 76.8 (C-3', 2''), 75.8 (C-5'), 73.9 (C-4''), 73.8 (C-2'), 70.6 (C-7, 4'), 67.5 (C-6''), 64.4 (C-5'').

Benzyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (17)

Colorless gum; FAB-MS m/z: 403 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.26-7.43 (5H, m, phenyl), 4.90 (1H, d, *J* = 11.7 Hz, H-7a), 4.66 (1H, d, *J* = 11.7 Hz, H-7b), 4.36 (1H, d, *J* = 8.2 Hz, H-1'), 4.34 (1H, d, *J* = 6.4 Hz, H-1''); ^{13}C-NMR (CD_3OD, 125 MHz): δ 137.9, 128.1, 128.0, 127.5 (phenyl), 104.0 (C-1''), 102.2 (C-1'), 76.8 (C-3'), 75.8 (C-5'), 73.9 (C-2'), 73.0 (C-3''), 71.2 (C-2''), 70.7 (C-7), 70.6 (C-2''), 68.3 (C-4''), 68.2 (C-6'), 65.5(C-5'').

Benzyl-β-D-xylopyranosyl-(1''→6')-β-D-glucopyranoside (18)

Colorless gum; FAB-MS m/z: 403 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.24-7.43 (5H, m, phenyl), 4.90 (1H, d, *J* = 11.5 Hz, H-7a), 4.66 (1H, d, *J* = 11.5 Hz, H-7b), 4.35 (1H, d, *J* = 8.0 Hz, H-1', 1''); ^{13}C-NMR (CD_3OD, 125 MHz): δ 137.9, 128.1, 128.0, 127.5 (phenyl), 104.4 (C-1''), 102.2 (C-1'), 76.8 (C-3'), 76.6 (C-5'), 75.9 (C-3''), 73.9 (C-2''), 73.8 (C-2'), 70.7 (C-7), 70.4 (C-4''), 70.0 (C-4'), 68.7 (C-6'), 65.7 (C-5'').

2-Phenylethyl-β-D-apiofuranosyl-(1''→6')-β-D-glucopyranoside (19)

Colorless gum; FAB-MS m/z: 439 $[M+Na]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.16-7.24 (5H, m, phenyl), 5.00 (1H, d, *J* = 2.3 Hz, H-1'), 4.24 (1H, d, *J* = 7.6 Hz, H-1), 4.03 (1H, dt, *J* = 9.9, 7.6 Hz, OCH_bHCH_2Ph), 3.76 (1H, dd, *J* = 11.1, 5.8 Hz, $OCHH_aCH_2Ph$), 2.93 (2H, t, *J* = 7.6 Hz, CH_2CH_2Ph); ^{13}C-NMR (CD_3OD, 125 MHz): δ 138.9, 128.8, 128.3, 126.0 (phenyl), 109.8 (C-1''), 103.3 (C-1'), 79.3 (C-3''), 76.8, (C-3', 2''), 76.8 (C-1), 75.7 (C-5'), 73.9 (C-4''), 73.8 (C-2'), 70.6 (OCH_2CH_2Ph), 70.6 (C-4'), 67.5 (C-6'), 64.5 (C-5''), 36.1 (CH_2CH_2Ph).

2-Phenylethyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (20)

Colorless gum; FAB-MS m/z: 417 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.14-7.26 (5H, m, phenyl), 4.36 (1H, d, *J* = 7.6 Hz, H-1'), 4.30 (1H, d, *J* = 7.6 Hz, H-1), 4.08 (1H, dt, *J* = 9.9, 7.6 Hz, OCH_bHCH_2Ph), 3.77 (1H, m, $OCHH_aCH_2Ph$), 2.93 (2H, t, *J* = 7.6 Hz, CH_2CH_2Ph); ^{13}C-NMR (CD_3OD, 125 MHz): δ 138.9, 128.8, 128.2, 126.0 (phenyl), 103.9 (C-1''), 103.2 (C-1'), 76.8 (C-3'), 75.8 (C-5'), 73.8 (C-2'), 73.0 (C-3''), 71.2 (C-2''), 70.6 (OCH_2CH_2Ph), 70.3 (C-2''), 68.3 (C-4''), 68.2 (C-6'), 65.7 (C-5''), 36.1 (CH_2CH_2Ph).

Aryl-β-D-glucopyranoside (21)

Colorless gum; FAB-MS m/z: 301 $[M+H]^+$; ^{1}H-NMR (CD_3OD, 500 MHz): δ 7.06 (2H, d, *J* = 8.2 Hz, H-2, 6), 6.70 (1H, d, *J* = 8.2 Hz, H-3, 5), 4.28 (1H, d, *J* = 8.2 Hz, H-1'); ^{13}C-NMR (CD_3OD, 125 MHz): δ 155.6(C-4), 129.7 (C-2, 6), 129.6 (C-1), 114.9 (C-3, 5), 103.2(C-1'), 76.9 (C-3'), 76.8 (C-5'), 73.9 (C-2'), 70.9 (C-7), 70.5 (C-4'), 61.6 (C-6').

***O*-deacetylation of compound 1**

A clear stock solution of the G/$GHNO_3$ reagent was prepared by dissolving guanidinium nitrate (6 mg) in MeOH/CH_2Cl_2 (10 mL, 9:1) and adding MeONa (1 mL, 1 M). Compound **1** (5 mg) in the stock solution (1 mL) was treated and the solution was stirred at room temperature for 1 h. When the *O*-deacetylation was complete, the mixture was neutralized by addition of Amberlite IR 120 H^+ and the solvent was removed. The residue was purified by HPLC [MeOH-H_2O (45:55, v/v)] to give **1a** (2 mg). The structure was identified by ^{1}H-NMR and MS spectral analysis.

Compound **1a**: Yellow solid; mp 252-253°C; ESI-MS *m/z* (rel. int.): 595 $[M - H]^-$; ^{1}H-NMR (500 MHz, DMSO-d_6): δ 12.45 (1H, brs, 5-OH), 7.68 (1H, dd, *J* = 8.8, 2.3 Hz, H-6'), 7.54 (1H, d, *J* = 2.3 Hz, H-2'), 6.82 (1H, d, *J* = 8.8 Hz, H-5'), 6.38 (1H, s, H-8), 6.18 (1H, s, H-6), 5.26 (1H, d, *J* = 7.6 Hz, H-1''), 4.06 (1H, *J* = 6.4 Hz, H-1''').

Acid hydrolysis of compound 1

Compound **1a** (1 mg) was heated in an ampoule with 1 mL of aq. 1.5 M HCl at 80°C for 2 h. After cooling, the reaction mixture was extracted with EtOAc. The EtOAc solvent was removed under reduced pressur and the residue was purified by HPLC [MeOH-H_2O (50:50, v/v) to give **1b**. The structure was identified by ^{1}H-NMR and MS spectral analysis. The aqueous layer of compound **1a** were subjected to HPLC analysis [CH_3CN-H_2O (85:15, v/v), 0.8 mL/min] and the sugar was confirmed as D-galactose and L-arabinose by comparison of their retention time and optical rotation with those of authentic samples. [R_t : 10.2 min (L-arabinose, positive optical rotation), 12.8 (D-galactose, positive optical rotation)]

Compound **1b**: Yellow solid; mp 312-313°C; ESI-MS *m/z* : 303 $[M+H]^+$; ^{1}H-NMR (500 MHz, CD_3OD): δ 7.66 (1H, dd, *J* = 8.2, 2.0 Hz, H-2'), 7.58 (1H, d, *J* = 2.0 Hz, H-6'), 6.90 (1H, d, *J* = 8.2 Hz, H-5'), 6.38 (1H, s, H-8), 6.18 (1H, s, H-6).

Test for cytotoxicity *in vitro*

Sulforhodamin B bioassays (SRB) were used as cytotoxicity screening methods (Skehan et al., 1990). Cytotoxicity assays for each compound were performed *in vitro* against four cultured human tumor cell lines at the Korea Research Institute of Chemical Technology. The cell lines used were A549 (non-small cell lung adenocarcinoma), SK-OV-3 (ovarian cancer cells), SK-MEL-2 (skin melanoma), and HCT15 (colon cancer cells). Doxorubicin was used as a positive control.

RESULTS AND DISCUSSION

Compounds **2**-**21** were identified by comparing the ^{1}H-, ^{13}C-NMR, and MS spectra of these compounds with the literatures. They were identified as quercetin 3-*O*-[2'''-*O*-acetyl-α-L-arabinopyranosyl]- (1'''→6'')-β-D-galactopyranoside (**2**) (Yoshitama et al., 1997), quercetin 3-*O*-α-L-arabinopyranosyl-(1'''→6'')-β-D-galactopyranoside (**3**) (Takemura et al., 2002), quercetin 3-*O*-β-D-galactopyranoside (**4**) (Lee et al., 2002), kaempferol 3,7-*O*-α-L-dirhamnopyranoside (**5**) (Mulinacci et al., 1995), diosmetin 7-*O*-β-D-glucopyranoside (**6**) (Son et al., 1994), diosmetin 7-*O*-β-D-xylopyranosyl-(1'''→6'')-β-D-glucopyranoside (**7**) (Park et al., 2009), *p*-hydroxybenzoic acid (**8**) (Lee et al., 2008), protocatechuic acid (**9**) (Sun et al., 2006), caffeic acid (**10**) (Lee et al., 2009), 6-hydroxy-3,4-dihydro-1-oxo-β-carboline (**11**) (Julia et al, 1973), (*Z*)-3-hexenyl-β-D-glucopyranoside (**12**), (*E*)-2-hexenyl-β-D-glucopyranoside (**13**) (Mizutani et al., 1988), (*Z*)-3-hexenyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**14**) (Kishida et al., 2005), oct-1-en3yl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**15**) (Wang et al., 1998), benzyl-β-D-apiofuranosyl-(1''→6')-β-D-glucopyranoside (**16**) (Wang et al., 1998), benzyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**17**) (Rosa et al., 1996), benzyl-β-D-xylopyranosyl-(1''→6')-β-D-glucopyranoside (**18**) (Otsuka et al., 1990), 2-phenylethyl-β-D-apiofuranosyl-(1''→6')-β-D-glucopyranoside (**19**), 2-phenylethyl-α-L-arabinopyranosyl-(1''→6')-β-D-glucopyranoside (**20**) (Ma et al., 2001), and aryl-β-D-glucopyranoside (**21**) (Schwab et al., 1988). Compounds **2**-**21** were isolated for the first time from this plant.

Compound **1** was isolated as a yellow solid, $[\alpha]_D^{25}$ –80° (c 0.08, MeOH). The molecular formula $C_{28}H_{30}O_{17}$ was determined by the HR-ESI-MS m/z 661.1375 $[M+Na]^+$ (calcd. 661.1375). The IR spectrum showed the bands of a hydroxyl group at 3401 cm^{-1} and α,β-unsaturated carbonyl group at 1646 cm^{-1}. In the ^{1}H-NMR spectra of **1**, the typical flavonoid signals were observed. The proton signal at δ_H 12.61 showed an aromatic C_5-OH. The proton signals at δ_H 7.77 (dd, J = 8.8, 2.3 Hz), 7.62 (d, J = 2.3 Hz) and 6.83 (d, J = 8.8 Hz) were assigned to three aromatic protons of the ABX system of the B ring, with two *meta*-coupled doublets at δ_H 6.42, and 6.20 (d, J = 2.0 Hz) for the A ring. The ^{13}C-NMR spectra of **1** showed a C=O at δ_C 178.1. The aglycone of **1** was identified as quercetin (Young et al., 1991). In addition, in the ^{1}H-NMR spectrum of **1** the signals of the two anomeric proton appeared at δ_H 5.26 (d, J = 7.6 Hz), and at δ_H 4.06 (d, J = 6.4 Hz) with characteristic coupling constants of a β- and α-configuration, respectively. In the ^{13}C-NMR spectrum of **1**, the signals at δ_C 102.6 and 103.5 corresponded to the galatosyl and arabinosyl anomeric carbon. The glycosidic position was established by an HMBC experiment, in which the long-range correlations were observed between the H-1'' (δ 5.26) of D-galatose and the C-3 (δ 134.2) of aglycone, and H-1''' (δ 4.06) of L-arabinose and C-6'' of D-galatose (Takemura et al., 2002). The ^{1}H- and ^{13}C-NMR spectra of **1** showed also acetyl group signals at δ_H 1.98 (3H, s) and δ_C 21.6 and 170.6, respectively. The H-4''' (δ 4.54) and C-4''' (δ 71.5) signals of **1** appeared more downfield than those of **3** (**3**, H-4''', δ 3.49; C-4''', δ 68.0). The acetyl group linkage was confirmed by HMBC data, where a correlation was observed between the H-4''' (δ 4.54) of L-arabinose and the C=O (δ 170.6) of the acetyl group as shown in Fig. 1. This indicated the presence of an acetyl group at C-4''' in **1**. The *O*-deacetylation of **1** afforded quercetin 3-*O*-α-L-arabinopyranosyl-(1→6)-β-D-galactopyranoside (**1a**), which was identified by co-TLC (R_f, 0.25, $CHCl_3$-MeOH-H_2O = 9:4:0.5) with **3** and by its ^{1}H-NMR (Takemura et al., 2002). Acid hydrolysis of quercetin 3-*O*-α-L-arabinopyranosyl-(1→6)-β-D-galactopyranoside yielded the aglycone, quercetin and a sugar (Takemura et al., 2002). The aglycone was confirmed by comparison of its ^{1}H-NMR, and ESI-MS data with literature values (Young et al., 1991), and the sugar was identified by co-TLC with authentic sugars ($CHCl_3$-MeOH-H_2O = 6:4:1, R_f value D-galatose 0.29, L-arabinose 0.55), and HPLC analysis (Takemura et al., 2002). Thus, the structure of 1 was determined as Quercetin 3-*O*-[4'''-*O*-acetyl-α-L-arabinopyranosyl]-

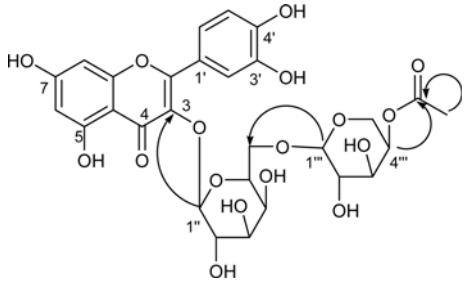

Fig. 1. Key HMBC correlations (H → C) of **1**

(1'''→6'')-β-D-galactopyranoside.

The isolated compounds, **2-21** were tested for cytotoxicity against four human tumor cells *in vitro* using the SRB assay. Of them the compound **11** exhibited weak cytotoxicity against A549, SK-OV-3, SK-MEL-2, and HCT15 cell lines with the IC_{50} values of 62.95, 60.04, 62.56, and 48.02 μM, respectively, and the other compounds showed little cytotoxicity (IC_{50} > 100 μM). IC_{50} values for the cytotoxicity of the control compound, doxorubicin, against A549, SK-OV-3, SK-MEL-2, and HCT15 cell lines were 0.039, 0.081, 0.074, and 0.076 μM, respectively.

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