Chemistry of Natural Compounds, Vol. 49, No. 5, November, 2013 [Russian original No. 5, September–October, 2013]

PHENOLIC COMPOUNDS FROM THE ROOTS OF *Brassica rapa* ssp. *campestris*

Qian Wu,[1] Myun-Ho Bang,[1] Jin-Gyeong Cho,[1] Dae-Young Lee,[2] Kyung-Tae Lee,[3] Hae-Gon Chung,[4] Myung-Sook Choi,[5] Tae-Sook Jeong,[6] Eun-Mi Ahn,[7] Geum-Soog Kim,[2] and Nam-In Baek[1]*

UDC 547:635.1:604

*A new benzyl α-D-fructofuranoside (**3**), along with six known phenol compounds, benzyl-β-D-glucopyranoside (**1**), dihydrosyringin (**2**), syringin (**4**), triandrin (**5**), phillyrin (**6**), and neoolivil-4-*O*-β-D-glucopyranoside (**7**), was isolated from the roots of* Brassica rapa *ssp.* campestris *L. for the first time. The structures of the compounds were established on the basis of NMR, MS, and IR spectroscopic data.*

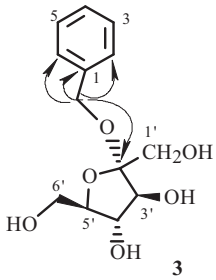
Keywords: *Brassica rapa* ssp. *campestris*, benzyl α-D-fructofuranoside, benzyl-β-D-glucopyranoside, dihydrosyringin, neoolivil-4-*O*-β-D-glucoside, phillyrin, syringin, triandrin.

Brassica rapa ssp. *campestris* L., a turnip, is a vegetable commercially cultivated in the west coast region of Ganghwa Island in Korea. The plant is an edible root vegetable with a conical shape and deep purple color and is well known for its ability to alleviate jaundice, combat liver diseases, relieve hangover and chronic constipation, and improve kidney function. Turnips are included in many food products such as Kimchi, a traditional Korean fermented vegetable dish. Some chemical constituents such as indole alkaloids [1, 2], sterols [1], and fatty acids [3], as well as ethanolic extracts from the roots of *B. rapa* ssp. *campestris*, have previously been reported to modulate the deleterious effects of diabetes [4], to prevent high-fat diet-induced obesity [5], and to prevent cisplatin-induced nephrotoxicity [6]. Our continuing research was carried out to search for other phytochemical constituents from the roots of *B. rapa* ssp. *campestris*.

The roots of *B. rapa* ssp. *campestris* were extracted with 95% aqueous EtOH, and the concentrated extract was partitioned with EtOAc, *n*-BuOH, and H_2O. From the *n*-BuOH fraction, seven phenolic compounds were isolated through repeated SiO_2, ODS, and Sephadex LH-20 column chromatographies. Six known compounds were identified, benzyl β-D-glucopyranoside (yield: 5.3×10^{-5}%, **1**) [7], dihydrosyringin (yield: 1.9×10^{-5}%, **2**) [8], syringin (yield: 9.1×10^{-6}%, **4**) [9, 10], triandrin (yield: 1.3×10^{-5}%, **5**) [9], phillyrin (yield: 1.8×10^{-5}%, **6**) [11–13], and neoolivil-4-*O*-β-D-glucopyranoside (yield: 1.3×10^{-5}%, **7**) [14, 15], through comparison of their spectroscopic data with those of the literature. Although they are known compounds, all of them are reported for the first time from this plant, even the entire Brassicaceae family.

1) Graduate School of Biotechnology, Department of Oriental Medicinal Materials and Processing, Kyung-Hee University, Yongin 446-701, South Korea, e-mail: nibaek@khu.ac.kr; 2) Department of Herbal Crop Research, National Institute of Horticultural & Herbal Science, RDA, Eumseong 369-873, South Korea; 3) Department of Biochemistry, College of Pharmacy, Kyung-Hee University, Seoul 130-701, South Korea; 4) Ganghwa Agricultural Research and Development Center, Incheon 417-833, South Korea; 5) Department of Food Science and Nutrition, Kyung-Pook National University, Daegu 702-701, South Korea; 6) National Research Laboratory of Lipid Metabolism & Atherosclerosis, Korea Research Institute of Bioscience and Biotechnology, Daejeon 305-333, South Korea; 7) Department of Herbal Foodceutical Science, Daegu-Haany University, Gyeongsan 712-715, South Korea. Published in *Khimiya Prirodnykh Soedinenii*, No. 5, September–October, 2013, pp. 734–737. Original article submitted September 19, 2012.

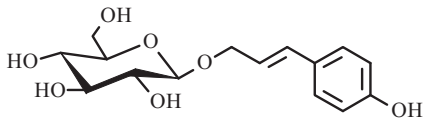
 0009-3130/13/4905-0852



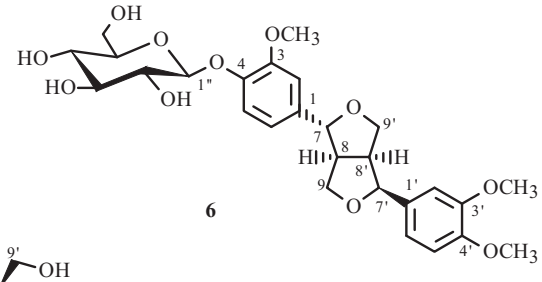
3

Fig. 1. The one-way arrows indicate the long-range correlations from hydrogen to carbon signals in the gHMBC spectrum.

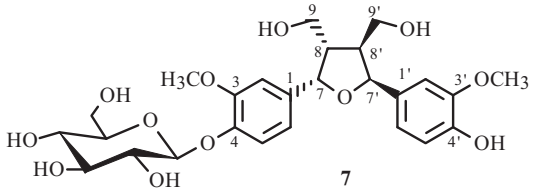
Compound **3** (yield: 5.4×10^{-6}%) is a colorless syrup, mp 88–89°C, $[\alpha]_D^{20}$ +44.9° (*c* 2.0, H_2O). It showed absorbance bands due to hydroxy (3360 cm^{-1}) and olefine (1550 cm^{-1}) groups in the IR spectrum. The molecular ion peak $[M - H]^-$ was detected at *m/z* 269 in the negative FAB-MS spectrum, and the molecular formula $C_{13}H_{18}O_6$ was determined by the molecular ion peak *m/z* 269.1020 $[M - H]^-$ (calcd for $C_{13}H_{17}O_6$, 269.1025) in the negative HR-FAB-MS. In the PMR (400 MHz, methanol-d_4, δ, ppm) spectrum, five olefine methine proton signals at δ 7.38 (2H, dd, J = 8.8, 1.2 Hz, H-2, 6), 7.30 (2H, dd, J = 8.8, 7.2 Hz, H-3, 5), and 7.23 (1H, tt, J = 7.2, 1.2 Hz, H-4) indicating a monosubstituted benzene ring structure, an oxygenated methylene proton signals at δ 4.71 (1H, d, J = 11.6 Hz, H-7a) and 4.58 (1H, d, J = 11.6 Hz, H-7b), and sugar moiety proton signals at δ 4.13 (1H, d, J = 4.4 Hz, H-3′), 3.92 (1H, dd, J = 7.2, 4.4 Hz, H-4′), 3.90 (1H, ddd, J = 7.2, 4.4, 2.8 Hz, H-5′), 3.80 (1H, d, J = 12.0 Hz, H-1′a), 3.77 (1H, dd, J = 12.8, 2.8 Hz, H-6′a), 3.72 (1H, d, J = 12.0 Hz, H-1′b), and 3.64 (1H, dd, J = 12.8, 4.4 Hz, H-6′b) revealed the presence of a fructose. In the ^{13}C NMR (100 MHz, methanol-d_4, δ, ppm) spectrum, one olefine quaternary carbon signal at δ 140.2 (C-1), five olefine methine carbon signals at δ 129.2 (C-3 and C-5), 128.8 (C-2 and C-6), and 128.3 (C-4), and an oxygenated methylene carbon signal at δ 64.6 (C-7) confirmed the presence of a benzyl alcohol moiety. An oxygenated quaternary carbon signal at δ 109.3 (C-2′), three oxygenated methine carbon signals at δ 84.2 (C-5′), 83.5 (C-3′), and 78.7 (C-4′), and two oxygenated methylene carbon signals at δ 62.7 (C-6′) and 61.8 (C-1′) confirmed the presence of an α-D-fructose moiety [16]. gHMBC was carried out in order to determine the positions of key signals (Fig. 1). In the gHMBC spectrum, the oxygenated methylene proton signals at δ 4.71 (H-7a) and 4.58 (H-7b) showed cross peaks with the olefine quaternary carbon signal at δ 140.2 (C-1), the olefine methine carbon signals at δ 128.8 (C-2, C-6), and the oxygenated quaternary carbon signal at δ 109.3 (C-2′), indicating that the oxygenated methylene carbon C-7 was located between C-1 of the benzene ring and C-2′ of the fructose via an ether bond. The presence of fructose was also confirmed by TLC comparison with an authenic fructose after acid hydrolysis. Thus, the structure was determined as benzyl-α-D-fructofuranoside. Even though it has been previously reported as a synthetic compound, there are no detailed reported NMR data for benzyl-α-D-fructoside. This is the first report of the isolation of compound **3** from the natural source and its identification using spectroscopic analysis.



5



6



7

EXPERIMENTAL

General. Optical rotation was measured on a JASCO P-1010 digital polarimeter (Tokyo, Japan). IR spectra were obtained using a PerkinElmer Spectrum One FT-IR spectrometer (Buckinghamshire, England). EI-MS, FAB-MS, and HR-FAB-MS were conducted on a JEOL JMSAX-700 mass spectrometer (Tokyo, Japan). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Unity Inova AS-400 FT-NMR spectrometer (Palo Alto, CA, USA). SiO_2 (Kieselgel 60, Merck, Darmstadt, Germany), octadecyl silica gel (ODS) (LiChroprep RP-18, 40–60 μm, Merck), Diaion HP-20 (Samchun, Korea), and Sephadex LH-20 (Amersham Pharmacia Biotech, Uppsala, Sweden) resins were used for column chromatography (CC). TLC analysis was carried out using Kieselgel 60 F_{254} and RP-18 F_{254S} (Merck) plates. The compounds were detected using a Spectroline ENF-240 C/F UV lamp (Spectronics Corporation, Westbury, NY, USA).

Plant Material. Roots of *B. rapa* ssp. *campestris* were provided by the Ganghwa Agricultural R & D Center, Incheon, Korea, in May 2009 and were positively identified by Dr. Hae-Gon Chung, Ganghwa Agricultural R & D Center. A voucher specimen (KHU090512) was deposited at the Laboratory of Natural Products Chemistry, Kyung Hee University, Yongin, Korea.

Isolation of Phenolic Compounds. Fresh turnip roots (77 kg) were chopped and extracted with 95% EtOH (770.0 L × 2) at room temperature for 24 hours. The extracts were filtered through filter paper and concentrated in a rotary vacuum evaporator to yield a dark brown mass (295 g). The extract was suspended in 8 L water and successively partitioned with EtOAc (8.0 L × 2) and *n*-BuOH (6.4 L × 2), yielding concentrated fractions of EtOAc (BRE, 39 g), *n*-BuOH (BRB, 117 g), and H_2O (139 g), sequentially. The *n*-BuOH fraction (BRB, 117 g) was fractionated into 14 fractions (BRB-1 to BRB-14) using Diaion HP-20 CC (10 × 45 cm) and eluted with H_2O (4.0 L)→MeOH (2.0 L)→acetone (4.0 L)→H_2O (2.0 L). BRB-3 (340 mg, V_{elute}/V_{total} 0.12–0.18) was subjected to ODS CC (4.0 × 7 cm) and eluted with MeOH–H_2O (1:2, 1.2 L) to get purified compound **1** [BRB-3-3, 41 mg, V_e/V_t 0.20 to 0.30; TLC (RP-18 F_{254s}) R_f 0.5, MeOH–H_2O 3:2]. BRB-4 (190 mg, V_e/V_t 0.19–0.23) was subjected to ODS CC (3 × 6 cm) and eluted with MeOH–H_2O (2:3, 1 L) to yield purified compound **2** [BRB-4-7, 15 mg, V_e/V_t 0.67–0.79; TLC (RP-18 F_{254s}) R_f 0.5, MeOH–H_2O 1:1]. BRB-6 (6.1 g, V_e/V_t 0.39–0.46) was subjected to a SiO_2 CC (6 × 15 cm) and eluted with $CHCl_3$–MeOH (6:1→2:1, each 8.0 L) and $CHCl_3$–MeOH–H_2O (6:4:1, 8.0 L) to yield 19 fractions (BRB-6-1 to BRB-6-19). Fraction BRB-6-2 (282 mg, V_e/V_t 0.06–0.08) was further purified by successive chromatography on a Sephadex LH-20 column (3 × 55 cm) and eluted with MeOH–H_2O (3:5→4:5, each 0.5 L) to obtain 10 fractions (BRB-6-2-1 to BRB-6-2-10). The BRB-6-2-4 fraction (50 mg, V_e/V_t 0.14–0.18) was further purified by ODS CC (3 × 5 cm) and eluted with MeOH–H_2O (1:5, 0.8 L) to yield purified compound **3** [BRB-6-2-4-8, 4 mg, V_e/V_t 0.27–0.36; TLC (RP-18 F_{254s}) R_f 0.5, MeOH–H_2O 1:1]. BRB-6-5 (360 mg, V_e/V_t 0.11–0.18) was further separated by ODS CC (3 × 5 cm) and eluted with MeOH–H_2O (1:2, 2.0 L) to obtain 10 fractions (BRB-6-5-1 to BRB-6-5-10). The BRB-6-5-3 fraction (51 mg, V_e/V_t 0.08–0.10) was further purified by SiO_2 CC (3 × 15 cm) and eluted with $CHCl_3$–MeOH–H_2O (22:3:1, 2.5 L) to yield purified compound **4** [BRB-6-5-3-8, 7 mg, V_e/V_t 0.07–0.10; TLC (RP-18 F_{254s}) R_f 0.5, MeOH–H_2O 1:2]. The BRB-6-5-4 fraction (40 mg) was also further purified by SiO_2 CC (3 × 12 cm) and eluted with $CHCl_3$–MeOH–H_2O (20:3:1, 2.0 L) to get purified compound **5** [BRB-6-5-4-12, 10 mg, V_e/V_t 0.10–0.15; TLC (RP-18 F_{254s}) R_f 0.5, MeOH–H_2O 1:2]. BRB-7 (4.2 g, V_e/V_t 0.45–0.51) was separated by SiO_2 CC (3 × 5 cm) and eluted with $CHCl_3$–MeOH (14:1→12:1→8:1→5:1→3:1, each 1.0 L) to obtain 14 fractions (BRB-7-1 to BRB-7-14). BRB-7-11 (61 mg, V_e/V_t 0.25–0.29) was further purified by ODS CC (3 × 5 cm) and eluted with MeOH–H_2O (1:2, 2.0 L) to obtain purified compound **6** [BRB-7-11-8, 14 mg, V_e/V_t 0.66–0.76; TLC (RP-18 F_{254s}) R_f 0.35, MeOH–H_2O 1:1]. The BRB-7-14 fraction (51 mg, V_e/V_t 0.31–0.33) was further purified by ODS CC (3 × 15 cm) and eluted with MeOH–H_2O (1:3→2:1, 2 L) to obtain purified compound **7** [BRB-7-14-9, 10 mg, V_e/V_t 0.58–0.60; TLC (RP-18 F_{254s}) R_f 0.6, MeOH–H_2O 3:2].

Benzyl-*β*-D-glucopyranoside (1). Yellow crystals (MeOH), mp 176–177°C (H_2O); $[\alpha]_D^{20}$ –24.0° (*c* 0.1, H_2O). UV (EtOH, λ_{max}, nm): 236. Positive FAB-MS *m/z* 271 $[M + H]^+$. PMR (400 MHz, pyridine-d_5, δ, ppm, J/Hz): 7.61 (2H, dd, J = 8.4, 1.2, H-2, 6), 7.35 (2H, dd, J = 8.4, 7.2, H-3, 5), 7.21 (1H, m, H-4),4.62 (1H, d, J = 12.4, H-7a), 4.60 (1H, d, J = 7.6, H-1′), 4.38 (1H, dd, J = 12.4, 2.0, H-6′a), 4.28 (1H, d, J = 12.4, H-7b), 3.90 (1H, dd, J = 12.4, 4.8, H-6′b), 4.05–3.55 (4H, overlap, H-2′, H-3′, H-4′, H-5′). ^{13}C NMR (100 MHz, pyridine-d_5, δ, ppm): 138.5 (C-1), 128.1 (C-2, C-6), 127.9 (C-3, C-5), 126.3 (C-4), 103.3 (C-1′), 78.6 (C-3′), 78.4 (C-5′), 75.7 (C-2′), 72.0 (C-7), 71.3 (C-4′), 62.2 (C-6′).

Dihydrosyringin (2). White needlelike crystals (MeOH), mp 130–132°C (H_2O); $[\alpha]_D^{20}$ –52.0° (*c* 0.5, MeOH). UV (MeOH, λ_{max}, nm): 276. Positive FAB-MS *m/z* 375 $[M + H]^+$. IR (CaF_2, ν, cm^{-1}): 3501, 1652. PMR (400 MHz, pyridine-d_5, δ, ppm, J/Hz): 6.65 (2H, br.s, H-2, 6), 5.64 (1H, d, J = 7.8, H-1′), 4.33–4.23 (5H, overlap, sugar moiety), 3.86 (2H, t, J = 7.2, H-9), 3.71 (6H, s, 3-OCH_3, 5-OCH_3), 2.78 (2H, t, J = 6.4, H-7), 1.99 (2H, m, H-8). ^{13}C NMR (100 MHz, pyridine-d_5, δ, ppm):

153.2 (C-3, C-5), 138.7 (C-4), 133.8 (C-1), 106.8 (C-2, C-6), 104.9 (C-1′), 78.3 (C-3′), 78.0 (C-5′), 75.7 (C-2′), 71.2 (C-4′), 62.9 (C-6′), 61.1 (C-9), 56.3 (3-OCH_3, 5-OCH_3), 35.2 (C-8), 32.8 (C-7).

Benzyl-α-D-fructofuranoside (**3**). Colorless syrup, mp 88–89°C; $[\alpha]_D^{20}$ +44.9° (*c* 2.0, H_2O). Negative FAB-MS *m/z* 269 $[M - H]^-$, HR-FAB-MS *m/z* 269.1020 (calcd for $C_{13}H_{17}O_6$, 269.1025). IR (CaF_2, ν, cm^{-1}):3360, 1550. PMR (400 MHz, methanol-d_4, δ, ppm, J/Hz): 7.38 (2H, dd, J = 8.8, 1.2, H-2, H-6), 7.30 (2H, dd, J = 8.8, 7.2, H-3, H-5), 7.23 (1H, tt, J = 7.2, 1.2, H-4), 4.71 (1H, d, J = 11.6, H-7a), 4.58 (1H, d, J = 11.6, H-7b), 4.13 (1H, d, J = 4.4, H-3′), 3.92 (1H, dd, J = 7.2, 4.4, H-4′), 3.90 (1H, ddd, J = 7.2, 4.4, 2.8, H-5′), 3.80 (1H, d, J = 12.0, H-1′a), 3.77 (1H, dd, J = 12.8, 2.8, H-6′a), 3.72 (1H, d, J = 12.0, H-1′b), 3.64 (1H, dd, J = 12.8, 4.4, H-6′b). ^{13}C NMR (100 MHz, methanol-d_4, δ, ppm): 140.2 (C-1), 129.2 (C-3, C-5), 128.8 (C-2, C-6), 128.3 (C-4), 109.3 (C-2'), 84.2 (C-5′), 83.54 (C-3′), 78.7 (C-4′), 64.6 (C-7), 62.7 (C-6′), 61.8 (C-1′).

Hydrolysis of Compound 3. Two milligrams of **3** was refluxed with 1 mL of 1 M HCl for 1 h. The identity of the sugar was confirmed by TLC (F_{254s}) analysis ($CHCl_3$–MeOH–H_2O, 6:4:1) of the reaction mixture with an authentic sample of D-fructose.

Syringin (4). White needlelike crystals (MeOH), mp 190–192°C (H_2O); $[\alpha]_D^{20}$ –18.0° (*c* 0.6, H_2O). UV (EtOH, λ_{max}, nm): 221, 226. Positive FAB-MS *m/z* 373 $[M + H]^+$. IR (CaF_2, ν, cm^{-1}): 3451, 1660. PMR (400 MHz, methanol-d_4, δ, ppm, J/Hz): 6.74 (2H, s, H-2, 6), 6.55 (1H, br.d, J = 16.0, 1.6, H-7), 6.33 (1H, dt, J = 16.0, 6.0, H-8), 4.21 (2H, dd, J = 6.0, 1.6, H-9), 3.86 (6H, s, 3-OCH_3, 5-OCH_3), 3.80–3.30 (6H, sugar moiety). ^{13}C NMR (100 MHz, methanol-d_4, δ, ppm): 154.3 (C-3, C-5), 135.5 (C-4), 135.2 (C-1), 131.2 (C-8), 130.0 (C-7), 105.4 (C-2, C-6), 105.3 (C-1′), 78.3 (C-3′), 77.8 (C-5′), 75.7 (C-2′), 71.3 (C-4′), 62.5 (C-6′), 57.0 (3-OCH_3, 5-OCH_3).

Triandrin (5). White needlelike crystals (EtOH), mp 178–180°C (H_2O); $[\alpha]_D^{20}$ –62.3° (*c* 0.5, H_2O). UV (EtOH, λ_{max}, nm): 264. Positive FAB-MS *m/z* 313 $[M + H]^+$. IR (CaF_2, ν, cm^{-1}): 3451, 1660. PMR (400 MHz, methanol-d_4, δ, ppm, J/Hz): 7.24 (2H, d, J = 8.4, H-2, 6), 6.72 (2H, d, J = 8.4, H-3, 5), 6.56 (1H, ddd, J = 16.0, 1.6, 1.6, H-7), 6.17 (1H, ddd, J = 16.0, 6.8, 6.0, H-8), 4.48 (1H, ddd, J = 12.4, 6.0, 1.6, H-9a), 4.35 (1H, d, J = 7.6, H-1′), 4.26 (1H, ddd, J = 12.4, 6.8, 1.6, H-9b), 3.80–3.20 (6H, sugar moiety). ^{13}C NMR (100 MHz, methanol-d_4, δ, ppm): 158.4 (C-4), 134.1 (C-7), 129.7 (C-1), 128.8 (C-2, C-6), 123.3 (C-8), 116.3 (C-3, C-5), 103.1 (C-1′), 78.1 (C-3′), 77.9 (C-5′), 75.1 (C-2′), 71.6 (C-4′), 71.0 (C-9), 62.5 (C-6′).

Phillyrin (6). White powder (MeOH). UV (MeOH, λ_{max}, nm): 207, 230, 278. Positive FAB-MS *m/z* 535 $[M + H]^+$. IR (CaF_2, ν, cm^{-1}): 3451, 1660. PMR (400 MHz, pyridine-d_5, δ, ppm, J/Hz): 7.60 (1H, d, J = 8.4, H-5), 7.24 (2H, br.s, H-2, 2′), 7.13 (1H, d, J = 8.4, H-5′), 7.03 (1H, d, J = 8.4, H-6), 7.00 (1H, dd, J = 8.4, 1.2, H-6′), 5.67 (1H, d, J = 6.0, H-1″), 4.94 (1H, d, J = 6.0, H-7′), 4.67 (1H, d, J = 6.8, H-7), 4.49 (1H, dd, J = 12.4, 2.0, H-6″a), 4.35 (1H, dd, J = 12.4, 5.2, H-6″b), 4.35–4.08 (4H, m, H-2″, 3″, 4″, 5″), 4.24 (1H, m, H-9a), 4.00 (1H, dd, J = 9.2, 8.4, H-9′a), 3.88 (1H, dd, J = 8.0, 6.4, H-9b), 3.78 (3H, 4′-OCH_3), 3.75 (6H, 3-OCH_3, 3′-OCH_3), 3.56 (1H, dd, J = 10.4, 9.2, H-9′b), 3.37 (1H, m, H-8′), 2.95 (1H, m, H-8). ^{13}C NMR (100 MHz, pyridine-d_5, δ, ppm): 150.3 (C-3), 150.1 (C-3′), 149.1 (C-4′), 147.5 (C-4), 136.4 (C-1), 132.2 (C-1′), 119.1 (C-6), 118.5 (C-6′), 116.6 (C-5), 112.6 (C-5′), 111.3 (C-2), 110.7 (C-2′), 102.4 (C-1″), 87.8 (C-7), 82.3 (C-7′), 78.8 (C-3″), 78.5 (C-5″), 74.9 (C-2″), 71.3 (C-4″), 71.3 (C-9), 70.0 (C-9′), 62.4 (C-6″), 56.1 (3-OCH_3), 56.0 (3′-OCH_3, 4′-OCH_3), 54.1 (C-8), 50.5 (C-8′).

Neoolivil-4-*O*-β-D-glucoside (7). Amorphous powder (EtOH); $[\alpha]_D^{20}$ –6.4° (*c* 0.1, MeOH). UV (EtOH, λ_{max}, nm): 228, 277. Positive HR-FAB-MS *m/z* 561.1902 $[M + Na]^+$. IR (CaF_2, ν, cm^{-1}): 3451, 2925, 1660, 1100. PMR (400 MHz, methanol-d_4, δ, ppm, J/Hz): 7.13 (1H, d, J = 8.4, H-5), 7.02 (1H, d, J = 2.0, H-2), 6.93 (1H, d, J = 1.6, H-2′), 6.91 (1H, dd, J = 8.4, 2.0, H-6), 6.79 (1H, dd, J = 8.0, 1.6, H-6′), 6.75 (1H, d, J = 8.0, H-5′), 4.87 (1H, d, J = 7.2, H-1″), 4.75 (1H, d, J = 4.4, H-7), 4.70 (1H, d, J = 4.4, H-7′), 4.24 (2H, m, H-9a, H-9′a), 3.87 (2H, m, H-9b, 9′b), 3.86–3.38 (6H, sugar moiety), 3.75 (6H, 3-OCH_3, 3′-OCH_3), 3.12 (1H, m, H-8, 8′). ^{13}C NMR (100 MHz, methanol-d_4, δ, ppm): 150.9 (C-3), 149.0 (C-3′), 147.5 (C-4), 147.2 (C-4′), 137.5 (C-1), 133.7 (C-1′), 120.0 (C-6′), 119.7 (C-6), 118.0 (C-5), 116.0 (C-5′), 111.6 (C-2), 110.9 (C-2′), 102.8 (C-1″), 87.4 (C-7′), 87.1 (C-7), 78.2 (C-3″), 77.8 (C-5″), 74.9 (C-2″), 72.7 (C-9, C-9′), 71.3 (C-4″), 62.5 (C-6″), 56.7 (3-OCH_3), 56.5 (3′-OCH_3), 55.5 (C-8′), 55.3 (C-8).

ACKNOWLEDGMENT

This research was funded by the Rural Development Administration (20110701-305-656-001-02-00), Republic of Korea.

REFERENCES

1. J. S. Kim, Y. H. Choi, J. H. Seo, J. W. Lee, Y. S. Kim, S. Y. Ryu, J. S. Kang, Y. K. Kim, and S. H. Kim, *J. Korean Soc. Appl. Biol. Chem*., **35**, 260 (2004).
2. M. H. Bang, D. Y. Lee, Y. J. Oh, M. W. Han, H. J. Yang, H. G. Chung, T. S. Jeong, K. T. Lee, M. S. Choi, and N. I. Baek, *J. Korean Soc. Appl. Biol. Chem*., **51**, 66 (2008).
3. M. H. Bang, D. Y. Lee, M. W. Han, Y. J. Oh, H. G. Chung, T. S. Lee, K. T. Lee, M. S. Choi, and N. I. Baek, *J. Korean Soc. Appl. Biol. Chem*., **50**, 235 (2007).
4. U. J. Jung, N. I. Baek, H. G. Chung, M. H. Bang, T. S. Jeong, K. T. Lee, Y. J. Kang, M. K. Lee, H. J. Kim, J. Y. Yeo, and M. S. Choi, *Clin. Nutr*., **27**, 167 (2008).
5. S. J. An, J. I. Han, M. J. Kim, J. S. Park, J. M. Han, N. I. Baek, H. G. Chung, M. S. Choi, K. T. Lee, and T. S. Jeong, *J. Med. Food*, **13**, 414 (2010).
6. Y. H. Kim, Y. W. Kim, Y. J. Oh, N. I. Baek, S. A. Chung, H. G. Chung, T. S. Jeong, M. S. Choi, and K. T. Lee, *Biol. Pharm. Bull*., **29**, 2441 (2006).
7. F. Toshiyuki, I. Hideyuki, and Y. Takashi, *Nat. Med*., **57**, 19 (2003).
8. K. Rie and K. Masao, *Ann. Rep. Tohoku Coll. Pharm.*, **45**, 128 (1998).
9. G. G. Zapesochnaya, V. A. Kurkin, V. B. Braslavskii, and N. V. Fiatova, *Chem. Nat. Compd*., **39**, 317 (2003).
10. M. C. Song, E. M. Ahn, M. H. Bang, S. Y. Kim, Y. D. Rho, B. M. Kwon, H. S. Lee, and N. I. Baek, *J. Korean Soc. Appl. Biol. Chem*., **52**, 562 (2009).
11. H. X. Kuang, Y. G. Xia, B. Y. Yang, J. Liang, Q. B. Zhang, and L. G. Yu, *Chin. J. Nat. Med*., **7**, 281 (2009).
12. J. H. Park, S. W. Yeon, J. G. Cho, D. Y. Lee, Y. S. Kim, and N. I. Baek, *J. Korean Soc. Appl. Biol. Chem*., **53**, 736 (2010).
13. M. Chiba, S. Hisada, S. Nishibe, and H. Theeme, *Phytochemistry*, **19**, 336 (1979).
14. L. Gongora, S. Manez, R. M. Giner, C. Recio, A. I. Gray, and J. L. Rios, *Phytochemistry*, **59**, 859 (2002).
15. M. Kikuchi and M. Kikuchi, *Chem. Pharm. Bull*., **53**, 49 (2005).
16. L. Poncini and G. N. Richards, *Carbohydr. Res*., **87**, 216 (1980).