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CHEMICAL CONSTITUENTS FROM THE STEM BARK OF *Acer barbinerve*

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The genus *Acer* (Aceraceae) is comprised of approximately 200 species that are widely distributed throughout Asia, North America, and Europe. More than 100 species are recorded in China [1]. Within this genus 15 species are exclusively distributed in Korea. The leaves, stems, and roots of some species have been used in Korean folk medicine for the treatment of arthralgia, fracture, and hepatic disorders [2]. *Acer barbinerve* Max. is indigenous to Korea and China, and it is a rare shrub growing to about 30 ft in height [2]. There are no phytochemical and biological studies previously reported with this species. In our investigation on the chemical constituents of the stem bark of *A. barbinerve*, 13 compounds were isolated from this plant for the first time.

The stem bark of *A. barbinerve* was collected from Jungseon, Gangwon Province of South Korea in June 2008 and authenticated by Prof. Wan-Geun Park, Kangwon National University. A voucher specimen (No. 0806-AB01) was deposited in the herbarium, Department of Forest Biomaterials Engineering, Kangwon National University, South Korea.

The air-dried stem bark of *A. barbinerve* (3.5 kg) was extracted with 70% aqueous acetone at room temperature. The extract was suspended in water and successively partitioned with *n*-hexane, CH_2Cl_2, EtOAc, and water. The EtOAc extract (48 g) was chromatographed on a Sephadex LH-20 column eluted with MeOH–H_2O (3:1) to give four fractions (I–IV). Fraction II was subjected to column chromatography on RP-18 silica gel with MeOH–H_2O (1:1, 1:3), and then purified on Sephadex LH-20 with MeOH–H_2O (1:2, 1:5, 1:7) and EtOH–hexane (3:1, 3:2, 5:4) to afford compounds **1** (13.7 g), **2** (4.8 g), **3** (54 mg), **11** (60 mg), **12** (52 mg), and **13** (72 mg). Fraction III was purified by repeated Sephadex LH-20 column chromatography eluted with MeOH–H_2O (1:2, 1:3, 1:5) to afford compounds **1** (2.9 g), **4** (18 mg), **5** (16 mg), **6** (19 mg), **7** (23 mg), **8** (20 mg), **9** (45 mg), and **10** (46 mg).

All compounds were identified by a combination of spectroscopic methods (MS, ^{1}H and ^{13}C NMR, including HMQC and HBMC). The spectroscopic data of all compounds were in good agreement with the literature data.

Methyl gallate (1): $C_8H_8O_5$, yellow amorphous powder, EI-MS *m/z* 184 $[M]^+$. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 3.82 (3H, s, OCH_3), 7.05 (2H, s, H-2, 6). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 52.32 (OCH_3), 110.06 (C-2, 6), 121.47 (C-1), 139.79 (C-4), 146.43 (C-3, 5), 169.06 (C-7) [3].

Methyl gallate-4-*O*-β-D-glucoside (2): $C_{14}H_{18}O_{10}$, yellow amorphous powder, ESI-MS *m/z* 369 $[M + Na]^+$, 347 $[M + H]^+$. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 3.22–3.80 (6H, m, Glc-H-2–6), 3.84 (3H, s, OCH_3), 4.69 (1H, d, J = 7.9, Glc-H-1), 7.05 (2H, s, H-2, 6). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 51.55 (OCH_3), 60.85 (Glc-C-6), 69.58 (Glc-C-4), 74.15 (Glc-C-2), 76.23 (Glc-C-3), 77.29 (Glc-C-5), 106.27 (Glc-C-1), 109.14 (C-2, 6), 127.41 (C-1), 137.46 (C-4), 150.61 (C-3, 5), 167.08 (C-7) [4].

Methyl gallate-3-*O*-β-D-glucoside (3): $C_{14}H_{18}O_{10}$, yellow amorphous powder, ESI-MS *m/z* 369 $[M + Na]^+$, 347 $[M + H]^+$. ^{1}H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 3.35–3.82 (6H, m, Glc-H-2–6), 3.85 (3H, s, OCH_3), 4.89 (1H, d, J = 7.5, Glc-H-1), 7.32 (1H, d, J = 1.8, H-2), 7.44 (1H, d, J = 1.8, H-6). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 51.64 (OCH_3), 62.25 (Glc-C-6), 70.58 (Glc-C-4), 75.20 (Glc-C-2), 77.61 (Glc-C-3), 78.52 (Glc-C-5), 104.62 (Glc-C-1), 112.18 (C-6), 113.94 (C-2), 122.12 (C-1), 143.58 (C-4), 147.03 (C-5), 149.41 (C-3), 167.16 (C-7) [5].

Gallic acid (4): $C_7H_6O_5$, brown amorphous powder, EI-MS *m/z* 170 $[M]^+$. ^{1}H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) data as described in [6].

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Protocatechinic acid (5): $C_7H_6O_4$, brown amorphous powder, EI-MS *m/z* 154 $[M]^+$. ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) data as described in [7].

Vanillic acid (6): $C_8H_8O_4$, yellow amorphous powder, EI-MS *m/z* 168 $[M]^+$. ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) data as described in [8].

***p*-Tyrosol (7)**: $C_8H_{10}O_2$, white amorphous powder, EI-MS *m/z* 138 $[M]^+$. ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) data as described in [9].

(+)-Catechin (8): $C_{15}H_{14}O_6$, yellow amorphous powder, EI-MS *m/z* 290 $[M]^+$. ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) data as described in [10].

(–)-Epicatechin (9): $C_{15}H_{14}O_6$, yellow amorphous powder, EI-MS *m/z* 290 $[M]^+$. ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR (100 MHz, CD_3OD) data as described in [10].

(–)-Epicatechin-3-*O*-gallate (10): $C_{22}H_{18}O_{10}$, brown amorphous powder, ESI-MS *m/z* 465 $[M + Na]^+$, 443 $[M + H]^+$. ^1H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 2.85 (1H, dd, J = 2.2, 17.3, H-4a), 3.00 (1H, dd, J = 4.5, 17.3, H-4b), 5.03 (1H, s, H-2), 5.53 (1H, m, H-3), 5.96 (2H, s, H-6, 8), 6.70 (1H, d, J = 8.2, H-5′), 6.81 (1H, dd, J = 2.0, 8.2, H-6′), 6.93 (1H, d, J = 2.0, H-2′), 6.95 (2H, s, Galloyl-H-2, 6). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 25.47 (C-4), 68.58 (C-3), 77.24 (C-2), 94.50 (C-8), 95.15 (C-6), 98.00 (C-10), 108.82 (Galloyl-C-2, 6), 113.72 (C-2′), 114.61 (C-5′), 117.99 (C-6′), 120.08 (Galloyl-C-1), 130.07 (C-1′), 138.41 (Galloyl-C-4), 144.56 (C-3′, 4′), 144.92 (Galloyl-C-3, 5), 155.89 (C-5, 9), 156.46 (C-7), 166.21 (Galloyl-C-7) [11].

Hirsutrin (11) (quercetin-3-*O*-β-D-glucoside): $C_{21}H_{20}O_{12}$, yellow amorphous powder, ESI-MS *m/z* 487 $[M + Na]^+$, 465 $[M + H]^+$. ^1H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 3.22–3.71 (6H, m, Glc-H-2–6), 5.25 (1H, d, J = 7.4, Glc-H-1), 6.19 (1H, d, J = 2.1, H-6), 6.38 (1H, d, J = 2.1, H-8), 6.87 (1H, d, J = 8.5, H-5′), 7.58 (1H, dd, J = 2.2, 8.5, H-6′), 7.71 (1H, d, J = 2.2, H-2′). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 62.58 (Glc-C-6), 71.24 (Glc-C-4), 75.76 (Glc-C-2), 78.14 (Glc-C-5), 78.41 (Glc-C-3), 94.75 (C-8), 99.91 (C-6), 104.35 (Glc-C-1), 105.75 (C-10), 116.03(C-2′), 117.60 (C-5′), 123.10 (C-1′), 123.24 (C-6′), 135.66 (C-3), 145.93 (C-3′), 149.88 (C-4′), 158.48 (C-9), 159.04 (C-2), 163.06 (C-5), 166.02 (C-7), 179.52 (C-4) [12].

Hyperin (12) (quercetin-3-*O*-β-D-galactoside): $C_{21}H_{20}O_{12}$, yellow amorphous powder, ESI-MS *m/z* 487 $[M + Na]^+$, 465 $[M + H]^+$. ^1H NMR (600 MHz, $(CD_3)_2SO$, δ, ppm, J/Hz): 3.30–3.66 (6H, m, Gal-H-2–6), 5.38 (1H, d, J = 7.7, Gal-H-1), 6.20 (1H, d, J = 1.2, H-6), 6.40 (1H, d, J = 1.2, H-8), 6.82 (1H, d, J = 8.5, H-5′), 7.53 (1H, d, J = 1.9, H-2′), 7.67 (1H, dd, J = 1.9, 8.5, H-6′), 12.63 (1H, s, 5-OH). ^{13}C NMR (125 MHz, $(CD_3)_2SO$, δ, ppm): 60.02 (Gal-C-6), 67.80 (Gal-C-4), 71.09 (Gal-C-2), 73.07 (Gal-C-3), 75.72 (C- Gal-5), 93.99 (C-8), 98.56 (C-6), 101.68 (Gal-C-1), 103.77 (C-10), 115.06 (C-2′), 115.82 (C-5′), 120.98 (C-1′), 121.89 (C-6′), 133.36 (C-3), 144.71 (C-3′), 148.35 (C-4′), 156.11 (C-9), 156.19 (C-2), 161.11 (C-5), 164.09 (C-7), 177.36 (C-4) [12].

Quercitrin (13) (quercetin-3-*O*-α-L-rhamnoside): $C_{21}H_{20}O_{11}$, yellow amorphous powder, ESI-MS *m/z* 471 $[M + Na]^+$, 449 $[M + H]^+$. ^1H NMR (400 MHz, CD_3OD, δ, ppm, J/Hz): 0.95 (3H, d, J = 6.1, Rha-CH_3), 3.36–4.23 (4H, m, Rha-H-2–5), 5.36 (1H, d, J = 1.4, Rha-H-1), 6.20 (1H, d, J = 2.0, H-6), 6.36 (1H, d, J = 2.0, H-8), 6.91 (1H, d, J = 8.2, H-5′), 7.31 (1H, dd, J = 2.1, 8.2, H-6′), 7.34 (1H, d, J = 2.1, H-2′). ^{13}C NMR (100 MHz, CD_3OD, δ, ppm): 17.69 (Rha-CH_3), 71.93 (Rha-C-5), 72.06 (Rha-C-3), 72.13 (Rha-C-2), 73.28 (Rha-C-4), 94.74 (C-8), 99.83 (C-6), 103.56 (Rha-C-1), 105.92 (C-10), 116.39 (C-2'), 116.96 (C-5′), 122.92 (C-6′), 122.99 (C-1′), 136.26 (C-3), 146.42 (C-3′), 149.80 (C-4′), 158.52 (C-9), 159.32 (C-2), 163.21 (C-5), 165.87 (C-7), 179.65 (C-4) [13].

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