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PHENOLIC COMPOUNDS FROM THE AERIAL PART OF *Geranium rotundifolium*

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Geranium rotundifolium L. (Geraniaceae) is an annual herbaceous plant that grows on rocky slopes and screes in the lower and middle mountain belts of Central Asia [1]. The goal of the present research was to study the chemical composition of *G. rotundifolium* distributed in the Balyklitau mountains, Forish District, Jizzakh Region, Uzbekistan.

Ellagitannin (hexahydroxydiphenic acid glucoside) and flavonoids (quercetin, kaempferol, afzelin, kaempferol rutinosido-4′-glucoside) were reported from the aerial part of *G. rotundifolium* [2–4].

Herein, we communicate results from studies of phenolic compounds in the EtOAc fraction (70 g) of the EtOH (70%) extract of the aerial part of *G. rotundifolium* (3.0 kg). This fraction was separated over a column of KSK silica gel (100–200 mesh; Tianjin Sinomed Pharmaceutical, China). Separate fractions were eluted by $CHCl_3$ and $CHCl_3$–MeOH mixtures of increasing gradient of the latter. Subsequent rechromatography of the obtained eluates over Sephadex LH-20 (particle size 25–100 μm; GE Healthcare Bio-Sciences AB, Sweden) and elution by EtOH–H_2O (8:2 and 7:3) isolated the 12 pure phenolic compounds gallic acid (**1**, 77 mg) [5], ethyl gallate (**2**, 52 mg) [6], kaempferol (**3**, 39 mg) [6], quercetin (**4**, 40 mg) [6], afzelin (**5**, 390 mg) [7], quercitrin (**6**, 145 mg) [7], juglanin (**7**, 95 mg) [8], avicularin (**8**, 90 mg) [8], astragalin (**9**, 74 mg) [8], isoquercetin (**10**, 108 mg) [9], kaempferol-7-*O*-α-L-rhamnopyranoside (**11**, 344 mg) [10], and kaempferitrin (**12**, 4.5 g) [11]. The chemical structures of the isolated compounds were elucidated by analyzing their spectral data (UV, IR, PMR, ^{13}C NMR, 2D NMR) followed by comparisons of them with the literature.

Gallic acid (1), white crystals, mp 236–238°C.

Ethyl gallate (2), white powder, mp 168–170°C.

Kaempferol (3), yellow compound, mp 278–279°C.

Quercetin (4), yellow crystals, mp 310–312°C.

Afzelin (5), yellow compound, mp 172–174°C.

Quercitrin (6), yellow compound, mp 186–187°C. UV spectrum (EtOH, λ_{max}, nm): 256, 353. IR spectrum (KBr, ν, cm^{-1}): 3234 (OH), 1658 (C=O), 1605, 1567, 1499 (Ar), 1069 (C–O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.61 (1H, s, 5-OH), 9.41 (1H, br.s, OH), 7.26 (1H, d, J = 2.2, H-2′), 7.21 (1H, dd, J = 8.3, 2.2, H-6′), 6.83 (1H, d, J = 8.3, H-5′), 6.36 (1H, d, J = 2.0, H-8), 6.17 (1H, d, J = 2.0, H-6), 5.21 (1H, d, J = 1.6, H-1″), 4.95, 4.73, 4.63 (3H each, br.s, Rha*p*-OH), 3.94 (1H, dd, J = 3.4, 1.7, H-5″), 3.05–2.21 (3H, m, H-2″, 3″, 4″), 0.77 (1H d, J = 5.9, H-6″). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 157.43 (C-2), 134.30 (C-3), 177.84 (C-4), 161.38 (C-5), 98.83 (C-6), 164.37 (C-7), 93.77 (C-8), 156.56 (C-9), 104.17 (C-10), 121.25 (C-1′), 115.74 (C-2′), 145.30 (C-3′), 148.55 (C-4′), 115.58 (C-5′), 120.83 (C-6′), 101.91 (C-1″), 70.72 (C-2″), 70.44 (C-3″), 71.26 (C-4″), 70.16 (C-5″), 17.63 (C-6″).

Juglanin (7), yellow compound, mp 228–230°C. UV spectrum (EtOH, λ_{max}, nm): 267, 349. IR spectrum (KBr, ν, cm^{-1}): 3389 (OH), 1656 (C=O), 1605, 1556, 1509 (Ar), 1089, 1067, 1040 (C–O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.58 (1H, br.s, 5-OH), 10.24 (1H, br.s, 4′-OH), 7.98 (2H, d, J = 8.9, H-2′, 6′), 6.84 (2H, d, J = 8.9, H-3′, 5′), 6.40 (1H, d, J = 2.0, H-8), 6.16 (1H, d, J = 2.0, H-6), 5.57 (1H, d, J = 1.2, H-1″), 5.51, 5.25, 4.65 (3H each, br.s, OH), 4.10 (1H, d, J = 3.5, H-2″), 3.68 (1H, m, H-5″b), 3.15–3.50 (3H, m, H-3″, 4″, 5″a). ^{13}C NMR spectrum (100 MHz,

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DMSO-d_6, δ, ppm): 156.47 (C-2), 133.47 (C-3), 177.73 (C-4), 161.27 (C-5), 98.80 (C-6), 164.40 (C-7), 93.28 (C-8), 156.90 (C-9), 104.05 (C-10), 120.81 (C-1′), 130.91 (C-2′, 6′), 115.51 (C-3′, 5′), 160.03 (C-4′), 108.11 (C-1″), 82.20 (C-2″), 77.15 (C-3″), 86.40 (C-4″), 60.91 (C-5″).

Avicularin (8), yellow compound, mp 199–201°C. The PMR and ^{13}C NMR spectra of **8** agreed with the published data.

Astragalin (9), yellow compound, mp 218–219°C. UV spectrum (EtOH, λ_{max}, nm): 267, 352. IR spectrum (KBr, ν, cm^{-1}): 3432 (OH), 1654 (C=O), 1609, 1503 (Ar), 1072 (C–O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.56 (1H, br.s, 5-OH), 10.23 (1H, br.s, 4′-OH), 7.98 (2H, d, J = 8.9, H-2′, 6′), 6.83 (2H, d, J = 8.9, H-3′, 5′), 6.37 (1H, d, J = 2.1, H-8), 6.15 (1H, d, J = 2.1, H-6), 5.41 (1H, d, J = 7.4, H-1″), 5.34 (1H, br.s, 3″-OH), 5.03 (1H, br.s, 2″-OH), 4.95 (1H, br.s, 4″-OH), 3.16 (1H, m, H-5″), 3.11 (1H, m, H-2″), 3.03 (1H, m, H-4″), 3.02 (1H, m, H-3″). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 156.28 (C-2), 133.21 (C-3), 177.50 (C-4), 161.28 (C-5), 98.86 (C-6), 164.52 (C-7), 93.80 (C-8), 156.49 (C-9), 103.96 (C-10), 120.98 (C-1′), 130.98 (C-2′, 6′), 115.20 (C-3′, 5′), 160.03 (C-4′), 100.90 (C-1″), 74.29 (C-2″), 77.58 (C-3″), 69.93 (C-4″), 76.46 (C-5″), 60.88 (C-6″).

Isoquercetin (10), yellow compound, mp 236–237°C. The PMR and ^{13}C NMR spectra of **10** agreed with the published data.

Kaempferol-7-*O*-α-L-rhamnopyranoside (11), yellow compound, mp 231–232°C. UV spectrum (EtOH, λ_{max}, nm): 252, 366. IR spectrum (ν_{max}, cm^{-1}): 3417 (OH), 1658 (C=O), 1592, 1555, 1497 (Ar), 1061, 1029 (C–O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.43 (1H, s, 5-OH), 10.18 (1H, br.s, 4′-OH), 9.53 (1H, br.s, 3-OH), 8.04 (2H, d, J = 8.9, H-2′, 6′), 6.89 (2H, d, J = 8.9, H-3′, 5′), 6.77 (1H, d, J = 2.1, H-8), 6.37 (1H, d, J = 2.1, H-6), 5.50 (1H, d, J = 1.8, H-1″), 5.17 (1H, d, J = 4.5, Rha*p*-OH), 4.95 (1H, d, J = 5.7, Rha*p*-OH), 4.81 (1H, d, J = 5.9, Rha*p*-OH), 3.81 (1H, br.s, H-5″), 3.20–3.70 (3H, m, H-2″, 3″, 4″), 1.08 (3H, d, J = 6.1, H-6″). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 147.62 (C-2), 136.17 (C-3), 176.19 (C-4), 160.49 (C-5), 98.98 (C-6), 161.52 (C-7), 94.50 (C-8), 155.86 (C-9), 104.81 (C-10), 121.67 (C-1′), 129.82 (C-2′, 6′), 115.63 (C-3′, 5′), 159.49 (C-4′), 98.47 (C-1″), 70.37 (C-2″), 70.22 (C-3″), 71.74 (C-4″), 69.99 (C-5″), 18.09 (C-6″).

Kaempferitrin (12), yellow needle-like crystals, mp 189–190°C. UV spectrum (EtOH, λ_{max}, nm): 265, 346. IR spectrum (KBr, ν, cm^{-1}): 3431 (OH), 1658 (C=O), 1603, 1493 (Ar), 1088, 1061 (C–O). ^{1}H NMR spectrum (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 12.56 (1H, s, 5-OH), 10.28 (1H, br.s, 4′-OH), 7.75 (2H, d, J = 8.8, H-2′, 6′), 6.88 (2H, d, J = 8.8, H-3′, 5′), 6.74 (1H, d, J = 2.1, H-8), 6.41 (1H, d, J = 2.1, H-6), 5.51 (1H, d, J = 1.7, H-1‴), 5.25 (1H, d, J = 1.5, H-1″), 5.16 (1H, d, J = 4.5, Rha*p*-OH), 4.99 (1H, d, J = 4.4, Rha*p*-OH), 4.94 (1H, d, J = 5.8, Rha*p*-OH), 4.81 (1H, d, J = 5.9, Rha*p*-OH), 4.77 (1H, d, J = 4.4, Rha*p*-OH), 4.66 (1H, d, J = 5.8, Rha*p*-OH), 3.94 (1H, br.s, H-5″), 3.80 (1H, br.s, H-5‴), 3.0–3.65 (6H, m, H-2″, 3″, 4″, 2‴, 3‴, 4‴), 1.09 (1H, d, J = 6.1, H-6‴), 0.76 (1H, d, J = 5.6, H-6″). ^{13}C NMR spectrum (100 MHz, DMSO-d_6, δ, ppm): 157.95 (C-2), 134.63 (C-3), 178.04 (C-4), 161.03 (C-5), 98.49 (C-6), 164.79 (C-7), 94.72 (C-8), 156.21 (C-9), 105.90 (C-10), 120.46 (C-1′), 130.86 (C-2′, 6′), 115.56 (C-3′, 5′), 160.26 (C-4′), 101.96 (C-1″), 70.82 (C-2″), 70.42 (C-3″), 71.20 (C-4″), 70.19 (C-5″), 17.61 (C-6″), 99.59 (C-1‴), 70.33 (C-2‴), 70.22 (C-3‴), 71.71 (C-4‴), 69.93 (C-5‴), 18.06 (C-6‴).

The analytical results indicated that the aerial part of *G. rotundifolium* was a rich source of biologically active phenolic compounds. Afzelin (**5**) was also isolated from this plant growing in Egypt [4]. The presence of afzelin in large quantities could be useful for chemotaxonomic classification of *Geranium* species. Compounds **2** and **6**–**12** were isolated from and identified in this plant for the first time by us. *G. rotundifolium* growing in this region of Uzbekistan was especially rich in kaempferitrin (**12**, 0.15% of air-dried plant mass), afzelin (**5**, 0.013%), and kaempferol-7-*O*-α-L-rhamnopyranoside (**11**, 0.011%).

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