

SECONDARY METABOLITES FROM THE AERIAL PART OF *Geranium saxatile*

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We isolated and identified previously gallic and ellagic acids and quercetin-3-*O*-glucoside from the aerial part of *Geranium saxatile* Kar. et Kir. [1].

In continuation of research on the chemical composition of the aerial part of *G. saxatile*, we chromatographed the EtOAc extract over a column (165 × 4.5 cm) of KSK silica gel with elution by CHCl₃ and CHCl₃:MeOH in various ratios with further re-chromatography of separate eluates over Sephadex LH-20 with elution by H₂O:MeOH with an increasing gradient of alcohol (MeOH:H₂O). A total of seven pure compounds was isolated.

Based on a comparison of spectral data of the isolated compounds (UV, IR, PMR, and ¹³C NMR) with the literature and directly with authentic samples, they were identified as ethylgallate (**1**) [2], isomucronulatol (**2**) [3], kaempferol (**3**) [4], quercetin (**4**) [5], myricetin (**5**) [6], hyperoside (**6**) [7], and rutinoid (**7**) [8].

Ethylgallate (ethyl 3,4,5-trihydroxybenzoate) (1), white powder, C₉H₁₀O₅, mp 168–170°C, *R_f* 0.24 (CHCl₃:MeOH, 9:1). UV spectrum (EtOH, λ_{max}, nm): 218, 276. IR spectrum (KBr, ν, cm⁻¹): 3450–3294 (OH); 2975, 2934 (OCH₃); 1707 (C=O); 1620, 1535 (aromatic C=C). ¹³C NMR spectrum (100 MHz, DMSO-d₆, δ, ppm): 165.8 (C=O), 145.6 (C-3,5), 138.4 (C-4), 119.7 (C-1), 108.5 (C-2,6), 60.0 (CH₂), 14.3 (CH₃) [2].

Isomucronulatol (7,2'-dihydroxy-3',4'-dimethoxyisoflavan) (2), pale-yellow needles, C₁₇H₁₈O₅, mp 151–152°C, *R_f* 0.68 (CHCl₃:MeOH, 9:1). UV spectrum (EtOH, λ_{max}, nm) was characteristic of isoflavan derivatives and had absorption maxima at 280.4 (0.36) and 290 (0.22). IR spectrum (KBr, ν, cm⁻¹): 3526, 3422 (OH); 2970, 2943 (OCH₃); 1618, 1590, 1466, 1436 (aromatic C=C); 1384, 1318, 1275, 1239, 1211, 1199, 1179, 1155, 1117 [3].

The molecular structure of the isoflavan isomucronulatol was established conclusively based on an x-ray crystal structure analysis.

Kaempferol (3,5,7,4'-tetrahydroxyflavone) (3), yellow needle-like crystals, C₁₅H₁₀O₆, mp 270–272°C, *R_f* 0.88 [*n*-BuOH:AcOH:H₂O (BAW), 4:1:2]. UV spectrum (EtOH, λ_{max}, nm): 265, 368. IR spectrum (KBr, ν, cm⁻¹): 3430–3320 (OH); 1650 (γ-pyrone C=O); 1590, 1540 (aromatic C=C) [4].

Quercetin (3,5,7,3',4'-pentahydroxyflavone) (4), light-yellow needle-like crystals, C₁₅H₁₀O₇, mp 310–312°C, *R_f* 0.36 (BAW, 4:1:2). UV spectrum (EtOH, λ_{max}, nm): 255, 371. IR spectrum (KBr, ν, cm⁻¹): 3367–3287 (OH); 1672 (γ-pyrone C=O); 1615 (aromatic C=C); 1492, 1430, 1385, 1296, 1174, 1102 [5].

Myricetin (3,5,7,3',4',5'-hexahydroxyflavone) (5), yellowish powder, C₁₅H₁₀O₈, mp 356–358°C. UV spectrum (MeOH, λ_{max}, nm): 210, 254, 375. IR spectrum (KBr, ν, cm⁻¹): 3427 (OH); 1667 (C=O); 1623, 1523 (C=C). ¹³C NMR spectrum (100 MHz, DMSO-d₆, δ, ppm): 146.9 (C-2), 136.0 (C-3), 175.9 (C-4), 156.2 (C-5), 98.3 (C-6), 164.1 (C-7), 93.7 (C-8), 160.9 (C-9), 103.1 (C-10), 121.0 (C-1'), 107.36 (C-2', C-6'), 145.9 (C-3'), 136.0 (C-4'), 145.9 (C-5') [6].

Hyperoside (5,7,3',4'-tetrahydroxyflavone-3-*O*-β-D-galactoside) (6), light-yellow powder, C₂₁H₂₀O₁₂, mp 218–220°C, *R_f* 0.23 (CHCl₃:MeOH:EtOAc, 10:3.5:3). UV spectrum (EtOH, λ_{max}, nm): 257, 358. IR spectrum (KBr, ν, cm⁻¹): 3319, 2974, 2904, 1655, 1607, 1089, 1055, 1020. ¹³C NMR spectrum (100 MHz, DMSO-d₆, δ, ppm): 156.2 (C-2), 133.5 (C-3), 177.5 (C-4), 161.2 (C-5), 98.6 (C-6), 164.1 (C-7), 93.5 (C-8), 156.3 (C-9), 103.9 (C-10), 121.2 (C-1'), 115.1 (C-2'), 144.8 (C-3'), 148.4 (C-4'), 115.9 (C-5'), 121.0 (C-6'), 101.8 (C-1''), 71.2 (C-2''), 73.2 (C-3''), 67.9 (C-4''), 75.8 (C-5''), 60.1 (C-6'') [7].

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Rutin (5,7,3',4'-tetrahydroxyflavone-3-O-rutinoside) (7), greenish-yellow powder, $C_{27}H_{30}O_{16}$, mp 196–198°C, R_f 0.68 (CHCl₃:MeOH:H₂O:AcOH, 9:3:0.5:0.5). UV spectrum (MeOH, λ_{max} , nm): 257, 356 [8].

Thus, isomucronulatol (**2**) was isolated for the first time from the genus *Geranium*; ethylgallate (**1**), kaempferol (**3**), quercetin (**4**), myricetin (**5**), hyperoside (**6**), and rutinoside (**7**), for the first time from the plant *G. saxatile*.

Pharmacological investigations showed that total proanthocyanidines from the aerial part of *G. saxatile* exhibited antihypoxic and antioxidant activity. Polymeric proanthocyanidines, the total of which we called geranyl, showed the greatest activity [9].

The study of the polyphenol composition of the aerial part of *G. saxatile* roots is continuing.

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