PHENOLIC ACIDS OF *Geranium pusillum*

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In continuation of research on phenolic compounds of the aerial part of *Geranium pusillum* L. (Geraniaceae) [1], the air-dried material was extracted exhaustively with ethanol (70%). The aqueous solution remaining after removal of alcohol was extracted with $CHCl_3$ to remove lipophilic substances. The purified aqueous extract developed a precipitate on standing. This was filtered off and recrystallized from pyridine to give yellowish crystals (**1**).

Phenolic compounds from the aqueous solution were extracted by ethylacetate. The ethylacetate fraction was separated over a polyamide column (eluent alcohol—water in various ratios) and rechromatographed repeatedly over silica gel (eluent $CHCl_3$—CH_3OH in various ratios) to isolate **2-4**, which were phenolic carboxylic acids according to qualitative reactions.

Compound 1 is slightly soluble in boiling water and alcohol, insoluble in ether, mp ~360°C (dec.).

UV spectrum (C_2H_5OH, λ_{max}, nm): 366, 255. IR spectrum (KBr, ν_{max}, cm^{-1}): 3260, 3250 (OH), 1720 (carbonyl), 1615 (double bond). R_f 0.43 [butanol—acetic acid—water (BAW) 40:12.5:29], 0.05 (15% CH_3COOH) [3, 4], 0.33 (glac. CH_3COOH—HCl—H_2O 30:3:10) [5].

The compound gives a color reaction with conc. CH_3COOH and $NaNO_2$ that is typical of free ellagic acid [6]. The melting point is not depressed by adding ellagic acid. The compound was characterized as ellagic acid.

Compound 2 is a yellowish crystalline material; very soluble in hot water, methanol, ethanol; insoluble in $CHCl_3$ and C_6H_6; mp 196-197°C.

UV spectrum (C_2H_5OH, λ_{max}, nm): 325, 299 sh, 235. R_f 0.82 (BAW 4:1:2), 0.28 (2% CH_3COOH), 0.78 (glac. CH_3COOH—HCl—H_2O 30:3:10) [7]. It gives a green color with ferric chloride solution (1%). Protocatechuic acid forms if the compound is fused with KOH. The melting point is not depressed by adding caffeic acid. Compound **2** was identified as caffeic acid [8].

Compound 3 crystallizes from water as colorless prisms, mp 210-212°C.

UV spectrum (C_2H_5OH, λ_{max}, nm): 230, 310. R_f 0.90 (BAW, 4:1:2), 0.30 (2% CH_3COOH), 0.84 (glac. CH_3COOH—HCl—H_2O 30:3:10) [7]. It gives a rose color with ferric chloride solution (1%). Alkaline destruction of the compound forms *p*-hydroxybenzoic acid. The melting point is not depressed by adding *p*-coumaric acid. Compound **3** was characterized as *p*-coumaric acid [9].

Compound 4 is a white crystalline material, very soluble in alcohol and hot water, mp 236-240°C.

UV spectrum (C_2H_5OH, λ_{max}, nm): 210, 274. R_f 0.66 (BAW, 4:1:2), 0.36 (2% CH_3COOH) [8], 0.64 (glac. CH_3COOH—HCl—H_2O 30:3:10) [7]. It gives a blue color with ferric chloride solution (1%). Compound **4** was gallic acid [1].

The study of the phenolic composition of *G. pusillum* L. is continuing.

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