FLAVONOIDS OF *Geranium pusillum*

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In continuation of a study of the flavonoids of the epigeal part of *Geranium pusillum* L. (Geraniaceae) [1], air-dried raw material that was collected during flowering was exhaustively extracted with ethanol (70%). The alcohol extract was evaporated in vacuum. The moist solid was treated with $CHCl_3$ to remove lipophilic substances. Flavonoids were extracted from the purified moist solid by ethylacetate (average 2% yield).

The ethylacetate fraction was chromatographed over a polyamide column (eluent ethanol—water in various proportions). Repeated rechromatography of the separate fractions gave flavonoid-like **1**-**6**. Bryant cyanidin reaction [2] established that two of these were aglycones whereas the others were glycosides.

The isolated flavonoids were identified using UV and IR spectra and chemical transformations compared with authentic samples.

Quercetin (1) (3,5,7,3′,4′-pentahydroxyflavone), yellow crystals, $C_{15}H_{10}O_7$, mp 310-312°C, R_f 0.36 (BAW, 4:1:2), 0.03 (15% CH_3COOH), UV spectrum (MeOH, λ_{max}, nm): 255, 364 sh, 370. The IR spectrum contains absorption bands for hydroxyl (3385-3300 cm^{-1}), γ-pyrone carbonyl (1660 cm^{-1}), and aromatic C=C (1565, 1516 cm^{-1}).

Acetylation of **1** by acetic anhydride in pyridine gave the pentaacetate with mp 196-198°C. Alkali fusion with KOH gave fluoroglucinol and protocatechuic acid [3, 4].

Kaempferol (2) (3,5,7,4′-tetrahydroxyflavone), yellow needles, $C_{15}H_{10}O_6$, mp 276-278°C, R_f 0.88 (BAW, 4:1:2), 0.05 (15% CH_3COOH), UV spectrum (EtOH, λ_{max}, nm): 265, 370. The IR spectrum contains absorption bands for hydroxyl (3400, 3300 cm^{-1}), γ-pyrone carbonyl (1650 cm^{-1}), and aromatic C=C (1580, 1540 cm^{-1}).

Acetylation of **2** by acetic anhydride in pyridine provided the tetraacetate with mp 184-186°C. Alkali fusion with KOH gives fluoroglucinol and *p*-hydroxybenzoic acid [4].

Hyperin (3) (quercetin-3-O-β-D-galactoside), light yellow needles, $C_{21}H_{20}O_{12}$, mp 236-238°C, $[\alpha]_D^{20}$ -59.0° (*c* 0.1, CH_3OH), R_f 0.54 (BAW, 4:1:2), 0.36 (15% CH_3COOH), UV spectrum (EtOH, λ_{max}, nm): 259, 360. Acid hydrolysis gave quercetin and D-galactose [4, 5].

Trifolin (4) (kaempferol-3-O-β-D-galactoside), yellow crystals, $C_{21}H_{20}O_{11}$, mp 259-260°C, $[\alpha]_D^{20}$ -35.0°C (*c* 0.1, C_2H_5OH), R_f 0.78 (BAW, 4:1:2), 0.24 (15% CH_3COOH), UV spectrum (MeOH, λ_{max}, nm): 267, 354. Acid hydrolysis gave kaempferol and D-galactose [4, 6].

Avicularin (5) (quercetin-3-O-α-L-arabofuranoside), light yellow needles, $C_{20}H_{18}O_{11}$, mp 208-210°C, $[\alpha]_D^{20}$ -159°C (*c* 0.1, C_2H_5OH), R_f 0.65 (BAW 4:1:2), 0.28 (15% CH_3COOH), UV spectrum (EtOH, λ_{max}, nm): 260, 360.

Acid hydrolysis gave quercetin and L-arabinose. Acetylation gave an acetyl derivative with mp 184-185°C. Mixing a sample of the acetyl derivative and an authentic sample of acetylated avicularin did not depress the melting point [4, 7].

Compound 6, yellow crystals, mp 205-209°C, R_f 0.46 (BAW, 4:1:2), UV spectrum (MeOH, λ_{max}, nm): 270, 350. Acid hydrolysis gave kaempferol, D-xylose, and D-galactose. The yield of aglycone was 46%. This indicates that the flavonoid is a bioside. The structure of this flavonoid is under investigation.

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