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FLAVONOIDS FROM *Geranium robertianum*

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In continuation of research on phenolic compounds from representatives of the *Geranium* L. genus growing in Georgia, the aerial part (1.0 kg) of *G. robertianum* L. (Roberts geranium) was treated by the literature method [1]. A yellow solid precipitated from the purified aqueous liquid at room temperature. It was filtered off and recrystallized from pyridine to afford **1**. Phenolic compounds were extracted from the mother liquor of **1** by ethylacetate. The total ethylacetate extract was chromatographed over a polyamide column ($CH_3OH:H_2O$ eluent in various ratios). The enriched total extract and fractions of pure compounds were rechromatographed over a silica-gel:polyamide column to isolate **2-6**.

Qualitative reactions found that **1-3** are phenolic acids [2] whereas **4-6** are flavonoids [3]. The isolated compounds were identified using UV and IR spectral data, chemical transformations, and determination of melting points of samples mixed with authentic specimens.

1 is poorly soluble in boiling water and alcohol and insoluble in ether, mp ~360°C (dec.). UV spectrum (C_2H_5OH, λ_{max}, nm): 366, 255. IR spectrum (KBr, ν_{max}, cm^{-1}): 3300, 3250 (OH); 1720 (>C=O); 1615 (>C=C<); R_f 0.41 (BAW 4:1:2) (I), 0.33 (ice, $CH_3COOH:HCl:H_2O$, 30:3:10) (II), 0.05 (15% CH_3COOH) (III) [4]. The compound gives a red color with conc. CH_3COOH and $NaNO_2$ that is characteristic of free ellagic acid. **1** was characterized as ellagic acid [4].

2 consists of yellow crystals that are very soluble in hot water, methanol, and ethanol and insoluble in $CHCl_3$ and benzene, mp 197-198°C. UV spectrum (C_2H_5OH, λ_{max}, nm): 325, 299(sh), 235. R_f 0.81 (I), 0.78 (II), 0.26 (2% CH_3COOH) (IV). Fusion of the compound with KOH forms protocatechic acid. **2** was identified as caffeic acid [4].

3 crystallizes from alcohol as white needles that are very soluble in alcohol and hot water, mp 238-240°C. UV spectrum (C_2H_5OH, λ_{max}, nm): 210, 274. R_f 0.66 (I), 0.64 (II), 0.36 (IV). **3** was identified as gallic acid [4].

The Bryant cyanidin reaction [3] established that one of the isolated flavonoids is a glycoside; two, aglycons.

4 is obtained as light yellow needles, MW 464 (spectrophotometry [5]), $C_{21}H_{20}O_{12}$, mp 236-238°C, $[\alpha]_D^{20}$ -59.0° (*c* 0.1, CH_3OH). UV spectrum (C_2H_5OH, λ_{max}, nm): 259, 360. R_f 0.54 (I), 0.36 (III). Acid hydrolysis of **3** produced quercetin [1] and D-galactose. A mixture of **3** with an authentic sample of hyperin did not give a depressed melting point. **4** was identified as quercetin-3-galactoside or hyperin [1].

5 forms white needles, MW 302 (spectrophotometry [5]), $C_{15}H_{10}O_7$, mp 310-312°C. UV spectrum (CH_3OH, λ_{max}, nm): 255, 364(sh), 370. IR spectrum (KBr, ν_{max}, cm^{-1}): 3385, 3300 (OH), 1660 (γ-pyrone >C=O); 1615, 1565 (>C=C<), R_f 0.76 (I), 0.03 (III). Fusion of **5** with KOH forms fluoroglucinol and protocatechic acid. Acetylation of **5** produced the pentaacetyl derivative with mp 196-198°C and identified it as 3,5,7,3′,4′-pentahydroxyflavone or quercetin [1].

6 forms white needles, MW 286 (spectrophotometry [5]), $C_{15}H_{10}O_6$, mp 276-278°C (EtOH). UV spectrum (C_2H_5OH, λ_{max}, nm): 265, 370. IR spectrum (KBr, ν_{max}, cm^{-1}): 3400, 3300 (OH); 1650 (γ-pyrone >C=O); 1580, 1540 (>C=C<), R_f 0.87 (I), 0.05 (III). Fusion of **6** with KOH forms fluoroglucinol and *p*-hydroxybenzoic acid. Acetylation of **6** produced the tetraacetyl derivative with mp 184-186°C. **6** was characterized on the basis of the results as 3,5,7,3′-tetrahydroxyflavone or kaempferol [1].

The study of the hydrolysates [6] of the total extract of *G. robertianum* identified **1-6**, which were isolated from this species for the first time.

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