FLAVONOIDS OF SOME SPECIES OF THE FAMILY *Scrophulariacea*

V. I. Frolova and S. F. Dzhumyrko

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We have continued a study of the chemical composition of the phenolic compounds of some species of the genus *Veronica* L., growing in the Northern Caucasus and gathered by us in the flowering phase [1, 2]. The freshly gathered herbage of *Veronica peduncularis* Bieb., *V. spicata* L., and *V. gentianoides* Vahl. (Kabkazskie Mineral'nye Vody) was successively extracted with ethanol, acetone (in the cold), and aqueous (50%) ethanol and with acetone on heating. When the extracts were concentrated, greenish-yellow deposits were obtained which, after preliminary purification (with petroleum ether, diethyl ether, chloroform, and water, successively) were crystallized from ethanol—acetone—water (5:4:1). The purified total flavonoids obtained were separated on columns with alkaline polyamide using for elution $CHCl_3$—CH_3OH mixtures in ratios of 9.5:0.5, 9:1, 8:2, 5:5, and 2:7. Three individual substances were isolated.

Substance (I) — yellow crystals, mp 237-239°C, $[\alpha]_D^{20}$ —70°. The Bargellini reaction was negative. In the UV spectrum, $\lambda_{max}^{CH_3OH}$ 305, 280, 225 nm; $\lambda_{max}^{CH_3COONa}$ 315, 270 nm; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 363, 305, 278 nm; $\lambda_{max}^{AlCl_3}$ 355, 327, 223 nm; $\lambda_{max}^{CH_3ONa}$ 330, 286 nm. The substance was readily hydrolyzed by 5% H_2SO_4 with the formation of equimolar amounts of an aglycone and of D-glucose. The aglycone formed amber-colored crystals with 250-252°C; the Bargellini test was positive [3]; acetyl derivative with mp 209-210°C. In the UV spectrum: $\lambda_{max}^{CH_3OH}$ 347, 336, 282 nm; with sodium acetate $\Delta\lambda$ + 29 nm; with $AlCl_3$ $\Delta\lambda_{max}$ + 32 nm; with CH_3COONa + H_3BO_3 $\Delta\lambda$ + 21 nm; with CH_3ONa $\Delta\lambda$ + 39 nm. From the products of chemical transformations, the aglycone was identified as 5,6,7-trihydroxy-4'-methoxyflavone [4].

Substance (II) formed light yellow needles with mp 198-204°C (from aqueous methanol). In the UV spectrum: $\lambda_{max}^{CH_3OH}$ 346, 285, 257 nm; $\lambda_{max}^{CH_3COONa}$ 356, 282, 260 nm; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 360, 283, 264 sh. nm; $\lambda_{max}^{AlCl_3}$ 426, 342 sh, 305, 276 nm; $\lambda_{max}^{AlCl_3+HCl}$ 374, 297, 261 nm; $\lambda_{max}^{CH_3ONa}$ 395, 303, 265 nm. The products of acid hydrolysis were D-glucose and an aglycone with the melting point above 360°C (with decomposition). Pentaacetate, mp 239-240°C. In the UV spectrum: $\lambda_{max}^{CH_3OH}$ 346, 283 nm; $\lambda_{max}^{CH_3COONa}$ 376, 305, 277 nm; $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 425 sh. 374, 290, 260 sh, nm; $\lambda_{max}^{AlCl_3}$ 425, 306, 273 nm, $\lambda_{max}^{AlCl_3+HCl}$ 374, 296, 260 nm; $\lambda_{max}^{CH_3ONa}$ 395, 345, 302 sh and 252 nm. The aglycone was identified as 3',4',5,6,7-pentahydroxyflavone [5, 6]. A mixture with an authentic sample gave no depression of the melting point.

Substance (III) could not be isolated in the crystalline state. R_f 0.17 (BAW (4:1;5)), 0.16 (15% AcOH). $\lambda_{max}^{CH_3OH}$ 346, 285 nm. On acid hydrolysis the glycoside was split into the aglycone 6-hydroxyluteolin and two molecules of D-glucose. The UV spectrum and a negative Bargellini reaction indicated the presence of the sugar residue in position 7 [7].

The IR spectra of the glycosides isolated contained absorption bands at 800 cm^{-1} showing β configuration of the glycosidic bond and at 1100-1010 cm^{-1} showing the pyranose form of the sugar ring.

The results of a comparison of the physicochemical indices with information in the literature permitted the substances isolated to be characterized as 4'-methoxyscutellarein 7-O-D-glucoside, 6-hydroxyluteolin 7-O-D-glucoside, and a 6-hydroxyluteolin 7-O-diglucoside, respectively [5-7].

From ethanolic extracts of the herbage of *Rhinanthus minor* L., *Scrophularia rupestris* Bieb., and *Rhynchocorys orientalis* (L). Benth., the total flavonoids of each species were obtained by the ethyl acetate method. Their analysis by preparative paper chromatography permitted the isolation and identification of the flavonoids apigenin, cosmosiin, cyanoroside, and diosmin.

Substances (I), (II), (III), cosmosiin, and cyanaroside were also detected by paper chromatography in ethanolic extracts of the epigeal parts of: *Veronica schistosa* E. Busch.,

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V. monticola Trautv., *V. orchidea* Crantz., *V. longifolia* L., *V. didyma* Ten., *V. persica* Poir., *V. filiformis* Smith., *V. chamaedrys* L., *V. umbrosa* Bieb., *V. multifida* L., *V. orientalis* Mill., *V. teucrium* L., *V. austriaca* L., *V. caucasica* Bieb., *V. anagallis-aquatica* L., *V. anagalloides* Guss. and *V. beccabunga* L. [8-10].

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RUTIN AND LUTEOLIN 7-RUTINOSIDE FROM THE LEAVES OF *Citrus unshiu*

A. G. Shalashvili and N. R. Rakviashvili

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We have investigated the flavonoid compounds of the leaves of *Citrus unshiu* Marc. (Unshiu mandarin) collected in the Sukhumi experimental station of subtropical crops of the All-Union Scientific-Research Institute of Plant-Growing. The leaves were fixed with steam and dried and were then comminuted and extracted with 80% methanol. The extracts were evaporated, and the aqueous residue was treated repeatedly with chloroform. Two-dimensional paper chromatography showed the presence in the extract obtained of not less than 12 phenolic compounds, predominantly represented by flavonoid glycosides. Fractionation of the combined phenolic compounds was carried out on a column of polyamide sorbent. Water and mixtures of water and methanol in various proportions were used as eluents. The fraction of flavonoid glycosides was separated on a column of microcrystalline cellulose (with water as the eluent) into subfractions of flavone and flavonol glycosides. Then individual compounds were isolated from the subfractions on a column of Sephadex LH-20 (eluent: acetone—methanol—water (2:1:1)). Two substances (I and II) were obtained.

The positions of the main absorption maxima of substances (I) and (II) in the UV spectrum characterized them as flavonol and flavone derivatives [1]. In the products of the acid hydrolysis [2] of substances (I) and (II) we detected quercetin (I), luteolin (II), and D-glucose and L-rhamnose (I and II) by PC in various solvent systems. On oxidative degradation [3], both substances gave the disaccharide rutinose (6-O-α-L-rhamnosyl-D-glucose).

It was established by qualitative reactions [4] and spectral investigations with ionizing and complex-forming reagents [1] that the rutinose was attached to the aglycones of substances (I) and (II) in position 3 and 7, respectively.

The physicochemical constants, spectral characteristics (UV, IR, and PMR spectra), and a chromatographic comparison with authentic compounds, and also literature information, permitted substances (I) and (II) to be identified as rutin and luteolin 7-rutinoside [5].

Institute of Plant Biochemistry, Academy of Sciences of the Georgian SSR, Tbilisi.
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