PHENOLIC COMPOUNDS OF *Rhodiola viridula* AND *Rh. heterodonta*

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In studying species of *Rhodiola* we have investigated the phenolic compounds of the hypogeal parts of *Rhodiola viridula* Boriss. and *Rh. heterodonta* (Hook et Thoms) Boriss., family Crassulaceae, collected in the Aksu-Dzhabagly reserve, KazSSR, in July, 1973.

The comminuted rhizomes were treated with 70% and 95% ethanol successively. The evaporated extracts were transferred into aqueous solutions which were then extracted successively with chloroform, ethyl acetate, and n-butanol. By column chromatography on a polyamide sorbent using mixtures of chloroform and water and of water and ethanol with increasing gradients of the second component, from *Rh. viridula* we isolated compounds (I-VII) and by preparative TLC (Kapron) in the ethanol–water (4:1) system, compound (X). From *Rh. heterodonta* we isolated substances (I-VI), (VIII), and (IX) and on separation by a method described previously [1], compounds (I), (II), and (VIII).

Compound (I), $C_{14}H_{20}O_7$, mp 158-159°C, $[\alpha]_D^{20}$ −31.2 (c 1.4; ethanol), on acid hydrolysis, gave p-tyrosol with mp 92-93°C (II) and glucose. The NMR spectrum of the TMS ether of the glucoside had the following signals: doublet at 4.16 ppm with J = 7 Hz (H-1 of β-glucose); the signals of four aromatic protons in the 6.6-7.2 ppm region; a triplet at 2.7-2.95 ppm (2H), J = 7 Hz), corresponding to the aliphatic β-protons of the tyrosol; and a multiplet in the 3.1-3.9 ppm region (6H of glucose) overlapped by the signals of the two protons of the CH_2 group of p-tyrosol present in the α-position. On the basis of UV, IR, and NMR spectra and the results of a comparison with an authentic sample, compound (I) was identified as salidroside (rhodioloside) [2, 3], and (II) as p-tyrosol.

Compound (III) with mp 238-240°C was identified as gallic acid by spectroscopy and by the GLC of its TMS derivative.

Compound (IV) with mp 273-276°C and compound (V) with mp 308-310°C were identified as kaempferol and quercetin, respectively.

Compound (VI) with mp 232-234°C, from its spectral and chromatographic properties, is umbelliferone.

Compound (VII) with mp 189-191°C, $[\alpha]_D^{20}$ −33.8° (c 0.1; methanol) was identified as rutin.

Compound (VIII) with mp 222-224°C, $[\alpha]_D^{20}$ −18.4° (c 0.26; ethanol) was identified by the results of UV spectroscopy with ionizing and complex-forming reagents, IR spectroscopy, and acid and enzymatic hydrolysis, as quercetin 3-O-β-D-glucopyranoside (isoquercitrin).

Compound (IX), with mp 168-171°C, $\lambda_{max}^{C_2H_5OH}$ 237, 298, 328 nm was identified by IR and UV spectroscopy with diagnostic reagents as ferulic acid.

Compound (X), with the composition $C_{15}H_{16}O_8$, mp 220-222°C, $[\alpha]_D^{20}$ −81.9° (c 0.08; ethanol), $\lambda_{max}^{C_2H_5OH}$ 250, 317 nm was split under the conditions of quantitative acid and enzymatic (β-glucosidase) hydrolysis into umbelliferone and glucose (1:1). On the basis of a polarometric analysis and of differential IR spectroscopy, compound (IX) was characterized as umbelliferone 7-O-β-D-glucopyranoside (skimmin) [4].

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THE POLYPHENOLIC COMPOUNDS OF *Epilobium hirsutum*. II

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Continuing an investigation of the polyphenolic compounds of *Epilobium hirsutum* [1], we have isolated the following flavonoid aglycones and glycosides: (I) with mp 275-277°C (from methanol); (II) with mp 307-310°C (from aqueous methanol); (III) with mp 357-360°C (from methanol); (IV) with mp 236-238°C (from aqueous methanol), $[\alpha]_D^{22}$ −52° (c 0.4; methanol); and (V) with mp 197-200°C (from aqueous methanol), $[\alpha]_D^{20}$ −19.8° (c 0.3; DMFA).

Color reactions and bathochromic shifts with complex-forming and ionizing reagents showed that (I) contained free hydroxy groups in positions 3, 4', 5, and 7, II in positions 3, 3', 4', 5, and 7, and III in positions 3, 3', 4', 5, 5', and 7.

In the products of alkaline degradation, by paper chromatography we found phlorogucinol (in all three substances) and p-hydroxybenzoic, protocatechuic, and gallic acids. The results obtained, and also a chromatographic comparison with authentic samples enabled the substances to be identified as kaempferol (I), quercetin (II), and myricetin (III).

On the basis of the results of UV spectroscopy with diagnostic reagents, the products of alkaline and enzymatic hydrolysis, and molecular rotation [2], it was established that substance (IV) was quercetin 3-O-β-D-glucopyranoside and substance (V) was myricetin rutinoside.

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