FLAVONOIDS OF Rhodiola litvinovii

E. A. Krasnov

UDC 547.972

We have previously reported the isolation from the epigeal part of Rhodiola litvinovii Boriss., family Crassulaceae, of two phenolic compounds — p-hydroxyacetophenone and picein [1]. Continuing our investigation of this plant, by two-dimensional paper chromatography we have detected in the rhizomes four and in the epigeal part three flavonoids. For their isolation, the comminuted rhizomes were extracted with 95% ethanol, and the concentrated ethanolic extracts were treated with water and were extracted with chloroform and with ethyl acetate. The dry ethyl acetate extract was separated on a column of Kapron with elution by water and aqueous ethanol. Substance (I) and (II) were isolated. On rechromatography using chloroform and chloroform—ethanol (8:2 and 7:3), and also preparative chromatography in a thin layer of Woelm polyamide in the ethanol—water (3:2) system we obtained substances (III) and (IV).

Substance (I), $C_{21}H_{20}O_{10}$, had mp 173-174°C [ethanol—water (1:1)], $[\alpha]_D^{20}$ $-166°$ (c 0.2; ethanol), R_f 0.47 and 0.64 (15% and 60% acetic acid; here and below, respectively, systems 1 and 2), $\lambda_{max}^{CH_3OH}$ 265, 346 nm. Quantitative acid hydrolysis gave the aglycone kaempferol and L-rhamnose in equimolecular amounts. From the bathochromic shifts in the UV spectra of the glycoside and aglycone with diagnostic reagents, free hydroxy groups were found in positions 4', 5, and 7. The glycoside suffered no change under the action of the β-hydrolases from the fungus Aspergillus oryzae.

On the basis of the results of a study of its chemical properties and UV and IR spectra, and polarimetry, substance (I) was identified as 3,4',5,7-tetrahydroxyflavone 3-O-α-L-rhamnopyranoside, or afzelin [2].

Substance (II) with mp 277-279°C, R_f 0.49 (system 2) was identical with the aglycone of afzelin, i.e., 3,4',5,7-tetrahydroxyflavone (kaempferol).

Substance (III) with mp 293-294°C, $\lambda_{max}^{CH_3OH}$ 225, 271, 326, 380 nm, R_f 0.44 (system 2) was identified by direct comparison with an authentic sample as 3,4',5-7,8-pentahydroxyflavone (herbacetin).

Substance (IV), $C_{21}H_{20}O_{11}$, had mp 271-272°C, $[\alpha]_D^{20}$ $-102°$ (0.2; methanol), ν_{CO} 1665 cm^{-1}, $\lambda_{max}^{CH_3OH}$ 268, 342, 385 nm, R_f 0.16 (system 1), 0.74 (system 2). Hydrolysis with 2% HCl (1 h) formed an aglycone (yield 65%) with mp 285-287°C, which was identified as herbacetin, and L-rhamnose. UV spectra of the glycoside with ionizing and complex-forming reagents showed the presence of OH groups in positions 3, 5, and 7. The formation of an intense crimson red coloration by the reaction of the aglycone with p-benzoquinone and a negative gossypetone test on the glycoside showed that the carbohydrate component was present at C_8 [3].

An intense yellow fluorescence of the substance on chromatograms in filtered UV light indicated the presence of a free hydroxy group at C_3. On the basis of the negative results of enzymatic hydrolysis, and the findings of IR spectroscopy and polarimetry, and also the absence of appreciable cleavage of the glycoside on acid hydrolysis under mild conditions [4], it was concluded that the sugar residue was α-L-rhamnopyranose.

Thus, the facts given show that substance (IV) has the structure of 3,4',5,7,8-pentahydroxyflavone 8-O-α-L-rhamnopyranoside, for which the name litvinolin is proposed.

LITERATURE CITED

1. E. A. Krasnov, L. A. Demidenko, and L. P. Zeman, Khim. Prir. Soedin., 421 (1973).
2. K. Dumkow, Planta Med., 19, 197 (1971).
3. A. G. Perkin, J. Chem. Soc., 103, 650 (1913).
4. A. Hunger and G. Reichstein, Helv. Chim. Acta, 35, 2 (1952).

Tomsk Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 851-852, November-December, 1979. Original article submitted June 15, 1979.

0009-3130/79/1506-0756$07.50