FLAVONOIDS OF THE EPIGEAL PART OF Rhodiola rosea. I.

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The flavonoids of the epigeal part of *Rhodiola rosea* L. (*Sedum rosea*, roseroot stonecrop), family *Crassulaceae* had not been studied previously, although there is information of their presence in the flowers and herbage of this plant [1, 2].

We have investigated the herbage and inflorescences in the fruit-bearing phases and the flowers of wild-growing and cultivated (Moscow province) roseroot stonecrop. It was found that the corresponding organs of the wild and cultivated plants did not differ in their chemical compositions. From the flowers of the plant under investigation we isolated flavonoid compounds (I-IV); from the inflorescences, compounds (I-V); and from the herbage, compounds (II, IV, V, VI, and VII). Among the substances isolated, four compounds (II, III, IV, and VI) were new.

Rhodionin (I) - yellow acicular crystals with the composition $C_{21}H_{20}O_{11}$, mp 232-235°C (decomp.), $[\alpha]_D^{20}$ -150° (c 0.2; ethanol) - was identified as herbacetin 7-rhamnoside [3].

Rhodionidin (II) — formed yellow crystals with the composition $C_{27}H_{30}O_{16}$, mp 209-211°C, $[\alpha]_D^{20}$ -32° (c 0.1; ethanol).

Rodiolgin (III) formed yellowish green crystals with the composition $C_{21}H_{20}O_{12}$, mp 176-178 178°C, $[\alpha]_D^{20}$ -11.3° (c 0.19; ethanol).

Rhodiolgidin (IV) formed yellow crystals with the composition $C_{27}H_{30}O_{17}$, mp 194-197°C (decomp.), $[\alpha]_D^{20}$ --30° (c 0.09; ethanol).

Rhodalin (V) - yellow crystals with the composition $C_{20}H_{18}O_{11}$, mp 261-264°C - was identified as herbacetin 8-xyloside [4].

Rhodalidin (VI) formed yellow crystals with the composition $C_{26}H_{28}O_{16}$, mp 242-245°C, $[\alpha]_D^{20}$ +48° (c 0.09; ethanol).

Caffeic acid (VII) — light yellow crystals with the composition $C_{9}H_{8}O_{4}$, M⁺ 180, mp 218-222°C — was identified from its PMR and mass spectra.

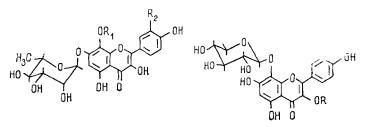
On acid hydrolysis, compounds (I, II, V, and VI) gave the same aglycone, herbacetin $(3,4^{*},5,7,8-pentahydroxyflavone, M^{+} 302)$, while compounds (III and IV) gave gossypetin $(3,3^{*}-4^{*},5,7,8-pentahydroxyflavone, M^{+} 318)$, identified by spectral characteristics and a direct comparison with authentic samples. The carbohydrate moieties of compounds (I) and (III) consisted of rhamnose; those of (II) and (IV), rhamnose and glucose; those of (V), xylose; and those of (VI), xylose and glucose.

The ratio of the numbers of aromatic and aliphatic acetoxy groups in the PMR spectra of the acetates of compounds (II, IV, and VI) indicated the diglycosidic nature of these substances. Under the conditions of enzymatic hydrolysis with β -glucosidase the diglycosides (II), (IV), and (VI) yielded intermediate monoglycosides which were identified (by TLC, UV spectroscopy, and acid hydrolysis) as rhodionin (I), rhodiolgin (III), and rhodalin (V), respectively. To determine the positions of the second carbohydrate residue in each case the diglycosides (II), (IV), and (VI) were subjected to methylation with diazomethane followed by acid hydrolysis.

The UV, PMR, and mass spectra of the native substances and of their derivatives in combination with a number of qualitative reactions permitted the following structures to be put forward for the compounds isolated. [See scheme on next page.]

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Rhodionin (I): $R_1 = R_2 = H$ Rhodalin (V): R = HRhodionidin (II): $R_2 = H$, $R = \beta$ -D-glucopyranosyl Rhodalidin (VI): $R = \beta$ -D-glucopyranosyl Rhodiolgin (III): $R_1 = H$; $R_2 = OH$ Rhodiolgidin (IV): $R_2 = OH$, R_1 , = β -D-glucopyranosyl

Thus, the structures of four new compounds isolated from the epigeal part of roseroot stonecrop - rhodionidin (II), rhodiolgin (III), rhodiolgidin (IV), and rhodalidin (VI) have been established.

It is interesting that no gossypetin derivatives have hitherto been known for the genus Rhodiola.

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