FLAVONOIDS OF SOME SPECIES OF *Sedum*

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Continuing a chemical study of some species of stonecrops from the flora of the Far East, by the method described previously [2] we have isolated compound (I) from *Sedum middendorffianum* [1], compounds (II-IV) from *S. selskianum* [2], and compounds (IV-IX) from *S. kamtschaticum* Fisch., collected in the flowering phase in the Khabarovsk territory.

To study these substances we used NMR and UV spectroscopy under the conditions given by Mabry et al. [3], and their chromatographic behavior on paper and in thin layers of polyamide and silica gel.

Compound (I), mp 228-230°C, was identified as quercetin 3-β-D-glucoside (isoquercitrin) on the basis of its UV, IR, and NMR spectra, the products of acid hydrolysis, and comparison with an authentic sample.

Compound (II), $C_{28}H_{32}O_{16}$, mp 222-224°C, on acid hydrolysis, gave rhamnose, glucose, and the aglycone — isorhamnetin. The UV spectra with additives and the NMR spectrum of the TMS ether in CCl_4 showed that the D-glucose is attached to the 3-OH group of the aglycone (the anomeric proton gives a doublet with J = 6.5 Hz at 5.83 ppm), and the L-rhamnose is attached to the 7-OH group (H-1, doublet with J = 2 Hz at 5.16 ppm; CH_3, doublet at 1.13 ppm, J = 6 Hz). Thus, compound (II) is 3-O-β-D-glucosyl-7-O-α-L-rhamnosylisorhamnetin (brassidin) [4].

Compound (III), $C_{28}H_{24}O_{16}\cdot 2H_2O$, mp 214-216°C, ν_{CO} 1660, 1710 cm^{-1} is cleaved in an acid medium into L-rhamnose, myricetin (M^+ 318), and gallic acid (M^+ 170). Its UV and NMR spectra show that myricetin has a substituent in position 3 — rhamnose acylated with gallic acid. Such a compound has not been described in the literature, and we have called it gallomyricitrin.

Compound (IV), mp 248-249°C, according to its IR, UV, and NMR spectra and comparison with an authentic sample, is 6,7-dihydroxycoumarin (esculetin).

Compound (V), $C_{21}H_{20}O_{12}\cdot 2H_2O$, mp 203-205°C, was identified on the basis of the products of acid hydrolysis and spectroscopy, and a direct comparison, as myricetin 3-O-α-L-rhamnopyranoside (myricitrin).

Compound (VI), mp 232-234°C, giving on acid hydrolysis quercetin and galactose, was identical according to its UV and NMR spectra with hyperoside.

Compounds (VII), mp 255-258°C, and (VIII), mp 198-202°C, having identical compositions and practically identical UV and NMR spectra, differ by the carbohydrate moiety attached to the 3-OH group of myricetin. The first is myricetin 3-β-D-glucoside (isomyricitrin) and the second is myricetin 3-β-D-galactoside.

Compound (IX), $C_{21}H_{20}O_{13}$, mp 244-246°C, λ_{max}^{MeOH} 258, 275, 380 nm; diagnostic reagents show the presence in it of 3,4',7-OH groups and an ortho-dihydroxy grouping. Acid hydrolysis gave D-glucose and an aglycone $C_{15}H_{10}O_8$ giving a positive gossypetone test and identical with 3,3',4',5,7,8-hexahydroxyflavone (gossypetin).

The NMR spectrum of the TMS ether of the glycoside in CCl_4 showed a two-proton multiplet at 7.8 ppm (H-2',6'), a doublet with J = 9 Hz at 6.77 ppm (H-5'), a singlet at 6.05 ppm

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(H-6), a doublet with J = 8 Hz at 4.92 ppm (H-1 of glucose), and a multiplet in the 3.0-3.7 ppm region (6 H of glucose). In DMSO, the glycoside gives the signal of a 5-OH group at 12.37 ppm.

Methylation of the glycoside with dimethyl sulfate followed by hydrolysis led to the production of the 3,3',4',5,7-pentamethyl ether of gossypetin, the mass spectrum of which contained the molecular ion with m/e 388 (100%). The ion of the side-chain phenyl group with m/e 165 (60.8%) contained two methoxy groups. This shows that the glucose must be present in ring A.

The facts given, taken together, permit compound (IX) to be identified as gossypetin 8-O-β-D-glucopyranoside (gossypin). This is the first time that a glycoside of gossypetin has been isolated from plants of the genus *Sedum*.

LITERATURE CITED

1. G. P. Shnyakina and G. G. Zapesochnaya, Khim. Prirodn. Soedin., 674 (1973).
2. G. P. Shnyakina and G. G. Zapesochnaya, Khim. Prirodn. Soedin., 673 (1973).
3. T. J. Mabry et al., The Systematic Identification of Flavonoids, Springer, New York (1970).
4. L. Hörhammer, H. Wagner, H. Krämer, and L. Farkas, Chem. Ber., 100, 2301 (1967).