FLAVONOIDS AND HYDROXYCOUMARINS OF Sedum ewersii

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We have studied the composition of the phenolic compounds of Sedum ewersii Ledb. (Ewers' stonecrop), family Crassulaceae collected in the flowering phase in the Gorno-Altai AO, village of Kebezen'. By two-dimensional chromatography on paper using chromogenic reagents it was shown that the epigeal part contains not less than eight substances of phenolic nature, five of which are flavonoids and two are coumarins.

To isolate these compounds, the epigeal part was extracted successively with petroleum ether, chloroform, and ethanol. The dry ethanolic extract was separated on a column containing Kapron with elution by mixtures of water and ethanol. The aqueous eluates yielded substances (I-III), and 20% ethanol yielded substance (IV). When the individual fractions obtained with 40-95% ethanol were rechromatographed on polyamide using mixtures of chloroform and ethanol with increasing concentrations of the latter, compounds (V-VII) were obtained, and substance (VIII) was isolated in small amount by preparative chromatography on paper in 15% acetic acid.

The compounds isolated were identified from the products of their acid and enzymatic hydrolysis, alkaline degradation, physicochemical properties, IR spectra, and UV spectroscopy with ionizing and complex-forming reagents [1, 2], and also by the molecular rotation calculations by Klyne's method [3]. The sugars were identified by PC and by GLC in the form of the trimethylsilyl ethers [4].

Substance (I) with mp 234-235°C was identified with umbelliferone, and substance (II) with mp 269-271°C was characterized as 6,7-dihydroxycoumarin, as was confirmed by comparison with a sample of esculetin which we had isolated previously from other species of Sedum: S. purpureum, S. hybridum, and S. aizoon.

Substance (III), mp 159-161°C, $[\alpha]_D^{21} - 64°$ (c 0.3; water) was identified as arbutin [5].

Substance (IV) with mp 187-190°C, $[\alpha]_D^{21} - 35°$ (c 0.2; methanol) was split on hydrolysis with 0.1% HCl, without the formation of intermediate products, into quercetin (46.1%) and rutinose; it was identified as rutin.

Substances (V) (mp 277-279°C) and (VI) (mp 310-313°C) were identified as kaempferol and quercetin, respectively.

Substance (VII), $C_{21}H_{20}O_{10}$, mp 229-233°C, $[\alpha]_D^{21} - 135.6°$ (c 0.1; ethanol), λ_{max}^{MeOH} 265, 366 nm. On quantitative acid hydrolysis, L-rhamnose and kaempferol (64.3%) were obtained. The compound was identified as kaempferol 7-O-α-L-rhamnopyranoside.

Substance (VIII), $C_{21}H_{20}O_{11}$, mp 187-188.5°C, λ_{max}^{MeOH} 266, 357 nm, λ_{max}^{+AcONa} 273, 367 nm, λ_{max}^{+MeONa} 263, 409 nm, $\lambda_{max}^{+AlCl_3/HCl}$ 276 (353), 406 nm. Kaempferol and D-glucose (1:1) were found in the products of acid hydrolysis and of enzymatic hydrolysis with β-glucosidase. IR spectroscopy and the value of $[M]_D$ showed the β configuration of the glucosidic bond and a pyranose ring in the sugar residue. Consequently, substance (VIII) is kaempferol 4'-O-β-D-glucopyranoside. A kaempferol 4'-glucoside (laminoside) has been isolated previously but the position of the carbohydrate substituent was determined only on the basis of color reactions and PC without a determination of the nature of the glycosidic bond and the size of the oxide ring [6].

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FLAVONE BIOSIDES OF Campanula patula

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In a further study of the phenolic compounds of Campanula patula (rambling bellflower) [1, 2] by repeated chromatography on polyamide we have obtained another two substances of flavonoid nature.

Substance (I) with the composition $C_{27}H_{30}O_{15}$ formed yellow crystals with mp 196-198°C (aqueous methanol), $[\alpha]_D^{18} -114.2°$ (c 0.63; methanol), $\lambda_{max}^{C_2H_5OH}$ 256, 268 sh., 355 nm.

Substance (II) with the composition $C_{27}H_{30}O_{16} \cdot 1/2\,H_2O$ formed yellow needles aggregated into druses with mp 206-209°C (methanol), $[\alpha]_D^{18} -80.8°$ [c 0.44; DMFA-methanol (5:2)], $\lambda_{max}^{C_2H_5OH}$ 257, 268 sh., 355 nm.

When the substances were heated with 5% H_2SO_4 on a boiling-water bath for 4 h they give the same aglycone-luteolin. In addition, from (I) D-glucose and L-rhamnose (1:1) were obtained, and form (II) only D-glucose. On milder hydrolysis of the glycosides (2% HCl, 100°C, 2 h), an intermediate product was isolated which we have identified from its physicochemical properties as cynaroside [1].

Rhamnodiastase cleaved each substance to the aglycone and a biose. In the products of the hydrolysis of (I) and (II) by the PC method we found, respectively, rutinose and gentiobiose, glycoside (I) being hydrolyzed completely in 48 h and (II) in 8 h.

The absence of a shift of the absorption bands in the UV spectra of the glycosides with sodium acetate showed that the bioses were attached at C_7.

When compounds (I) and (II) were acetylated with acetic anhydride in pyridine, their full acetates (III and IV) were obtained with mp 142-144°C (petroleum ether-ether) and 233-236°C (methanol), respectively. In the NMR spectra of (III) and (IV) (ν = 100 MHz, $CDCl_3$, δ scale), the aromatic protons of luteolin form a characteristic group of signals in the 6.62-7.85 ppm region, and the signals of three aromatic acetyl groups are found at 2.48, 2.40, and 2.36 ppm. The carbohydrate moiety of (III) gives two groups of proton signals in the 4.7-5.1 ppm and 3.6-4.1 ppm regions with a ratio of intensities of 8:4, the signal of the anomeric proton of α-rhamnose at 4.78 ppm, and a doublet at 1.19 ppm (J = 6.5 Hz) of the CH_3 group of rhamnose, which is characteristic for rutinose [3]. In the NMR spectrum of (IV), the protons of the biose appear in the 4.9-5.4-ppm (7H) and 3.6-4.3 ppm (6H) regions, and the anomeric proton of the second β-glucose molecule in the form of a doublet at 4.58 ppm (J = 7.5 Hz).

Information on the structure of the carbohydrate chain was also obtained by the exhaustive methylation of the biosides by Hakomori's method [4]. By PC, TLC, and GLC the products of the hydrolysis of the methyl ether of (I) were shown to include 2,3,4-tri-O-methyl-D-glucose and 2,3,4-tri-O-methyl-L-rhamnose. When the permethylate of (II) was subjected to methanolysis, 2,3,4-tri-O-methyl-D-glucose and 2,3,4,6-tetra-O-methyl-D-glucose were identified.

Thus, substance (I) has the structure of luteolin 7-O-[α-L-rhamnopyranosyl-(1→6)-O-β-D-glucopyranoside], and substance (II) that of luteolin 7-O-[β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranoside].

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