FLAVONOID COMPOUNDS FROM THE FLOWERS OF Sempervivum ruthenicum

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We have previously established that the epigeal part of the plant Sempervivum ruthenicum contains a large complex of phenolic compounds [1, 2].

We have found that the flavonoids accumulate mainly in the flowers and to a smaller extent in the leaves of the plant, and the stems contain only traces of these substances.

In a study of the products of the acid hydrolysis of purified extracts from the flowers, leaves, and stems, it was found that they contain the aglycones quercetin, kaempferol, isorhamnetin, and scutellarein.

By two-dimensional paper chromatography of a methanolic extract of the flowers in ethyl acetate–formic acid–water (10:2:3) (system 1) and 15% acetic acid (system 2) we have found no less than 18 substances of flavonoid nature in it. The total flavonoids isolated from the flowers amounted to 85% of the weight of the dry raw material.

These substances were separated on a column of Kapron. Ethanol elution gave five substances: (VI) (10% ethanol), (VII)* (20% ethanol), (VIII) and (IX) (40% ethanol), and (X) (50% ethanol). The R_f values of these compounds in system 1 were 0.35, 0.70, 0.76, 0.75, and 0.39, respectively.

Substance (VI) consisted of yellow needles with mp 213-215°C [from aqueous acetone (1:1)], $[\alpha]_D^{20}$ –35° (50% methanol). The UV spectrum of this compound (λ_{max} 345 and 290 nm) is characteristic for flavonoids [3]. From the products of the hydrolysis of this compound with 2% sulfuric acid we isolated an aglycone with mp 345-347°C and sugar components identified as D-glucose and L-rhamnose. The study of this compound is continuing.

Substance (VII), $C_{21}H_{20}O_{12}$, mp 238-239°C [from aqueous acetone (1:1)], $[\alpha]_D^{20}$ –60° (ethanol). From the products of acid hydrolysis we obtained galactose (phenylosazone with mp 185-186°C) and an aglycone, $C_{15}H_{10}O_7$, with mp 310-312°C (mp of the acetate 199-201°C) identified as quercetin [4].

Substance (VIII), $C_{22}H_{22}O_{12}$, mp 166-169°C [from aqueous acetone (1:1)], $[\alpha]_D^{20}$ –59.8°. From the products of its hydrolysis with sulfuric acid we isolated D-glucose and an aglycone $C_{16}H_{12}O_7$ with mp 303-305°C (mp of the acetyl and methyl derivatives 207-209°C and 151-153°C, respectively). Qualitative reactions and UV and IR spectroscopy [5] showed the presence in it of hydroxy groups in the 3, 5, 7, and 4' positions and of a methoxy group in the 3' position, which permits it to be characterized as 3,4',5,7-tetrahydroxy-3-methoxyflavone (isorhamnetin).

Substance (IX), $C_{22}H_{22}O_{12}$, mp 253-255°C, $[\alpha]_D^{20}$ –58.9°, gave an acid hydrolysis galactose and an aglycone identified as isorhamnetin.

Substance (X), $C_{21}H_{18}O_{12}$, mp 210-213°C, $[\alpha]_D^{20}$ –131.2°, is resistant to enzyme preparations from Aspergillus oryzae and rhamnodiastase, but is cleaved by the enzyme of the pancreatic juice of the grape snail. In the hydrolysis products we found an aglycone and glucuronic acid [R_f 0.30 in the butan-1-ol–

* Substance (VII) was contaminated with very small amounts of (VI) and (VIII) and it was purified by rechromatography on a column of Kapron using ethanol–chloroform (1:4) as the eluent.

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pyridine–water (6:4:3) system]. Similar products were obtained when this substance was hydrolyzed with 2% sulfuric acid. The aglycone had the composition $C_{15}H_{10}O_6$, mp 345-347°C (acetyl and methyl derivatives melting at 236-238°C and 161-163°C, respectively). The UV spectra of this compound [λ_{max} 345 and 290 nm (ethanol), 370 and 280 nm (sodium acetate), 385 and 320 nm (sodium ethoxide), and 390 and 304 nm (aluminum chloride)] show that it contains hydroxy groups in the C_5, C_6, C_7, and C_4' positions. Consequently, this aglycone is 4',5,6,7-tetrahydroxyflavone.

The substances isolated were identified from their elementary analyses, bathochromy, products of acid hydrolysis and alkaline degradation, UV and IR spectra, mixed melting points with authentic samples, R_f values, and qualitative reactions as quercetin 3-O-β-D-galactopyranoside (VII), isorhamnetin 3-O-β-D-glucoside (VIII), isorhamnetin 3-O-β-D-galactoside (IX), and scutellarein 7-O-β-D-glucuronide (X).

We are the first to have isolated these substances from the family Crassulaceae.

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