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FLAVONOIDS OF Solidago canadensis AND S. virgaurea

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Continuing an investigation of goldenrod [1], we give the results of a study of two species of the plant Solidago canadensis L. Canada goldenrod) and S. virgaurea L. (Eurpean goldenrod), family Asteraceae (Compositae), collected at the beginning of the flowering period.

The dried and comminuted flowers and leaves of S. canadensis were extracted with 95% ethanol, the extract was evaporated until the solvent had been driven off completely, and the residue was diluted with water. To free the flavonoids from accompanying substances, the extract was treated successively with chloroform, butanol, and ethyl acetate. The flavonoid substances were separated on polyamide sorbent with elution by ethanol–chloroform (1:4) and were then crystallized from water–acetone (1:1).

Substances (I-III) were isolated from the ethyl acetate extract. From their qualitative reactions, physicochemical properties, and UV spectra with diagnostic reagents [2], and also by chromatography with markers, the substances isolated were identified as a number of aglycones of the flavonol group.

Substance (I) – composition $C_{15}H_{10}O_6$; mp 275-277°C; UV spectrum: 371, 272 nm (in methanol)* – was 3,4',5,7-tetrahydroxyflavone (kaempferol).

Substance (II) – composition $C_{15}H_{10}O_7$; mp 311-314°C. The UV spectrum (370, 257 nm, in methanol) did not differ from that of 3,3',4',5,7-pentahydroxyflavone (quercetin).

Substance (III) – composition $C_{16}H_{12}O_7$; mp 305°C (decomp.); UV spectrum: 368, 254 nm (in methanol) – was identified as 3,4',5,7-tetrahydroxy-3'-methoxyflavone (isorhamnetin).

The separation on polyamide of the butanolic extract yielded substances (IV-VII) which, according to the preliminary results of a chemical study, were flavonoid biosides. D-glucose and L-rhamnose were detected in the products of the hydrolysis with 5% hydrochloric acid of substance (IV-VII), together with the aglycones kaempferol, isorhamnetin, rhamnetin (3,3',4',5-tetrahydroxy-7-methoxy flavone), and quercetin, respectively.

From their UV spectra with diagnostic reagents it was established that in all the substances isolated the sugar components were present in position 3 in the form of biosides. Rhamnose was the terminal sugar residue. All the substances isolated were hydrolyzed by the enzyme rhamnodiastase, which confirmed the β configuration of the glycosidic center of the glucose.

Substance (IV) – composition $C_{27}H_{30}O_{15}$; mp 173-175°C; UV spectrum, 350, 266 nm (in methanol) – was identified as kaempferol 3-O-β-D-glucorhamnoside.

Substance (V) – composition $C_{28}H_{32}O_{16}$; mp 171-173°C; UV spectrum: 353, 255 nm (in methanol) – consisted of isorhamnetin 3-O-β-D-glucorhamnoside.

Substance (VI) –composition $C_{28}H_{32}O_{16}$; mp 184-187°C; UV spectrum: 357, 257 nm (in methanol) – was identified as rhamnetin 3-O-β-D-glucorhamnoside.

Substance (VII) – composition $C_{27}H_{30}H_{16}$; mp 188-192°C; UV spectrum: 358, 258 nm (in methanol) – was identical with rutin (quercetin 3-O-β-D-rutinoside).

*The absorption maxima in the UV spectra of substances (I-VII) are given.

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Seven compounds identical with those described above were isolated from S. virgaurea.

Thus, free flavonols and their biosides have been detected in S. canadensis and S. virgaurea. The flavonoid compositions of the species of goldenrod studies are similar to one another; differing only by the ratios of the individual components.

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FLAVONOIDS OF Salix acutifolia

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We have investigated the flavonoid composition of the leaves of Salix acutifolia Willd. (sharpleaf willow) collected in August in Gomel' province (Belorussian SSR)

The dry comminuted leaves (1 kg) were exhaustively extracted with 80% ethanol. The ethanolic extracts were concentrated in vacuum, diluted with water, and treated with chloroform.

The purified aqueous fraction was extracted with diethyl ether and with ethyl acetate. The ethereal and ethyl acetate fractions so obtained were chromatographed on columns of polyamide sorbent. The chromatography of the ethereal fraction with elution by chloroform–ethanol containing increasing concentrations of the latter yielded substances (I), (II), and (III). Substances (IV), (V), and (VI) were isolated from the ethyl acetate fraction of the aqueous ethanolic mixture.

Substance (I) – $C_{15}H_{10}O_7$; mp 309-312°C; acetate with mp 198-199°C; λ_{max} 255, 270, 372 nm.

Substance (II) – $C_{15}H_{10}O_6$; mp 328-330°C; the acetate had mp 224-226°C; λ_{max} 255, 268, 350 nm.

Substance (III) – $C_{15}H_{10}O_5$; mp 349-351°C; acetate with mp 183-185°C; λ_{max} 268, 337 nm.

Substance (IV) – $C_{21}H_{20}O_{11}$; mp 226-268°C; $[\alpha]_D^{20}$ −54.7° (formamide); λ_{max} 257, 268, 351 nm.

Substance (V) – $C_{21}H_{20}O_{10}$; mp 222-225°C; $[\alpha]_D^{20}$ −142.8° (formamide); λ_{max} 269, 332 nm.

Substance (VI) – $C_{21}H_{20}O_{12}$; mp 243-245°C; $[\alpha]_D^{20}$ −59° [methanol–pyridine (5:1)]; λ_{max} 256, 268, 364 nm.

From their physical constants, the characteristics of their IR, UV, and PMR spectra, the products of their acid hydrolysis, the reuslts of elementary analyses, and comparisons of them with literature information, and also on the basis of the absence of depressions of the melting points of mixtures with authentic samples, we identified substance (I) as quercetin [2], (II) as luteolin [1], (III) as apigenin [3], (IV) as cynaroside [1], (V) as cosmosiin [3], and (VI) as quercimeritrin [2].

Substance (VII) and (VIII) were minor components and they were identified by paper chromatograpy with markers as isoquercetin and rutin, respectively.

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