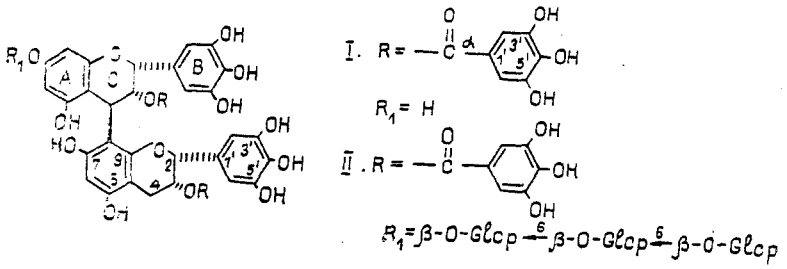

A study of the products of enzymatic cleavage of rhodisinoside and of the acid hydrolysis of its permethylate showed that the sugar moiety consisted of three D-glucose residues linked with the aglycon by a β-glycosidic bond and with one another by β-C-6 ← C-1 bonds (the presence of β-glucose was confirmed by the ^{13}C NMR characteristics). In galloylated catechin glycosides the sugars are usually attached to the aglycon in position 5 or 7. Because position 5 of the "upper" and position 7 of the "lower" epicatechin blocks (II) are sterically hindered, we suggest that the most probable position of attachment of the sugar moiety is the C-5 position of the "lower" or the C-7 position of the "upper" epigallocatechin block. On the basis of the facts given above, we suggest for rhodisin and rhodisinoside the most probable structures and relative configurations (I) and (II).

The study of the structures of the other proanthocyanidins is continuing.

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FLAVONOIDS OF Salsola collina

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We have investigated the epigeal part of Salsola colina Pall., family Chenopodiaceae, collected in the beginning of October in Novosibirsk province.

The air-dry comminuted herbage (80 kg) was extracted with 80% ethanol. From the n-butanol-soluble part of the evaporated extract previously treated with hexane and chloroform we have isolated six flavonoid compounds by column chromatography on polyamide and silica gel.

Compound (I) was tricin, $C_{17}H_{14}O_7$, mp 282-284°C. MS (EI), m/z: 330, 178, 152. UV spectrum: $\lambda_{max}^{CH_3OH}$ 250, 271, 352 nm [1]. Acetate of (I), $C_{23}H_{20}O_{13}$, mp 248-250°C. The CSs of the protons of (I) in the PMR spectrum coincided with those given in the literature [2]. ^{13}C NMR spectrum (DMSO-d_6): 164.4 (C-2); 103.8 (C-3); 182.0 (C-4); 161.6 (C-5); 99.1 (C-6); 163.8 (C-7); 94.4 (C-8); 157.5 (C-9); 104.6 (C-10); 120.6 (C-1'); 104.6 (C-2', C-6'); 148.4 (C-3', C-5'); 140.0 (C-4'); 56.6 (OCH_3). The assignment of the signals of the carbon atoms in the ^{13}C NMR spectrum of (I) was made on the basis of a comparison with the results for apigenin and tricetin [3].

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Compound (II) was tricin 7-O-β-D-glucopyranoside, $C_{23}H_{24}O_{12}$, mp 244-246°C. FAB-MS, m/z: 493 $(M + H)^+$, 331 $(M + H - \text{hexose})^+$. UV spectrum: $\lambda_{max}^{CH_3OH}$ 245, 270, 352 nm [2]. Compound (II) was identified on the basis of the results of NMR spectroscopy and its UV spectra with ionizing and complex-forming additives.

Compound (III) was quercetin 3-O-β-D-glucopyranoside, $C_{21}H_{20}O_{12}$, mp 220-222°C, $[\alpha]_D^{20}$ −66.2° (c 0.1; CH_3OH). FAB-MS, m/z: 465 $(M + H)^+$, 303 $(M + H - \text{hexose})^+$. UV spectrum: $\lambda_{max}^{CH_3OH}$ 257, 260 nm. The ^1H and ^{13}C NMR spectra of (III) coincided with those given in the literature [1, 3].

Compound (IV), was isorhamnetin, $C_{16}H_{12}O_7$, mp 303-305°C. MS (EI), m/z: 316, 152, 151. UV spectrum: $\lambda_{max}^{CH_3OH}$ 255, 269 sh., 372 nm [1]. The ^1H and ^{13}C NMR spectra coincided with those given in the literature [1, 4].

Compound (V) was isorhamnetin 3-O-β-D-glucopyranoside, $C_{22}H_{22}O_{12}$, mp 170-172°C, FAB-MS, m/z: 479 $(M + H)^+$, 317 $(M + H - \text{hexose})^+$. $[\alpha]_D^{20}$ −58° (c 0.3; CH_3OH). UV spectrum: $\lambda_{max}^{CH_3OH}$ 255, 355 nm [1]. The change in the CS of the C-3 signal in (V) as compared with (IV) (−3.6 ppm), and also the presence in the ^{13}C NMR spectrum of the signals of the carbon atoms of a β-D-glucose residue at 101.0 (C-1"), 74.5 (C-2"), 77.5* (C-3"), 70.4 (C-4"), 76.6* (C-5"), and 60.7 (C-6") and of the signal in the PMR spectrum of the anomeric H-1" proton (doublet at 5.55 ppm, J = 7 Hz) confirmed the structure of (V).

Compound (VI) was isorhamnetin 3-O-[O-α-rhamnopyranosyl-(1 → 6)-β-D-glucopyranoside (narcissin), $C_{28}H_{32}O_{16}$, mp 176-178°C. FAB-MS, m/z: 647 $(M + H)^+$. $[\alpha]_D^{20}$ +112° (c 0.85; CH_3OH). UV spectrum: $\lambda_{max}^{CH_3OH}$ 254, 268 sh., 358 nm [1].

On acid hydrolysis, (VI) formed glucose, rhamnose, and isorhamnetin. In the PMR spectrum of (VI) the anomeric protons H-1" of the β-D-glucose residue and H-1"' of the α-L-rhamnose residue appeared at 5.44 ppm (d, J = 7 Hz) and 4.42 ppm (br.s), respectively. The position of the C-6" of the glucose residue at 67.0 ppm in the ^{13}C NMR spectrum of (VI) showed the 1 → 6 type of bond between the carbohydrate residues. The CSs of the carbon atoms of (VI) coincided with those for isorhamnetin 3-rutinoside [3].

This is the first time that compounds (I-VI) have been detected in Salsola collina. Isorhamnetin 3-O-glycoside has previously been detected in S. kali [4], and isorhamnetin 3-rutinoside in S. kali, S. blauca, and S. macera [5, 6].

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