FLAVONOID COMPOSITION OF THE POLLEN (POLLEN PELLETS) FROM *Salix caprea* AND *S. alba*

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We have previously reported the fatty-acid composition of pollen (pollen pellets) from *Salix caprea* L. (goat willow) and *S. alba* L. (white willow) [1].

Continuing the study of the chemical composition of the pollen (pollen pellets) collected by bees from these plants, we have detected in them no less than 5–6 compounds of flavonoid nature. The isolation of these compounds in the individual state proved difficult. Extraction by the usual method [2, 3] was unsuccessful, and therefore to determine the composition of the flavonoids 25 g of air-dry pollen was carefully triturated in a mortar and suspended in aqueous ethanol, and the suspension was treated with an equal volume of dilute sulfuric acid [4]. The mixture was boiled for 1–2 h and, after cooling, the solution was filtered and was treated successively with diethyl ether and ethyl acetate. The diethyl ether fraction contained the aglycones quercetin and kaempferol, and the ethyl acetate fraction contained the same aglycones and unhydrolyzed glycosides. After neutralization with barium carbonate, the hydrolysate was found to contain the same sugars as were present in the pollen before hydrolysis (fructose, glucose, galactose and traces of rhamnose). After the acid treatment, the pollen was extracted with 60% ethanol, in this way another aqueous ethanolic fraction was obtained which contained glycosides. Three compounds were isolated from the combined glycoside-containing fractions by chromatography on a column of polyamide (eluants: water and dilute solutions of ethanol).

Substance (I) — yellow crystals; mp 175°C. UV spectra: $\lambda_{max}^{C_2H_5OH}$ 350, 300 sh, 267; + $AlCl_3$: $\Delta\lambda$ + 52 nm; + CH_3COONa: $\Delta\lambda$ + 6; + H_3BO_3 + CH_3COONa: $\Delta\lambda$ 0. From its R_f values in various systems — 1) butan-1-ol–CH_3COOH–H_2O (4:1:5); 2) 15% CH_3COOH; and 3) H_2O (0.69, 0.40 and 0.13, respectively) — the substance was identified as kaempferol 3-O-glucopyranoside (astragalin).

Substance (II) (UV spectrum: 257, 375 nm) gave no bathochromic shift in the presence of freshly fused sodium acetate; + $AlCl_3$: $\Delta\lambda$ + 50 nm; + H_3BO_3 + CH_3COOH: $\Delta\lambda$ + 10 nm. From its R_f values (0.30 in system 1 and 0.10 in system 2), it corresponded to quercitin 7-O-β-D-glucopyranoside (quercimeritrin).

Substance (III) formed pale yellow crystals. UV spectra: $\lambda_{max}^{C_2H_5OH}$ 260, 273 sh, 356 nm; + $AlCl_3$: 274, 298 sh, 334, 440 nm; + CH_3COONa: 260, 295 sh, 423 nm; + H_3BO_3 + CH_3COONa: 275, 380 nm. On hydrolysis it formed quercetin and D-glucose. A mixture with quercetin 3,7-di-O-glucoside gave no depression of the melting point. In their glycoside composition, the pollens of the goat and white willows are identical, but they differ from the pollen of the brittle willow.

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FLAVONOIDS OF *Ephedra lomatolepis*

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The detection of flavonoids and phenolic acids in *Ephedra equisetina* Bge. (Mongolian ephedra) has been reported previously [1–3]. We have continued the chemical investigation of the plants of the *Ephedra* genus. By two-dimensional paper chromatography, in the epigeal part of *E. lomatolepis* Sch. collected in the Alma-Ata province in the fruit-bearing period we have detected more than 20 substances of polyphenolic nature. From a methanolic extract, by column chromatography on polyamide with elution by chloroform–methanol with increasing concentrations of the latter, we have isolated a substance with mp 251–253°C (from aqueous ethanol), $[\alpha]_D^{24}$ –64.3° (c 0.28; CH_3OH). UV spectra, nm: 274, 336, 384 (CH_3OH); + CH_3COONa: 272, 342, 384; + CH_3COONa + H_3BO_3: 276, 338, 382; + CH_3ONa: decomp; + $AlCl_3$: 254, 364, 442, + $AlCl_3$ + HCl: 254, 364, 442; + $ZrOCl_2$: 266, 394, 490; + $ZrOCl_2$ + citric acid: 266, 376, 428.

The positions of the main absorption maxima of the substance in the UV spectrum characterize it as a flavonol derivative. The substance is a glycoside, as is shown by the existence of optical rotation and by the results of acid hydrolysis, giving an aglycone corresponding in melting point and spectral characteristics of herbacetin [4] and glucose. The PMR spectrum of the substance in deuteropyridine includes the signals of five of the protons of herbacetin: 8.7 ppm (d, J = 8 Hz, H-2', 6'); 7.2 ppm (d, J = 8 Hz, H-3', 5'); 6.5 ppm (s, H-6). In the stronger field there is a doublet with J = 6 Hz (δ 5.7 ppm) characteristic for the anomeric proton of a β-glucose residue, the remaining protons of which give signals in the δ 4.4–3.8 ppm region.

The UV spectra of the flavonoid shows that the hydroxy groups in position 3, 4', and 5 are free. Consequently, the glucose can be attached either at the C-7 or the C-8 position. A positive gossypetin reaction for the substance and its aglycone, characterizing the presence of a 5,8-dihydroxy grouping [5], excludes attachment at C-8. The pyranose nature of the glucose ring follows from an analysis of the specific rotation characteristics.

On the basis of the facts obtained, the structure of 3,4',5,8-tetrahydroxyflavone 7-O-β-D-glucopyranoside has been established for the substance isolated. Herbacetin 7-glucoside has been detected previously in *Gossypium* [6] and *Mimultus luteus* [7]. This is the first time that it has been isolated from plants of the domestic flora.

In addition to herbacetin 7-glucoside, we isolated two other substances of flavan nature from *Ephedra lomatolepis*. Since the substances are labile, their separation was performed through their acetyl derivatives on columns of Chromatin–silicic acid, with elution by benzene–acetone (1:1 and 1:2) [8]. The acetate of flavan 1 had mp 163–165°C (from ethanol), $[\alpha]_D^{24}$ –27.1° (acetone), and the acetate of flavan 2 had mp 155–157°C (from ethanol), $[\alpha]_D^{24}$ –25.8° (acetone). Both flavones gave a positive proanthocyanidin reaction and underwent acid cleavage with the formation of catechins, which characterize them as proanthocyanidins [9].

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