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FLAVONOIDS OF SOME PLANTS OF THE GENUS *Haplophyllum*

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Continuing a study of the components of the genus *Haplophyllum* A. Juss. for the presence of flavonoids, we have investigated the epigeal part of *H. latifolium* Kar. et Kir. collected in the flowering period in May, 1979, on the territory of the Syrdar'ya sovkhoz [communal farm] Chimkent province. The dried and comminuted raw material was extracted six times at room temperature with 70% ethanol. The concentrated ethanolic extract was diluted with water and was shaken successively with chloroform, ethyl acetate, and n-butanol. The ethyl acetate fraction was chromatographed on a column of silica gel in a chloroform–methanol gradient system. The individual flavonoids (I-III) were isolated.

Flavonoic (I) — $C_{16}H_{12}O_8$, M^+ 332, mp 335-337°C (decomp.) λ_{max} ethanol 261, 276, 340, 386 nm, was identified as haplogenin (3,4',5,7,8-pentahydroxy-3'-methoxyflavone) [1, 2].

Flavonoid (II) — $C_{24}H_{24}O_{14}$, mp 193-194°C (from ethanol) was identified as haploside A [1].

Flavonoid (III) — $C_{22}H_{22}O_{13}$, mp 211-213°C (from aqueous ethanol) — was identified as haploside B (haplogenin 7-O-β-D-glucopyranoside) [3].

The identification of flavonoids (I-III) was performed on the basis of the results of a study of spectral characteristics and was confirmed by comparison with authentic samples.

The dried and comminuted epigeal part of *H. perforatum* (N.B.) Kar. et Kir. collected in the budding period in Chimkent province was exhaustively extracted with 60% ethanol. The ethanol was distilled off in vacuum and the aqueous residue was freed from lipophilic substances by treatment with chloroform and was slowly passed through a column of polyamide sorbents. Then the column was washed with water and the flavonoids were desorbed with ethanol. The eluates were evaporated in vacuum and the residue was dried and subjected to preparative TLC on silica gel L 5/40 μ in the chloroform–methanol (4:1) system. Haplogenin and flavonoid (IV) with the composition $C_{17}H_{14}O_8$, mp 272-274°C (with sublimation), which was identified as limocitrin [4], were isolated.

Haploside B was isolated from the ethyl acetate fraction of an ethanolic extract of the epigeal part of *H. obtusifolium* Ledeb. by column chromatography on silica gel in the ethyl acetate–chloroform (8:2) system and was identified as in [3].

It was shown by TLC and qualitative reactions that the epigeal part of a plant *Haplophyllum* sp. collected in the environs of the village of Ayakagitma, Navoi region, UzSSR, likewise contained flavonoids. The ethyl acetate fraction of an ethanolic extract of the epigeal part of this plant was separated on a column of silica gel in the chloroform–ethanol system. This led to the isolation of an individual flavonol glycoside (V) — $C_{22}H_{22}O_{12}$, mp 163-165°C (from methanol), λ_{max} ethanol 257, 267, 360 nm. The acid hydrolysis of compound

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(V) led to an aglycon with mp 305-307°C, M^+ 316, λ_{max} ethanol 255, 266, 372 nm, identified as isorhamnetin (IR spectrum, mixed melting point), and D-glucose. By a study of IR, UV, and PMR spectra, and also on the basis of the results of acid hydrolysis, flavonoid (V) was identified as isohamnetin 3-O-β-D-glucopyranoside.

This is the first time that flavonoids (I-V) have been detected in the above-mentioned species of *Haplophyllum*.

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KAEMPFEROL GLYCOSIDES FROM *Astragalus dipelta*

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We have investigated the epigeal part of *Astragalus dipelta* Bunge, family Fabacaeae collected in the flowering–fruit-bearing period in the Uganmskii range close to the village of Khumsan for the presence of flavonoid compounds.

The dried comminuted raw material was exhaustively extracted with 70% ethanol. The ethanolic extracts were concentrated in vacuum and treated with chloroform. The purified aqueous extract was deposited on a column of polyamide and was eluted with aqueous solutions of ethanol. Analysis of some of the eluates obtained showed that they contained a mixture of flavonol glycosides. On rechromatography of individual fractions under the same conditions, substances (I-IV) were obtained.

Substance (I) (eluted with 20-25% ethanol) was identified as astragalin (kaempferol 3-O-β-D-glucopyranoside), $C_{21}H_{20}O_{11}$, mp 179-180% (ethanol), $[\alpha]_D^{20}$ − 16° (s 0.5; ethanol), λ_{max} 355, 270 nm [1].

Substance (II) (eluted with 20-25% ethanol) was robinin (kaempferol 7-O-β-rhamnopyranoside 3-O-β-robinobioside) $C_{33}H_{40}O_{19}$, mp 190-191°C (water), $[\alpha]_D^{20}$ − 120.4° [pyridine–ethanol (1:1)], λ_{max} 350, 265 nm [2].

Substance (III) (eluted with 25% ethanol) was trifolin (kaempferol 3-O-β-D-galactopyranoside), $C_{21}H_{20}O_{11}$, mp 229-231°C (ethanol), $[\alpha]_D^{0}$ − 18.1° (s 0.13; ethanol), λ_{max} 355, 266 nm [2].

Substance (IV) (eluted with 30-35% ethanol) was populin (kaempferol 7-O-β-D-glucopyranoside), $C_{21}H_{20}O_{11}$, mp 269-271°C (ethanol), $[\alpha]_D^{20}$ − 48.2° (s 0.1; ethanol), λ_{max} 365, 221 nm [2].

The structures of the glycosides isolated were confirmed by the results of elementary analysis, by UV and IR spectroscopy, and by the results of a study of the products of acid and enzymatic hydrolysis, and also by comparison with authentic samples.

The quantitative determination of the kaempferol glycosides was performed by a spectrometric method from the maximum densities of the spots directly on chromatograms treated with aluminum chloride.

The following amounts were found, %: astragalin — 0.09; robinin — 0.02; trifolin — 0.06; populnin — 0.03.

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