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DIACETYLISOSTACHYFLASIDE AND ACETYLISOSTACHYFLASIDE FROM *Stachys atherocalyx*

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From the herbage of *Stachys atherocalyx* C. Koch. we have isolated two new acylated flavone glycosides which we have called diacetylisostachyflaside and acetylisostachyflaside.

Diacetylisostachyflaside ($C_{31}H_{34}O_{18}$, mp 186-188°C) and acetylisostachyflaside ($C_{29}H_{32}O_{17}$, mp 174-178°C) have R_f values of 0.67 and 0.57, respectively, in solvent system 1) butan-1-ol–acetic acid–water (4:1:2), and 0.36 and 0.47, respectively, in system 2 (50% acetic acid).

Qualitative chemical reactions, chromatographic behavior, and the results IR and PMR spectroscopy characterized the compounds under investigation as glycosides of a flavone nature.

The PMR spectrum of diacetylisostachyflaside has the signals of two acetyl groups (signals at δ 1.85 and 1.62), of which the first belongs to an axial and the second to an equatorial acetoxy group of a carbohydrate component [1]. In the spectrum of acetylisostachyflaside, only the signal at δ 1.85 appears. The presence of acetyl substituents was also confirmed by the formation of acetohydroxamic acid [2]. Diacetylisostachyflaside and acetylisostachyflaside were hydrolyzed by 5% sulfuric acid with the formation of an aglycone, D-glucose, D-mannose, and acetic acid. From its physicochemical properties and the results of UV, IR, and PMR spectroscopy, the aglycone $C_{15}H_{10}O_6$, mp 298-301°C) was identified as 4',5,7,8-tetrahydroxyflavone (isoscutellarein) [3].

Both glucosides were stable to the action of rhamnodiastase and emulsin, but the esterases of the grape snail hydrolyzed them to the de-acetyl derivative – isostachyflaside [4]. An intermediate product in the enzymatic hydrolysis of diacetylisostachyflaside was acetylisostachyflaside. Different rates of the stripping off of the acetyl groups attached to equatorial and axial hydroxyls was also observed on mild alkaline hydrolysis with a 1.5% solution of potassium bicarbonate.

The position of the equatorial acetoxy group in the diacetylisostachyflaside molecule was determined from the products of periodate oxidation [5]. The absence of D-glucose and D-mannose in the degradation products excluded the presence of acetyl groups at C-3 and C-4 of both sugar residues. Attachment of the acetyl derivatives was possible at the C-6 hydroxyls of the D-glucose or D-mannose residues.

The bioside nature of the compounds studied was shown by oxidative degradation according to Chandler and Harper [6].

Neither glycoside was hydrolyzed by 0.5% caustic soda solution which shows the 1→2 order of the bond between the sugars [7].

The position of the carbohydrate component, the order of attachment of the D-glucose and D-mannose residues and the configuration of the glycosidic bonds were determined as described for isostachyflaside [4].

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Thus, the structure of acetylisostachyflaside can be represented as 4',5,7,8-tetrahydroxyflavone 4'-O-{acetyl[O-β-D-mannopyranosyl)-(1→2)-β-D-glucopyranoside]}, and that of diacetylisostachyflaside as 4',5,7,8-tetrahydroxyflavone 4'-O-{diacetyl[O-β-D-mannopyranosyl-(1→2)-β-D-glucopyranoside]}.

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PHENOLIC COMPOUNDS OF THE EPIGEAL PART OF *Valeriana*. IV. COMPOSITION OF THE FLAVONOIDS OF THREE CENTRAL ASIAN SPECIES OF THE GENUS *Valeriana*

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Continuing the search for promising species of the genus *Valeriana* L. among the flora of Central Asia [1], we have investigated the inflorescences, leaves, and stems of *Valeriana chionophila* Pop. et Kult. [∿ snow-loving valerian], *V. ficariifolia* Boiss. [∿ fig-leaved valerian], and *V. fedtschenkoi* Coincy (Fedchenko's valerian) — low-growing high-mountain plants, the first two of which are found, in the USSR, only in Central Asia [2]. According to the results of two-dimensional paper chromatography, the epigeal organs of the plants mentioned contain hydroxycinnamic acids and flavonoids. The inflorescences were the richest in flavonoids, the leaves contained a smaller amount, and there was very little in the stems. Using a procedure described previously [3], with the aid of column chromatography on polyamide sorbent from the individual extracts we isolated in the pure state two flavonoid glycosides (I and II), and from hydrolysates of the extracts five aglycones (III-VII).

Substance (I) was present in all the samples analyzed, while (II) was present in the inflorescences and the leaves of *V. fedtschenkoi* and also in the leaves of *V. chionophila*. According to their mobilities on two-dimensional chromatograms, the results of acid and enzymatic hydrolysis, and of UV spectroscopy with the addition of diagnostic reagents [4], substance (I) was characterized as luteolin 7-O-β-D-glucoside, and (II) as diosmetin 7-O-β-D-glucoside. On the basis of the results of physicochemical investigations and comparison with authentic samples isolated previously [3, 5, 6], the aglycones were identified as acacetin (substance III), apigenin (IV), diosmetin (V), luteolin (VI), and quercetin (VII). The inflorescences of the plants contained glycosides of all the aglycones mentioned with a predominance of the derivatives of (V) and III).

In addition to flavonoids, in the epigeal and, particularly, the hypogeal organs of the species of valerian mentioned we detected valepotriates, among which, by the results of TLC in comparison with known characteristics [7], we identified valtrate and dihydrovaltrate.

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