# C-GLYCOSIDES OF SPECIES OF Dipsacaceae. II.

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We have previously reported that plants of the family Dipsacaceae contain C,O-glycosides of flavones [1].

From the freshly gathered leaves of Knautia montana (MB) D. C., by extraction with methanol and purification by recrystallization from 80% methanol we have obtained a substance 2 with the composition $C_{28}H_{33}O_{16}$, mp 245-248°C. Its IR spectrum showed the absorption bands characteristic for C-glycosides (1010-1040 $cm^{-1}$) [2]. IR spectrum: $\lambda_{max}$ $CH_3$ OH 350, 262, 270 nm; $CH_3COONa$ 350, 270 nm; $H_3BO_3$ + $CH_3$ COONa 350, 270 nm; $AlCl_3$ 385, 278 nm; $C_2H_5ONa$ 403, 273 nm. Substance 2 has no hydroxy group at $C_7$ as is shown by the absence of bathochromy with sodium acetate.

For exhaustive hydrolysis we used a mixture of 30% solutions of sulfuric and acetic acids. After hydrolysis for 10 h, the aglycone, D-glucose, and L-arabinose had been formed. According to UV spectroscopy, alkaline degradation, demethylation with hydriodic acid, and a mixed melting point with an authentic sample, the aglycone was chrysoeriol.

When substance 2 was hydrolyzed with 5% sulfuric acid, during the first hour D-glucose was split off with the formation of substance 2a having mp 230-232°C (from 80% methanol) and the composition $C_{22}H_{22}O_{11}$. Analysis of the UV spectrum showed the presence in substance 2a of free hydroxy groups at $C_7$ and $C_5$. In the IR spectrum, absorption bands in the 1000-1100-$cm^{-1}$ region corresponded to vitexin and bands in the 2800-3600-$cm^{-1}$ region to a C-glycoside of luteolin. Acetylation with acetic anhydride in the presence of anhydrone took place incompletely. The hydroxy group at $C_5$ did not undergo acetylation, which is characteristic for C-glycosides [3]. The melting point of the acetyl derivatives was 145-147°C. UV spectrum: $\lambda_{max}$ 258, 300 nm.

The NMR spectrum of the acetyl derivative had the following chemical shifts ($CDCl_3$, 32°C): in the 1.7-2.5-ppm region – the signals of the protons of aliphatic acetyl groups (12 H); 2.28-2.48 ppm – the signals of the protons of aromatic acetyl groups (9 H); 3.98 ppm – the signal of an $OCH_3$ group; the proton at $C_1$" of the glucose appeared in the form of a doublet at 4.75 ppm (J = 6 Hz); 3.90-5.28 ppm – the signals of the H-5", H-4", H-3", and H-2" protons of glucose; 6.48 ppm H-3; 6.78 ppm (doublet) (J = 4 Hz) H-5; 7.46 ppm H-2"; and in the 7.68 ppm region a doublet (J = 2 Hz) representing the signal of the H-6' proton. The absence of the signal of a $C_8$ proton showed that this compound is an 8-C-glucoside, the glucose being present in it in the pyranose form. The spin–spin coupling constant of the proton at $C_1$" is smaller than that observed for the $\beta$ anomer [4, 5]. Consequently, the glucose may be present in the $\alpha$ form. An 8-C-glucoside of chrysoeriol has already been described in the literature under the name of scoparin [5]. Substance 2a may be considered its isomer; we have called it episcoparin, and the substance 2 isolated from Knautia montana is a new glycoside – 4',5-dihydroxy-3'-methoxyflavone 7-O-$\beta$-D-glucopyranoside -8-C-$\alpha$-D-glucopyranoside, or episcoparin 7-O-$\beta$-D-glucopyranoside, which we have called knautinoside.

## LITERATURE CITED

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