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FLAVONES OF *TRIFOLIUM PANNONICUM*

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Abstract—Hispidulin-7-glycoside, luteolin-7-glucoside and luteolin-7-glucuronide were isolated from leaves of *Trifolium pannonicum.*

Plant. Trifolium pannonicum L. *Source.* Botanical Garden of the College, Hannover. *Uses.* Formerly as forage plant. *Previous work* on *T. campestre.*[1]

Leaves. The MeOH extract of deep frozen leaves was separated first with light petroleum (b.p. 60–70°) and then with EtOAc. The substances of the latter phase were fractionated on polyamide Woelm with $CHCl_3$–MeOH–butanone-2 (CMB) in a gradient from 14:2:1 to 10:2:1, and subsequently by prep. PC with *n*-BuOH–HOAc–H_2O (4:1:2·2) (BAW).

Hispidulin-7-glycoside. Light yellow needles from MeOH-water. m.p. 226–235°. λ_{max}^{EtOH} 275 and 332 nm; $\lambda_{max}^{AlCl_3}$ 285 infl., 300 and 352 nm; λ_{max}^{NaOAc} 275, 337 and 399 nm; $\lambda_{max}^{NaOAc+H_3BO_3}$ 275 and 335 nm; λ_{max}^{NaOEt} 274 and 395 nm. PC: 15% HOAc, R_f 0·43; BAW, R_f 0·73. TLC on polyamide with CMB 9:4:2, R_f 0·8. Acid hydrolysis (32% HCl[2]) to hispidulin (UV, IR and co-chromatography with authentic substance[3]). Alkaline cleavage (10% KOH, N_2[4]) of the aglycone to 4-hydroxyacetophenone and presumably iretol. 4-hydroxy acetophenone: λ_{max}^{EtOH} 218 and 276 nm; $\lambda_{max}^{0·1nHCl}$ 275 nm; $\lambda_{max}^{0·1nNaOH}$ 217 and 325 nm; TLC: CMB 24:2:1, R_f 0,67 (compare 4-methoxyacetophenone from pectolinarigenin: λ_{max}^{NaOH} 216 and 277 nm; TLC: CMB, R_f 0·94; also presumably iretol). Methylation of hispidulin with dimethylsulphate in acetone and K_2CO_3 yielded the tetramethyl ether (UV[3], PC, TLC).

Luteolin-7-β-D-glucoside. UV, PC, TLC; acid hydrolysis to luteolin and glucose; aglycone-sugar ratio 1:0·8; cleavage with β-glucosidase.

Luteolin-7-β-D-glucuronide. UV, PC, TLC; cleavage with β-glucuronidase of *Helix pomatia* to luteolin.

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