C-GLYCOSIDES OF Desmodium canadense

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By paper chromatography in the ethyl acetate-formic acid-water (10:2:3) system, from an extract of the leaves of <u>Desmodium canadense</u> (L.) DC. (Canada tickclover), family Leguminosae, no less than ten substances of flavonoid nature have been isolated which have been denoted provisionally by the letters A (R_f 0.23), B (0.17), C (0.30), D (0.36), E (0.31), F (0.57), G (0.38), H (0.61), I (0.43), and J (0.37).

These substances are not hydrolyzed by 20% acid at the boil for 5 h. Their relatively high polarity on chromatography in 2% acid and their resistance to hydrolysis show that they contain C-glycosidic bonds. C-Glycosides have been found previously in <u>Desmodium caudatum</u> [1].

Substances D, F, H, and I were isolated by chromatography on polyamide. According to chemical and spectral investigations, the flavonoids H and D are C-glycosides of apigenin (5,7,4-trihydroxyflavone) and flavonoids I and F are C-glycosides of luteolin (5,7,3',4'-tetrahydroxyflavone).

Flavonoid H, $C_{21}H_{20}O_{10}$, has mp 195-198°C, $[\alpha]_D^{20}$ +48° (methanol). UV spectrum: $\lambda_{\max}^{\text{init}}$ 271, 333 nm, $\lambda_{\max}^{+NaCH_{a}COO}$ 278, 380 nm, $\lambda_{\max}^{+NaOCH_{a}}$ 278, 330, 395 nm, $\lambda_{\max}^{+H_{a}BO_{a}+NaCH_{a}COO}$ 271, 310 nm, $\lambda_{\max}^{+AlCI_{a}}$, 278, 304, 350, 380 nm. Apigenin and glucose were isolated from the products of acid hydrolysis according to Kiliani [2].

When the products of the isomerization of flavonoid H with 5% acid [3] were chromatographed on polyamide, two substances were isolated. One of them proved to be identical with the initial flavonoid. The second substance, $C_{21}H_{20}O_{10}$, was obtained with mp 264-265°C, $[\alpha]_D^{20} - 35^\circ$ (methanol). IR spectrum: λ_{\max}^{init} 272, 333 nm; $\lambda_{\max}^{+NaCH_{3}COO}$ 280, 372 nm; $\lambda_{\max}^{+NaOCH_{3}}$ 280, 335, 395 nm; $\lambda_{\max}^{+H_{3}BO_{3}+NaCH_{3}COO}$ 271, 331 nm; $\lambda_{\max}^{+AlCl_{3}}$ 280, 306, 345, 380 nm. The facts given, and also the results of a chromatographic investigation, permit the second substance to be identified as vitexin (5,7,4'-trihydroxyflavone 8-C- β -D-glucopyranoside), which is obviously an isomer of flavonoid H.

In its physicochemical properties and chromatographic behavior with an authentic sample, H is identical with saponaretin (5,7,4'-trihydroxyflavone 8-C-glucopyranoside).

Flavonoid D has the composition $C_{27}H_{30}O_{15}$, mp 225-230°C, $[\alpha]_D^{20}$ +97° (methanol). UV spectrum: λ_{\max}^{init} 272, 335 nm, $\lambda_{\max}^{+NaCH_3COO}$ 282, 388 nm; $\lambda_{\max}^{+NaOCH_4}$ 282, 333, 398 nm; $\lambda_{\max}^{+H_3BO_4+NaCH_3COO}$ 275, 323, 350 nm; $\lambda_{\max}^{+AlCI_3}$ 283, 305, 388 nm. Apigenin and glucose were again isolated from the products of the Kiliani acid hydrolysis [2] of flavonoid D.

By comparing the physicochemical properties of the known C-glycosides of apigenin and flavonoid D we established that this compound is vicein (5,7,4'-trihydroxyflavone 6,8-di-C-glucopyranoside).

Flavonoid I has the composition $C_{21}H_{20}O_{11}$, mp 220-223°C $[\alpha]_D^{20}$ +21° (methanol). UV spectrum: $\lambda_{\max}^{\text{init}}$ 255, 270, 348 nm; $\lambda_{\max}^{+\text{NaCH}_{3}\text{COO}}$ 277, 390 nm; $\lambda_{\max}^{+\text{NaOCH}_{3}}$ 269, 405 nm; $\lambda_{\max}^{+\text{H}_{4}\text{BO}_{3}+\text{NaCH}_{3}\text{COO}}$ 265, 372 nm; $\lambda_{\max}^{+\text{AiCI}_{3}}$ 277, 427 nm. When flavonoid I was subjected to Kiliani hydrolysis [2], luteolin and glucose were found.

According to its physicochemical properties, paper-chromatographic behavior, and a comparison with an authentic sample, flavonoid I was identified as homoorientin (5,7,3',4'-tetrahydroxyflavone 8-C-glucopyranoside).

Khar'kov Scientific-Research Institute of Pharmaceutical Chemistry. Translated from Khimiya Prirodnykh Soedinenii, No.5, pp. 634-635, September-October, 1970. Original article submitted April 13, 1970.

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Flavonoid F had mp 172-175°C, $[\alpha]_D^{20}$ +16° (methanol). UV spectrum: $\lambda_{\max}^{\text{init}}$ 257, 265, 353 nm; $\lambda_{\max}^{+\text{NaCH}_{2}\text{COO}}$ 273, 390 nm; $\lambda_{\max}^{+\text{NaOCH}_{2}}$ 272, 408 nm; $\lambda_{\max}^{+\text{H}_{3}\text{BO}_{3}+\text{NaCH}_{2}\text{COO}}$ 262, 375 nm; $\lambda_{\max}^{+\text{AICI}_{3}}$ 274, 434 nm. Luteolin was found in the products of acid hydrolysis according to Kiliani. A spectrophotometric molecular weight determination showed that flavonoid F contains not less than two sugar residues. A study of the nature of the sugar components and the position of their attachment is continuing.

LITERATURE CITED

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