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GLYCOFLAVONOIDS OF RANUNCULUS REPENS

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Literature data on the flavonoids of the Ranunculaceae is contradictory [1–3].

By paper chromatography, we have found not less than six substances of flavonoid nature in the herb Ranunculus repens L. (creeping buttercup) [4]. After three rechromatographings on columns of polyamide sorbent, we obtained two individual substances—A and B.

Substance A had mp 263–265° C, R_f 0.4 in 15% CH_3COOH, $\lambda_{max}^{C_2H_5OH}$ 228, 340 mμ. Substance B differs from A mainly only by its R_f value; mp 262–264° C, R_f 0.59, $\lambda_{max}^{C_2H_5OH}$ 265, 340 mμ. On acid hydrolysis, these flavonoids undergo mutual isomerization. An enzyme preparation from the fungus Aspergillus oryzae did not cleave substances A and B. Then each of the flavonoids was hydrolyzed with Kiliani's mixture [5]. The aglycones were separated on a small layer of polyamide sorbent. Both glycosides were shown to contain apigenin. In aqueous solutions after neutralization with the ion-exchange resin AB-17 (OH^- form), D-glucose and traces of D-arabinose were found. The presence of free hydroxy groups in positions 5, 7, and 4' was established by UV spectroscopy: in flavonoid A $\lambda_{max}^{+CH_3COONa}$ 271, 380 mμ, $\lambda_{max}^{+CH_3COONa+H_3BO_3}$ 268, 340 mμ, $\lambda_{max}^{+C_2H_5ONa}$ 266, 405 mμ, $\lambda_{max}^{+ZrOCl_2}$ 266, 390 mμ, and in flavonoid B $\lambda_{max}^{+CH_3COONa}$ 269, 379 mμ, $\lambda_{max}^{+CH_3COONa+H_3BO_3}$ 267, 339 mμ, $\lambda_{max}^{+C_2H_5ONa}$ 264, 410 mμ $\lambda_{max}^{+ZrOCl_2}$ 262, 395 mμ.

As already shown in the case of derivatives of scutellarein [6] and various C-diglycosides [7] a substituent in position 6 causes steric hindrance in the formation of a zirconyl complex, which appears as a decrease in the bathochromic shift to 20–30 mμ. Thus, the substances studied are rotation isomers [8]. Substance A may be characterized as 5,7,4'-trihydroxyflavone 8-C-β-D-glucopyranoside or vitexin. Substance B is also a 8-C-β-D-glucopyranoside of 5,7,4'-trihydroxyflavone and has the trivial name saponaretin.

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FLAVONOIDS OF RANUNCULUS ILLYRICUS

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In a study of the flavonoids of Ranunculus illyricus L. (Illyrian buttercup) we have obtained four individual substances. On the basis of a physicochemical investigation and a spectroscopic study in the UV region, flavonoid I was identified as vitexin and II as saponaretin. Substance III has mp 264–265° C, $\lambda_{max}^{C_2H_5OH}$ 258, 267, 350 mμ and substance IV mp 238–240° C, $\lambda_{max}^{C_2H_5OH}$ 258, 267, 350 mμ.

Acid hydrolysis showed the mutual isomerization of the flavonoids III and IV, the equilibrium shifting in the direction of substance IV prolonged hydrolysis. No carbohydrate moiety was found in the hydrolysate. These flavonoids underwent no change when treated with the enzymes of the fungus Aspergillus oryzae. The products of the hydrolysis of both substances by Kiliani's mixture [1] proved to be the aglycone luteolin and, as the carbohydrate moiety, D-glucose; traces of D-arabinose were detected. According to the rotation theory of the structure of C-glycosides [2], the carbohydrate residue may be attached in positions 6 or 8, which is shown by the magnitude of the bathochromic shift of the substances with the zirconyl ions. As has been shown by a study of derivatives of scutellarein [3] and C-diglycosides [4], a substituent in position 6 causes a decrease in the bathochromic shift to 20–30 mμ. The bathochromic shift of an ethanolic solution with the addition of zirconyl chloride was 70 mμ for the flavonoid III and 60 mμ for IV. This gives us grounds for stating that the carbohydrate substituents of the two glycosides are attached to the aglycone luteolin in position 8 and the substances are therefore rotation isomers. The trivial names of the flavonoids are as follows: III is orientin and IV is homoorientin.

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CATECHINS AND FLAVONOLS OF THE ROOTS OF RUMEX RECHINGERIANUS

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The catechins were extracted from the roots of Rumex Rechingerianus (moisture content 62.9%) collected in October by steeping them in ether until the reaction with 1% vanillin in concentrated hydrochloric acid was negative. The ethereal extracts were evaporated to dryness in a current of nitrogen. The residue was dissolved in methanol and chromatographed on a mixture of cellulose and Kapron (1 : 1). The dry residue from the evaporation of the eluates was dissolved in ether saturated with water, and the solution was chromatographed on silica gel. The stationary solvent was water and the mobile solvent ether and a mixture of ether and ethyl acetate [1]. The separated catechins were crystallized from water. The catechins isolated were (+)-catechin, (—)-epicatechin, and (—)-epicatechin gallate, which were identified from their melting points, elementary compositions, specific rotations, qualitative reactions, and the results of paper chromatography with reference samples.

The amount of catechins in the roots was determined spectrophotometrically from the absorption of the colored spots of the catechins directly on the chromatograms after treatment with silver nitrate [2]. The measurements were carried out in a SF-4A spectrophotometer at λ = 460 mμ.

Flavonols have been found in the roots of Rumex Rechingerianus [3]. The substances were separated by chromatography on polyamide using aqueous methanol of various concentrations as eluant. After repeated chromatography of the individual fractions and crystallization from aqueous ethanol, four individual flavonols were isolated. On alkaline cleavage (heating with 50% caustic potash at 150° C) they formed phloroglucinol and protocatechuic acid and on reduction (magnesium in concentrated hydrochloric acid) they formed cyanidin.

The features of the UV spectra with ionizing and complex-forming reagents [4, 5], the elementary compositions, the results of acid hydrolysis, and comparison with reference samples on paper chromatography in various systems of solvents enabled the following flavonols to be identified: quercetin, quercitrin, hyperoside, and rutin.

The amount of flavonols in the roots was determined spectrophotometrically from the intensity of the absorption of the colored spots of the flavonols directly on the chromatograms after treatment with aluminum chloride. The measurements were carried out in an SF-4A spectrophotometer at λ = 430 mμ. The following amounts were found (%): (+)-catechin, 0.152; (—)-epicatechin, 0.121; (—)-epicatechin gallate, 0.177; quercetin, 0.16; quercitrin, 0.066;