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;

hyperoside, 0.01; and rutin, 0.001 (on the weight of the absolutely dry raw material).

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4',5,6,7-TETRAMETHOXYFLAVONE FROM MARRUBIUM PEREGRINUM

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We have previously isolated from Marrubium peregrinum [1] in high yield a substance $C_{19}H_{18}C_6$ with two forms of crystals from ethanol and mp 141–142° C, 161–162° C, $[\alpha]_D \pm 0°$, M^+ 342.

On a thin layer of alumina (activity grade III) in the benzene—ethanol (9 : 1) system the substance had a R_f value of 0.65 (spot revealed in UV light or by the action of iodine); in silica gel containing gypsum in the benzene—acetone (9 : 1) system, R_f = 0.5 (the same blue fluorescence in UV light or a yellow coloration on spraying with concentrated H_2SC_4).

This paper gives information enabling the structure of this compound to be established.

The substance has four methoxyl groups and no free hydroxyl groups. It is not hydrogenated under the usual conditions on catalysts and readily forms bright yellow salts with strong acids. These results, and also the features of the UV spectrum [λ_{max} (ethanol) 265 and 370 mμ (log ε 4.23, 4.50)] and the IR spectrum (KBr; 2820, 1643, 1633, 1516 cm^{-1}) give grounds for assigning the substance to the flavone group.

When the compound was oxidized by Jones' method [2] with heating to 80° C, an acid $C_8H_8O_3$ was obtained. The mass spectrum of the latter had the peak M^+ 152, an intense ion with m/e 135 (M −17) and a fragment with m/e 107 (m* 85) formed from it. This shows the stepwise elimination of a carboxyl group.

The splitting off of formaldehyde from the fragment with m/e 107 leads to the appearance of a phenyl ion with m/e 77 (m* 55.5) which shows that the acid is a methoxybenzoic acid. By comparing the melting point of the acid (173–175° C) and its methyl ester (48° C) with literature data, it can be stated that it is p-methoxybenzoic (anisic acid).

Consequently, the natural flavone contains one methoxyl group in position 4' of ring B.

On the basis of information that the family Labiatae usually contains 5,6,7- or 5,7,8-trihydroxyflavones [3], and also of the results of a comparison of the UV spectra of the substance and those of various substituted flavones, it was concluded that the native product is 4',5,6,7-tetramethoxyflavone (I) identical with tetramethylscutellarein [4], which has not previously been found in plants.

This was definitely confirmed by the IR spectrum, thin-layer chromatography, and the absence of a depression of the melting point of a mixture with an authentic sample of 4',5,6,7-tetramethoxyflavone which was kindly given to us by Ya. Streletskii (Budapest, Hungary). The mass spectrometric measurements of the samples was carried out by Dr. L. Doleiš (Prague).