UDC 547.972

GLYCOFLAVONOIDS OF RANUNCULUS REPENS

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, p. 180, 1969

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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9 January 1969

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UDC 547.972

FLAVONOIDS OF RANUNCULUS ILLYRICUS

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Khimiya Prirodnykh Soedinenii, Vol. 5, No. 3, pp. 180–181, 1969

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.