Acid hydrolysis by Kiliani's method [2] gave apigenin and D-glucose mixed with a small amount of D-arabinose. The proportion of aglycone in the glycosides investigated was 58.9% for A and 61.5% for A-2 (calculated: 62.2%). The ratio of the intensities of the maxima of the long-wave absorption in the UV spectra of the glycosides and the aglycone indicate that both substances are monoglucosides [3].

The results of a comparison of the optical activity of the glycosides and their acetates with known C-glucosides [4], and also spectral differential analysis in the IR region [5], make it possible to assume that their carbohydrate moiety is in the pyranose form and has an equatorial or β-configuration of the bond with the aglycone.

From its physicochemical properties and a chromatographic comparison with an authentic sample, substance A-2 was identified as vitexin. Consequently, the initial compound A from which the vitexin was obtained must be saponaretin.

Thus, it has been shown that one of the flavonoid components of the leaves of Glycyrrhiza glabra is apigenin 6-C-β-D-glucopyranoside, or saponaretin.

The sample of vitexin was given to us by V. S. Batyuk of the Khar'kov Chemical and Pharmaceutical Scientific Research Institute.

REFERENCES

1. V. I. Litvinenko and N. P. Maksyutina, KhPS[CNC], 420, 1965.
2. H. Kiliani, Ber., 63, 2866, 1930.
3. G. Netien and Ph. Lebreton, Ann. Pharm. fr., 22, no. 1, 69, 1964.
4. W. E. Hillis and D. H. S. Horn, Austral. J. Chem., 18, 531, 1965.
5. I. P. Kovalev and V. I. Litvinenko, KhPS[CNC], 233, 1965.

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Khar'kov Chemical and Pharmaceutical Scientific Research Institute

ISOLATION OF SCUTELLARIN FROM CENTAUREA DEPRESSA

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The epigeal part of Centaurea depressa M. B. collected in Uzbekhistan (village of Burchumull, Tashkent Oblast) in the period of full flowering in 1964 has yielded a mixture of flavonoids comprising, from the results of paper chromatography, six substances. In addition, the ethyl acetate treatment of an extract acidified with mineral acid has yielded yet another flavonoid compound with the composition $C_{21}H_{18}O_{12}$ in the form of light yellow crystals sparingly soluble in water. Even after repeated recrystallization from methanol, the substance had no sharp melting point and began to darken at 210-215°C.

The IR spectrum showed the presence of the groups C = C, >C = C<, and 4'-OH (1661, 1615, 820, 835 cm^{-1}), and also absorption bands characteristic for hydroxy groups in ring A of the flavones, UV spectrum: λ_{max} 335 and 285 mμ.

When the substance was boiled with a mixture of glacial acetic acid and 10% sulfuric acid for 5 hr, hydrolysis took place with the formation of an aglycone having mp >340°C. UV spectrum: λ_{max} 338, 286 mμ. Melting point of the acetyl derivative 236-237°C. From the R_f value and the color reactions on paper chromatography in various systems of solvents, the aglycone was identical with a reference sample of scutellarein. The carbohydrate part of the glycoside was glucuronic acid (demonstrated by paper chromatography, revealed with a solution of p-anisidine hydrochloride in butan-1-ol).

With a solution of ferric chloride, the glycoside gave a green color, it reduced an ammoniacal silver solution in the cold, and did not give a bright yellow fluorescence with Wilson's reagent.

A mixture of it with the scutellarin isolated from Erigeron canadensis L. showed no depression of the melting point. On the basis of these results the substance was identified as a glucuronide of scutellarein (5, 6, 7, 4'-tetrahydroxyflavone). The investigation of the other flavonoids of this plant is continuing.

The sample of scutellarin from Erigeron canadensis L. was kindly given to us by Dr. V. Plouvier (Paris).

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THE QUERCIMERITRIN CONTENT OF SOME SPECIES OF CENTAUREA

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By the chromatography on Kapron of an ethanolic extract of the epigeal part of Centaurea cyanus L. (cornflower) prepared in the Kiev Botanical Gardens in 1965, we have isolated a flavonol glycoside with mp 247–249° C, mol. wt. 466.8.

The IR spectrum of the substance exhibited the following absorption bands: 3380, 3420, 1160, 1615, 1085, 1055, 1025, 940, 905, 885, 850, 800, 735, 705 cm^{-1} (UR-10 spectrometer, tablets in KBr), which indicates the presence of hydroxy groups in ring A of the chromone nucleus and in the lateral phenyl radical, and the presence of a carbonyl group, a double bond, and a sugar in the pyranose form. In the UV: $\lambda_{max}^{CH_3OH}$ 375, 255; $\lambda_{max}^{C_2H_5OH}$ 372, 257; $\lambda_{max}^{C_2H_5ONa}$ 361, 291 ($\Delta\lambda$ + 3, + 34); $\lambda_{max}^{CH_3COONa}$ 370, 258 ($\Delta\lambda$ + 1); $\lambda_{max}^{CH_3COONa+H_3BO_3}$ 395, 259 ($\Delta\lambda$ + 23, + 2); $\lambda_{max}^{AlCl_3}$ 424, 364 ($\Delta\lambda$ + 52). Acid hydrolysis of the glycoside gave the aglycone with mp 309° C. The acetyl derivative had mp 192° C. By paper chromatography and its UV and IR spectra, the aglycone was identified as quercetin. Enzymatic hydrolysis with the enzyme from the fungus Aspergillus oryzae also gave quercetin, together with D-glucose.

On the basis of the above results, the glycoside was identified as 3, 5, 7, 3', 4'-pentahdroxyflavone 7-β-D-glucopyranoside, which is known under the name of quercimeritrin (quercetin 7-β-D-glucopyranoside). We have isolated the same glycoside from the flowers of C. cheiranthifolia Willd. collected in 1965 in the region of the Teberda reserve at a height of 3000 m. No quercimeritrin has been found in other species of centaury that we have investigated (C. ciscaucasica Sosn., C. nigrifimbria (C. Koch) Sosn., C. micranthos Gmel., C. rutenica Lam., C. solstitialis L., and C. sumensis Kaleh).

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ANTHOCYANINS OF THE SEEDS OF RHEUM TATARICUM II

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The anthocyanins of the rhubarbs of the family Polygonaceae Lind. have not been studied previously. The anthocyanins were extracted from the raw material with methanol containing 1% of hydrochloric acid. The resulting extract was chromatographed on a column of silica gel using the organic phase of the butan-1-ol–acetic acid – water (4:1:5) system as the mobile solvent and the aqueous phase as the stationary solvent.

The paper chromatography of the anthocyanin fraction in various systems of solvents showed the presence of two anthocyanins in the fraction. The combined anthocyanins were separated by preparative paper chromatography in the acetic acid–concentrated hydrochloric acid–water (5:1:5) system. The sharply separated zones were cut out and eluted with methanol containing 0.01% of hydrochloric acid. Hydrolysis of the anthocyanins under severe conditions showed that the two compounds were glycosides of the same aglycone cyanidin.

The ratio fo the intensity of the light absorption of a solution at 440 mμ to the intensity at the corresponding maximum was twice as great for anthocyanin 1 as for anthocyanin 2, which indicates the diglucosidic structure of the latter [1].