

COUMARINS OF THE ROOTS OF HERACLEUM ANTASIATICUM

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It is known [1] that the fruit of the endemic species Heracleum antasiaticum Manden, which grows in the Caucasus, contains sphondin, pimpinellin, isopimpinellin, bergapten, isobergapten, and angelicin (substance 5).

The present paper gives the results of a study of the furocoumarins of the root of this plant. The coumarins were isolated by a procedure described previously [2]. Four substances were isolated in the individual crystalline state, three of them being identified as sphondin  $C_{12}H_8O_4$ , mp 190–192° C,  $R_f$  0.10; psoralen  $C_{11}H_6O_3$ , mp 139–140° C,  $R_f$  0.14; and angelicin  $C_{11}H_6O_3$ , mp 138–140° C,  $R_f$  0.29 [the  $R_f$  values given are for the petroleum ether–formamide system].

The fourth substance,  $C_{21}H_{22}O_4$ , mp 96–97° C,  $R_f$  0.79, on acid hydrolysis formed 5,8-dihydroxypsoralen  $C_{11}H_6O_5$ , mp 239–242° C, which was converted by methylation into isopimpinellin  $C_{13}H_{10}O_5$ , mp 149–150° C,  $R_f$  0.15. The physicochemical properties and reaction products of this substance show that it was cnidicin, 5,8-diisopentenylloxypso-ralen, previously found only in Cnidium dubium [3]. Psoralen and cnidicin have not previously been detected in plants of the genus Heracleum.

Paper chromatography in the petroleum ether–formamide system yielded small amounts of isopimpinellin ( $R_f$  0.15), bergapten ( $R_f$  0.21), isobergapten ( $R_f$  0.41), and pimpinellin ( $R_f$  0.44).

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Khar'kov Chemical and Pharmaceutical  
Scientific Research InstituteGLYCOFLAVONIDS OF GLYCYRRHIZA GLABRA

I. Saponaretin and Vitexin

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In a study of the individual compounds of Glycyrrhiza glabra L., we have attempted to investigate the flavonoids of the epigeal part of this plant.

In a quantitative analysis by two-dimensional paper chromatography we found about ten substances of flavonoid nature in the herb collected in the flowering phase. The flavonoids were separated on polyamide sorbent to give in the individual state substance A with the composition  $C_{21}H_{20}O_{10}$ , mp 262–264° C (ethanol–water),  $[\alpha]_D^{+55.0^\circ}$  (c 0.2; methanol),  $R_f$  0.59–0.61 (15% acetic acid); giving an acetate  $C_{35}H_{34}O_{17}$ , mp 165–167° C,  $[\alpha]_D^{-32.4^\circ}$  (c 0.05; acetone). Substance A underwent no decomposition on enzymatic hydrolysis with emulsin and yeast  $\alpha$ -glucosidase, while acid hydrolysis led to the formation of a new compound A-2,  $C_{21}H_{20}O_{10}$ , mp 263–265° C (alcohol–water),  $[\alpha]_D^{-15.0^\circ}$  (c 0.1; methanol),  $R_f$  0.25–0.27 (15% acetic acid); giving an acetate  $C_{35}H_{34}O_{17}$  with mp 256–257° C (alcohol),  $[\alpha]_D^{-70.1^\circ}$  (c 0.05; acetone).

From the results of a spectroscopic investigation in the UV region using ionizing and complex-forming reagents [1], both substances were shown to be flavone derivatives with free phenolic groups in positions 5, 7, and 4'.

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  $\beta$ -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- $\beta$ -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.

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#### ISOLATION OF SCUTELLARIN FROM CENTAUREA DEPRESSA

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The epigeal part of *Centaurea depressa* M. B. collected in Uzbekistan (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:  $\lambda_{max}$  335 and 285  $m\mu$ .

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  $>340^{\circ}C$ . UV spectrum:  $\lambda_{max}$  338, 286  $m\mu$ . 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.