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FLAVONOIDS OF THE BARK OF SALIX ELBURSENSIS

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The flavonoids of the leaves of Salix purpurea L. (purpleosier willow) [1], which, according to A. K. Skvortsov, must be regarded as Salix elbursensis Boiss [2, 3], have been studied previously. The latter is endemic to the region of the Caucasus and Iran and belongs to the section Purpuraea L.

The dried comminuted bark (1.5 kg) from branches of 1 to 5 years' growth was exhaustively extracted with 70% ethanol. The ethanolic extract was concentrated in vacuum, diluted with water and treated first with chloroform and then with ethyl acetate. The ethyl acetate extract was evaporated to small bulk, and the flavonoids were precipitated by means of dry chloroform. The deposit that separated was dissolved in the minimum amount of 50% ethanol, and diethyl ether was added to saturation. The mixture was left in the refrigerator at 3-4° C. After 10-12 days, 5, 7, 4'-trihydroxyflavone 5-β-D-glucopyranoside (salipurposide) [4], $C_{21}H_{22}O_{10} \cdot 1.5\ H_2O$, with mp 226-227° C (water), λ_{max} 328, 282 mμ crystallized out; melting point of the acetyl derivative 182-183° C (96% ethanol).

The cambial layer was separated from the bark (0.8 kg) of growth more than 50 years old in the form of a lemon yellow strip, and it was dried, comminuted, and extracted in a Soxhlet apparatus with diethyl ether saturated with water. The extract was concentrated to 1/2 of its initial volume and was placed in a refrigerator at 3-4° C.

The precipitate that deposited after a day was washed with dry ether and dissolved in the minimum amount of anhydrous acetone, and the solution was filtered. The filtrate was brought to the boil and 2 to 3 volumes of hot water was added. On cooling, the mixture deposited bright orange crystals of 4, 2', 4', 6'-tetrahydroxychalcone 6'-β-D-glycopuranoside (isosalipurposide) [5], $C_{21}H_{22}O_{10} \cdot 2H_2O$, mp 171-173° C (water), λ_{max} 368 mμ.

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FLAVONOIDS OF CENTAUREA DEPRESSA

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From the flowerheads of Centaurea depressa M. B. growing in Uzbekhistan we extracted the combined flavonoids with 96% ethanol. Paper chromatography established the presence in the extract of six flavone and flavonol compounds [1].

Hydrolysis of the substances isolated from the acidic aqueous fraction gave an aglycone with the composition $C_{15}H_{10}O_5$, mp 340° C, which was identified on the basis of its acetate with mp 236-237° C and the products of alkaline fusion as scutellarein. The carbohydrate part of the glycosides consisted of β-D-glucuronic acid.

Two glycosides were isolated from the same fraction. One with the composition $C_{21}H_{18}O_{12}$ had no sharp melting point. On the basis of spectral analyses and the bathochromic shift we identified it as scutellarein 7-β-D-glucuronoside. The second glycoside of this fraction was similar in properties to that described above and is, apparently, scutellarein 5-β-D-glucuronoside.

From the ethyl acetate fraction we isolated a substance with the composition $C_{21}H_{20}O_{12} \cdot H_2O$, mp 220-222° C (248-250° C, anhydrous). IR spectrum: $\lambda_{max}^{CH_3OH}$ 360, 250 mμ (lg ε 4.32, 4.42) and $\lambda_{min}^{CH_3OH}$ 240, 385 mμ. On hydrolysis it yielded quercetin with mp 305° C and D-glucose in a molar ratio of 1:1. The glycoside was readily hydrolyzed

by emulsin. Its IR spectra had bands at 1080, 1055, 1028 and 890 cm^{-1} (β-pyranose form of the sugar) [3]. This compound was identified as isoquercitrin.

The second glycoside of the same fraction was also a quercetin glycoside. Its IR spectrum had two maxima at 350 and 256 mμ. It gave a characteristic bathochromic shift for the presence of an ortho-dihydroxy grouping in position 3' and 4' [4]. Complete hydrolysis yielded quercetin and D-glucose, and partial hydrolysis gave quercimeritrin (quercetin 7-O-β-glucopyranoside). Because of the small amounts available, it was impossible to identify the substance in more detail.

The third compound of the ethyl acetate fraction was also a glycoside. Hydrolysis gave an aglycone which, from its Rf values in various systems and its UV spectra, is apigenin. The carbohydrate moiety of the glycoside is being studied.

The fourth compound of this fraction was identified as scutellarein.

We have isolated scutellarin from the flowerheads of Centaurea depressa previously [2].

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PROANTHOCYANIDINS OF POLYGONUM CORIARIUM

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We have previously [1, 2] reported the isolation and identification of the catcheins of the roots of Polygonum coriarium. In this paper we give the results of a study of the proanthocyanidins.

A concentrated methanolic extract of the roots of P. coriarium was treated sucessively with chloroform, ether, ethyl acetate, and acetone. From the ethyl acetate extract, in addition to catechins, we obtained leucodelphinidin and leucocyanidin.

The acetone extract was concentrated and the residue was treated repeatedly with butan-1-ol–acetic acid–water (4 : 12 : 28). The upper layer was chromatographed on a column of cellulose. The mobile phase was the same solvent. Three fractions were obtained. Paper chromatography showed that the first contained a mixture of (–)-epigallocatechin, leucodelphinidin, and leucocyanidin, while the second appeared in the form of a band, and the third remained stationary at the starting line. The third fraction was treated with a small amount of water and the solvent was distilled off under vacuum in the form of the azeotrope at 40–45° C. The concentrated butanolic solution was treated with a threefold volume of petroleum ether. The precipitate that deposited—a gray powder with a pinkish tinge—was dissolved in water, and gave all the reactions of phenols. Hydrolysis with 0.5 M HCl formed delphinidin, (–)-epigallocatechin gallate, (±)-epigallocatechin, and (–)-epigallocatechin. Enzymatic hydrolysis with tannase led to the formation of gallic acid, and alkaline cleavage to the formation of gallic acid and phloroglucinol.

The lower aqueous layer obtained in the treatment with butan-1-ol–acetic acid–water mixture was treated with butan-1-ol, and the solvent was distilled off under vacuum in the form of the azeotrope. The concentrate was treated with petroleum ether. The precipitate that then deposited was filtered off and was washed successively with hot ethyl acetate and butan-1-ol. The substance obtained, with mp 192–193° C, gave the same products as the first substance on acid and enzymatic hydrolysis and also on alkaline cleavage.

Consequently, the main components of the substances isolated—the proanthocyanidins of the roots of Polygonum coriarium are leucodelphinidin, (–)-epigallocatechin gallate (±)-gallocatechin, and (–)-epigallocatechin.