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POLYPHENOLIC COMPOUNDS OF *Hypericum hirsutum*

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In a study of the epigeal part of *Hypericum hirsutum* L. (hairy St. John's wort) collected in the People's Republic of Bulgaria (central Rhodope) in the flowering period we have found a complex of phenolic substances comprising more than 17 components. The majority of them have been assigned to the flavonoids, catechins and phenolcarboxylic acids, and there are two representatives of anthocyan compounds and one substance is hypericin.

The combined polyphenols were exhuastively extracted with 80% ethanol in the presence of an antioxidant (potassium metabisulfite), the extracts were concentrated in vacuum until the ethanol had been eliminated completely, the aqueous residue was treated with chloroform to eliminate ballast substances, and then the polyphenolic compounds were extracted by repeated treatment with ethyl acetate, the extracts were combined, and the solvent was distilled off in vacuum. The catechins were extracted from the dry residue by treatment with water-saturated diethyl ether. They were separated on a column of silica gel in a current of nitrogen. When the column was eluted with water-saturated diethyl ether, two substances were isolated.

Substance (I), mp 174-176°C (from water). $[\alpha]_D^{20}$ +15.8° [c 0.69; acetone–water (1:1)]; mp of the acetate 130-131°C; identified as (+)-catechin.

Substance (II), with mp 242-243°C (from water), $[\alpha]_D^{20}$ −68° [c 0.23; acetone–water (1:1)]; mp of the acetate 151-152°C; identified as (−)-epicatechin.

Substances (I) and (II) were identified from their degradation products (phloroglucinol and protocatachuic acid) and by comparison with authentic samples, and from the absence of depressions of the melting points of mixtures with authentic samples of (+)-catechin and (−)-epicatechin. This is the first time that substances (I) and (II) have been isolated from *H. hirsutum*. They proved to be identical with the catechins that we have found previously in *H. perforatum* L. and *H. degenii* Bornm. [1, 2].

The combined flavonoids (after the elimination of the catechins) were separated by column chromatography on cellulose and on polyamide and by preparative chromatography on paper. Four compounds of flavonoid nature (III-VI) were isolated. They were identified on the basis of spectrophotometric investigations with the aid of ionizing and complex-forming agents, a comparative analysis of IR spectra, from the products of alkaline, acid, and enzymatic hydrolysis, and by comparison with authentic samples.

Substance (III) with mp 306-308°C was identified as quercetin, and substance (IV), with mp 235-237°C was characterized as quercetin 3-O-β-galactopyranoside or hyperoside [3, 4].

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According to the results of preliminary investigations, substance (V) with mp 261-263°C and substance (VI) with mp 222-223°C are C-glycosides. On acid hydrolysis, each substance formed an equilibrium mixture of two compounds, which is characteristic for C-glycosides. The study of the structures of these substances is continuing.

Rutin was found in the complex of polyphenolic compounds of hairy St. John's wort by two-dimensional paper chromatography and comparison with an authentic sample. Rutin is a minor component for this species.

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ALKALOIDS OF *Papaver lisae*

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By methanolic extraction of *Papaver lisae* raw material collected in the flowering period in May, 1976 in the Khulamo-Bezengiiskii gorge, Kabardino-Balkarsk ASSR we have obtained the combined alkaloids: 0.09% from the epigeal part and 1.28% from the roots, calculated on the weight of the dry raw material. By separating the total alkaloids of the epigeal part and the roots of the plant into fractions of phenolic and nonphenolic bases [1] and by column chromatography we have isolated five alkaloids in the pure form. Thin-layer chromatography (alumina of activity grade II; chloroform–ethanol (30:1) system) showed the identity of the qualitative compositions of the combined alkaloids of the epigeal part and of the fruits and that it consisted of at least nine components.

We have isolated two bases from the fraction of nonphenolic bases.

Base I, with the composition $C_{22}H_{25}NO_6$, mp 177-178°C (ether–ethanol); R_f 0.39; $[\alpha]_D$ $-239 \pm 4°$ (c 0.35; chloroform). IR spectrum: λ_{max} 3605 cm^{-1} (OH). NMR spectrum (δ, ppm): 1H singlet at 6.58; 1H singlet at 6.33 (isolated ArH protons); 2H singlet at 5.85 (CH_2O_2); 2H singlet at 4.65 ($ArCH_2$–OH); 3H singlet at 3.98 (OCH_3); 6H singlet at 3.84 (2 OCH_3); one OH multiplet group in the interval from 3.80 to 2.10.

Mass spectrum: fragments with m/e 399 (M^+), 368 (M − 31), 206, 204, 195, 194, 179. According to literature characteristics, the base (I) isolated was identical with (–)-mecambridine [2, 3] oreophiline [4].

Base (II), isolated from the same fraction, had mp 207-208°C (chloroform–ethanol–acetone), and on the basis of thin-layer chromatography a mixed melting point, and a comparison of spectra, it was identified as protopine [5].

From the phenolic fraction of the combined alkaloids we isolated another three bases.

Base (III) with mp 185-186°C (ethyl acetate), $[\alpha]_D$ 200 ± 5° (c 0.5; chloroform); R_f 0.72; mixed melting point at mp 185-186°C. The IR, NMR, and mass spectra of this alkaloid were identical with those of a sample of (+)-isocorydine.

Base (IV), the one present in greatest amount, had the composition $C_{17}H_{23}NO_3$, mp 234-235°C (acetone); $[\alpha]_D$ −83 ± 1° (c 1.0; ethanol) R_f 0.13. Mass spectrum of the base, m/e (% intensity): 289 (50), 228 (100), 270 (5), 260 (70), 242 (10), 191 (10), 185 (10). Accord-

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