NUCHENSEIN — A NEW FLAVONE FROM *Teucrium nuchense*

O. V. Slyun'kova, S. F. Dzhumyrko,
V. A. Kompantsev, É. T. Oganesyan,
and V. I. Glyzin

UDC 547.918

Some species of germander have been investigated previously [1-7]. We have studied the flavonoid composition of the epigeal part of *Teucrium nuchense* C. Koch, family Lamiaceae [8], collected in the vegetation period in the environs of Pyatigorsk (Mt. Mashuk) in July, 1974. A preliminary chromatographic analysis showed the presence in it of 16 substances of polyphenolic nature, six of which were flavonoids. For their isolation, the raw material (1.6 g) was extracted with ethanol, and the concentrated extracts were diluted with water and purified with chloroform and were then treated with ethyl acetate. The ethyl acetate extract yielded six flavonoid compounds by chromatography on alkaline polyamide in gradient chloroform–methanol and water–ethanol systems.

Substance (I), $C_{17}H_{14}O_7$, mp 258-259°C (methanol), R_f 0.87 (BAW (4:1:5) system; Filtrak F No. 1); 0.70 (C_6H_6–EtOAc–AcOH(70:30:2)); and 0.41 (15% AcOH). On the basis of the Bryant [9] and Bargellini [10] tests and that with a mixture of 1% solutions of $FeCl_3$ and potassium ferrocyanide, it was suggested that substance (I) was a flavone aglycone with vicinal substitution in ring A [11]. UV spectrum, nm 348, 272 (257) (CH_3OH); 353, 268 (+CH_3COONa); 378, 265 (CH_3COONa + H_3BO_3); 365, 282 (263) (+$AlCl_3$ + HCl); 367, 282 ($AlCl_3$); 393, 273 (+CH_3ONa). The size of the bathochromic shift of the maximum of the long-wave band by 15 mm in the presence of aluminum chloride and hydrochloric acid confirmed that there was an oxygen-containing substituent in position 6 [12]. On the basis of the NMR spectrums (HA-100; CCl_4; 0 — TMS), we established that substance (I) had —OCH_3 groups in positions C-7 and C-4', represented by singlets at 3.88 and 3.78 ppm each with an intensity of 3 proton units. The presence of protons in the C-2' and C-6' positions was shown by a multiplet in the 7.28 ppm region (2H). The signal of a proton in the C-5' position appears in the form of a doublet in the 6.80 ppm region with an intensity of one proton unit. A singlet in the 6.34 region corresponds to a proton in the C-3 position, and the presence of a proton at C-8 is shown by a singlet in the 6.32 region with an intensity of one proton unit [13].

Demethylation with hydriodic acid gave 3',4',5,6,7-pentahydroxyflavone [14].

On the basis of the results of the investigations performed and also its IR spectrum and the results of alkaline degradation, substance (I) was shown to be 3',5,6-trihydroxy-4',7-dimethoxyflavone. It proved to be new, and we called it nuchensein. The other flavonoids obtained from the plant were characterized by physicochemical methods as: (II), luteolin 7-O-β-D-glucopyranoside; (III), 3', 4', 5,7-tetrahydroxyflavone; (IV), 4',5,7-trihydroxyflavone; (V), 5,6,7-trihydroxyflavone; and (VI), 4',5,6,7-tetrahydroxyflavone.

A quantitative spectrophotometric determination was made by means of the cyanadin reaction of the total flavonoids [15] of the herb *Teucrium nuchense*; it proved to be 3.16%.

LITERATURE CITED

1. T. Pfeiffer and O. Manns, Pharmazie, 12, 401 (1957).
2. T. Pfeiffer, Planta medica, 14, 117 (1966).
3. I. A. Damirov, Proceedings of the First All-Union Congress of Pharmacists [in Russian], Pyatigorsk (1967), p. 287.
4. J. Petricic, N. Basisic-Poljak, and A. Radosevic, Acta Pharmac. Jugosl., 18, 105 (1968).
5. J. Grzybek, Dissert. Pharmac. Pharmacol., 20, No. 5, 563 (1968).
6. T. V. Zinchenko and V. A. Bandyukova, Farmats. Zh., 49 (1969).
7. J. Grzybek, Dissert. Pharmac. Pharmacol., 21, No. 3, 253 (1969).

Pyatigorsk Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 268-269, March-April, 1978. Original article submitted November 16, 1977.

 0009-3130/78/1402-0226$07.50

8. S. V. Yuzepchuk, Flora of the USSR [in Russian], Moscow–Leningrad, Vol. XX (1954), p. 52.
9. E. F. Bryant, J. Amer. Pharm. Assoc., 39, 480 (1950).
10. G. Bargellini, Gazz. Chim. Ital., 49, 47 (1919).
11. T. P. Popova, V. I. Litvinenko and I. P. Kovalev, Khim. Prirodn. Soedin., 729 (1973).
12. J. A. Mears and T. J. Mabry, Phytochem., 11, 411 (1972).
13. T. J. Mabry, K. R. Markham, and M. B. Thomas, The Systematic Identification of Flavonoids, Springer-Verlag, New York (1970).
14. I. B. Gillet, Angew. Chem., 69, 679 (1957).
15. A. V. Simonyan, A. L. Shinkarenko, and É. T. Oganesyan, Farmatsiya, 4, 30 (1973).

POLYPHENOLIC COMPOUNDS OF *Hypericum hirsutum*

G. Kitanov, Kh. Akhtardzhiev, and K. F. Blinova

UDC 547.972

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].

Pharmaceutical Faculty of the Medical Academy of Sofia. Leningrad Institute of Pharmaceutical Chemistry. Translated from Khimiya Prirodnykh Soedinenii, No. 2, p. 269, March-April, 1978. Original article submitted November 16, 1977.

0009-3130/78/1402-0227$07.50