We have isolated ostruthin from the roots of <u>Libanotis condensata</u> (L.) Grantz,, family Umbelliferae, in which the presence of pteryxin (3'-acetyl-4'-angeloyl-2', 2'-dimethyl-3', 4'-dihydropyrano-5', 6':8, 7-coumarin) had been established previously [7]. The presence of ostruthin has also been detected in other species of the genus Libanotis by paper chromatography.

Thus, the presence of ostruthin in plants containing furo- and pyranocoumarins makes it possible to confirm modern ideas on the biogenesis of coumarin derivatives in plants. Evidently, 6- and 8-alkyl-derivatives of Umbelliferone are distributed among coumarin-containing plants more widely than is reflected in the literature. The limited nature of the information on this group of coumarins is probably connected with inadequate attention to the fractions of phenolic hydroxycoumarins.

REFERENCES

- 1. E. Späth and I. Bruck, Ber. Dtsch. Chem. Ges., 70, 1023, 1937.
- 2. L. Erdmann, J. Pract. Chem., 16, 42, 1939.
- 3. V. I. Zaretskii, N. S. Vul'fson, L. S. Chetverikova, and V. G. Zaikin, ZhOKh, 34, 3655, 1964.
- 4. G. K. Nikonov and A. A. Ivashenko, ZhOKh, 33, 2740, 1963.
- 5. G. K. Nikonov, M. E. Perel'son, and M. G. Pimenov, KhPS [Chemistry of Natural Compounds], 2, 285, 1966.
- 6. V. V. Vandyshev, G. K. Nikonov, and M. G. Pimenov, Proceedings of the 1st Conference of Pharmacists [in Russian], Moscow, p. 39, 1967.
 - 7. G. K. Nikonov, F. V. Babilev, and N. E. Ermatov, KhPS [Chemistry of Natural Compounds], 2, 214, 1966.

15 May 1968

All-Union Scientific-Research Institute for Medicinal Plants
Institute of the Chemistry of Natural Compounds AS USSR

UDC 615.82

IRIDOIDS OF BETONICA FOLIOSA

V. I. Litvinenko and B. N. Aronova

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 5, p. 319, 1968

Iridoids are a group of natural compounds belonging to cyclopentanoid monoterpenes of a glycosidic nature [1,2]. They are widely distributed in the families Rubiaceae, Scrophulariaceae, Globulariaceae, Plantaginaceae, and others. These compounds have also been discovered in some plants of the family Labiatae (Mellitis, Ajuga, etc.) [1-3]. On studying the chemical composition of the herb <u>Betonica foliosa Rupr.—Stachys betonicaeflora Rupr.</u>, we detected in a methanolic extract on paper-chromatographic analysis [BAW system (4:1:2)] two substances of an iridoid nature the spots of which gave a blue-violet coloration with the benzidine—trichloroacetate reagent [2].

To characterize these compounds further, we attempted to isolate them and developed the following method. The raw material was extracted with 50% methanol. The extracts, evaporated to an aqueous residue, were treated several times with butanol. The dried butanolic extracts were evaporated to dryness, the residue was dissolved in a small volume of methanol, and the solution was diluted with water and filtered. The filtrate was freed from flavonoids and aromatic acids, respectively, on columns of Kapron and of alumina, and was evaporated to dryness. The residue was dissolved in ethanol and the impurities were precipitated with an excess of acetone. The purified combined iridoids were recrystallized from a mixture of ethanol and acetone (1:3) and ethanol—petroleum ether (1:1). A white crystalline substance with mp 154-155° C was isolated which was identified by its physicochemical properties, qualitative reactions, chromatographic behavior, and IR spectra as harpagide acetate [3]. A second substance obtained from the mother liquors may be identified, from its reaction products and a comparison with the substance obtained from the saponification of harpagide acetate, as harpagide [2, 3].

REFERENCES

- 1. R. Hänsel, Planta Medica, suppl., 61, 1966.
- 2. G. Gröger and P. Simchen, Pharmazie, 22, 315, 1967.
- 3. M. L. Scarpati, M. Guiso, and L. Panizzi, Tetrah. Let., no. 39, 3439, 1965.

20 November 1967

Khar kov Chemical and Pharmaceutical Scientific-Research Institute Kirgiz Scientific-Research Institute for the

Protection of Maternity and Childhood

UDC 615,32

PHENOLIC COMPOUNDS OF BETONICA FOLIOSA

V. I. Litvinenko and B. N. Aronova

Khimiya Prirodnykh Soedinenii, Vol. 4, No. 5, pp. 319-320, 1968

We have studied the epigeal part of <u>Betonica foliosa</u> Rupr. — <u>Stachys betonicaeflora</u> Rupr. collected in the flowering phase in the foothills of the Kirgiz range in the region of Issyk-Ata, for its content of phenolic compounds.

Chromatographic analysis of the extracts (extractant-50% methanol; system for chromatography-0.1 N HCl) showed the presence of five substances which, on the basis of qualitative reactions, UV spectra of the spots on paper, and the results of a comparison with authentic samples, where identified as caffeic (R_f 0.20), 4-caffeoylquinic (R_f 0.40), chlorogenic (R_f 0.50), neochlorogenic (R_f 0.70), and 1-caffeoylquinic (R_f 0.80) acids. Thus, the tanning substances previously found in these plants [1] form a complex of depsinoids of caffeic and quinic acids.

By two-dimensional chromatography [1) n-BAW (4:1:2) and 2) 15% CH₃COOH] and one-dimensional chromatography (60% CH₃COOH) four flavonoids were found in the extract of <u>Betonica foliosa</u> (<u>Stachys betonicaeflora</u>). All of these substances were isolated by fractional extraction with butanol from aqueous solutions and were separated on a column of Kapron. Three individual compounds, (A,B, and C) were obtained.

Substance A, from its physicochemical constants, UV spectrum, and a comparison with an authentic sample, proved to be identical with orientin [2].

Substance B has been provisionally characterized as an apigenin glycoside with a substituent in position 4'.

Substance C is also an apigenin derivative, of an aglycone nature, with methoxy groups in positions 7 and 4'.

We are the first to have found C-glycosides in plants of the family Labiatae.

REFERENCES

1. B. N. Aronova, Collection of Scientific Papers of the Kirgiz Scientific-Research Institute for the Protection of Maternity and Childhood [in Russian], Frunze, no. 2, p. 77, 1964.

2. A. I. Tikhonov, P. E. Krivenchuk, V. I. Litvinenko, and I. P. Kovalev, Farm. zh., no. 3, 53, 1965.

20 November 1967

Khar'kov Chemical and Pharmaceutical Scientific-Research Institute

Kirgiz Scientific-Research Institute for the Protection of Maternity and Childhood