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ALKALOIDS OF *Corydalis stricta*

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UDC 547.943

The alkaloids of the epigeal part and roots of *Corydalis stricta* have been studied. Of the 23 alkaloids isolated, N-methylcorypalline proved to be new, and its structure has been determined. Stilopine hydroxymethylate and pycnarrhine have been isolated from the genus *Corydalis* for the first time, and cheilanthiofoline **isocorypalmine, scoulerine, isoboldine,** reticuline, N-methylcoclaurine, coreximine, juziphine, pancorydine, corypalline, wilsonirine, stilopine, adlumidine, dihydrosanguinarine, adlumine, and bicucculine have been isolated from this species of plant for the first time.

We have investigated the alkaloid composition of the epigeal part and roots of the plant *Corydalis stricta* Steph. [1] collected in the flowering period in the environs of the settlement of Rabat (Pamir). d-β-Hydrastine and protopine have been isolated **previously** from the epigeal part of *C. stricta*, and protopine and sanguinarine from the roots [2]. Chloroform extraction of the epigeal part of *C. stricta* yielded 1.57% of total alkaloids. From the nonphenolic fraction of the total we isolated stilopine, adlumidine, bicucculine, protopine [3], and d-β-hydrastine [4], and from the phenolic part scoulerine, coreximine [4], isoboldine, juziphine, [3], and corypalline [5]. From the quaternary fraction of alkaloids we isolated in the form of iodides stilopine hydroxymethylate [6] and pycnarrhine [7]. All the alkaloids obtained were identified on the basis of spectral characteristics and comparison with authentic samples.

The roots of *C. stricta* collected at the same growth site contained 0.63% of total alkaloids. The separation of this material gave sanguinarine, bicucculine, protopine, wilsonirine, pancorydine, and pancorynine [8]. From the quaternary fraction of total alkaloids we isolated in the form of iodides stilopine hydroxymethylate and a new optically inactive base with mp 238-239°C. Its UV spectrum contained a single absorption maximum at 287 nm (log ε 4.14). Its IR spectrum showed absorption bands at (cm^{-1}) 3370 (hydroxy group), 1530, 1610, and 1620 (aromatic ring). Its mass spectrum had the peaks of ions with m/z 207, 206, 177, 164, 150, 142, 127. The PMR spectrum showed signals in the form of a six-proton singlet at 2.85 ppm from a N-dimethyl group, a three-proton singlet at 3.50 ppm from a methoxy group, and a two-proton singlet at 4.06 ppm from an isolated methylene group. In the aromatic region of the spectrum there were two single-proton singlets at 6.34 and 6.40 ppm, and a four-proton multi-

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 490-493, July-August, 1983. Original article submitted June 3, 1982.

0009-3130/83/1904-0461$07.50

EXPERIMENTAL

For chromatography we used type KSK silica gel. UV spectra were taken on a Hitachi spectrometer (in ethanol), IR spectra on a UR-20 instrument (tablets with KBr), mass spectra on a MKh-1303 mass spectrometer, and PMR spectra on a JNM-4H 100/100 MHz instrument (HMDS as internal standard, δ scale, CF_3COOH).

Isolation and Separation of the Total Alkaloids. The epigeal part of the air-dry plant *C. stricta* (80 kg) was extracted with chloroform [3], giving 759.01 g of ethereal nonphenolic fraction, 113.05 g of ethereal phenolic fraction, and 386.53 g of total chloroformic alkaloids. The nonphenolic material was treated with methanol, which led to the separation of 189.76 g of a mixture of crystals of d-bicucculine and d-β-hydrastine. When the mother liquor was treated with methanol again, 145.58 g of protopine was obtained. The mother liquor after the separation of the crystals was chromatographed on a column of silica gel with elution of the alkaloids by benzene and benzene–methanol in various proportions. The benzene eluate yielded 5.6 g of stilopine and 3.5 g of adlumidine. The fractions eluted by benzene–methanol (99:1) gave 83.93 g of bicucculine, and the (98:2) and (97:3) eluates gave 169.3 g of a mixture of crystals consisting of d-bicucculine and d-β-hydrastine. The benzene–methanol (95:5) eluate gave 22.9 g of protopine. The total phenolic material was chromatographed on a column of silica gel, and the alkaloids were eluted with benzene, mixtures of benzene and methanol in various proportions, and methanol. The benzene–methanol (99:1, 98:2, and 97:3) eluates yielded 62 g of scoulerine, and the (95:5) eluates 1.2 g of coreximine, 0.1 g of isoboldine, and 0.2 g of juziphine. Elution with benzene–methanol (9:1) gave 1.81 g of corypalline. The total chloroformic material was treated with methanol, which led to the separation of 162 g of a mixture of crystals consisting of d-bicucculine and d-β-hydrastine.

The aqueous alkaline solution after the extraction of the tertiary alkaloids was acidified with 10% sulfuric acid, and a saturated solution of potassium iodide was added. Then the iodides of the quaternary alkaloids were extracted with chloroform, which gave 2.5 g of iodides from which, after treatment with methanol, 0.5 g of stilopine hydroxymethylate was isolated. The mother liquor was chromatographed on a column of silica gel with elution of the alkaloids by chloroform–ethanol in various proportions. From the chloroform–ethanol (99:1) eluate was isolated an additional 0.1 g of stilopine hydroxymethylate and 0.1 g of pycnarrhine.

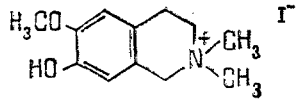
The air-dried roots of *C. stricta* (1.4 kg) were extracted with chloroform, which gave 4.16 g of combined ethereal (0.56 g of phenolic and 3.60 g of nonphenolic fractions) and 4.66 g of combined chloroformic alkaloids. The total nonphenolic material was treated with methanol, which led to the separation of sanguinarine (0.12 g) and bicucculine (2.3 g). When the mother liquor was treated with methanol again, protopine (0.75 g) separated out. The mother liquor from the combined nonphenolic material was chromatographed on a column of silica gel, and the alkaloids were eluted with benzene and with mixtures of benzene and methanol in various proportions. This gave an additional 0.03 g of sanguinarine, 0.20 g of bicucculine, and 0.15 g of protopine. The total chloroformic material (4.66 g) was chromatographed on a column of silica gel, and the alkaloids were eluted with chloroform and mixtures of chloroform and methanol in various proportions. The chloroform eluates yielded 1.07 g of pancorydine and 0.42 g pancorynine, and the total phenolic material yielded 0.25 g of wilsonirine.

The residual alkaline solution was acidified with 10% sulfuric acid and treated with a saturated solution of potassium iodide, and the alkaloids were extracted with chloroform. This gave 0.2 g of iodides of quaternary alkaloids. The iodides were treated with methanol, and 0.5 g of stilopine hydroxymethylate was isolated. The mother solution was chromatographed on a column of silica gel, and elution with chloroform–methanol (95:5) gave 0.07 g of N-methylcorypalline.

The air-dried plant collected in Mongolia (1.85 kg) was extracted with chloroform. This gave 20 g of total ethereal and 10.5 g of total chloroformic alkaloids. The total ethereal material was separated into phenolic (2.31 g of ethereal and 0.3 g of chloroformic fraction) and nonphenolic (17.39 g) parts.

The total phenolic ethereal material (2.31 g) was separated on a column of silica gel. Benzene and mixtures of benzene and ethanol in various proportions were used for elution. The benzene eluates yielded 0.2 g of cheilanthifoline, the (99:1) fraction 0.2 g of isocorypalline, and the (98:2) fraction 1.0 g of scoulerine. The fractions eluted by the (94:6)

plet at 2.70-3.45 ppm. The facts given above permit the base to be assigned to the quaternary tetrahydroisoquinoline alkaloids. A direct comparison of the base with corypalline methiodide showed their identity. Thus, the base isolated is N-methylcorypalline, which has not previously been described in the literature.



The epigeal part of *C. stricta* gathered in Mongolia in the flowering period contained 1.65% of total alkaloids. On the separation of this material we obtained cheilanthifoline [6], isocorypalmine, scoulerine, isoboldine, reticuline, N-methylcoclaurine, sanguinarine, dihydrosanguinarine [9], stilopine, adlumidine, adlumine [3], bicucculine, d-β-hydrastine [4], and protopine.

mixture gave 0.4 g of reticuline and those by the (9:1) mixture 0.22 g of N-methylcoclaurine. The nonphenolic part of the total alkaloids were treated with methanol, which led to the separation of 10.1 g of a mixture of crystals consisting of d-β-hydrastine, bicucculine, adlumidine, and protopine. The mother liquor (7.29 g) was chromatographed on a column of silica gel. The alkaloids were eluted with benzene and mixture of benzene and ethanol in various proportions. The benzene eluates yielded 0.4 g of stilopine, the (99:1) eluates 0.5 g of adlumidine and 0.3 g of sanguinarine, and the (98:2) eluates (0.02 g of dihydrosanguinarine. From the fractions eluted by the (96:4) mixture were isolated 0.02 g of adlumine and 2.0 g of d-β-hydrastine, and from the (94:6) fractions 1.5 g of bicucculine. The (9:1) fraction gave 0.4 g of protopine. The total chloroformic sum was treated with methanol, giving 5.6 g of a mixture of crystals consisting of d-β-hydrastine and bicucculine.

SUMMARY

From the roots and epigeal part of the plant *Corydalis stricta* have been isolated 23 alkaloids, 19 of which have not been isolated from these species previously, while one alkaloid — N-methylcorypalline — proved to be new, and its structure has been established.

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