Chemistry of Natural Compounds, Vol. 29, No. 4, 1993

ALKALOIDS OF *Nitraria komarovii*.
XV. VASICINONE AND DEOXYVASICINONE N-OXIDES

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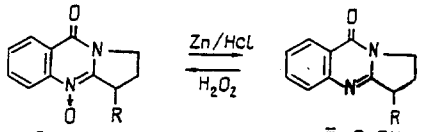
Two new alkaloids have been isolated from the epigeal part of Nitraria komarovii — *the N-oxides of vasicinone and of deoxyvasicinone. Their structures have been established on the basis of spectral results and chemical transformations.*

Continuing our investigations of the alkaloids of *Nitraria komarovii* [1], we have isolated two new alkaloids ((I) and (II)) from the benzene fraction of the total bases. From their spectral characteristics they were assigned to the quinazolone alkaloids. Base (I), optically inactive, had the composition $C_{11}H_{10}N_2O_3$ and differed from vasicinone by one oxygen atom. In other respects its mass-spectrometric fragmentation was close to that of vasicinone [2]. The presence in the IR spectrum of (I) of bands characteristic for N-oxides, the appearance in its mass spectrum of intense peaks of the ions $(M - 16)^+$ and $(M - 17)^+$, and the ready solubility of the compound in water showed its N-oxide nature. When *dl*-vasicinone (III) was oxidized with perhydrol in alcohol a base identical with (I) in all its characteristics (PMR, IR, and mass spectra, and R_f) was obtained.

When (I) was reduced with zinc in hydrochloric acid, base (III) was obtained with mp (211-121°C) [2] and mass and IR spectra identical with those for *dl*-vasicinone. At the same time, in addition to (III), bases (IV) and (V) with mp 110-111°C and 86-87°C were obtained, and these were identified by direct comparison with authentic specimens of deoxyvasicinone and deoxypeganine, respectively.

A broadened signal in the PMR spectrum of (I) at 5.62 ppm for the proton of a hydroxy group and an absorption band in the IR spectrum corresponding to the stretching vibrations of an OH group in the lower-frequency region (ν^{KBr} 3160 cm^{-1} and ν^{CHCl_3} 3200 cm^{-1}) as compared with vasicinone (ν^{KBr} 3400 cm^{-1}) showed the formation in the molecule of the compound under investigation of an intramolecular hydrogen bond [3], the presence of which was confirmed by recording the IR spectrum in chloroform. When the solution was diluted four-fold, the position and intensity of the absorptiopn band at 3200 cm^{-1} did not change. An intramolecular hydrogen bond can be formed with the participation of the proton of the hydroxy group if the N-oxidic oxygen is present at N-1.



I. R=OH
II. R=H
III. R=OH
IV. R=H

The facts mentioned above show that the alkaloid isolated was the N-oxide of vasicinone at N-1 and has structure (I). Vasicinone N-oxide has not previously been isolated plant material, although its existence has been shown indirectly [4].

Base (II), with mp 152-153°C (acetone), composition $C_{11}H_{10}N_2O_2$, differed from deoxyvasicinone by one oxygen atom; for the rest, its mass-spectral fragmentation was similar to that of deoxyvasicinone [2]. The presence in the mass spectrum of (II) of intense peaks of the $(M - 16)^+$, $(M - 17)^+$, and $M - 18)^+$ ions, and also the solubility of the alkaloid in polar solvents (ethanol, methanol, and water), permitted the assumption that base (II) was a N-oxide.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 580-582, July-August, 1993. Original article submitted March 1, 1993.

0009-3130/93/2904-0509$12.50

When (II) was reduced with zinc in hydrochloric acid, deoxyvasicinone and deoxypeganine were obtained (IR and mass spectra). When deoxyvasicinone (IV) was oxidized with perhydrol in alcohol, base (II) was identified.

Thus, the base isolated was deoxyvasicinone N-oxide, with the structure (II), and it is a new alkaloid.

EXPERIMENTAL

UV spectra were taken on an EPS-3T spectrophotometer (Hitachi), mass spectra on a MKh1310 spectrometer, and IR spectra on a UR-20 instrument in tablets molded with KBr and in $CHCl_3$ solution. For recording in solution, we used nondismountable cells with NaCl windows and thicknesses of the absorbing layers of 1.01 and 5 mm. PMR spectra were taken in $CDCl_3$ on a Tesla-567A (100 MHz instrument) with HMDS as internal standard.

For TLC we used silica gel of types KSK and L 5/40. The solvent systems used for chromatography were those given in [1, 5]. The extraction and separation of the total bases were described in the same papers [1, 5].

Vasicinone N-Oxide (I). Fractions 6 and 7, together with the mother liquors from fractions 8-12 after the isolation of *dl*-vasicinone, were rechromatographed on a column of silica gel. Elution was performed with chloroform–alcohol (10:1), and 12- to 15-ml fractions were collected. On crystallization from acetone, fractions 7-12 yielded 107 mg of base (I) with mp 203-204°C. Mass spectrum of (I), m/z (%): 218 (M^+, 4), 202 [$(M-16)^+$, 100], 201 (20), 186 (18), 185 (23), 174 (12), 155 (6), 146 (60), 130 (19), 119 (35). UV spectrum: $\lambda_{max}^{C_2H_5OH}$ (nm): 209, 226, 270, 305, 316, (lgε 4.51; 4.63; 4.06; 3.76; 3.67).

The following absorption bands were present in the IR spectrum: 775 (o-disubstituted benzene ring), 1110, 1280 (=N→O), 1330, 1470, 1570 and 1610 (C=C), 1630 (C=N), 1690 (N–C=O), 2860, 2930 and 2960 (–CH_2-groups), 3160 (–OH) cm^{-1}. PMR spectrum: (δ, ppm): 2.25 and 2.54 (m, 2H-10), 3.98 and 4.24 (m, 2H-11), 5.17 (t, H-9), 5.62 (br.s, OH), 7.38 (m, H-6), 7.62 (m, H-7 and H-8), 8.20 (d, H-5).

Oxidation of dl-Vasicinone. A solution of 83 mg of *dl*-vasicinone (III) in 5 ml of alcohol was treated with 2 ml of perhydrol, and the mixture was left for a week. The solvent was distilled off, and the residue was chromatographed on a column of silica gel with elution by chloroform–ethanol (8:1). Fractions of 5-6 ml were collected, and fractions No. 2-5 were crystallized from acetone to give 27 mg of base (I), mp 203–204°C.

Reduction of Vasicinone N-Oxide. Base (I) (47 mg) was dissolved in 5 ml of 8% hydrochloric acid and was reduced with granulated zinc at room temperature for 7 h. The reaction mixture was decomposed with 10% caustic soda solution and extracted with chloroform, and the chloroform was distilled off. Chromatography in a thin layer of silica gel showed the formation of three substances, with one of them predominating. The mixture was separated chromatographically on a column of silica gel, with elution by mixtures of chloroform and ethanol in various ratios (20:1, 10:1, and 4:1). This gave 6 mg of base (IV) with mp 110-111°C (acetone), 19 mg of base (III) with mp 211-212°C (alcohol–acetone) and 8 mg of base (V) with mp 86-87°C (pet. ether).

Deoxyvasicinone N-Oxide (II). The mother solutions from fractions 2-5 after the isolation of deoxyvasicinone and from fractions 2-6 after the isolation of vasicinone N-oxide were combined and rechromatographed, as described above. By crystallization, fractions 2-7 yielded 48 mg of base (II).

Mass spectrum, m/z (%): 202 (M^+, 13), 186 (100), 185 (100), 184 (17), 169 (8), 160 (26), 157 (25), 130 (42), 129 (39), 119 (19), 116 (16), 103 (58), 90 (23).

UV spectrum (II): $\lambda_{max}^{C_2H_5OH}$ (nm): 229, 270, 304, 315 (lg ε 4.42; 4.10; 3.94; 3.88).

IR spectrum (II): 770 (o-disubstituted benzene ring), 840, 880, 1025, 1170, 1270 and 1285 (=N→O), 1335, 1380, 1470, 1570, and 1610 (C=C), 1630 (C=N), 1685 (N–C=O), 2930 and 2965 (–CH_2 groups), 3050 (Ar–H).

PMR spectrum (II): (δ, ppm): 2.22 (m, 2H-10), 3.08 (t, 2H-9), 4.10 (t, 2H-11), 7.32 (m, H-6), 7.55 (m, H-7 and H-8), 8.12 (d, H-5).

Oxidation of Deoxyvasicinone. A solution of 71 mg of deoxyvasicinone (IV) in 5 ml of alcohol was treated with 2 ml of perhydrol, and after 10 days the solvent was distilled off. The residue was chromatographed on a column of silica gel with elution by chloroform–ethanol (10:1), with the collection of 4- to 5-ml fractions. By crystallization from acetone, fractions 3-7 yielded 24 mg of base (II), with mp 152-153°C.

Reduction of Deoxyvasicinone N-Oxide. Base (II) (34 mg) was dissolved in 5 ml of 8% hydrochloric acid and was reduced with granulated zinc, as described above. The mixture was separated by chromatography on a column of silica gel with

elution by chloroform–ethanol (5:1). This gave 16 mg of base (IV) with mp 110-111°C, and 7 mg of base (V) with mp 86-87°C.

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