Chemistry of Natural Compounds, Vol. 36, No. 1, 2000

ALKALOIDS OF *Nitraria komarovii.* STRUCTURES OF KOMARIN AND PEGANOL-N-OXIDE

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UDC 547.944/945

Two alkaloids are isolated from the aerial portions of Nitraria komarovii. *Their structures are determined using spectral data and chemical transformations.*

Key words: alkaloid, *Nitraria*, *Nitraria komarovii*, komarin, peganol-N-oxide, shoberidin, nitrarin, peganol, deoxypeganin.

In continuation of studies of alkaloids from the aerial portions of *Nitraria komarovii* Jljin et Lava [1, 2], we used column chromatography to isolate optically inactive base **1** [mp 224-225°C (alcohol), $C_{20}H_{17}N_3$, M^+ 299 (mass spectrometry)] from the total $CHCl_3$ extract.

The UV spectrum of **1** contains the following maxima: λ_{max} (C_2H_5OH) 210, 252, 306, and 370 nm (lg ε 4.41, 4.16, 4.08, and 3.80). The maxima undergo bathochromic shifts when the solution is made alkaline: (λ_{max} 214, 292, 320, and 425 nm). This is characteristic of anhydronium bases.

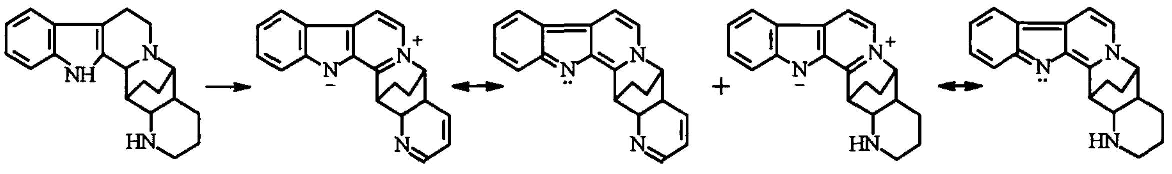
The IR spectrum of **1** exhibits aborption bands characteristic of an *o*-disubstituted benzene ring (755 cm^{-1}), a substituted indole (1460, 1490, 1580, and 1630 cm^{-1}), and others.

PMR spectra show the following signals (δ, ppm): 1.62 (m, 4H), 3.34 (m, 2H), 4.29 (m, 2H). Aromatic protons resonate in the range 7.0-8.2 ppm as a multiplet (9H). A broad one-proton signal appears at 9.32 ppm.

Analysis of the spectral data suggest that structure **1** is most probable for the alkaloid.

We attempted to correlate the chemical properties of **1** with those of nitrarin (**2**) [3]. For this, nitrarin was dehydrated using selenium anhydride in boiling isopropanol. Shoberidin (**3**) [4], an unidentified base (mp 214-215°C), and base **1** (mp 223-224°C), identical to the natural product, were isolated from the products.

Thus, the spectral data and chemical transformations for the alkaloid named komarin suggest the structure **1**.



2 **1** **3**

The benzene extract of the total bases isolated from the aerial portion of *N. komarovii* yielded optically inactive base **4** [mp 182-183°C (alcohol)], $C_{11}H_{12}N_2O_2$.

The UV spectrum of **4** (alcohol) contains absorption maxima (λ_{max}) at 207 and 270 nm (lg ε 4.08 and 3.62). The mass spectrum has the following peaks, *m/z*: 204 (M^+, 4), 203 (3), 188 (8), 187 (11), 186 (7), 172 (48), 171 (100), 143 (9), 129 (11), 116 (15), 89 (13).

Analysis of the spectral data suggested structure **4**, a quinazoline alkaloid. The molecular composition of **4** is one O atom greater than peganol (**5**). Otherwise, their mass spectral fragmentation patterns are similar.

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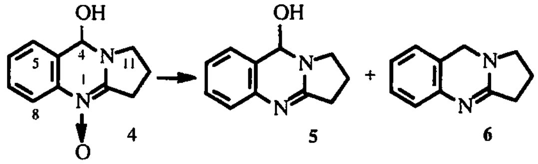
0009-3130/00/3601-0076$25.00

The presence in the IR spectrum of bands characteristic of an N-oxide, the appearance in the mass spectrum of peaks for ions $(M - 16)^+$, $(M - 17)^+$, and $(M - 18)^+$, and the high solubility in water suggest that **4** is an N-oxide.

Reduction of **4** with zinc in HCl produced **5** (mp 178-180°C, dec.) and **6** (mp 86-87°C). These were identified as peganol and deoxypeganin [5], respectively.



Thus, the isolated base is peganol-N-oxide and has structure **4**. The alternative structure with the N-oxide on N-3 is eliminated from consideration on the basis of the PMR spectra (the signal of C-11 would be significantly shifted).

EXPERIMENTAL

UV spectra were recorded in alcohol on a Lambda 16 UV/Vis spectrometer. PMR spectra were recorded in a deuterochloroform—deuteromethanol mixture and in $CDCl_3$ on a Tesla BS 567 A/100 MHz spectrometer with 0 = HMDS. IR spectra were recorded on UR-20 and Perkin—Elmer System 2000 FT-IR spectrometers in pressed KBr pellets. Mass spectra were measured on an MX-1310 spectrometer; on a Kratos MS-25 RF.

Extraction and separation of total bases and solvent systems for TLC have been previously described [1, 2, 6, 7].

Komarin (1). The $CHCl_3$ extract (43.21 g) of the total bases was separated by column chromatography using silica gel. The eluents were $CHCl_3$—acetone—ethanol (5:4:1) and then $CHCl_3$—methanol in various ratios (10:1, 10:2, 4:1, and 1:1). Fraction of 50-60 ml were collected.

Fractions 8-17 were combined and rechromatographed on a silica-gel column by eluting with $CHCl_3$—ethanol (10:1). Fractions of 13-15 ml were collected. Base **1** (mp 224-225°C) was isolated from fractions 11-20 by crystallization from alcohol—acetone.

IR spectrum (ν_{max}, cm^{-1}): 755, 1170, 1340, 1460, 1490, 1580, 1630, 1650, 2860, 2940, 3065.

Dehydration of Nitrarin by Selenium Anhydride. Nitrarin (0.8 g) was dissolved in isopropanol (30 ml) in a round-bottomed flask and treated with selenium anhydride (0.8 g). The solution was refluxed for 6 h and filtered. The solvent was removed. The alkaloids were isolated from the solid by the usual method and separated on a silica-gel column by elution with $CHCl_3$—ethanol (4:1) and then $CHCl_3$—methanol—ammonia (4:1:0.1). Fractions of 10-15 ml were collected.

Base **1** (76 mg, mp 223-224°C, alcohol), shoberidin (41 mg), and an unidentified base (53 mg, mp 214-215°C, alcohol—acetone) were isolated from separate fractions.

Peganol-N-oxide (4). The mother liquor (fractions 7-11) of the benzene part of the total bases after isolation of deoxyvasicinone was rechromatographed on a silica-gel column. The eluent was $CHCl_3$—ethanol (6:1). Fractions of 8-10 ml were collected. Base **4** (67 mg, mp 182-183°C, alcohol) was obtained by crystallization from alcohol of fractions 15-22.

PMR spectrum ($CDCl_3$, δ, ppm): 0.75 (m, 1H), 1.16-2.13 (m, 3H), 3.30 (m, 1H), 3.89 (m, 1H), 5.80 (s, 1H), 6.95-7.40 (m, 4H), 7.80 (br. s).

IR spectrum (ν_{max}, cm^{-1}): 781, 881, 1006, 1076, 1169, 1190, 1293, 1423, 1455, 1479, 1568, 1599, 1620, 2697, 2826, 2875, 2934, 2977, 3062.

Reduction of Peganol-N-oxide. Base **4** (41 mg) was dissolved in HCl (5 ml, 8%) and reduced by granulated zinc at room temperature for 7 h. The solution was made alkaline using 10% NaOH solution and extracted with $CHCl_3$. The $CHCl_3$ was removed. The mixture was separated by column chromatography on silica gel using elution by $CHCl_3$—ethanol (5:1) to produce **5** (18 mg, mp 178-180°C, dec., alcohol) and base **6** (17 mg, mp 86-87°C, petroleum ether).

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