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ALKALOIDS OF *Nitraria komarovii*. N-ALLYLNITRARINE AND KOMAROVIDININE N-OXIDE

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Two new alkaloids, N-allylnitrarine and komarovidinine N-oxide were isolated from the aerial part of Nitraria komarovii. *Their structures were established by chemical transformations and spectral data.*

Key words: alkaloid, *Nitraria*, nitrarine, komarovidinine, N-allylnitrarine, komarovidinine N-oxide.

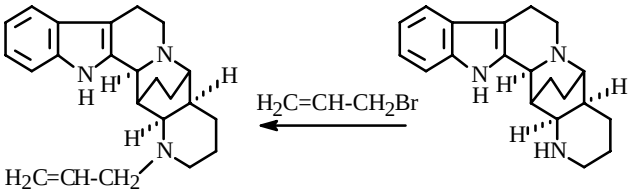
In continuation of our studies of the alkaloids from the aerial part of *Nitraria komarovii* Iljin et Lava [1], column chromatography of the $CHCl_3$ extract of the total alkaloids yielded optically inactive **1**, mp 269-271°C (alcohol), of composition $C_{23}H_{29}N_3$. The molecular weight is 347 (mass spectrometry).

The IR spectrum of **1** has absorption bands characteristic of an *o*-disubstituted benzene ring (773 cm^{-1}), a substituted indole (1468, 1495, 1622, 1641 cm^{-1}), and others.

The UV spectrum of **1** exhibits maxima (λ_{max}, C_2H_5OH) at 222, 265-272, 280 (sh), and 388 nm (4.72, 3.85, 3.84, 3.52) that are characteristic of a nonconjugated indole chromophore [2].

The spectral data indicate that **1** is an indole. Its molecular weight differs from that of nitrarine (**2**) and isonitrarine by 40 amu. The PMR spectrum contains signals of aromatic and alicyclic protons in addition to signals characteristic of an allyl group at 3.30 (2H, d, J = 10 Hz), 5.25 (2H, m), and 5.87 ppm (1H, m).

Direct comparison of the physicochemical and spectral data of **1** with those of an authentic sample of N-allylnitrarine that was obtained via allylation of nitrarine (**2**) with allyl bromide indicated that they are identical.



1 **2**

N-Allylnitrarine is isolated for the first time from a natural source.

These same total alkaloids yielded **3** (mp 263-264°C), $C_{20}H_{11}N_3O$.

The UV spectrum of **3** in alcohol exhibits absorption maxima (λ_{max}) at 210, 229, 266, 295-306, 387, 406, and 432 nm (4.68, 4.67, 4.38, 4.04, 4.10, 4.40, 4.57) that change upon acidification to (λ_{max}, $C_2H_5OH + H^+$) 208, 266, 310, 291, 414, and 445 nm. The presence of absorption bands in the visible range indicates that the alkaloid is a condensed polycyclic aromatic compound.

The molecular weight of **3** differs from that of the known alkaloid komarovidinine by 16 amu. Otherwise, their mass-spectral fragmentation patterns are similar.

The presence in the IR spectrum of **3** of bands characteristic of an N-oxide (1241, 1261, and 1284 cm^{-1}) [3]; of strong peaks in the mass spectrum for ions $[M - 16]^+$, $[M - 17]^+$, and $[M - 18]^+$; and poor solubility in all organic solvents suggest that this compound is an N-oxide.

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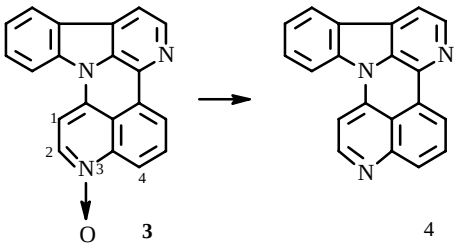
Reduction of **3** by Zn/HCl produced **4**, mp 254-255°C, which was identified as komarovidinine [4].



3 4

Comparison of the PMR spectra of komarovidinine and **3** indicates that the signals of the aromatic protons for C-1 and C-2 shift to weak field by 0.3 ppm. This is consistent with **3** being komarovidinine N-oxide at N-3.

Thus, komarovidinine-N-oxide has the structure of **3** and is a new alkaloid.

EXPERIMENTAL

PMR spectra were recorded in a $CDCl_3$—CD_3OD mixture on a Tesla BS 567 A/100 MHz spectrometer with HMDS as an internal standard; UV spectra, in alcohol on an EPS-3T (Hitachi) spectrophotometer and a UV/Vis Lambda 16 spectrometer; IR spectra, in KBr pellets on a Perkin—Elmer System 2000 FT-IR spectrometer; mass spectra, on an MX-1310 spectrometer and a Kratos MS-25 RF GC—MS.

Extraction and separation of the total alkaloids have been described in detail [5, 6].

For TLC we used KSK and L 5/40 silica gels; for chromatography, the solvent systems reported in the literature [7, 8].

The $CHCl_3$ extract of the total alkaloids (43.21 g) was chromatographed on a silica-gel column with elution by $CHCl_3$—$(CH_3)_2CO$—C_2H_5OH (5:4:1) and $CHCl_3$—C_2H_5OH mixtures in various ratios (10:1, 10:2, 4:1, and 1:1). Fractions of 50-60 ml were collected. Individual fractions yielded known alkaloids and the following ones:

N-Allylnitrarine (1). Fractions 18-27 were combined and rechromatographed on a silica-gel column with elution by $CHCl_3$—CH_3OH (5:1). Fractions of 15-17 ml were collected. Fractions 10-20 were combined and crystallized from alcohol. Yield of **1**, 96 mg, mp 269-271°C.

Alkylation of Nitrarine by Allyl Bromide. N-Allylnitrarine. A solution of nitrarine (**2**, 0.2 g) in ethanol (5 ml) was treated with freshly distilled allylbromide (2 ml) and refluxed for 5 h. The solvent was removed after the reaction was finished. Water was added. The solution was basicified with NaOH solution (10%) and extracted with $CHCl_3$. The $CHCl_3$ was removed. The solid was separated by chromatography on a silica-gel column with elution by $CHCl_3$—C_2H_5OH (5:1). Yield 0.11 g of N-allylnitrarine, mp 269-271°C (alcohol).

Mass spectrum, *m/z* (%): 347 (M^+, 52), 324 (10), 306 (23), 289 (10), 264 (24), 263 (21), 225 (76), 224 (100), 223 (81), 169 (47), 168 (44), 144 (36), 123 (85), 98 (62).

IR spectrum (ν_{max}, cm^{-1}): 773, 852, 880, 891, 925, 937, 951, 970, 995, 1008, 1050, 1081, 1122, 1143, 1155, 1164, 1195, 1232, 1261, 1277, 1334, 1385, 1423, 1468, 1495, 1622, 1641, 2815, 2862, 2932, 3046, 3120, 3382.

PMR (δ, ppm): 1.21 (m), 1.70 (m), 2.20 (m), 2.90 (m), 3.30 (2H, d, J = 10 Hz), 3.75 (m), 4.21 (m), 4.62 (1H, br. s), 5.25 (2H, m), 5.87 (1H, m), 7.13 (2H, m), 7.46 (2H, m).

Komarovidinine N-oxide (3). Fractions 7-15 were combined and rechromatographed on a silica-gel column with elution by $CHCl_3$—C_2H_5OH (6:1). Fractions of 10-15 ml were collected. Fractions 8-17 were crystallized from alcohol—acetone. Yield 43 mg of **3**, mp 263-264°C.

Mass spectrum, *m/z* (%): 309 (8), 293 (100), 292 (29), 291 (22), 146.5 $[M - 16]^{++}$ (5).

IR spectrum (ν_{max}, cm^{-1}): 739, 771, 823, 966, 1120, 1241, 1261, 1284, 1333, 1384, 1431, 1453, 1485, 1510, 1602, 1615, 3062.

PMR (δ, ppm): 7.39 (d, H-1, J = 6 Hz), 7.44 (m, H-11), 7.54 (m, H-5), 7.65 (3H, m, H-6, H-12, H-13), 7.80 (d, H-9, J = 7 Hz), 8.05 (m, H-4), 8.09 (m, H-10), 8.25 (d, H-8, J = 5.5 Hz), 8.60 (d, H-2, J = 7 Hz).

Reduction of Komarovidinine N-oxide. Komarovidinine (4). Alkaloid **3** (24 mg) was dissolved in HCl (5 ml, 10%) and reduced with granulated Zn at room temperature for 14 h. The solution was basicified with NaOH (10%) and extracted with

$CHCl_3$. The solvent was removed. The solid was crystallized from benzene. Yield of **4**, 17 mg, mp 254-255°C.

Mass spectrum, *m*/*z* (%): 293 (M^+) and 146.5 (M^{++}).

PMR (δ, ppm): 7.10 (d, H-1, J = 6.5 Hz), 7.32 (d, H-11, J = 8 Hz), 7.45 (m, H-5), 7.54 (2H, m, H-12 and H-13), 7.63 (m, H-6), 7.76 (d, H-9, J = 7 Hz), 7.81 (m, H-4), 7.96 (dd, H-10, J = 7 and 2 Hz), 8.17 (d, H-8, J = 5 Hz), 8.36 (d, H-2, J = 8 Hz).

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