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ALKALOIDS FROM *Nitraria schoberi*. O-ACETYLNITRARAINE

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The new alkaloid O-acetylnitraraine was isolated from the aerial part of Nitraria schoberi. *Its structure was established using spectral data and chemical transformations.*

Key words: *Nitraria*, *N. schoberi*, alkaloid, nitraraine, O-acetylnitraraine.

We investigated alkaloids from the aerial part of *Nitraria schoberi* L. collected during flowering in Surkhandar'ya District of the Republic of Uzbekistan. Column chromatography of the benzene fraction of the total bases isolated the following known alkaloids: schoberine [1a], nitraraine [1b], nitraramine [1c], dehydroschoberine [1d], sibiridine [2], vasicinone [1e], peganol [1f], tetramethylenetetrahydro-*β*-carboline N-oxide [1g], and the new base **1**, mp 93-95° (CH_3OH). Peganol was isolated from this species for the first time.

The $CHCl_3$ fraction of the total bases afforded nitrarine [1b], isonitrarine [1h], schoberidine [1a], nitramidine [1h], isoschoberidine [1j], and N-methylnitrarine [3].

Base **1** had formula $C_{22}H_{26}N_2O_2$, $[\alpha]_D$ ±0, 350 $[M]^+$.

The UV spectrum of **1** exhibited the following absorption maxima: 227, 281, 292(sh) (log ε 4.55, 4.01, 3.91). These are typical of an unconjugated indole chromophore [4].

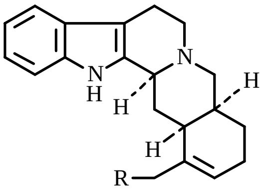
The IR spectrum of **1** contained absorption bands due to vibrations of *o*-disubstituted benzene (743 cm^{-1}), C–O (1027), substituted indole (1455, 1472, 1575, 1625), ester carbonyl (1718), active H (3232), and a trisubstituted double bond (722-870). The mass spectrometric fragmentation of **1** was similar to that of yohimbine alkaloids [5, 6].

The PMR spectrum of **1** gave signals for indole N–H protons at 7.91 ppm (br.s, 1H), aromatic indole protons at 6.87-7.49 ppm, and olefinic protons at 5.35 ppm (br.s, 1H).

The spectral data showed that the alkaloid belonged to the yohimbine class. Acidic hydrolysis of **1** afforded nitraraine (**2**) [7].

Direct comparison of **1** with O-acetylnitraraine showed that they were identical.

Thus, **1** is O-acetylnitraraine and was isolated from this plant for the first time.



1, 2

1: R = $OCOCH_3$
2: R = OH

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EXPERIMENTAL

UV spectra were recorded in alcohol on a Lambda 16 UV/Vis spectrometer; IR spectra, on a Perkin—Elmer System 2000 FT—IR spectrometer in KBr disks; mass spectra, on a Kratos MS-25 RF GC—MS; PMR spectra, on a Tesla Bs 567 A spectrometer at 100 MHz and HMDS = 0. TLC used KSK and L silica gel (5/40 μm) and Silufol plates. Chromatography used the following solvents: C_6H_6:CH_3OH (4:1, 1), $CHCl_3$:$(CH_3)_2CO$:C_2H_5OH (5:4:1), 2), $CHCl_3$:CH_3OH (6:1, 3; 4:1, 5), $CHCl_3$:C_2H_5OH (5:1, 4), $CHCl_3$:CH_3OH:NH_4OH (4:1:0.1, 6), $CHCl_3$:$(CH_3)_2CO$:C_2H_5OH:NH_4OH (5:4:1:0.1, 7). The developers were Dragendorff's reagent or I_2 vapor.

Extraction of the Aerial Part of *Nitraria schoberi*. The aerial part of *N. schoberi* (3.2 kg) collected in June 2002 was moistened with aqueous NH_4OH (8%), left for 2 h, and extracted with $CHCl_3$ (10 times) The condensed $CHCl_3$ extracts were extracted with H_2SO_4 (10%). The acidic extract was made basic with KOH solution (10%) and extracted with C_6H_6 and then $CHCl_3$. The basic solution was saturated with NH_4Cl. The phenolic part was extracted with $CHCl_3$ to afford the following total alkaloids. Nonphenolic part: C_6H_6 total 6.15 g; $CHCl_3$ total 5.2 g. Phenolic part: $CHCl_3$ total 0.35 g. Total yield 11.60 g (0.36% of the air-dried plant mass).

The C_6H_6 part of the total bases (6.15 g) was separated by column chromatography over silica gel with elution by $CHCl_3$:CH_3OH in various ratios (20:1, 15:1, 10:1, 6:1, 4:1) and collection of fractions (10-15 mL). Separate fractions afforded the following known alkaloids: schoberine, dehydroschoberine, nitraraine, nitraramine, sibiridine, vasicinone, peganol, and tetramethylenetetrahydro-*β*-carboline N-oxide.

O-Acetylnitraraine (1). Fractions 22-27 were combined and evaporated. The solid was crystallized from CH_3OH to afford **1** (56 mg), mp 93-95°C.

Hydrolysis of 1. Base **1** (0.04 g) was dissolved in H_2SO_4 (5 mL, 2 N) and heated to 90°C for 2 h. After the reaction was finished, the solution was made basic with KOH solution (10%) and extracted with $CHCl_3$. The solvent was evaporated. The solid was crystallized from alcohol to afford **2** (0.026 g), mp 280-281°C.

Synthesis of 1. A mixture of nitraraine (0.08 g), freshly purified pyridine (1 mL), and freshly distilled acetic anhydride (1 mL) was left at room temperature for 5 d. The solvent was removed in vacuo. The resulting solid was treated with water (2 mL) and made basic with conc. NH_4OH until the pH was 7. The resulting solid was filtered off, washed with water and CH_3OH, and crystallized from CH_3OH to afford O-acetylnitraraine (0.067 g), mp 93-95°C.

Mass spectrum (*m/z*): 350 (44), $[M]^+$, 349 (26) $[M - 1]^+$, 307 (4) $[M - 43]^+$, 291 (35) [M - CH_3COO], 277 (4) [M - 73], etc.

IR spectrum (λ_{max}, cm^{-1}): 744, 822, 847, 870, 976, 1008, 1027, 1091, 1140, 1170, 1255, 1286, 1304, 1323, 1363, 1385, 1439, 1456, 1472, 1493, 1625, 1648, 1718, 2850, 2907, 2926, 2998, 3056, 3232.

The $CHCl_3$ part of the total bases (5.2 g) was separated by column chromatography over silica gel with elution by $CHCl_3$:CH_3OH in various ratios (20:1, 10:1, 4:1, 2:1). Separate fractions afforded the known alkaloids nitrarine, isonitrarine, schoberidine, nitramidine, isoschoberidine, and N-methylnitrarine.

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