Chemistry of Natural Compounds, Vol. 39, No. 3, 2003

ALKALOIDS FROM PLANTS OF THE *Nitraria* GENUS. STRUCTURE OF SIBIRIDINE

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UDC 547.944/945

The new alkaloid sibiridine was isolated from the aerial parts of Nitraria sibirica *and* N. schoberi. *Its structure was established using spectral data and chemical transformations. Its synthesis was carried out.*

Key words: *Nitraria, N. sibirica, N. schoberi,* alkaloid, synthesis, sibiridine.

In continuation of the study of alkaloids from the aerial part of *Nitraria sibirica* Pall., the new base **1** was isolated from the benzene fraction of the total bases [1] by column chromatography: $C_{15}H_{13}NN^{+}OH^{-}$, mp 192-193°C, named by us sibiridine.

The mass spectrum of **1** exhibits peaks with *m/z* 222, 221, and 220 in addition to peaks of ions arising from quinoline and pyridine parts of the molecule [2].

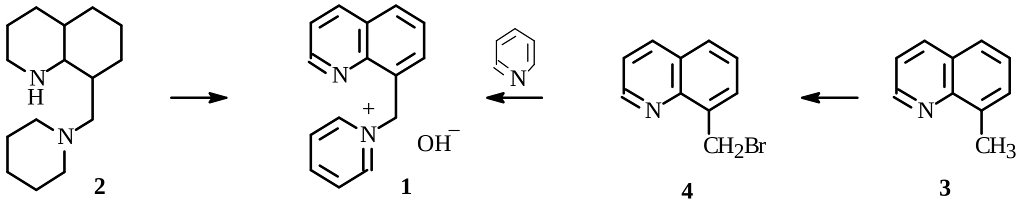
The IR spectrum contains absorption bands at 1665, 1631, 1585, 1538, 1500, 1475, and 1453 (conjugated C=C and C=N systems) and 865, 843, 807, 776, 767, and 742 cm^{-1} (out-of-plane deformations of aromatic rings).

The PMR spectrum of **1** has at weak field a complicated group of signals characteristic of aromatic protons.

Sibiridine was found to be identical to one of the dehydrogenation products of dihydroschoberine (**2**) by Pd-black.

Structure **1** was most probable based on spectral data and the formation from dihydroschoberine via dehydrogenation.

We synthesized a compound of this structure from 8-bromomethylquinoline and pyridine by the scheme given below.



8-Methylquinoline (**3**) was synthesized from *o*-toluidine by the Scraup method [3]. 8-Bromomethylquinoline (**4**) was prepared by bromination of 8-methylquinoline by the literature method [4]. Alkylation of pyridine by 8-bromomethylquinoline afforded **1**, which was identical in physicochemical properties and spectral data to the natural alkaloid sibiridine.

Thus, sibiridine is (quinol-8-yl)methylpyridinium hydroxide and is a new type of nitrogenous base.

1 was also isolated from the benzene fraction of the total alkaloids from *N. schoberi* L. collected in June 1995 near Ayakhagitm village of Bukhara region of the Republic of Uzbekistan.

EXPERIMENTAL

Information on the instruments used to record spectra, the solvent systems used for TLC, and the conditions for extraction and separation of total bases have been published [5, 6].

Isolation of Sibiridine (1) from *N. sibirica*. Fractions 27-37 after chromatography of the benzene fraction and mother liquors of fractions after separation of dihydroschoberine [5] were combined and separated chromatographically over a silica-gel

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column with elution by $CHCl_3$:C_2H_5OH (9:1). Fractions of 6-7 mL were collected. Fractions 17-21 afforded **1** upon crystallization from ethanol, 27 mg, mp 192-193°C.

IR spectrum (KBr, ν_{max}, cm^{-1}): 641, 742, 767, 776, 807, 843, 865, 913, 957, 978, 1000, 1040, 1069, 1131, 1142, 1171, 1192, 1216, 1247, 1265, 1321, 1385, 1453, 1475, 1500, 1538, 1585, 1631, 1665, 1708, 2225, 3068, 3128.

UV spectrum (EtOH, λ_{max}, nm): 220, 280-295, 307, 320 nm (4.1, 3.51, 3.46, 3.54).

Mass spectrum, *m/z* (%): 222, 221 (0.5) $[M]^+$, 220 (0.5), 130 (28), 129 (100), 128 (36), 103 (22), 102 (69), 91 (11), 78 (18), 77, 76, 75.

PMR spectrum (CD_3OD, δ, ppm): 7.85-9.20, 4.8 (br.s).

Dehydrogenation of Dihydroschoberine (2) over Pd-black. Dihydroschoberine (37 mg) was mixed with Pd-black (21 mg). The mixture was immersed into a sand bath heated to 180°C, held for 40 min at 180-200°C, and cooled. The mixture was dissolved in $CHCl_3$:CH_3OH. The Pd was filtered off. The solvent was distilled off. The solid was worked up as usual and chromatographed over a silica-gel column with elution by $CHCl_3$:C_2H_5OH (10:1). Crystallization of individual fractions from alcohol isolated base **1** (9 mg), mp 192-193°C.

8-Bromomethylquinoline (4). A suspension of N-bromosuccinimide (1.5 g) in CCl_4 (10 mL) was heated to 60°C, treated in portions with 8-methylquinoline (1.5 g), and boiled for 1 h on a water bath. Upon completion of the reaction, the insoluble part was filtered off. The filtrate was evaporated. The solid was washed with water. Crystallization from petroleum ether afforded **4**, 0.5 g, mp 83-84°C.

Preparation of 1 from Pyridine and 8-Bromomethylquinoline (4). A solution of pyridine (2 mL) in acetone (5 mL) was treated in portions with 8-bromomethylquinoline (0.5 g) in acetone (5 mL) and boiled on a water bath for 2 h. The solvent was removed. Water was added. The solution was made basic with NaOH solution (10%) and extracted with $CHCl_3$. The $CHCl_3$ was evaporated. The solid was crystallized from alcohol. Yield 0.51 g of base **1**, mp 192-193°C.

Isolation of Sibiridine (1) from *N. schoberi*. The benzene fraction (14.26 g) of total bases [6] was chromatographed over a silica-gel column with elution by $CHCl_3$:C_2H_5OH in various ratios (20:1, 15:1, 10:1, 5:1, and 4:1). Fractions of 40-50 mL were collected.

The mother liquors of fractions 9-15, 16-21, and 22-29 were combined after isolation of nitraraine, deoxyvasicinone, and tetramethylenetetrahydro-*β*-carboline, respectively, and rechromatographed over a silica-gel column with elution by $CHCl_3$:C_2H_5OH (6:1). Fractions of 15-20 mL were collected.

After isolation of dihydronitraraine, the mother liquors of fractions 14-21 were separated over a silica-gel column with elution by $CHCl_3$:CH_3OH (10:1). Fractions of 10-15 mL were collected.

Removal of solvent from fractions 24-35 and crystallization from alcohol produced **1**, 23 mg, mp 192-193°C.

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