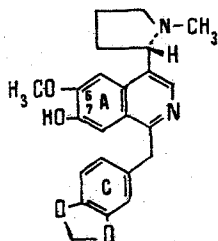


or C₇. In the NMR spectrum of (I) the signal of the C₈ aromatic proton is shifted by 20 Hz (7.47 ppm) downfield as compared with that in the spectrum of macrostomine, and the protons of ring C (6.53, 6.60 ppm) and the methylene protons (4.32 ppm) are shifted upfield by approximately 10 Hz. These displacements are apparently connected with a change in the orientation of the benzyl part of the molecule of (I) relative to macrostomine and are due to the replacement of the methoxy group at C₇ in macrostomine by the hydroxy group in arenine.

The facts given above and the correlation of O-methylarenine with macrostomine show that arenine has the structure (I) with the S configuration of the asymmetric center



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ALKALOIDS OF *Peganum nigellastrum*

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UDC 547.944/945

The main area of *Peganum nigellastrum* Bge. is the desert regions of Mongolia. The alkaloid composition of this plant has been little studied. Peganine and harmine have been found in the epigeal part by chromatography. We have investigated *Peganum nigellastrum* collected in the South Gobi iamak of Mongolia in the flowering phase. Chloroform extraction yielded 1.57% of combined alkaloids. The mixture of bases was separated into three fractions; A, B, and C. Fraction A was obtained by treating an acid extract with chloroform, fraction B consisted of the precipitate that deposited from the acid solution on alkalization, and fraction C was obtained by treating the filtrate with chloroform. Each fraction was separated further by preparative chromatography. Individual substances were crystallized or converted into salts.

Fraction A yielded a base in the form of a crystalline hydrochloride. From the latter a base was recovered with mp 110-111°C, mol. wt. 186; the R_f value of the substance on TLC [Al₂O₃; chloroform-benzene-methanol (5:4:1)] coincided with that of deoxyvasicinone [2], and a mixture with an authentic sample gave no depression of the melting point. The second base from this fraction was identified by TLC and a mixed melting point with an authentic sample of vasicinone [2].

From a base isolated from fraction B was obtained a nitrate with mp 166-168°C, which was identical with *dl*-peganine nitrate.

A base obtained from fraction C was identified as deoxyvasicinone.

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Thus, *dl*-peganin, vasicinone, and deoxyvasicinone have been obtained from *Peganum nigellastrum*.

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ALKALOIDS OF *Berberis integerrima*

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UDC 547.944/945

Continuing the separation of the combined alkaloids of the leaves of *Berberis integerrima* Bge. [1], we have isolated a phenolic base (I) with mp 125–126°C (benzene), $[\alpha]_D +57^\circ$ (c 0.2; ethanol). Methylation of (I) with diazomethane yielded glaucine. According to its mass and NMR spectra, (I) must contain two hydroxy and two methoxy groups. A direct comparison of (I) with isoboldine [2] showed their identity.

A phenolic base (II) with mp 192–193°C, $[\alpha]_D +90^\circ$ (c 0.16; CHCl_3) gave a crystalline hydrochloride with mp 204–205°C. The UV spectrum [$\lambda_{\text{max}}^{\text{ethanol}}$ 222, 282, 306 nm (log ϵ 4.49, 4.04, 4.06)] characterized (II) as a 1,2,9,10-substituted aporphine. The mass spectrum coincided with that of thalicmidine (III). The NMR spectra of (II) and (III) differed by the signal of the N-methyl group: in (II) it was displaced downfield to 3.08 ppm. The facts given above permit (II) to be identified as thalicmidine N-oxide [3]. In actual fact, the reduction of (II) with Zn/HCl or NaBH_4 yielded (III). Oxidation of the latter with hydrogen peroxide gave (II).

Another phenolic base (IV) was isolated in the form of an oil with $[\alpha]_D +20.6^\circ$ (c 0.06; ethanol). UV spectrum: $\lambda_{\text{max}}^{\text{ethanol}}$ 230 nm (shoulder), 285 nm (log ϵ 4.09, 3.76). Mass spectrum: m/e 329 (M^+), 192 (100%), 178, 137. The NMR spectrum taken in CDCl_3 showed signals in the form of singlets from a N- CH_3 group (2.39 ppm), two OCH_3 groups (3.76 ppm), five aromatic protons in the form of three singlets at 6.24, 6.45, and 6.61 ppm, and two one-proton doublets at 6.51 and 6.68 ppm. This enabled (IV) to be assigned to the benzyltetrahydroisoquinoline bases. The benzyl and the isoquinoline moieties of (IV) contain hydroxy and methoxy groups. When (IV) was methylated with methyl iodide in an alkaline medium, a methiodide was obtained with mp 217–218°C, which was identified as the methiodide of laudanosine by comparison with an authentic sample. Consequently, (IV) contains substituents in positions 3', 4', 6, and 7.

The mutual arrangement of the hydroxy and methoxy groups was determined with the aid of proton-proton double resonance from the results of measurements of the intramolecular NOE. According to these results, the positions of the hydroxy and methoxy groups in (IV) correspond to reticuline [4].

The detection of reticuline among the protoberberine, aporphine, and bisoclaurine alkaloids of the barberry is interesting from the biogenetic point of view: it shows that in the barberry biogenesis probably takes place by the route as has been shown by experiments with labeled atoms for *Hydrastis canadensis* [5].

An alkaloid (V) was isolated in the form of an amorphous substance. It formed a crystalline hydrochloride with mp 228–229°C. The UV spectrum of (V) [$\lambda_{\text{max}}^{\text{ethanol}}$ 223, 271, 306 nm (log ϵ 4.39, 3.95, 3.96)] is characteristic for aporphine alkaloids with substituents in positions 1, 2, 10, and 11. The NMR spectrum taken in CDCl_3 showed the signals from three OH groups in the 3.84 ppm (6H, s) and 3.65 ppm (3H, s) regions, of a N- CH_3 group at 3.41 ppm (3H, s) and from aromatic protons at 6.80 ppm (1H, s), 6.75 ppm (1H, d), and 6.77 ppm (1H, d).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. M. I. Kalinin Andizhan Medical Institute. Translated from *Khimiya Prirodnykh Soedinenii*, No. 3, p. 419, May–June, 1978. Original article submitted January 6, 1978.