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NEW HOMOAPORPHINE BASE FROM *Merendera robusta*

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The alkaloid composition of the bulb casing of Merendera robusta *Bge. (Liliaceae) was investigated. The tropolone alkaloid colchicine was identified. A new homoaporphine base for which the structure methylmerenderine hydroxide was established by spectral and chemical methods was isolated.*

Key words: *Merendera robusta* Bge., homoaporphine base, merenderine, methylmerenderine hydroxide, methylmerenderine iodide.

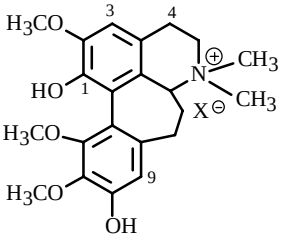
Large merendera (*Merendera robusta* Bge.) is a widely distributed colchicine-bearing plant of Central Asia that is a promising source for colchicine production [1]. The principal alkaloids of the leaves and stems of this plant are tropolone compounds colchicine and colchamine. The homoaporphine base merenderine (bechuanine) was also found in the plant [2, 3]. In addition to several minor tropolone alkaloids, their photochemical isomers, and homoaporphines [4], homoproaporphine bases [3, 5] that differ from previously known analogs in the configuration of the substituents [6] were also isolated from the leaves and stems. This may be due to a slightly different biosynthetic pathway for the large merendera alkaloids than that previously described [7].

Thus, alkaloids in the leaves and stems of merendera are studied to a certain extent whereas they are still uninvestigated in other plant parts such as flowers, seeds, fruit skin, and bulbs and their casing.

Our goal was to isolate alkaloids from the bulb casing. Alkaloids were extracted using acetic acid (3%). This produced the neutral alkaloids (0.04%), from which colchicine was positively identified. The mixture of basic alkaloids (0.02%) contained compounds without a tropolone ring.

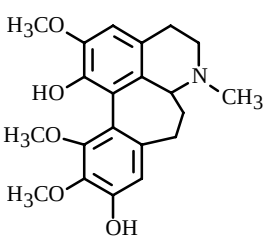
Furthermore, a small quantity of unknown base **1** was isolated from the aqueous mother liquor after extracting neutral and basic alkaloids.

Base **1** has the composition $C_{22}H_{28}O_5N^+OH^-$. The UV spectrum has absorption maxima at 260 and 290 nm. The IR spectrum contains absorption bands for benzene rings and methylene and hydroxyl groups (1460, 1600, 3460-3600 cm^{-1}). The PMR spectrum exhibits signals corresponding to two biphenyl aromatic protons (6.70 and 6.65 ppm), three methoxyls (3.88×2 and 3.67 ppm), and an N-dimethyl group (3.43 and 3.30 ppm) of an isoquinoline system.



1, 3

1: X = OH;
3: X = I



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The spectral properties indicated that the compound belongs to the group of homoaporphine bases, which are found in several colchicine-bearing plants of the lily family [8, 9], including large merendera [4]. The presence of the amine with two methyls, the signals of which appear at relatively weak field, indicates that the N in it is quaternary. This is consistent with the good solubility in water.

Comparison of the PMR spectra and chromatographic mobilities of **1** and known homoaporphine alkaloids showed the greatest similarity to the merenderine (**2**) derivative methylmerenderine iodide (**3**). However, **1** gave a negative reaction for halides.

Methylmerenderine iodide was converted to **1** by treatment with silver hydroxide hydrate. The isolated compound was identified by its PMR spectrum and chromatographic behavior as **1**, confirming at the same time the positions of the two hydroxyls and the quaternary N.

Thus, **1** has the structure 1,10-dihydroxy-2,11,12-trimethoxyhomoaporphine. The hydroxy-methylate is the first quaternary homoaporphine base isolated from this plant.

EXPERIMENTAL

UV spectra were recorded on an SF-4A spectrometer in CH_3OH; IR spectra, on a UR-10 dual-beam spectrometer in KBr; PMR spectra, on a Varian XL-100 instrument in $CDCl_3$.

The purity and identity of the compounds were monitored by paper chromatography (PC). Radial PC on Filtrak paper was performed using the mobile phases *n*-butanol:HCl:H_2O (50:7.5:13.5, system 1) and *n*-butanol:CH_3COOH (5%) (1:1, organic layer, system 2). Spots of the compounds were developed using modified Dragendorff's reagent and iodine vapor.

Isolation of Alkaloids. Ground bulb casing (11.0 kg) of large merendera collected in Tashkent district in various years and vegetative periods was extracted five times with acetic acid (3%). Fractions of alkaloids were obtained according to the previously described method [4]:

Neutral alkaloids	4.46 g	(0.04%)
Bases	1.98 g	(0.02%)
Total alkaloids	6.44g	(0.06%)

Colchicine (R_f 0.34, system 2) was identified in the neutral alkaloids by comparison with an authentic sample. Unidentified compounds with R_f values 0.26, 0.45, 0.71, and 0.92 were observed in the bases.

Isolation of Methylmerenderine Hydroxide (1). After extracting neutral and basic alkaloids, the $CHCl_3$ mother liquor was evaporated. The solid was treated with $CHCl_3$:CH_3OH (2:1). Purification of the extracts over Al_2O_3 afforded **1** (26 mg) with R_f 0.71 and 0.42 (systems 1 and 2, respectively).

PMR spectrum (ppm): 6.70 and 6.65 (2H, two s, H-3 and H-9), 6.16 (OH), 3.88 (6H, s, $2OCH_3$), 3.67 (3H, s, OCH_3), 3.34 and 3.30 [6H, two s, $(CH_3)_2N^+$].

Methylmerenderine Iodide (3). A mixture consisting of merenderine (**2**), CH_3OH (3 mL), and CH_3I (0.5 mL) was refluxed for 2 h. The solvent was distilled off. The solid was treated with acetone to afford an amorphous compound with R_f 0.44 (system 2).

PMR spectrum (ppm): 6.72 and 6.68 (2H, two s, H-3 and H-9), 6.20 (OH), 3.94 (6H, s, $2OCH_3$), 3.72 (3H, s, OCH_3), 3.48 and 3.34 [6H, two s, $(CH_3)_2N^+$|].

Preparation of 1,10-Dihydroxy-2,11,12-trimethoxyhomoaporphine (1) from Methylmerenderine Iodide (3). Compound **3** (0.3 g) was dissolved in CH_3OH (5 mL) and treated on a shaker with AgOH, which was freshly prepared from $AgNO_3$ (0.3 g) and KOH (0.1 g). The precipitate was filtered off. The filtrate was evaporated in vacuum without heating and washed with dry acetone.

A noncrystalline compound with an R_f value and PMR spectrum identical to those of **1** from the plant was isolated.

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