

THE STRUCTURE OF MERENDERINE

M. K. Yusupov, A. A. Trozyan,
Kh. A. Aslanov, and A. S. Sadykov

UDC 547.944.6

We have previously [1] reported the isolation from *Merendera raddeana* of a new base - merenderine - with the composition $C_{21}H_{25}O_5N$, mp 229-230°C, $[\alpha]_D + 105^\circ$, M^+ 371 (mass spectrometrically). From the nature of its UV spectrum (Fig. 1) [λ_{max} 258, 296 nm ($\log \epsilon$ 4.11, 3.89), λ_{min} 248, 282 nm ($\log \epsilon$ 3.97 and 3.72)] merenderine may be assigned to the group of homoaporphine alkaloids [2-4].

The IR spectrum of the base (Fig. 2) has absorption bands of hydroxy groups (3560 and 3470 cm^{-1}), of aromatic nuclei (1600 , 1577 cm^{-1}), and of methylene groups (1455 cm^{-1}). The NMR spectrum of merenderine (Fig. 3) has the signals of three aromatic methoxy groups (δ 3.80, 3.80, and 3.67 ppm), of a N-methyl group (2.20 ppm), and of two aromatic protons in the form of singlets (6.60 and 6.69 ppm). On methylation with diazomethane, this substance formed a dimethyl ether, and on acetylation a diacetyl derivative, which shows the presence of two phenolic hydroxy groups in the initial base. The positions of the hydroxy and the methoxy groups were determined on the basis of the constants of the homoaporphine alkaloids isolated from colchicine-containing species of plants of the family Liliaceae having substituents at the C_2 , C_3 , C_4 , C_5 , and C_6 atoms of rings A and D [4].

The results of a comparison of the composition and physical constants of merenderine with known homoaporphine alkaloids showed that the base is similar to bechuanine [5], but differs from the latter by a higher specific rotation. The spectral characteristics of an optical isomer of this base - floramultine - are known from the literature. On comparing the NMR spectra of the latter and of merenderine, and also those of their diacetyl derivatives, we found that they were very similar (δ , in ppm):

Compound	Methoxy groups	Aromatic protons
Floramultine	3.55; 3.84; 3.89	6.54; 6.59
Diacetylfloramultine	3.44; 3.78; 3.82	6.71; 6.63
Merenderine	3.55; 3.88; 3.90	6.69; 6.60
Diacetylmerenderine	3.52; 3.80; 3.81	6.70; 6.62

This shows the almost identical position of the functional groups in their aromatic rings. However, the signal of one of the aromatic protons (6.69 ppm) in the NMR spectra of merenderine appears in a weaker field than in the case of floramultine (6.54 ppm) which can be explained by the influence of a hydroxy group located on a neighboring carbon atom. Consequently, we have assumed that both hydroxy groups in merenderine, in

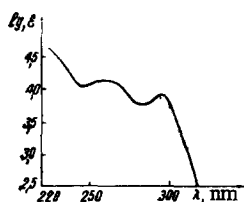


Fig. 1. UV spectrum of merenderine (methanol).

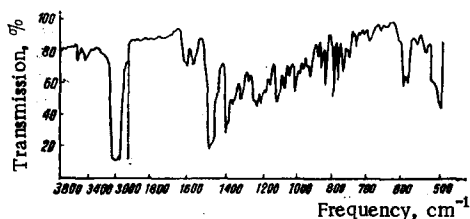


Fig. 2. IR spectrum of merenderine (paraffin oil).

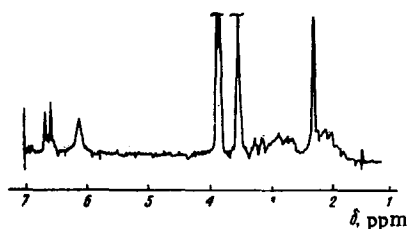


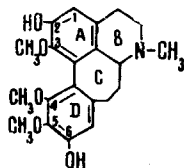
Fig. 3. NMR spectrum of merenderine ($CDCl_3$).

V. I. Lenin Tashkent State University. Translated from *Khimiya Prirodnykh Soedinenii*, No. 6, pp. 777-779, November-December, 1972. Original article submitted April 29, 1972.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

contrast to the situation in floramultine, are located in α positions to aromatic protons. To confirm this we studied the double resonance of merenderine, and were unable to observe a nuclear Overhauser effect, which shows the absence of an interaction of aromatic protons with O-methyl groups.

On the basis of the information given, we propose for merenderine the structure of 2,6-dihydroxy-3,4,5-trimethoxyhomoaporphine:



EXPERIMENTAL

Merenderine. The mixture of phenolic bases (1.3 g) was chromatographed on 25 g of alumina (activity grade II). Elution with chloroform yielded 0.56 g of merenderine with mp 229–230°C. $[\alpha]_D^{20} + 105^\circ$ (c 0.57; chloroform).

Merenderine is readily soluble in chloroform, sparingly soluble in methanol, acetone, and water, and insoluble in ether and petroleum ether. It forms a colorless solution in concentrated sulfuric acid. Ethanolic solutions are colored faintly green by ferric chloride.

The hydrochloride was obtained by adding to an acetone suspension of merenderine an acetone solution of hydrogen chloride; mp 220°C (decomp.).

The methiodide was isolated by adding to a methanolic solution of merenderine an excess of methyl iodide and heating the mixture for 10–15 min; mp 150°C (with charring).

Methylation. A solution of diazomethane in petroleum ether was added to a methanolic solution of 50 mg of merenderine. The mixture of solvents was evaporated off, and the dry residue was purified by chromatography on alumina. This gave the dimethyl ether of merenderine; M^+ 399 (mass spectrometrically). The substance contained five methoxy groups (3.80 and 3.70–3.60 ppm in pyridine).

Acetylation. Merenderine (60 mg) was acetylated with acetic anhydride in the presence of anhydrous sodium acetate. A product with M^+ 455 (mass spectrometrically) and with two O-acetyl groups (2.40 and 2.26 ppm) was isolated.

SUMMARY

On the basis of the UV, IR, mass, and NMR spectra and double resonance, the structure of 2,6-dihydroxy-3,4,5-trimethoxyhomoaporphine has been proposed for merenderine.

LITERATURE CITED

1. A. A. Trozyan, M. K. Yusupov, and A. S. Sadykov, *Khim. Prirodn. Soedin.*, 541 (1971).
2. J. Holubek, *Spectral Data and Physical Constants of Alkaloids*, Vol. VI, Heyden, London (1970).
3. A. R. Battersby, R. B. Bradbury, R. B. Herbert, M. H. G. Munro, and R. Ramage, *Chem. Commun.*, 450 (1967).
4. A. R. Battersby, R. Ramage, A. F. Cameron, C. Hannaway, and F. Santavy, *Helv. Chim. Acta*, **54**, 1084 (1971).
5. J. L. Kaul, B. K. Moza, F. Santavy, and P. Vrublovsky, *Collection Czech. Chem. Commun.*, **29**, 1689 (1964).