

NONPHENOLIC ALKALOIDS OF *TELITOXICUM GLAZIOVII*

MARY D. MENACHERY* and DENISE L. EDGREN

Penn State Altoona Campus, Ivyside Park, Altoona, Pennsylvania 16601-3760

Telitoxicum (Menispermaceae) is a genus of woody vines found in the Amazon basin (1,2). Chemical investigation of the species *Telitoxicum peruvianum* has revealed the presence of oxoaporphines and azaffluoranthenes, as well as telazoline [1] (3), the first representative of a new structural type of alkaloid. In continuation of our work on *Telitoxicum* species, we now report the isolation and structural determination of the new alkaloid, teladiazoline [2], from the nonphenolic alkaloids of *Telitoxicum glaziovii* Moldenke. The known bases *O*-methylmoschatoline [3] (4), lysicamine [4] (4), and telazoline [1] (3) were also isolated from *T. glaziovii* and identified from spectral data.

Teladiazoline [2], $C_{18}H_{14}N_2O_3$, crystallizes from MeOH/CHCl₃ as reddish orange needles, mp 197–199 (dec). The uv spectrum exhibits maxima at 254, 294, 378, and 502 nm. The ¹H nmr (200 MHz, CDCl₃) of teladiazoline shows two 3-H singlets at δ 4.11 and 4.15, corresponding to two methoxyl groups. The rest of the spectrum consists of six aromatic protons. Of these, the pair of doublets at δ 8.11 and 8.88

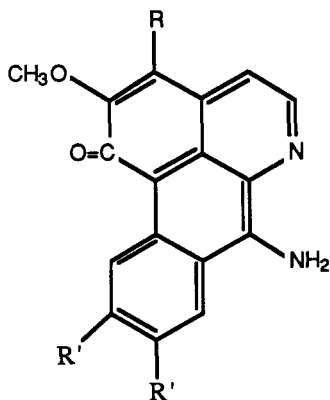
($J = 5$ Hz) are assigned to the B-ring protons of this compound from decoupling studies. The singlet aromatic proton signal of telazoline is missing in the nmr of teladiazoline, and the 8.11 doublet of 2 is deshielded by the adjacent methoxyl relative to the corresponding proton (7.66) of telazoline.

The rest of the spectrum consists of a pair of multiplets at δ 7.74 and 7.48 and a pair of doublets at δ 8.62 and 8.52 (1H each, $J = 8$ Hz). From decoupling experiments and comparison with the ¹H nmr of telazoline, we conclude that these signals correspond to the ring protons of the D ring of an aporphine alkaloid. The tentative structure 2 is suggested for teladiazoline, which becomes the third oxidized aporphine isolated, the second being pancorinine [5] (5).

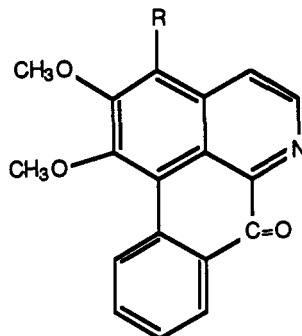
EXPERIMENTAL

PLANT MATERIAL.—The plant material was collected from the state of Para, Brazil by N. T. Silva. A voucher specimen identified by Dr. B. A. Krukoff was placed in the New York Botanical Garden herbarium.

Woody stems were air-dried and powdered. Ground plant material (2.1 kg) was moistened with NH₄OH-H₂O (1:1) and extracted exhaus-



- 1 R=H, R'=H
2 R=OMe, R'=H
5 R=H, R'=OMe



- 3 R=OMe
4 R=H

tively with EtOAc-EtOH (9:1). The extract was concentrated and then partitioned between CH_2Cl_2 and 1% H_3PO_4 , followed by 2% H_2SO_4 , to obtain the CH_2Cl_2 -soluble neutral fraction (16.1 g). Acidic extracts were made alkaline with NH_4OH and extracted with CH_2Cl_2 . Both acid extracts gave identical tlc's and were mixed to give the total base fraction. The total base fraction was partitioned between CH_2Cl_2 and 5% NaOH three times to give the nonphenolic bases (0.84 g) and the phenolic bases (0.39 g).

The nonphenolic base fraction was chromatographed over a column of Si gel (50 g) by elution with CH_2Cl_2 ; the polarity of the solvent was gradually increased by the addition of increasing amounts of MeOH. *O*-Methylmoschatoline [3] (2 mg) and lysicamine [4] (18 mg) were obtained from the column with CH_2Cl_2 -MeOH (99:1). Spectral data were in agreement with those reported for these compounds.

Crude teladiazoline [2] eluted from the column with CH_2Cl_2 -MeOH (98.5:1.5). Further purification by cc over Si gel using CHCl_3 /MeOH in increasing polarity gave teladiazoline as the second compound eluted from the column. Recrystallization from CHCl_3 /MeOH gave reddish orange needles (4 mg): mp 197–199° (dec); uv λ max (EtOH) 254 (log ϵ 4.42), 294 (4.40), 325 sh (3.69), 378 (3.01), 502 nm (3.91); ^1H nmr (200 MHz, CDCl_3) δ 8.88 (1H, d, $J = 5$ Hz), 8.62 and 8.52 (1H each, d, $J = 8$ Hz), 8.11 (1H, d, $J = 5$ Hz), 7.74 and 7.48 (1H each, m), 4.15 and

4.11 (3H each, s); hrms m/z calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_3$, 306.0999, found 306.0996.

Telazoline [1] was obtained from the column after the elution of teladiazoline with the same solvent system. Recrystallization from MeOH/ CHCl_3 gave reddish-brown cubic crystals (6 mg). ^1H -nmr, uv, and ir spectra were identical with those of an authentic sample of telazoline.

ACKNOWLEDGMENTS

We are grateful to Dr. Michael P. Cava, University of Alabama, for the plant material and helpful discussions. We also thank Dr. M.V. Lakshmikantham, University of Alabama, for sending the spectra of authentic telazoline. A Biomedical Research Support Grant from the Pennsylvania State University supported the research.

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Received 13 May 1988