The Isolation and Structure of Karachicine – a New Alkaloid from *Buxus papilosa*

Atta-ur-Rahman* and Mehrun Nisa

H. E. J. Research Institute of Chemistry
University of Karachi, Karachi-32/Pakistan

Z. Naturforsch. **39b,** 839 (1984);
received April 28, 1983

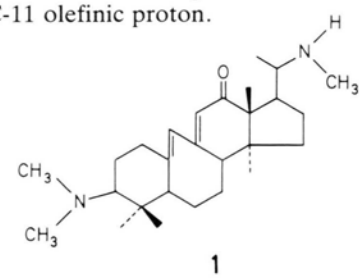
Steroidal Alkaloid, *Buxus papilosa,*
Structure Elucidation, Febrifuge Rheumatism

A new alkaloid, karachicine, has been isolated from the leaves of *Buxus papilosa* to which structure **1** has been assigned.

Buxus papilosa, C. K. Schn, Linn. (Buxaceae) grows abundantly in the northern regions of Pakistan. It has found use in the indigenous system of medicine as a febrifuge, for relief or rheumatism and for the treatment of a number of other ailments. In previous publications we have reported the isolation and structure of four new alkaloids, papilamine, moenjodaramine, harappamine and papilicine [1–4], from the alcoholic extracts of the air-dried leaves of the plant. We now report the structure of another new alkaloid "karachicine" **1** from the leaves of the same plant.

The alcoholic extracts of the leaves of *Buxus papilosa* were evaporated to a gum. The gummy mass was partitioned between 10% HCl and chloroform. The acid-soluble material was separated, basified with ammonia to pH 11 and extracted with chloroform. Evaporation of the organic extracts afforded the crude alkaloids. Karachicine was isolated as a colourless amorphous material by chromatography of the crude mixture of the alkaloids on a neutral alumina column, and was further purified by preparative t.l.c. on alumina plates.

The IR spectrum of the substance showed a band at 1680 cm^{-1}, indicating the presence of a six-membered α,β-unsaturated ketone. Other bands were present at 3400 cm^{-1} (NH) and 2840 (C–H). The UV spectrum showed maxima at 210, 241, 248 and 257 nm with weak absorptions at 283 and 291 nm indicating the presence of a conjugated 9(10→19) *abeo*-diene system [5]. The proton NMR spectrum ($CDCl_3$) showed four singlets corresponding to the four tertiary methyl groups at δ 0.58, δ 0.68, δ 1.13 and δ 1.21. The secondary methyl protons resonated as a doublet at δ 0.75 (J=6.6 Hz). Two singlets at δ 2.03 and δ 2.09 (3 H each) were assigned to the $-N(CH_3)_2$ groups at C-3, while another singlet at δ 2.41 was assigned to the N-methyl group at C-20. A singlet at δ 5.16 was assigned to the olefinic proton at C-19 while another singlet at δ 5.93 was ascribed to the C-11 olefinic proton.



1

The mass spectrum of karachicine showed the molecular ion peak at m/z 412.3446 corresponding to the formula $C_{27}H_{44}N_2O$ (calcd 412.3453). The substance showed base peak at m/e 58.0064 corresponding to the composition $C_3H_8N^+$, which is attributed to the ion $CH_3CH{=}N^+(H){-}CH_3$, commonly encountered in alkaloids bearing a $-CH(CH_3){-}NHCH_3$ grouping on ring D [6]. A peak at m/z 85.0911 was in accordance with the composition $C_5H_{11}N$ (calcd 85.0891) corresponding to the fragment $\dot{C}H_2{-}CH_2{-}CH{=}N^+(CH_3)_2$ formed by the cleavage of ring A [6]. A peak at m/z 71.0856 ($C_4H_9N^+$) was attributed to the fragment $\dot{C}H_2{-}CH{=}N^+(CH_3)_2$ formed by the cleavage of ring A.

The only two positions of the carbonyl group which would explain its absorption at 1680 cm^{-1} are C-1 and C-12. It was apparent from the mass spectral fragmentation that the carbonyl group was not located in ring A. Hence its positioning at C-12 appears reasonable and is consistent with the downfield shift of the C-11 proton (δ 5.93) as compared to the corresponding proton found in papilicine [4] (δ 5.49), moenjodaramine [2] (δ 5.55), harappamine [3] (δ 5.56) or buxenine C [7] (δ 5.52).

In the light of above spectroscopic studies structure **1** is proposed for karachicine.

[1] Atta-ur-Rahman, S. Farhi, G. A. Miana, Mehrun Nisa, and W. Voelter, submitted for publication.
[2] Atta-ur-Rahman, Mehrun Nisa, and S. Farhi, Planta Medica **49,** 126 (1983).
[3] Atta-ur-Rahman and Mehrun Nisa, Heterocycles **20**(1), 69 (1983).
[4] Atta-ur-Rahman, Mehrun Nisa, and Talat Zamir, Z. Naturforsch. **39b,** 127 (1984).
[5] F. Khuong-Huu, D. Herlem-Gaulier, Q. Khuong-Huu, E. Stanislas, and R. Goutarel, Tetrahedron **22,** 3321 (1966).
[6] Biochemical Applications of Mass Spectrometry edited by G. R. Waller and O. C. Dermer, p. 783, John Wiley and Sons, New York 1980.
[7] M. Shamma, V. St. Georgiev, G. A. Miana, and F. Sultana Khan, Phytochemistry **12,** 2051 (1973).

* Reprint requests to Prof. Dr. Atta-ur-Rahman.
0340–5087/84/0600–0839/$ 01.00/0