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

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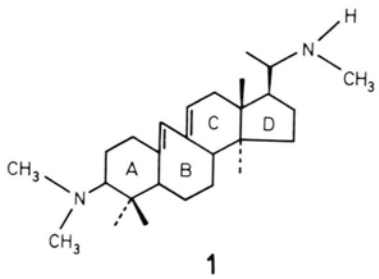
A new alkaloid, "papilicine", has been isolated from the leaves of *Buxus papilosa* to which structure (1) has been assigned on the basis of spectroscopic studies.

Buxus species have been used in the indigenous system of medicine as febrifuge, for relief of rheumatism and for the treatment of a number of other ailments. *Buxus papilosa* C. K. Schn., Linn. (Buxaceae) is a shrub which grows abundantly in the northern regions of Pakistan. We have previously reported the isolation of three new alkaloids "papilamine", "moenjodaramine" and "harappamine" from the leaves of this plant [1–3]. We now report the isolation of a new alkaloid "papilicine" from the leaves of the plant for which structure **1** is proposed on the basis of spectroscopic evidence.



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Papilicine was isolated by column chromatography on silica gel, the "papilicine" – containing fraction being eluted with 40% $CHCl_3$ – 60% MeOH. It was further purified by preparative t.l.c. whereby the pure alkaloid was obtained as a colourless gum, $[\alpha]_D(CHCl_3)$ + 47.6°.

The IR spectrum of the substance showed bands at 1080 cm^{-1} (C–N), 1600 cm^{-1} (C=C), 2840 cm^{-1} (N–H) and 2940 cm^{-1} (C–H). The UV spectrum showed maxima at 241 and 248 nm and shoulders at 210 and 257 nm characteristic of the presence of a 9(10→19) *abeo-diene* system [4]. The proton NMR spectrum ($CDCl_3$) showed four singlets, corresponding to the four tertiary methyl groups at δ 0.69, δ 0.71, δ 0.75 and δ 1.01. The secondary (C-21) methyl group resonated as a doublet at δ 0.97 (J = 7 Hz). A three proton singlet resonating at δ 2.46 was assigned to the $-NCH_3$ group attached to C-20, while another peak resonating at δ 2.28 and integrating for 6 protons was assigned to the $-N(CH_3)_2$ group at C-3. The isolated olefinic proton at C-19 resonated at δ 5.91 as a singlet while a multiplet centred at δ 5.49 was assigned to the C-11 olefinic proton.

The mass spectrum of the compound afforded the molecular ion at m/z 398.3665 which corresponded to the formula $C_{27}H_{46}N_2$ (calcd 398.3660). The substance showed a base peak at m/z 58.0658 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 [5], or to the ion $CH_2{=}N^+(CH_3)_2$ found in alkaloids bearing a $N{-}(CH_3)_2$ grouping on ring A [5]. A peak at m/z 85.0887 corresponded to the fragment $CH_2{-}CH_2{-}CH{=}N^+(CH_3)_2$ formed by the cleavage of ring A along with the side chain. A peak at m/z 71.0734 ($C_4H_9N^+$) was consistent with the fragment $CH_2{-}CH{=}N^+(CH_3)_2$ formed by the cleavage of ring A.

In the C-13 NMR spectrum of the compound the olefinic carbon atoms could be clearly distinguished at δ 128.42, δ 128.62, δ 136.30 and δ 138.45 which were assigned to C-11, C-19, C-10 and C-9 respec-

Table I. Assignments to carbon atoms.

Carbon	Chemical shift [ppm]	Carbon	Chemical shift [ppm]
1.	37.18	14.	48.47
2.	22.02	15.	30.16
3.	71.48	16.	25.62
4.	38.31	17.	51.06
5.	44.82	18.	16.99
6.	23.08	19.	128.62
7.	26.66	20.	58.43
8.	49.42	21.	15.05
9.	138.45	28.	17.92
10.	136.30	29.	24.88
11.	128.42	30.	15.87
12.	33.13	$Na{-}CH_3$	44.47
13.	43.24	$N_b{-}CH_3$	39.90

Gated spin echo measurements carried out on Bruker WP-100 SY NMR spectrometer with the following settings: Pulse 1 = 5.4 sec., Pulse 2 = 10.8 sec., D_1 = 2.5 sec., D_2 = 0.008 sec., O_1 = 30 Hz, O_2 = 1750 Hz, SW = 6000 Hz.

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tively. The two tertiary carbon atoms bearing the N-substituents, C-3 and C-20, were found to resonate at δ 71.48 and δ 58.43 respectively. The assignments to various carbon atoms are shown in Table I. The assignments were supported by gated spin echo measurements.

In the light of above studies structure **1** is proposed for "papilicine".

[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 Med. (in press).
[3] Atta-ur-Rahman and Mehrun Nisa, Heterocycles **20** (1), 69 (1983).
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[5] "Biochemical Applications of Mass spectrometry" edited by G. R. Waller and O. C. Dermer, John Wiley and Sons, New York 783 (1980).