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

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Z. Naturforsch. **40b,** 565–566 (1985); received June 28, 1984

Buxus papilosa, Steroidal Alkaloids, Structure Elucidation, NMR Spectra, Mass Spectra

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

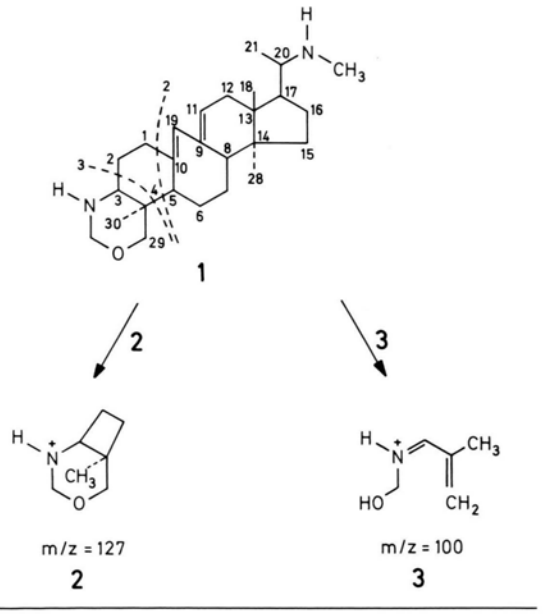
Buxus papilosa C. K. Schn, Linn. (Buxaceae) is very abundant in the northern regions of Pakistan. *Buxus* species have been used in the indigenous system of medicine as a febrifuge, for relief of rheumatism and for the treatment of a number of other ailments. We have previously reported the isolation of six new alkaloids from the leaves of this plant [1–6]. We now report the isolation of another new alkaloid "papilinine" from the leaves of the same plant.

Papilinine was isolated by column chromatography on a neutral alumina column, the papilinine containing fraction being eluted with 30% $CHCl_3$ –70% MeOH. It was further purified by preparative t.l.c. The pure alkaloid was obtained as a colourless gum, $[\alpha]_D$ ($CHCl_3$): +29.4°.

The IR spectrum of the substance showed bands at 1380 (C–N), 1600 (C=C), 2840 (C–H) and 2940 cm^{-1}. The UV spectrum showed maxima at 238 nm (ε 18763) and 245 nm (ε 19900) and shoulders at 203 and 253 nm (ε 8571 and ε 13077 respectively). The UV was characteristic of the presence of an 9(10→19) *abeo*-diene system [7]. The proton NMR spectrum ($CDCl_3$) showed three singlets, corresponding to the three tertiary methyl groups at δ 0.70, δ 0.74 and δ 1.02. The secondary (C-21) methyl group resonated as a doublet at δ 0.72 (J = 5 Hz). A three-proton singlet resonating at δ 2.10 was assigned to the N–CH_3 group attached to C-20. A set of AB doublets resonating at δ 3.23 and δ 3.79 were assigned to the C-29 methylene protons (J = 9 Hz), while another set of AB doublets centered at δ 3.56 and δ 4.42 (J = 7 Hz) were ascribed to the methylene protons α-to the C-3 nitrogen. A singlet at δ 5.97 was assigned to the olefinic proton at C-19 while a multiplet at δ 5.51 was ascribed to the C-11 olefinic proton**.

The mass spectrum of papilinine showed the molecular ion peak at m/z = 398.3307 corresponding to the formula $C_{26}H_{42}N_2O$ (calcd 398.3296). The substance showed a base peak at m/z 58.0659 corresponding to the composition $C_3H_8N^+$ (calcd 58.0660), which may be formed by the cleavage of $CH_3CH=N^+(H)-CH_3$ fragment from ring D [8]. A peak at m/z 71.0738 was in accordance with the composition $C_4H_9N^+$ (calcd 71.0734) and was attributed to the fragment $CH_2-CH_2-CH=N^+(H)CH_3$ or $CH_2(CH_3)C=N^+(H)CH_3$ formed by the cleavage of ring A, or ring D. The peak at 127.0999 was consistent with the fragment **2** formed by cleavage of ring A, and the peak at m/z 100.0766 was in accordance with the composition $C_5H_{10}NO$ (calcd 100.0762) and was attributed to the fragment **3.** In the light of above spectroscopic studies structure **1** is proposed for papilinine.

Papilinine may be a biosynthetic precursor of "harappamine" reported by us recently [3]. It is a third member of a new group of alkaloids, first reported by us [2], bearing both a tetrahydro-oxazine ring and a 9(10→19) *abeo*-diene system.



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0340–5087/85/0400–0565/$ 01.00/0

** After high resolution studies the assignments of the chemical shifts of the tertiary methyl groups of harappamine have been revised as δ 0.68, δ 0.76 and δ 1.03 while the C-21 methyl group resonates ad δ 0.72 (J = 7.7 Hz).

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