THE ISOLATION AND STRUCTURE OF "HARAPPAMINE"—A NEW ALKALOID FROM 
BUXUS PAPILOSA

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ABSTRACT—A new alkaloid "harappamine" has been isolated from the 
leaves of Buxus papillosa which has been assigned structure (1).

Buxus papillosa (Buxaceae) is a plant which grows abundantly in the northern 
regions of Pakistan. A number of alkaloids have previously been reported 
from this plant. In the previous communication we have reported the isola-
tion of "moenjodaramine" (2) from the leaves of this plant which was found 
to have a novel pentacyclic skeleton bearing both a tetrahydrooxazine ring 
and a 9(10-19) abeo-diene system. "Harappamine" was isolated by chromatography of the crude mixture of alka-
loids on a neutral alumina column. A number of alkaloidal fractions were 

tained, the "harappamine" containing fraction being eluted with 50% pet-
ether/60% CHCl₃.

The infra-red spectrum of the substance showed bands at 3400 cm⁻¹ (N-H), 
2840 cm⁻¹ (C-H) and 1650 cm⁻¹ (C=C). The U.V. spectrum showed maxima at 
238 and 246 nm and shoulders at 205 and 253 nm, characteristic of the pre-
sence of a 9(10-19) abeo-diene system. The proton NMR spectrum (CDCl₃) 
showed three singlets, corresponding to the three tertiary methyl groups 
at δ 1.03, δ 1.06 and δ 1.12. The secondary (C-21) methyl group resonated 
as a doublet at δ 0.72 (J=7.7 Hz). Two singlets at δ 2.10 and δ 2.41 were 
assigned to the two N(CH₃) groups at C-20 and C-3 respectively. A set of 
AB doublets resonating at δ 3.24 and δ 3.82 were assigned to the C-29

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methylene protons \((J_{AB} = 10.6 \text{ Hz})\), while another set of AB doublets centred at \(\delta 3.57\) and \(\delta 4.42\) \((J_{AB} = 7.4 \text{ Hz})\) were attributed to the methylene protons \(\alpha\)-to the C-3 nitrogen. The isolated olefinic proton at C-19 resonated as a singlet at \(\delta 5.98\), while a multiplet centred at \(\delta 5.56\) was ascribed to the C-11 olefinic proton. A comparison of the NMR spectrum of "harappamine" with that of "moenjodaramine" which has also been reported as a synthetic derivative by the French group,\(^8\) showed the NMR spectra of the two substance were virtually identical, with "harappamine" containing one less \(N\)-methyl group than (2).

The mass spectrum of "harappamine" showed a molecular ion peak at \(m/z 412.3454\) corresponding to the formula \(C_{27}H_{44}N_2O\) \(\text{(calcd. 412.3453)}\). The substance showed a base peak at \(m/z 58.0660\) corresponding to the composition \(C_3H_8N^+\). This may be attributed to the ion \(\text{CH}_3\text{CH} = N(H)\text{-CH}_3\) commonly encountered in alkaloids bearing a \(\text{-CH(CH}_3\text{-NHCH}_3\text{)}\) grouping on ring \(D\), or to the ion \(\text{CH}_2_2 = N(\text{CH}_3)_2\) found in alkaloids bearing a \(\text{-N(CH}_3\text{)}_2\) grouping on ring \(A\).\(^7\) Another peak at \(m/z 57.0625\) corresponded to the fragment \(\text{CH}_2_2 = N(\text{CH}_3)_2\). A peak at \(m/z 85.0887\) was in accordance with the composition \(C_5H_11N\) \(\text{(calcd. 85.0891)}\) corresponding to the fragment \(\text{CH}_2_2 = N(\text{CH}_3)_2\) 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 \(\text{CH}_2_2 = N(\text{CH}_3)_2\) formed by cleavage of ring \(A\) accompanied by an intramolecular proton transfer.

In the light of above studies structure (1) is proposed for "harappamine".

REFERENCES


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