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CARBAZOLE AND 3-METHYLCARBAZOLE FROM *GLYCOSMIS PENTAPHYLLA*

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Key Word Index—*Glycosmis pentaphylla*; Rutaceae; root bark; alkaloids; carbazole; 3-methylcarbazole.

Abstract—Carbazole and 3-methylcarbazole have been isolated from the root bark of *Glycosmis pentaphylla*. This is the first report of the isolation of the former from a plant source.

INTRODUCTION

Glycosmis pentaphylla, an Indian medicinal plant, has been reported to elaborate carbazole alkaloids [1–4]. In the course of our investigations on the identification of carbazole alkaloids in plant extracts by GC and HPLC, the presence of carbazole (1) and 3-methylcarbazole (2) was detected in the petrol extract of the root bark of *G. pentaphylla*. This prompted further chemical investigation of the plant; we now report the isolation of 1 and 2 from the root bark.

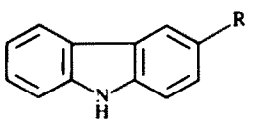
RESULTS AND DISCUSSION

The neutral fraction of the petrol extract of the root bark of *G. pentaphylla* was chromatographed over silica gel. A fraction from the petrol–benzene (1:1) eluate showed the presence of two compounds (A and B) which were separated by prep. TLC. Compound A, $C_{12}H_9N$ ($[M]^+$ *m/z* 167), mp 245° gave a UV spectrum which indicated the presence of a carbazole skeleton [5]. The IR and ^1H NMR spectral data suggested that A is carbazole (1). Compound B, $C_{13}H_{11}N$ ($[M]^+$ *m/z* 181), mp 207° was identified as 3-methylcarbazole (2) from its UV [5], IR [6] and ^1H NMR spectral data.

The identities of compounds A and B with carbazole and 3-methylcarbazole, respectively, were confirmed by comparisons with authentic samples (mmp, TLC, UV and IR).

This is the first report of the isolation of carbazole from a plant source. 3-Methylcarbazole, however, has been reported earlier from the genus *Clausena* [7, 8]. All the phytocarbazoles previously reported have a 3-methyl group or the oxidative functional variants of the 3-methyl group, namely CH_2OH, CHO, COOH and COOMe. Therefore, the isolation of carbazole from a plant source is significant from biogenetic considerations.

It was suggested earlier [9] that the aromatic C-methyl group of the carbazoles of Rutaceae could be oxidized *in vivo* to formyl and carboxylic acid groups. Carbazole may simply represent another phase in the oxidative pathway of the 3-methylcarbazoles, that is where oxidation has given the carboxylic acid which has then undergone decarboxylation.



1 R = H
2 R = Me

EXPERIMENTAL

Isolation of alkaloids. Air-dried finely powdered root bark (2 kg) of *G. pentaphylla* was extracted with petrol in a Soxhlet for 48 hr. The solvent was then distilled and the residue taken up in Et_2O. The Et_2O extract was separated into acidic, basic and neutral fractions. The neutral fraction after removal of Et_2O was taken up in C_6H_6 and chromatographed over silica gel (600 g). The column was eluted with petrol, petrol–C_6H_6 (1:1), C_6H_6, C_6H_6–$CHCl_3$ (1:1) and $CHCl_3$ in succession. From the petrol–C_6H_6 (1:1) eluate a colourless solid was obtained which showed the presence of two compounds (A and B) by TLC on silica gel (petrol–HOAc, 10:1; R_f 0.53 and 0.63, respectively). The two compounds were separated by repeated prep. TLC (silica gel GF_{254}) and purified further by sublimation under vacuum to furnish carbazole 1 (8 mg), mp 245°, and 3-methylcarbazole 2 (30 mg), mp 207°, respectively.

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INDOLE ALKALOIDS FROM *ALSTONIA SCHOLARIS*

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Key Word Index—*Alstania scholaris*; Apocynaceae; leaves; indole alkaloids; rhazimanine; alstonamine.

Abstract—A new indole alkaloid, alstonamine and a sitsirikine type indole alkaloid, rhazimanine, have been isolated from the leaves of *Alstonia scholaris*.

INTRODUCTION

As a part of our continuing programme on the isolation and structural studies on chemical constituents of medicinal plants, we wish to report here the isolation and structure of a new alkaloid alstonamine (**1**) from the leaves of *Alstonia scholaris* along with the known alkaloid rhazimanine (**2**) [1], which has not been previously reported from this plant.

RESULTS AND DISCUSSION

The crude alkaloidal mixture obtained from the alcoholic extract of the leaves of *A. scholaris* was selectively extracted with chloroform at different pH values. The fraction obtained at pH 9 was subjected to CC followed by prep. TLC. This resulted in the isolation of two alkaloids: a slower moving new alkaloid named alstonamine (**1**), and the faster moving rhazimanine (**2**) [1] which has not been previously reported from this plant.

Alkaloid (**1**) was obtained as a colourless amorphous solid $[\alpha]_D^{20} + 46$ ($CHCl_3$, *c* 2). The UV spectrum was characteristic of the indole chromophore showing maxima at 222, 283, 290 and minima at 249, 287 nm. The IR spectrum showed absorptions at 3300 cm^{-1} (NH) and 1725 cm^{-1} (ester C=O). The EI-mass spectrum showed the $[M]^+$ at *m/z* 338 which was confirmed by FD-mass spectrometry. The empirical formula was established by high resolution mass spectrometry as $C_{20}H_{22}N_2O_3$ (measured 338.1632, calc. 338.1630). Other significant peaks were observed at *m/z* 307, 251, 206, 157, 170 and 122. From the ^{1}H NMR and mass spectral data it was apparent that alstonamine (**1**) was closely related to vallesamine [2]. The $[M]^+$ of (**1**), however, was 2 mu less than that of vallesamine [2] suggesting the presence of an extra degree of unsaturation.

The ^{1}H NMR spectrum (300 MHz) of alstonamine (**1**) was very similar to that reported for vallesamine [3]. The main difference was the absence of the signals for the methyl protons and the presence of two broadened doublets centred at δ4.21 (18βH, $J_{18\beta,18\alpha}$ = 14.25 Hz, $J_{18\beta,19}$ = 3.4 Hz) and δ4.50 (18αH, $J_{18\alpha,18\beta}$ = 14.2, $J_{18\alpha,19}$ = 5.42 Hz) which were assigned to the 18β and 18α protons, respectively. The C-6α and C-6β protons were found to resonate as sets of AB doublets at δ4.87 and δ4.02, respectively, ($J_{6\alpha,6\beta}$ = 16.29 Hz). Another set of AB doublets occurred at δ4.38 and δ3.85 which were assigned to the H-17α and H-17β protons, respectively ($J_{17\alpha,17\beta}$ = 12.45 Hz). The ester methyl resonated as a 3 H singlet at δ3.88 while the olefinic protons resonated as a multiplet at δ5.53. The close correspondence of these ^{1}H NMR signals with those of vallesamine, the absence of the 18-methyl protons and the presence of an additional double doublet (broadened by homoallylic coupling) for the C-18 methylene protons indicated that the C-18 carbon had undergone cyclization with the C-17 hydroxyl group to generate a new 7-membered ring in alstonamine.

In order to confirm the assignments in the ^{1}H NMR spectrum a comprehensive series of homodecoupling experiments was carried out. Irradiation of the doublet for the H-18β proton at δ4.21 led to a collapse of the H-18α proton to a simple doublet ($J_{18\alpha,19}$ = 3.42 Hz) with the disappearence of the larger geminal coupling of 14.25 Hz. It also led to a simplification of the multiplet at δ3.45 for the C-21α/C-21β protons and of the multiplet at δ3.69 of the H-15 proton. Irradiation at the chemical shift for the 17α proton (δ4.38) resulted in the collapse of the doublet at δ3.85 due to the H-17β proton into a singlet. The chemical shifts, coupling constants and proton–proton connectivities were confirmed by recording a 2D-COSY 45 spectrum [4] (Fig. 1) and 2D-*J* resolved spectrum [5].

Both alstonamine (**1**) and vallesamine displayed similar chemical shifts for the aromatic carbons in the ^{13}C NMR spectrum (Table 2). The methylene carbons C-17 and C-18 adjacent to the ethereal oxygen appeared at δ70.99 and δ77.15, respectively. The carbons C-6, C-3 and C-21 α to N_b showed resonances at δ49.40, 43.32 and 55.43, respectively. The ester methyl occurred at δ52.45, while the