7.17 (1H, *d*, $J = 8$ Hz, H-6′), 8.20 (1H, *s*, H-2), 8.30 (1H, *d*, $J = 8$ Hz, H-5); ^{13}C NMR [25.2 MHz, $(CD_3)_2SO$]*: 60.5 (OMe), 102.6 (C-8), 107.7 (C-5′), 111.8 (C-1′), 115.7 (C-6), 116.8 (C-4a), 122.2 (C-3), 126.1 (C-6′), 127.6 (C-5), 136.3 (C-3′), 149.5† (C-2′), 151.1† (C-4′), 154.8 (C-2), 157.9 (C-8a), 162.9 (C-7), 176.0 (C=O); EIMS (probe) 70 eV, m/z (rel. int.): 300 $[M]^+$ (100), 285 (30), 282 (50), 254 (20), 164 (10), 137 (30).

7,2′,4′-Triacetoxy-3′-methoxyisoflavone. Mp 151–153° from petrol–$CHCl_3$; ^{1}H NMR [60 MHz, $(CD_3)_2$ CO]: $\delta 2.10$ (3H, *s*, 1 OAc), 2.30 (6H, *s*, 2 OAc), 3.80 (3H, *s*, OMe), 7.10–7.50 (4H, *m*, H-6, H-8, H-5′, H-6′), 8.17 (1H, *s*, H-2), 8.2 (1H, *d*, $J = 8$ Hz, H-5′); EIMS (probe) 70 eV, m/z (rel. int.): 426 $[M]^+$ (5), 384 (90), 342 (100), 300 (30), 282 (80), 164 (5), 137 (15).

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*δ (TMS) = δ $(CD_3)_2SO + 39.5$ ppm.

†Signals may be interchanged.

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STRICTAMINE-*N*-OXIDE FROM *RHAZYA STRICTA*

ATTA-UR-RAHMAN and SAJIDA KHANUM

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

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Key Word Index—*Rhazya stricta*; Apocynaceae; alkaloids; strictamine; NMR.

Abstract—A new alkaloid, strictamine-*N*-oxide has been isolated from the leaves of *Rhazya stricta*.

INTRODUCTION

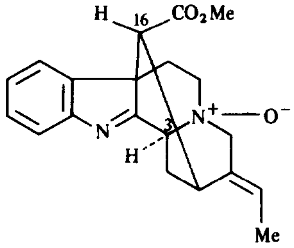
Rhazya stricta is a small glabrous erect shrub which is abundantly distributed in various parts of Pakistan [1–3] and is reported in the indigenous medicinal system as a curative for chronic rheumatism and as a bitter tonic for sore throats and in fever [4, 5]. Extracts of *R. stricta* showed a marked leucopenic effect in rats when given orally and a number of cytotoxic alkaloids have been reported from this plant [6, 7].

RESULTS AND DISCUSSION

Chromatography of the alcoholic extracts of the leaves afforded a substance which gave a UV spectrum typical of the indolenine chromophore. The IR spectrum ($CHCl_3$) showed the presence of an ester carbonyl group. High resolution mass spectrometry afforded the $[M]^+$ at m/z 338.1625 which corresponded closely with the mass calculated for the formula $C_{20}H_{22}N_2O_3$ (338.1630) while the rest of the spectrum was very similar to that reported for strictamine [8, 9].

The ^{1}H NMR spectrum ($CDCl_3$) showed a three-proton double doublet at $\delta 1.625$ ($J_1 = 7$ Hz, $J_2 = 2.5$ Hz) assigned to the methyl of an ethylidene group. A one proton quartet at $\delta 5.75$ ($J = 7$ Hz) was assigned to the olefinic proton of the ethylidene group. The ester methyl group resonated as a three-proton singlet at $\delta 3.73$. A characteristic one-proton doublet for the C-3 proton appeared at the rather downfield position of $\delta 5.61$ ($J = 6.25$ Hz) on account of the deshielding influence of the vicinal quaternary nitrogen. Another doublet at $\delta 2.15$ ($J = 3.25$ Hz) was assigned to the C-16 proton, the upfield shift being on account of the shielding influence of the indolenine nucleus on which it overlies [6, 8].

The aromatic protons resonated as complex multiplets in the region between $\delta 7.21$–8.77. Because of the strong similarities of the ^{1}H NMR and the mass spectrum with those of strictamine, as well as the polar nature of the compound it was suspected that the substance isolated was strictamine-*N*-oxide. For confirmation of this the material was subjected to deoxygenation in dichloromethane with phosphorus trichloride. After 25 min at 30° complete conversion to a faster moving material on TLC



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was observed. Usual work up afforded a white crystalline material which was identified as strictamine by comparison of its physical and spectral data (co-chromatography, mp, $[\alpha]_D$, IR, UV, NMR, mass spectrum) with those reported in the literature.

In order to ascertain that strictamine-*N*-oxide is a genuine natural product and not an artifact of isolation, strictamine was separately exposed to identical extraction and separation procedures but no conversion to the corresponding *N*-oxide was discernible. Further confirmation of this was obtained by detection of strictamine-*N*-oxide by TLC in freshly prepared crude extracts.

EXPERIMENTAL

*Isolation of strictamine-*N*-oxide.* The EtOH extract of the fresh leaves of *R. stricta* Decaisne was concd and taken up in 10% HOAc. The non-alkaloidal portion was removed by extraction into EtOAc. The aq. acidic soln was basified with aq. NH_3 and extracted with EtOAc to afford the crude alkaloids (170 g). This alkaloidal material was subjected to preliminary fractionation by flash chromatography over a silica gel column. Elution with petrol, C_6H_6, $CHCl_3$, EtOAc and finally with MeOH afforded a number of fractions. The fraction obtained on elution with petrol–$CHCl_3$ (4:5) was concd and again subjected to flash chromatography over a silica gel column, elution being carried out with $CHCl_3$–MeOH (43:7). This afforded a mixture of four alkaloids which were separated by CC on neutral alumina. A slower moving alkaloid thus obtained in a crude state was further purified on precoated prep. TLC plates (Merck aluminum oxide Type EF-254) in $CHCl_3$–MeOH (19:1). A pure substance was thus obtained as a colourless amorphous material (12 mg), $[\alpha]_D$ $-75°$, which gave an orange colouration with Dragendroff's reagent and a dark pink colour with $CeSO_4$ soln. $[\alpha]_D$ ($CHCl_3$) $-75°$; IR $\nu_{max}^{CHCl_3}$ 1740 cm^{-1}: UV λ_{max}^{MeOH} nm (log ε): 213 (3.15), 262 (2.66); λ_{max}^{MeOH} 238 nm (log ε 2.59); ^1H NMR ($CDCl_3$); δ1.625 (3H, *dd*, $J_1 = 7$ Hz, $J_2 = 2.5$ Hz, C=CH–$\underline{\mathrm{Me}}$), δ5.75 (1H, *q*, $J = 7$ Hz, C=CH–Me), δ3.73 (3H, *s*, OMe), δ5.61 (1H, *d*, $J = 6.25$ Hz, C-3H), δ2.15 (1H, *d*, $J = 3.2$ Hz, C-16H), δ7.21–8.77 (4H, *m*, ArH); HRMS: $[M]^+$ 338.1625 (calc. for $C_{20}H_{22}N_2O_3$, 338.1630); $m/z = 322.1657$ (100%, calc. for $C_{20}H_{22}N_2O_2$, 322.168 $[M-O]^+$, 294, 263, 230 and 122.0971 (calc. for $C_8H_{12}N$, 122.0969).

*Conversion of strictamine-*N*-oxide to strictamine.* Strictamine-*N*-oxide (7 mg) was dissolved in 0.5 ml CH_2Cl_2 and 0.1 ml PCl_3 added. The mixture was stirred for 25 min at 30° and after basification with aq. NH_3 to pH 14, extraction with $CHCl_3$ afforded a white crystalline material which was identified as strictamine by comparison of its physical and spectral data (co-chromatography, mp, $[\alpha]_D$, IR, UV, NMR, MS) with those reported in the lit.

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