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SHORT COMMUNICATION

THE ALKALOIDS OF *RHAZYA ORIENTALIS*

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Abstract—Picralinal (1), picrinine (3), vallesiachotamine (4) as well as a fourth amorphous, but homogeneous indole alkaloid of a dimeric type have been isolated from *Rhazya orientalis*.

The alkaloids of the Asian shrub *Rhazya stricta* have been extensively studied.[1] We have now carried out a preliminary investigation of the alkaloids of *R. orientalis* (Apocynaceae) the only other known member of the *Rhazya* genus.[2] This shrub is indigenous in Thrace, Macedonia and Turkey. We have examined the basic constituents of the roots, stems and leaves of plants grown in Britain. Analysis by thin layer chromatography (TLC) of crude extracts showed those from the leaves and stems to have comparable alkaloidal compositions, whereas that of the root extract was quite different. The leaf and stem extracts were accordingly examined together and the root extract separately.

Leaf and Stem Alkaloids

Two crystalline alkaloids have been obtained from leaf and stem extract by preparative TLC. The first of these proved to be identical with picralinal (1), a base previously fully characterized[3] as a degradation product of picraline (2). This compound has not previously been reported as naturally occurring. The second crystalline base from the leaves and stems was shown to be identical with another degradation product of picraline[3] namely picrinine (3). This base has also been reported to occur in *Alstonia scholaris*[4] and *Rauwolfia vomitoria*.[5]

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[4] A. CHATTERJEE, B. MUKHERJEE and A. B. RAY, *Tetrahedron Letters* 3633 (1965).

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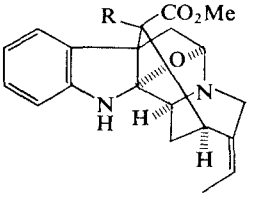
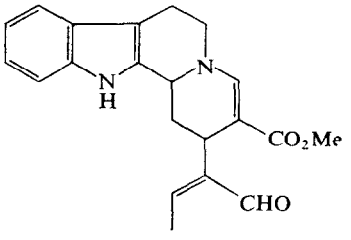


R

1 CHO

2 CH_2OAc

3 H



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Root Alkaloids

Two homogenous bases have been obtained so far from the roots of *Rhazya orientalis* again by preparative TLC. The first of these was crystalline and though only a minute quantity was isolated it was positively identified as vallesiachotamine[6] (4) by comparison with a sample of this alkaloid isolated[7] from the leaves of *R. stricta.* The second root base was amorphous and proved to be a dimeric alkaloid which was shown to be identical (i.r. and mass spectrum) with tetrahydrosecamine, $C_{42}H_{56}N_4O_4$, one of a group of novel dimeric indole alkaloids isolated from *R. stricta.*[8]

EXPERIMENTAL

Extraction. Five plants (each 45 cm high) drawn in the autumn were dried at room temperature. The leaves and stems (35 g) and roots (52 g) were separately extracted with MeOH at room temperature for 24 hr. The evaporated extracts were treated with 3 N HCl, the aqueous solution washed with Et_2O, basified with K_2CO_3 and extracted with Et_2O to give crude basic material.

Leaf and stem basic extracts (190 mg). This material was separated by TLC on Kieselgel developing with benzene/EtOAc/MeOH (2/2/1). The band at R_f 0·4 (30 mg) was eluted and crystallized from EtOH to give picrinine, m.p. 207–210° dec., mixed m.p. with an authentic sample[3] (m.p. 211–219°) 210–220° dec., identical by TLC. The band at R_f 0·5 (36 mg) was eluted and crystallized from MeOH to give picralinal, m.p. 169–170° dec., mixed m.p. with an authentic sample[3] (m.p. 168–169°) 168–170° dec., identical by TLC.

Root basic extract (357 mg). The benzene soluble portion of the crude extract was passed in benzene solution down a column of neutral Al_2O_3 (activity III) and the column washed through with Et_2O. The total eluate was evaporated and the residue subjected to preparative TLC using the same system as above. The

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[7] Z. Z. DABROWSKI, G. F. SMITH and G. N. SMITH, unpublished results.

[8] D. A. EVANS, G. F. SMITH, G. N. SMITH and K. S. J. STAPLEFORD, manuscript in preparation.

band at R_f 0·7 (5 mg) was eluted and crystallized from MeOH/Et_2O to give vallesiachotamine, m.p. 236–240° dec., mass spectrum and u.v. absorption identical with those reported[6] and identical in TLC behaviour with a sample of the alkaloid from *Rhazya stricta*.[7] The band at R_f 0·2 (81 mg) was eluted and purified further by subjection to a second TLC. The easily autoxidized glass thus obtained was shown to be identical with *tetrahydrosecamine* from *R. stricta*,[8] amorphous, ν_{max} (CS_2) 3420m, 1739s, 1728s, 740s cm^{-1}; λ_{max} (EtOH) 225, 285, 293 nm (ϵ 51200, 13700, 12300); τ ($CDCl_3$) 5·75 (1H), 6·22, 6·23, 6·26, 6·35 (6H, 4 singlets, 2 × C$H_3$0-), *ca.* 9·05 (6H, 2 triplets, 2 × CH_3CH_2-); *m/e* 680 (M^+, 19%), 554 (1), 168 (1), 126 (100).

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