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ATALAPHYLLININE, A NEW ACRIDONE BASE FROM *ATALANTIA MONOPHYLLA*

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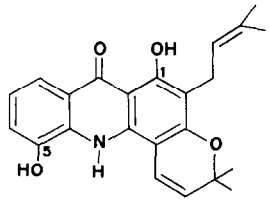
Key Word Index—*Atalantia monophylla*; Rutaceae; acridone alkaloid; atalaphyllinine.

Atalantia monophylla, a shrub distributed in certain parts of India, is reported to be used in chronic rheumatism and paralysis [1]. From the petrol extract of the dried roots, a new alkaloid, *N*-methylbicycloatalaphylline, was isolated [2] besides other known constituents reported earlier [3–5]. TLC investigation of the crude extract indicated the presence of more alkaloids in minute quantities.

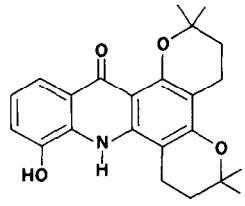
The crude alkaloid mixture left after isolation of pure components from petrol extract, on repeated column chromatography over silica gel, furnished a new base atalaphyllinine, $C_{23}H_{23}NO_4$ (M^+ 377), mp 205–7°. The alkaloid exhibited UV and IR spectra (see Experimental) characteristic of 9-acridones [6]. The NMR spectrum of atalaphyllinine showed signals at 15·44 δ (1H,*S*) and 9·50 δ (1H, *br*) which disappeared on deuteration. The low field signal is clearly due to the chelated hydroxyl at position 1 while the upfield signal is due to the hydroxyl proton at position 5 of the acridone nucleus. A one proton singlet at 10·58 δ (also washed out on deuteration) was attributed to an –NH function. Out of the three aromatic protons two appeared as multiplet between 7·45–7·57 δ and the third proton appeared further down field at 8·24 δ (*d*,*d*).

The alkaloid bears one dimethylallyl side chain, of which the olefinic proton resonated at 5·5 δ (1H, *m*), while the methylene protons appeared at 3·78 δ (2H,*d*) and another *iso*pentenyl side chain as a dimethylchromene system was evident with the appearance of two doublets at 5·94 and 7·24 δ (1H each, *J* 10·2 Hz). Presence of the latter moiety was further substantiated from the MS of the base where the base peak appeared at M-15, due to the formation of stable benzopyrylium cation. The methyl protons of gem-dimethyls appeared at 1·49 δ (3H,S), 1·89 δ (6H,S) and 2·02 δ (3H,S) respectively.

The above data together with MS fragmentation peaks at *m/e* 377 (M^+), 362 (100%), 334, 322, 306 and 294 are in excellent accord with structure (**1**) for atalaphyllinine.



(1)



(2)

Chemical correlation of the above structure was obtained by cyclization of atalaphyllinine with formic acid when a sticky mass was obtained, which was hydrogenated and working up of the hydrogenated product followed by preparative TLC led to the isolation of a yellow compound mp 250–51° which was found to be identical with bicycloatalaphylline (2) from mmp and superimposable IR spectra.

EXPERIMENTAL

Mp's are uncorrected. NMR spectra were recorded in $CDCl_3$ with a few drops of DMSO-d_6. All chromatography was carried out on Si gel (E. Merck).

Atalaphylline. This compound crystallized from C_6H_6–EtOAc (4:1) as yellow needles, mp 205–7°; λ_{max}^{EtOH} 347, 305, 293·5, 264 nm (log ϵ, 4·34, 4·12, 4·05, 3·85), ν_{max} 3300(*br*), 1640, 1605, 1570, 1525, 1475); (found: C, 72·98; H, 5·99; N, 3·65; $C_{23}H_{23}NO_4$ requires: C, 73·20; H, 6·10; N, 3·71%). NMR: 15·44 (1H, *s*, –OH), 9·50 (1H, br, –OH), 10·58 (1H, *s*, –NH), 8·24 (1H, *dd*; *J* 8·8 Hz, C_8-Ar-H), 7·45–7·57 (2H, *m*, Ar-H), 7·24 and 5·94 (1H, *d*, *J* 10·2 Hz each for α, β -Hs of chromene ring), 5·5 (1H, *m*), 3·78 (2H, *d*), 2·02 (3H, *s*, C–Me), 1·89 (6H, *s*, 2C–Me), 1·49 (3H, *s*, C–Me). MS: *m/e* 377 (M^+), 362 (100%), 334, 322, 306, 294.

Cyclization of atalaphyllinine. Atalaphyllinine (25 mg) was heated at 80–100° for 4 hr with HCO_2H (2 ml) and then left at room temp overnight. H_2O was added and the soln extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$ aq. H_2O, dried (Na_2SO_4) and evaporated. The residue was chromatographed over Si gel (2 g) in C_6H_6–EtOAc (1:1) to yield a gummy mass, homogeneous by TLC in several solvent systems.

Hydrogenation of cyclized product of atalaphyllinine. A soln of above gummy mass in dry EtOH (5 ml) was shaken with H_2 (1 atom) in the presence of PtO_2 (30 mg) for 6 hr. The soln was filtered, evaporated and preparative TLC of the residue (solvent: C_6H_6–EtOAc MeOH, 40:10:1) furnished a product yield 40%) which was crystallised from CH_2Cl_2–hexane in yellow crystals, mp 250° (dec.) (M^+ 379). This product gave brown colour with $FeCl_3$.

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MINOR COUMARINS OF *BOENNINGHAUSENIA ALBIFLORA*

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Like many other Rutaceae, *Boenninghausenia albiflora* contains many coumarins [1–4] only three of which are novel: nodakenetin acetate [1], 3-(1,1-dimethyl allyl)-xanthyletin [2] and the dimeric coumarin, matsukaze lactone [4]. Investigation of the minor constituents of leaves and stems of *B. albiflora* led to the isolation of three further coumarins; angelical (**1**), 6-(*trans*-1-buten-3-onyl)-7-methoxycoumarin (**2**) and daphnoretin (**3**) along with methyl *p*-coumarate. All these compounds were characterised mainly on the basis of their spectral properties.

Coumarin (**2**), $C_{14}H_{12}O_4$ (M^+ 244), mp 225°, showed UV absorption at λ_{max}^{EtOH} 285 nm (log ϵ 4·4) and 225 (4·09); IR, ν_{max}^{KBr} 1718 cm^{-1} (coumarin lactone CO), 1664 (α,β-unsaturated CO) and 976 (*trans*-disubstituted alkene). The PMR spectrum (100 MHz, $CDCl_3$, δ) had signals for a ketomethyl group (2·38, *s*, 3H), two *trans*-disubstituted olefinic protons (6·74 *d* and 7·80 *d*, *J* 16 Hz), coumarin 3- and 4-protons (6·29 *d* and 7·64 *d*, AB system, *J* 10 Hz), two aromatic protons (6·83 *s* and 7·62 *s*, 1H each, H-8 and H-5) and a methoxy group (3·96, *s*, 3H). The MS showed the base peak at *m/e* 213, the genesis of which may be rationalised by the loss of OMe from the ion (**4**), the latter being formed by isomerisation of the side chain double bond of the