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ALKALOIDS FROM A NEW DAPHNANDRA SP. ISOLATION AND STRUCTURE OF PSEUDOREPANDULINE

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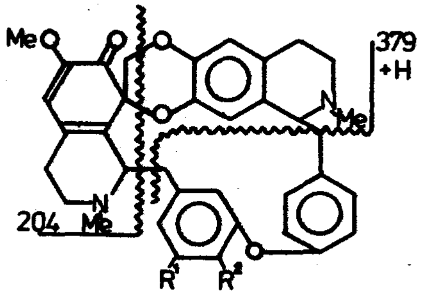
The genus Daphnandra (Monimiaceae) is at present being reclassified, and taxonomic studies[1] have revealed a new species, at present unnamed, which appears to be of very limited occurrence and confined to Mt. Springbrook in southern Queensland. We have examined a specimen of leaves and terminal twigs, from which a crude alkaloid fraction was separated by standard procedures. Repeated ptlc on silica gel plates treated with 0.5N KOH resulted in the isolation of three major alkaloids, O,N-dimethylmicranthine[2], micranthine[2] and (+) tenuipine[3], identical (mp and mixed mp, tlc, ir, nmr and [α]) with authentic samples of the corresponding bases; although each occurs in other Daphnandra spp, they had not previously been found together.

A further alkaloid [mp 168-173 (decomp.), $[\alpha]_D^{18}$ + 229 ($CHCl_3$)] seemed at first to correspond to repanduline[4], the unique yellow biscoclaurine base for which structure I has been proposed: the colour, R_f values, uv and ir spectra of the two alkaloids are very similar, also the nmr spectra, but the latter differ inasmuch as the two-proton multiplet at δ5.94 in the repanduline spectrum due to the methylenedioxy protons is replaced by an extra methoxyl proton resonance at δ3.98 in the spectrum of the new alkaloid, which we have named pseudorepanduline. There are differences also in the aromatic region of the two spectra consistent with the presence of an extra aromatic proton and an unsymmetrically trisubstituted benzene ring in pseudorepanduline. This feature is also suggested by the presence of a 790 cm^{-1} peak in the ir spectrum of the latter which is absent from that of repanduline, the only notable difference between the two spectra. Structure II



I. R^1-R^2 = O-CH_2-O

II. R^1 = H, R^2 = OMe.

indicated by these data for pseudorepanduline is further supported by its mass spectrum (M^+606.2723; calc. for $C_{37}H_{38}N_2O_6$: 606.2730), in which the same fragments occur at m/e 204 and 379 as for repanduline, due to the cleavages shown.

Structure I proposed for repanduline[4] rests largely on spectroscopy supported in part by degradative evidence; the latter is, however, incomplete owing to difficulties inherent in the presence of the methylenedioxy group, which interferes in the Birch reduction of the arylether groups. The isolation of pseudorepanduline in sufficient quantity for degradation could permit uncertainties in the structures of both alkaloids to be resolved, but the rarity and difficulty of collection of the new Daphnandra species makes it an unsuitable source. A careful examination[5] of other species, however, has revealed the presence of pseudorepanduline in the much more plentiful and accessible north Queensland D. dielsii, in which it occurs along with repanduline[6] and yet another repanduline analogue[5]; we shall report further on all three elsewhere.

There are at least three minor alkaloids present in the new Daphnandra sp, one of which [mp 188-194 (decomp.), $[\alpha]_D^{20}$ - 150 ($CHCl_3$)] was shown to be 1,2-dehydromicranthine from spectroscopic data [nmr: 3.85, 2.55δ (each S, 3H); uv: λ_{max} 335 nm (log ε_{max} 3.4)] and through the identity of its borohydride reduction product with micranthine; a second, which could not be obtained pure, corresponded closely in its properties with O-methylmicranthine, while a third has not yet been identified.

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