

STUDIES ON THE SYNTHESIS AND CONFORMATIONAL ANALYSIS
OF SOME DIBENZO[a,g]QUINOLIZIDINES

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Biotransformation of ($\pm$)-reticuline into ($\pm$)-coreximine, ($\pm$)-scoulerine and ($\pm$)-norreticuline with a whole rat or a homogenized rat liver was demonstrated by tracer experiments with carbon-14 and tritium labelled ($\pm$)-reticuline. Thus the biotransformation was found to occur with a rat liver 9,000 g supernatant, which was exceedingly catalysed by NADPH and magnesium chloride. Tritium labelled ($\pm$)-laudanosine was also incorporated into ($\pm$)-norlaudanosine, ($\pm$)-xylopinine and ($\pm$)-tetrahydropalmatine using the rat liver 9,000 g supernatant in the presence of NADPH.

Secondly, the total syntheses of retroprotoberberines, ($\pm$)-mecambridine and ($\pm$)-orientalidine have been accomplished. Namely, hydroxymethylation of the phenolic tetrahydroprotoberberine yielded O-demethylmecambridine, which on methylation with diazomethane afforded ($\pm$)-mecambridine. A treatment of O-demethylmecambridine with methylene chloride and sodium hydride in dimethylformamide gave ($\pm$)-orientalidine.

Thirdly, the structure of a new 8-methylprotoberberine, corytenchirine, isolated from Corydalis ochotensis in Taiwan, was elucidated. Careful reduction of coralyne sulphoacetate gave a mixture of coralydine and its stereoisomer, the latter of which was identical with the O-methyl ether of corytenchirine. On the basis of the spectral data, the structure of corytenchirine was deduced to 13a(S)-5,6,13,13a-tetrahydro-11-hydroxy-2,3,10-trimethoxy-8(R)-methyl-8H-dibenzo[a,g]quinolizidine.

Finally, the conformational analysis of some protoberberine alkaloids by carbon-13 NMR measurement was carried out. The preferential conformation of tetrahydroprotoberberine is easily assignable by comparison of the chemical shift of C(6) in carbon-13 NMR spectroscopy. It is possible, furthermore, to distinguish the 9,10- and 10,11-disubstituted tetrahydroprotoberberines by the difference in chemical shift of C(8).