

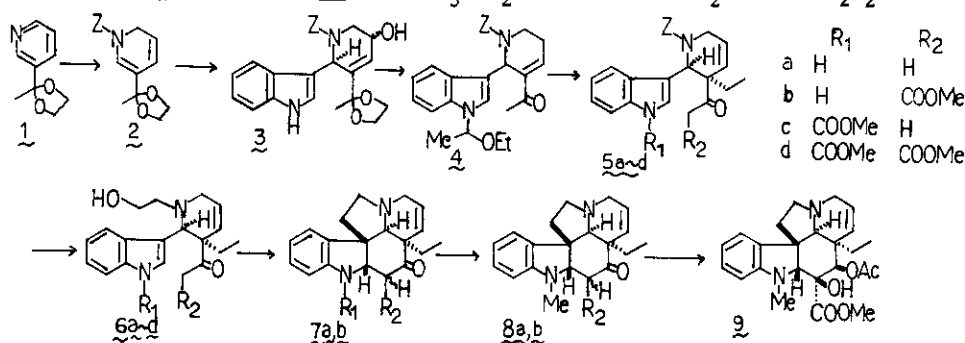
A NOVEL SYNTHESIS OF ASPIDOSPERMA ALKALOIDS USING SIMULTANEOUS
CYCLIZATION AT 2 AND 3 POSITIONS OF INDOLE RING

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A formal synthesis of ($\pm$)-vindorosine (9) was performed by a novel type of cyclization reaction (6a, 6d + 7a, 7b) which consists of two carbon-carbon bond formations at the C-2 and C-3 positions in the indole ring. The key compounds (6a and 6d) were prepared as follows. The ketal (1) was reduced with a bulky reducing reagent, $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OMe})_2\text{H}_2$, in the presence of $\text{ClCOOCH}_2\text{Ph}$ in THF to afford 1,6-dihydropyridine derivative (2), which was submitted to our oxygenative nucleophile introduction reaction¹⁾ to form compound (3). 3 was converted to 5a via 4 in six steps and the desired compound (6a) was obtained from 5a through 5c. The methane-sulfonate of 6a was treated with $(\text{Me}_3\text{Si})_2\text{NK}$, in THF at -70°C at first then at room temperature for 1 h to give the pentacyclic compound (7a). Alternatively, 6d derived from 5a by way of 5d [i) $(\text{Me}_3\text{Si})_2\text{NK}$, THF; ii) CO_2 ; iii) CH_2N_2], was



subjected to the same cyclization reaction using $t\text{-BuOK}$ in place of $(\text{Me}_3\text{Si})_2\text{NK}$ to furnish a more functionalized compound (7b). 7a and 7b were methylated with CH_2O and NaBH_3CN to afford 8a and 8b, which were identified with Büchi's samples²⁾ which were transformed to ($\pm$)-vindorosine (9).

REFERENCES

- 1) M. Natsume, et al, *Tetrahedron Lett.*, 3473 (1979).
- 2) G. Büchi, et al, *J. Am. Chem. Soc.*, 93, 3299 (1971).