

PLANNING AND OPERATION IN THE MULTISTEP  
ALKALOID SYNTHESIS

Yasuo Inubushi

Faculty of Pharmaceutical Sciences, Kyoto University

Kyoto 606, Japan

[I] Synthesis of Serratinine, 8-Deoxyserratinine and Fawcettimine

A preliminary planning (indicated by  $\Rightarrow$ ) includes three unsettled steps (A,B,C).  
A The selective addition direction was secured by using 2-methyl-5-acrylic ester-1,4-benzoquinone. B The desired selectivity was obtained using excess pyrrolidine-AcOH in MeOH. C The nitrogen containing rings were constructed via an aziridinium ring. Reduction of the triketone gave dl-serratinine.<sup>1)</sup> A preliminary planning includes three matters for investigation (D,E,F). D The stereoselective addition of butadiene was found in the presence of Lewis acids. E The desired selectivity was obtained using morpholine-camphoric acid in Et<sub>2</sub>O-HMPA. F The nitrogen containing ring was constructed through epoxides completing synthesis of dl-8-deoxyserratinine and dl-fawcettimine.<sup>2)</sup>  
[II] Synthesis of Pumiliotoxin C and Synthetic Approach to Histrionicotoxin

The first synthesis of pumiliotoxin C was achieved starting from tetrahydroindanone.<sup>3,4)</sup> The stereoselective synthesis was completed using the bicyclo[2.2.2]octane derivative synthesized by the Diels-Alder reaction of acrylonitrile with new type diene 1,3-bis(trimethylsilyloxycyclohexa)-1,3-diene. The key intermediate possessing three of four chiral centers of the toxin was obtained from the bicyclo compound in one operation. Alkylation of lactam carbonyl gave pumiliotoxin C.<sup>5)</sup> Synthesis of perhydrohistrionicotoxin has been reported by several groups<sup>4)</sup> and an alternative synthesis is undertaking.

References

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