STUDIES ON THE SYNTHESIS OF THE DIMERIC INDOLE ALKALOIDS THE STEREOSPECIFIC SYNTHESIS OF (±)-DIHYDROCLEAVAMINE AND A NEW SYNTHESIS OF (±)-QUEBRACHAMINE AND ITS (±)-14, 15-DEHYDRODERIVATIVE

Seiichi Takano, Susumi Hatakeyama, Michiyasu Hirama, Tsutomu Araki, Shin-ichi Yamada,

Masaaki Sato, Tsutomu Sugahara, Kozo Shishido, and Kunio Ogasawara

Pharmaceutical Institute, Tohoku University,

Aobayama, Sendai 980

Novel syntheses of the entitled compounds and their related compounds via sulfur containing intermediates have been reported.

Hydroboration followed by oxidation of an epimeric mixture of 2-(2-ethylally1)-3-thioxo-1,2,3,5,6,1lb-hexahydro-1lH-pyrrolo[1,2-a]- β -carboline afforded the primary alcohol;2-(2-ethyl-3-hydroxypropy1)-3-thioxo-1,2,3,5,6,1lb-hexahydro-1lH-pyrrolo[1,2-a]- β -carboline as a single stereoisomer which was then led to (+)-dihydrocleavamine.

A new synthesis of (\pm) -quebrachamine was accomplished by two different ways, in which the one employed the thio-Claisen rearrangement to construct crucial intermediate, while the other used the α -diketomonorhioketal cleavage reaction and in the latter a introduction of 14,15-double bond of quebrachamine was accomplished by the thermolysis of the corresponding sulfoxide.