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Bioinspired Collective Total Synthesis of (±)-Rhynchines A-E

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Total Synthesis of (±)-Rhynchine E

Significance: In 2021, a new class of structurally unique monoterpene indole alkaloids was isolated from *Uncaria rhynchophylla*, rhynchines A–E. Zhao and co-workers now report the first racemic total synthesis of rhynchine E as well as rhynchine A-D. A biosynthetic relationship of the rhynchines natural products to hirsuteine, which is also commonly found in the isolation plant, was proposed.

Comment: The synthesis commenced with the formation of tetracyclic triester **E** from pyridinium salt **C**, through a Pictet–Spengler reaction. Subsequent treatment with NaBH3CN in AcOH, triggered conjugated reduction and a 1,2-migration, forming the core tetrahydroazepine G. The tetrahydrofuran ring of (±)-rhynchine E was formed via C-H oxidation using $K_3[Fe(CN)_6]$.

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Category

Synthesis of Natural

(±)-rhynchine E

Pictet-Spengler reaction

1,2-migration

aldol addition

C-H oxidation

Krapcho decarboxylation

