

Sarlah Group **Synthesis of kingianins (A, D, F), kingianic acid E and endiandric acid A**

Kingianin natural products and endiandric acids

- isolated *as racemate* from the leaves of *Endiandra kingiana* and *Endiandra intorsa*.
- proposed biosyntheses for both natural products involve formation of bicyclo[4.2.0]-octadiene as a key intermediate, followed by intermolecular Diels-Alder dimerization for kingianins, and intramolecular Diels-Alder reaction for endiandric acids and kingianic acids.

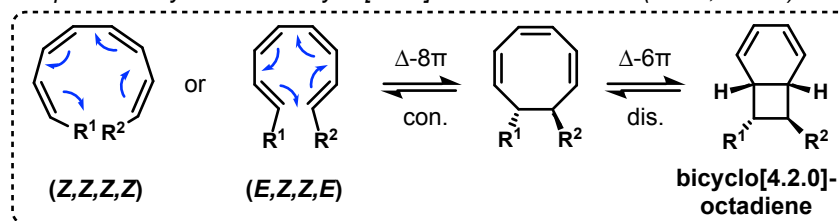
Bicyclo[4.2.0]octadiene structure in nature

- bicyclo[4.2.0]octadienes in nature are proposed to form through spontaneous (non-enzymatic) 8π - 6π electrocyclization sequence from either (Z,Z,Z,Z)-tetraene or (E,Z,Z,E)-tetraene.
- Nicolaou's biomimetic synthesis of endiandric acids A-G provided the first experimental support for (E,Z,Z,E)-tetraene to be a viable biosynthetic precursor.

Unified approach towards kingianin natural products and endiandric acids: A. L. Lawrence, M. S. Sherburn, et. al, *ACIE*, 2013, 52, 4221; *Chem. Sci.*, 2015, 6, 3886.

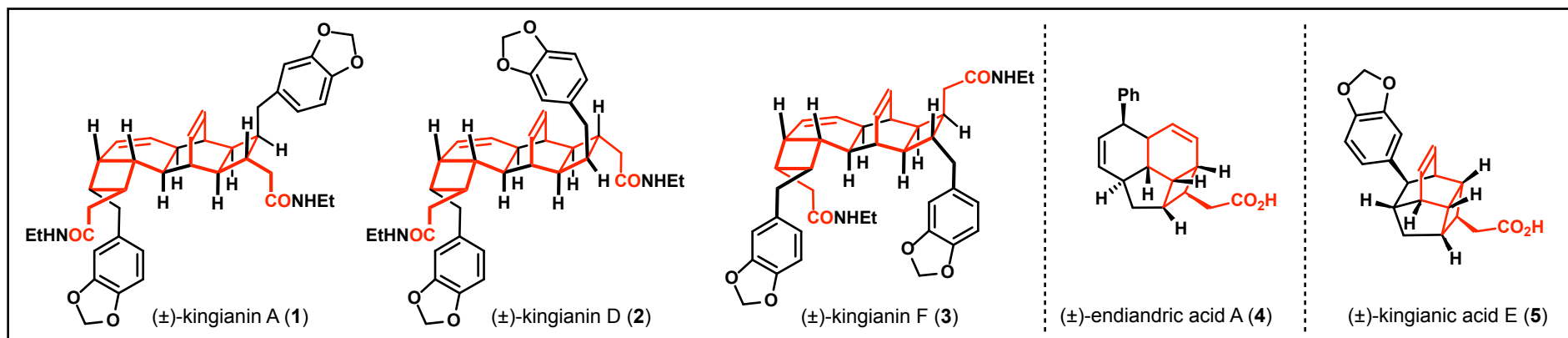
- utilized (Z,Z,Z,Z)-tetraene for the first time (all prior total syntheses proceeded via (E,Z,Z,E)-tetraene derivatives).
- radical cation Diels-Alder reaction was used to induce challenging intermolecular Diels-Alder dimerization.

Proposed biosynthesis of bicyclo[4.2.0]octadiene structure (Black, 1980s)



This work

Nicolaou (1982)
Moses (2011), etc.



intermolecular Diels-Alder dimerization

intramolecular Diels-Alder reaction

alkylation; partial reduction;
 8π - 6π electrocyclization sequence

Sarlah Group **Synthesis of kingianins (A, D, F), kingianic acid E and endiandric acid A**

A. L. Lawrence, M. S. Sherburn, *et. al*, *ACIE*, **2013**, 52, 4221; *Chem. Sci.*, **2015**, 6, 3886.

