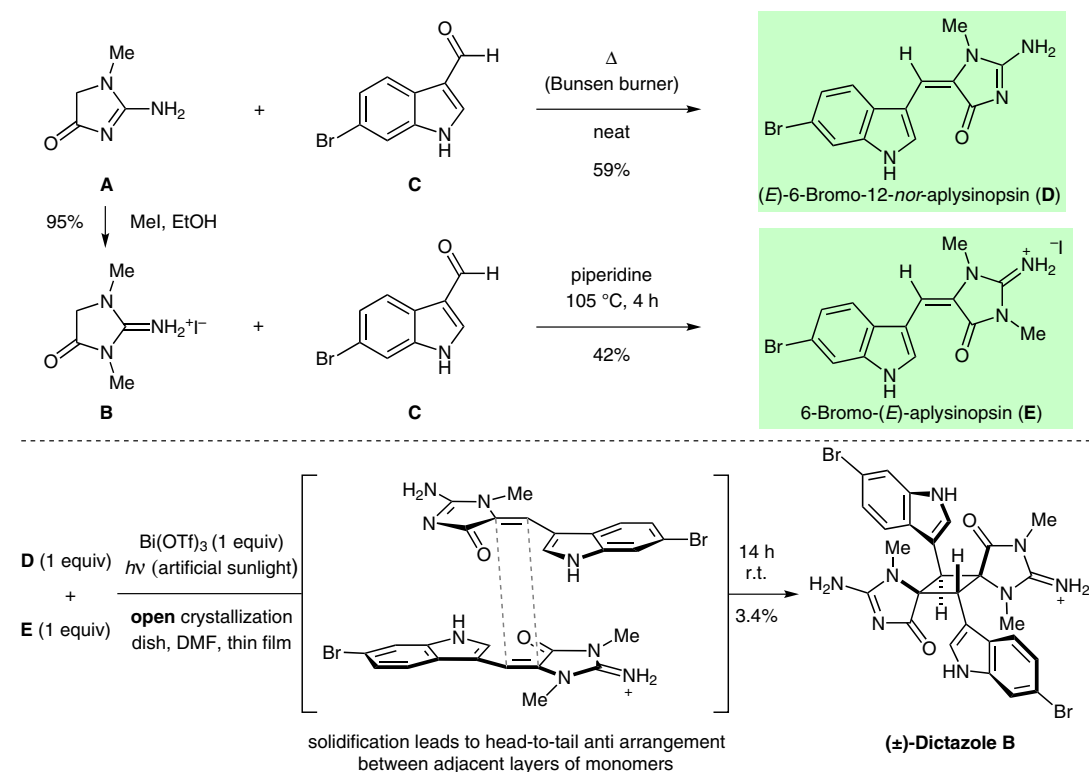


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 Spontaneous Biomimetic Formation of (±)-Dictazole B under Irradiation with Artificial Sunlight  
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## Biomimetic Synthesis of (±)-Dictazole B by Irradiation with Artificial Sunlight



**Significance:** The aplysinopsins are a class of biosynthetically related alkaloids whose members were isolated from several sponges and stony corals collected in shallow waters reachable by sunlight. Three basic types of molecular scaffolds were identified so far: (1) monomeric creatinine indoles such as **D** and **E**, (2) cyclobutane-containing alkaloids such as dictazole **B**, that could arise from photochemical heterodimerization and, (3) tetrahydrocarbazoles possibly stemming from cyclobutane ring expansion. In this work, careful experimentation made it possible for the first time to photochemically dimerize such aplysinopsin monomers, leading not only to the first and potentially biomimetic synthesis of dictazole **B**, but also substantiating the aforementioned biosynthetic proposal.

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**Comment:** Aplysinopsin-type monomers have previously been reported not to undergo any photochemical cycloadditions in solution with the only observable reaction being *E/Z*-isomerization. This finding was again verified in the course of this work. However, a fortuitous discovery was finally made during a routine LC/MS measurement of a monomer sample that had stood as a solid for weeks in the laboratory. Careful analysis of its chromatogram revealed the presence of minute amounts of the homodimer. After extensive screening of conditions it was found that also the requisite heterodimerization could be achieved, with best results being obtained when a thin film of **D** and **E** with Bi(OTf)<sub>3</sub> as an additive in DMF was left standing to crystallize while irradiating with artificial sunlight.

Category

Synthesis of Natural Products and Potential Drugs

Key words

dictazole B

aplysinopsins

biomimetic synthesis

[2+2] photocycloaddition

dimerization

**SYNFACTS**  
*of the month*

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