

Polyketide synthase chimeras reveal key role of ketosynthase domain in chain branching.

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Abstract

Biosynthesis of rhizoxin in *Burkholderia rhizoxinica* affords an unusual polyketide synthase module with ketosynthase and branching domains that install the δ -lactone, conferring antimitotic activity. To investigate their functions in chain branching, we designed chimeric modules with structurally similar domains from a glutarimide-forming module and a dehydratase. Biochemical, kinetic and mutational analyses reveal a structural role of the accessory domains and multifarious catalytic actions of the ketosynthase.

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