

Mechanistic characterization of three sesquiterpene synthases from the termite-associated fungus *Termitomyces*.

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Abstract

Three terpene synthases from the termite associated fungus *Termitomyces* were functionally characterized as (+)-intermedeol synthase, (–)-cadinene synthase and (+)-germacrene D-4-ol synthase, with the germacrene D-4-ol synthase as the first reported enzyme that produces the (+)-enantiomer. The enzymatic mechanisms were thoroughly investigated by incubation with isotopically labeled precursors to follow the stereochemical courses of single reaction steps in catalysis. The role of putative active site residues was tested by site directed mutagenesis of a highly conserved tryptophan in all three enzymes and additional residues in (–)-cadinene synthase that were identified by homology model analysis.

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