

Structural determinants of reductive terpene cyclization in iridoid biosynthesis.

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Abstract

The carbon skeleton of ecologically and pharmacologically important iridoid monoterpenes is formed in a reductive cyclization reaction unrelated to canonical terpene cyclization. Here we report the crystal structure of the recently discovered iridoid cyclase (from *Catharanthus roseus*) bound to a mechanism-inspired inhibitor that illuminates substrate binding and catalytic function of the enzyme. Key features that distinguish iridoid synthase from its close homolog progesterone 5 β -reductase are highlighted.

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