A flavoprotein dioxygenase steers bacterial tropone biosynthesis via coenzyme A-ester oxygenolysis and ring epoxidation

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Bacterial tropone natural products such as tropolone, tropodithietic acid, or the roseobacticides play crucial roles in various terrestrial and marine symbiotic interactions as virulence factors, antibiotics, algaecides, or quorum sensing signals. We now show that their poorly understood biosynthesis depends on a shunt product from aerobic CoA-dependent phenylacetic acid catabolism that is salvaged by the dedicated acyl-CoA dehydrogen-ase-like flavoenzyme TdaE. Further characterization of TdaE revealed an unanticipated complex catalysis, comprising substrate dehydrogenation, noncanonical CoA-ester oxygenolysis, and final ring epoxidation. The enzyme thereby functions as an archetypal flavoprotein dioxygenase that incorporates both oxygen atoms from O-2 into the substrate, most likely involving flavin-N5-peroxide and flavin-N5-oxide species for consecutive CoA-ester cleavage and epoxidation, respectively. The subsequent spontaneous decarboxylation of the reactive enzyme product yields tropolone, which serves as a key virulence factor in rice panicle blight caused by pathogenic edaphic Burkholderia plantarii. Alternatively, the TdaE product is most likely converted to more complex sulfurcontaining secondary metabolites such as tropodithietic acid from predominant marine Rhodobacteraceae (e.g., Phaeobacter inhibens).

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