A dedicated glutathione S-transferase mediates carbon-sulfur bond formation in gliotoxin biosynthesis.

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Abstract

Gliotoxin is a virulence factor of the human pathogen Aspergillus fumigatus , the leading cause of invasive aspergillosis. Its toxicity is mediated by the unusual transannular disulfide bridge of the epidithiodiketopiperazine (ETP) scaffold. Here we disclose the critical role of a specialized glutathione S-transferase (GST), GliG, in enzymatic sulfurization. Furthermore, we show that bishydroxylation of the diketopiperazine by the oxygenase GliC is a prerequisite for glutathione adduct formation. This is the first report of the involvement of a GST in enzymatic C-S bond formation in microbial secondary metabolism.

Beteiligte Forschungseinheiten

Biomolekulare Chemie Christian Hertweck Mehr erfahren

Molekulare und Angewandte Mikrobiologie Axel Brakhage Mehr erfahren

Leibniz-HKI-Autor*innen



Axel A. Brakhage

Details



Pranatchareeya Chankhamjon

Details



Thorsten Heinekamp

Details



Christian Hertweck

Details



Peter Hortschansky

Details



Daniel H. Scharf

Details



Kirstin Scherlach

Details

Identifier

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