Metabolic pathway rerouting in *Paraburkholderia rhizoxinica* evolved long-overlooked derivatives of coenzyme F420.

Braga D, Last D, Hasan M, Guo H, Leichnitz D, Uzum Z, Richter I, Schalk F, Beemelmanns C, Hertweck C, Lackner G (2019) Metabolic pathway rerouting in *Paraburkholderia rhizoxinica* evolved long-overlooked derivatives of coenzyme F420. *ACS Chem Biol* 14(9), 2088-2094.

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Abstract

Coenzyme $F_{420}$is a specialized redox cofactor with a negative redox potential. It supports biochemical processes like methanogenesis, degradation of xenobiotics or the biosynthesis of antibiotics. Although well-studied in methanogenic archaea and actinobacteria, not much is known about F_{420} in Gram-negative bacteria. Genome sequencing revealed F_{420} biosynthetic genes in the Gram-negative, endofungal bacterium Paraburkholderia rhizoxinica, a symbiont of phytopathogenic fungi. Fluorescence microscopy, high-resolution LC-MS, and structure elucidation by NMR demonstrated that the encoded pathway is active and yields unexpected derivatives of F_{420} (3PG-F_{420}). Further analyses of a biogas-producing microbial community showed that these derivatives are more widespread in nature. Genetic and biochemical studies of their biosynthesis established that a specificity switch in the guanylyltransferase CofC re-

programmed the pathway to start from 3-phospho-d-glycerate, suggesting a rerouting event during the evolution of F_{420} biosynthesis. Furthermore, the cofactor activity of 3PG-F_{420} wasvalidated, thus opening up perspectives for its use in biocatalysis. The 3PG-F_{420} biosynthetic gene cluster is fully functional in Escherichia coli, enabling convenient production of the cofactor by fermentation.

Involved units

Biomolecular Chemistry Christian Hertweck Read more

Chemical Biology of Microbe-Host Interactions Christine Beemelmanns Read more

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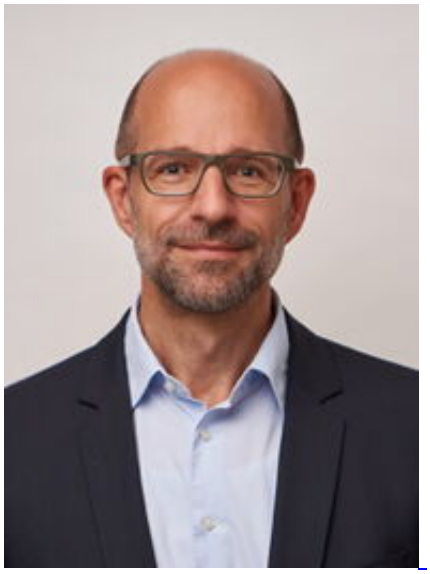
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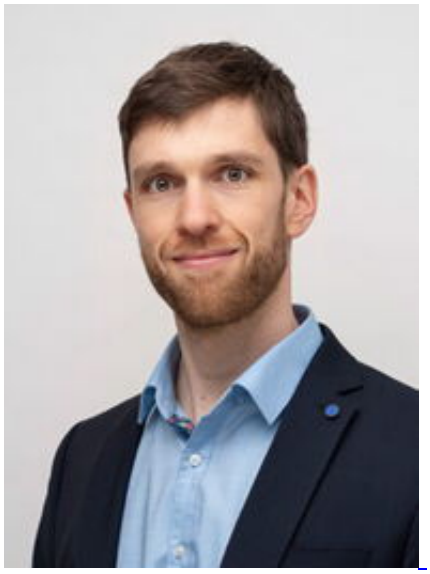
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