

Structure elucidation of the syringafactin lipopeptides provides insight in the evolution of nonribosomal peptide synthetases.

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Abstract

Modular biosynthetic machineries such as polyketide synthases (PKSs) or nonribosomal peptide synthetases (NRPSs) give rise to a vast structural diversity of bioactive metabolites indispensable in the treatment of cancer or infectious diseases. Here, we provide evidence for different evolutionary processes leading to the diversification of modular NRPSs and thus, their respective products. Discovery of a novel lipo-octapeptide family from *Pseudomonas*, the virginiafactins, and detailed structure elucidation of closely related peptides, the cichofactins and syringafactins, allowed retracing recombinational diversification of the respective NRPS genes. Bioinformatics analyses allowed us to spot an evolutionary snapshot of these processes, where recombination occurred both within the same and between different biosynthetic gene clusters. Our systems

feature a recent diversification process, which may represent a typical paradigm to variations in modular biosynthetic machineries.

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