

On-line enzymatic tailoring of polyketides and peptides in thiotemplate systems.

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Abstract

Non-ribosomal peptide synthetases (NRPS) and type I polyketide synthases (PKS) are versatile thiotemplate systems for the programmed assembly of biosynthetic building blocks. Typically, the post-PKS/NRPS enzymes tailor the resulting chains to yield the bioactive natural product scaffolds. However, more and more examples have surfaced showing that important structural modifications take place while the intermediates are still bound to the assembly line. A growing number of enzymatic domains and trans-acting enzymes as well as their recruiting areas in the modules have been identified and characterized. In addition to the widespread on-line alkylations, hydroxylations and heterocyclizations into oxazole/thiazole residues, on-line modifications lead to a variety of ring systems such as cycloethers, lactones, lactams, glutarimides, cyclopropanes, decalins and cyclic biaryls.

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