

## **Ascocorynin biosynthesis, an exception from the rule?**

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Genes coding for non-reducing NRPS-like enzymes are widely distributed among fungal genomes. Metabolites produced by these enzymes contribute to various biological activities such as phytotoxicity, quorum sensing or the formation of a protective melanin. The common domain structure of these enzymes consists of an adenylation (A), thiolation (T) and thioesterase (TE) domain. Thereby, the A-domain is responsible for activation of two identical aromatic alpha-keto acids that derive from either phenylalanine, tyrosine or tryptophan. The activated alpha-keto acids are subsequently condensed by the thioesterase domain that forms specific interconnecting core structures such as benzoquinones, furanones, butyrolactones or dioxolanones. While it is believed that the A-domain is strictly specific for a single substrate, there may be exceptions from this rule. *Ascocoryne sarcooides*, an endophytic ascomycete, produces large quantities of a compound named ascocorynin. This benzoquinone is characterised by a phenyl- and a hydroxyphenyl-side chain, implying the activation of phenylpyruvate and hydroxyphenylpyruvate. Genome mining identified the existence of a single non-reducing NRPS-like enzyme assumed to be involved in ascocorynin biosynthesis. Subsequent gene expression analyses, heterologous gene expression and metabolite identification eventually revealed the biosynthetic pathway of this unusual NRPS-like product.