A tale of four kingdoms - isoxazolin-5-one- and 3-nitropropanoic acid-derived natural products.

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Abstract

This review reports on natural compounds that derive from the isoxazolinone ring as well as the 3-nitropropanoic acid (3-NPA) moiety. These structural elements occur in compounds that have been identified in plants, insects, bacteria and fungi. In particular, plants belonging to the family of legumes produce such compounds. In the case of insects, isoxazolin-5-one and 3-NPA derivatives were found in leaf beetles of the subtribe Chrysomelina. A number of these natural products have been synthesized so far. In the case of the single compound 3-NPA, several synthetic strategies have been reported and some of the most efficient routes are reviewed. The toxicity of 3-NPA results from its ability to bind covalently to the catalytic center of succinate dehydrogenase causing irreversible inhibition of mitochondrial respiration. As a motif that is produced by many species of plants, leaf beetles and fungi, different detoxification mechanisms for 3-NPA have evolved in different species. These mechanisms are based on amide formation of 3-NPA with amino acids, reduction to β-alanine, ester formation or oxidation to malonic acid semialdehyde. The biosynthetic pathways of 3-NPA and isoxazolin-5-one moieties have been studied in fungi, plants and leaf

beetles. In the case of fungi, 3-NPA derives from aspartate, while leaf beetles use essential amino acids such as valine as ultimate precursors. In the case of plants, it is supposed that malonate serves as a precursor of 3-NPA, as indicated by feeding of ^{14}C-labeled precursors to *Indigofera spicata*. In other leguminous plants it is suggested that asparagine is incorporated into compounds that derive from isoxazolin-5-one, which was indicated by ^{14}C-labeled compounds as well. In the case of leaf beetles it was demonstrated that detection of radioactivity after ^{14}C-labeling from a few precursors is not sufficient to unravel biosynthetic pathways.

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