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Review

# Non-protein amino acids in plant defense against insect herbivores: Representative cases and opportunities for further functional analysis

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ABSTRACT

Chemical defense against herbivores is of utmost importance for plants. Primary and secondary metabolites, including non-protein amino acids, have been implicated in plant defense against insect pests. High levels of non-protein amino acids have been identified in certain plant families, including legumes and grasses, where they have been associated with resistance to insect herbivory. Non-protein amino acids can have direct toxic effects via several mechanisms, including misincorporation into proteins, obstruction of primary metabolism, and mimicking and interfering with insect neurological processes. Additionally, certain non-protein amino acids allow nitrogen to be stored in a form that is metabolically inaccessible to herbivores and, in some cases, may act as signals for further plant defense responses. Specialized insect herbivores often possess specific mechanisms to avoid or detoxify non-protein amino acids from their host plants. Although hundreds of non-protein amino acids have been found in nature, biosynthetic pathways and defensive functions have been elucidated in only a few cases. Next-generation sequencing technologies and the development of additional plant and insect model species will facilitate further research on the production of non-protein amino acids, a widespread but relatively uninvestigated plant defense mechanism.



**Contents**



## 1. Introduction

In addition to the 20 common amino acids used for protein biosynthesis, plants also produce numerous non-protein amino acids (Bell, 1976). Some of these, such as L-ornithine, L-homoserine, and L-*S*-adenosylmethionine, are important intermediates in primary metabolism that can be detected in most plant species. There are also uncommon amino acids found as secondary metabolites, whose occurrence is often limited to a small number of plant families. Hundreds of such non-protein amino acids have been identified, with seeds of various legumes being very common sources (Fowden, 1981). Several comprehensive reviews, including a recent one, have covered surveys of these amino acids (Barrett, 1985; Rosenthal, 1982; Vranova et al., 2010) and therefore will not be repeated here.

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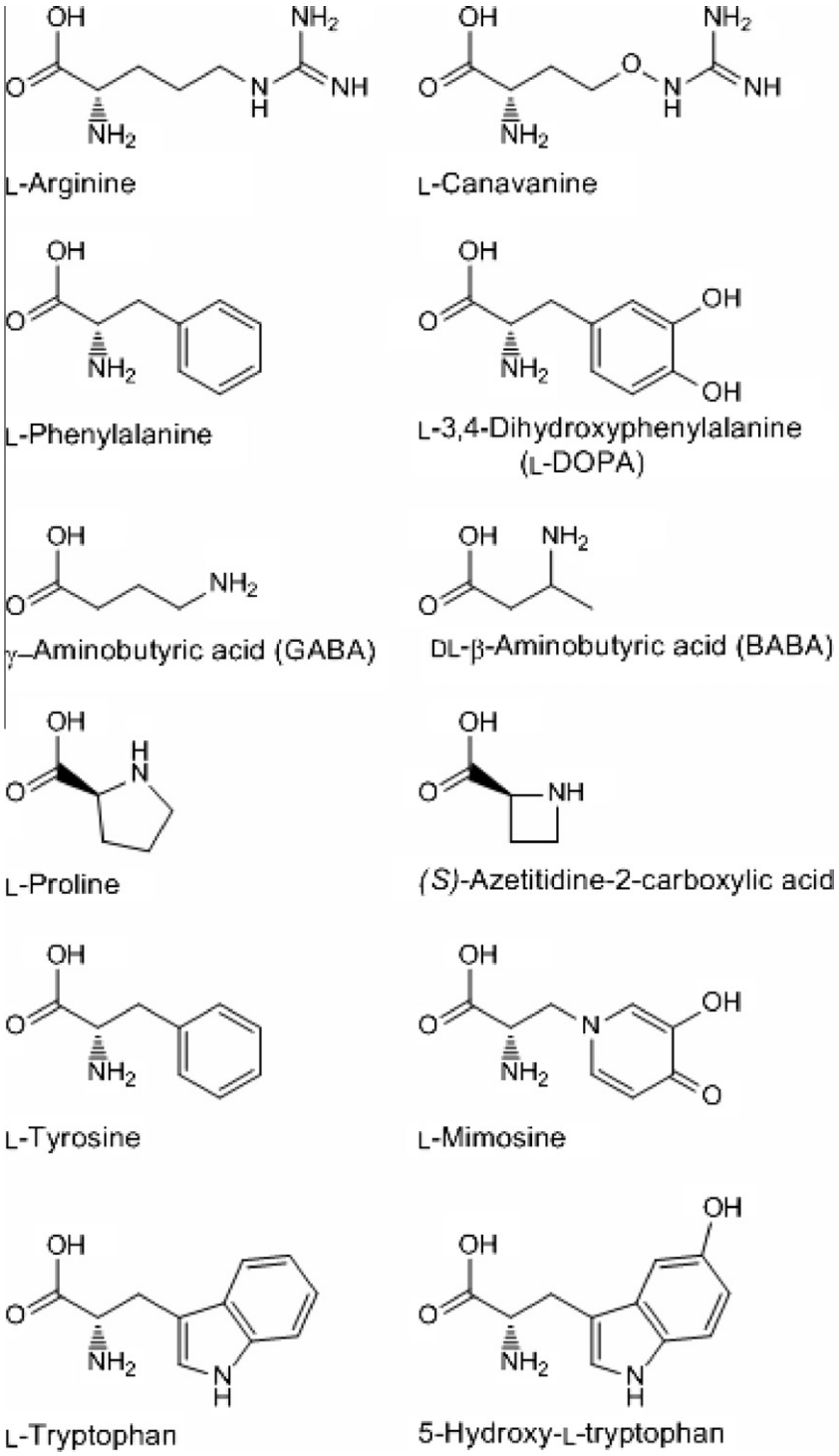


**Fig. 1.** Comparison of amino acid structures. Amino acids on the left are ubiquitous amino acids found in plants, whereas those on the right are respective non-protein analogs that have been found in certain plant species.

Among many possible functions of non-protein amino acids, their participation in plant defense against herbivores is of particular interest. During their entire life cycles, sessile plants rely on chemical defenses as one of the most important strategies to protect themselves from numerous insect herbivores (Levin, 1976; Swain, 1977; Wittstock and Gershenzon, 2002). Many of these chemical toxins, repellents, or barriers are plant secondary metabolites such as alkaloids, glucosinolates, terpenoids and phenolics (Schoonhoven et al., 2005). Non-protein amino acids also play important roles in this process by serving as intermediates in the biosynthesis or catabolism of primary metabolites, acting as nitrogen/carbon storage compounds and, in some cases, possessing direct defensive functions against herbivores (Rosenthal, 1991).

Although numerous non-protein amino acids have been described, relatively little is known about the biosynthesis of these compounds. Studies towards the elucidation of biosynthetic pathways, using isotope labeling and enzyme purification, suggest that uncommon non-protein amino acids can have three different