

# Proline, Cysteine and Glycine: The Stress Responsive Amino Acids and their Roles in Metal Tolerance in Plants

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**Abstract**—The Amino acids are crucial to plant growth and are also the first point of affect due to stress. The tolerance in plants to various stresses is also controlled by amino acids. The amino acids - proline, cysteine and glycine which are the special cases structurally are known to be induced under stress primarily. Certain other amino acids like histidine and glutamic acid are also induced under certain abiotic stresses. Proline and cysteine are the dominant amino acids involved in stress tolerance. Proline has been reported to accumulate in tissues/organs of plants subjected to various abiotic stresses including heavy metal toxicity and appears to be a preferred organic osmoticum for many plants. Under stress like drought, salinity and heavy metal, oxidative stress is produced. Proline acts as non-enzymatic antioxidants and help plant tolerate stress. Cysteine and glycine are important components of plant chelators, which help in lowering the toxicity of metals on the other hand. Total amino acid contents as a whole may degrade in sensitive species hinting towards metabolic dys-regulation and senescence either caused by the metal directly and oxidative stress caused thereby or also due to some signalling molecules induced by the stress action. While in tolerant species several stress related amino acids may get induced more, leading to enhanced tolerance to stress. Therefore, amino acid metabolic changes play a key role in understanding the tolerance in plants against abiotic stress.

## 1. INTRODUCTION

Amino acids are the building blocks of proteins among which, histidine, proline, cysteine and glycine along with other amino acids are known to be induced significantly upon heavy metal exposure [13]. Metal induced production of ROS may also modify amino acids leading to their loss. Amino acids can be peroxidized by free radicals turning them into second toxic messengers in cells and tissues consequently, even resulting in the oxidation and depletion of vital antioxidants in vivo [26]. Reactive oxygen (ROS)-mediated oxidation of proteins, free amino acids and proteins can lead to hydroxylation of aromatic groups and aliphatic amino acid side chains, nitration of aromatic amino acid residues, nitrosylation of sulfhydryl groups, sulfoxidation of methionine residues, chlorination of aromatic groups and primary amino groups, and to conversion of some amino acid residues to carbonyl derivatives. Oxidation can lead also to cleavage of the polypeptide chain

and to formation of cross-linked protein aggregates. Furthermore, functional groups of proteins can react with oxidation products of polyunsaturated fatty acids and with carbohydrate derivatives (glycation/ glycoxidation) to produce inactive derivatives [27].

All On the other hand, histidine, proline, cysteine and glycine along with other amino acids are known to be induced significantly upon heavy metal exposure [30,13]. Proline and cysteine are the two most important amino acids involved in stress tolerance but not much is known about their free to bound ratios. Proline has been reported to accumulate in tissues/organs of plants subjected to various abiotic stresses including heavy metal toxicity and appears to be a preferred organic osmoticum for many plants [28]. Amino acids or protein content, along with other mineral nutrients in the food crops, will affect a great portion of the world population, especially in developing countries where rice grain is the main source of protein. Thus, quantification of various amino acids in response to different concentrations of As seems imperative in rice [26].

## 2. AMINO ACIDS AS AFFECTED BY STRESS

Amino acid content is depressed by high As exposure [1,2,10] as also are readily peroxidized by the free radicals generated [26]. Ile, Leu, Lys, and Val which, are highly susceptible to free radicals and their subsequent reactions with protective agents, such as ascorbate or glutathione, decreases the antioxidant potential of cells and tissues [26,4]. Histidine, an important enzyme co-factor known to accumulate more in heavy metal stress [10,19]. Proline is known to play a protective role in plants against active oxygen or hydroxyl radicals [27], further metal tolerant populations of some plants have been shown to have higher constitutive content of proline as compared to non-tolerant counterparts [27].

A study by Mishra and Dubey [26] on rice showed enhanced free proline content on increasing concentrations of arsenite which has also been observed in this study. On the

other hand free to bound ratio of proline was more enhanced in HARG corresponding to As accumulation suggesting release from protein bound contents. This corresponds with previous independent observations on free proline and As toxicity that on higher As accumulation cells signal higher accumulation of stress related metabolites [16,18] like proline to protect cells from membrane damage [26], but, when the de-novo synthesis is hampered by arsenite toxicity plant can extract Pro bound in proteins [20, 31] as well.

### 3. PROLINE- THE KEY STRESS RESPONSIVE AMINO ACID

The proteinogenic amino acid proline functions as an osmolyte, radical scavenger, electron sink, stabilizer of macromolecules, and a cell wall component [20, 31]. Under salinity, proline accumulates to whole tissue concentrations up to 1 mol l<sup>-1</sup> [10]. The root proline content in *Lactuca sativa* increased proportionally with an increase in Cd concentration causing a 13-fold rise at 100 µM Cd [10]. Zn and Cu-induced proline rise in *Lemna minor* was fairly rapid; it was measurable within 6 h of metal treatment [10]. Similarly, a Cu-dependent increase in the proline level of detached rice leaves was detected within 4 h [21]. The metal-tolerant populations of three different species namely, *Armeria maritima*, *Deschampsia cespitosa*, and *Silene vulgaris* have been reported to possess substantially elevated constitutive proline levels in different plant parts even in the absence of excess metal ions when compared with their non-tolerant relatives [10,31].

### 4. HISTIDINE – THE CHELATOR

Nearly three-quarters of all known metal hyperaccumulator plants are Ni accumulators. The Ni-hyperaccumulation trait in *Alyssum* species (Brassicaceae) has been demonstrated to be specifically linked to the ability for free histidine production [21,10]. Zn administration to tomato and soybean strongly affected amino acid concentrations. A study of metal complex equilibria in xylem fluids suggests that the major portion of Cu and Ni was bound to asparagine and histidine [31,10].

### 5. CYSTEINE

Cysteine is a central metabolite required in antioxidant defense and metal detoxification via glutathione / phytochelatin synthesis [10]. Glycine and Glu are also the fundamental metabolites for phytochelatin and chlorophyll synthesis [10,21].

### 6. OTHER IMPORTANT AMINO ACIDS

Glu with Asp are important for other amino acid synthesis by transamination, while serine participates in ion transport [31, 24]. Methionine is the precursor of ethylene, involved in cell signalling to heavy metal stress [26,10] Alanine also reported to increase in the presence of As was enhanced more in

[LARG 30]. More metal accumulation leads to enhanced H<sub>2</sub>O<sub>2</sub> production which is known to trigger abscisic acid (ABA) induced stomatal closure, impeding plant growth, but some amino acids i.e., His, Met and Asp and Glu promote stomatal opening as well and revert the ABA effect [31].

## 7. CONCLUSION

Amino acids play a key role in metal tolerance. Cysteine, Glycine and Glutamic form the basis of chelating response of the plant to mitigate the stress. Hystidine, Methionine and proline play a key role in antioxidant defence against the metal stress.

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