



Glucosinolate Metabolism and its Role in Plant Defense

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Abstract

Glucosinolates are sulfur and nitrogen containing plant secondary metabolites found commonly in the Brassicaceae and related plant families. The glucosinolates are found naturally and give pungent smell in many plants such as mustard, cabbage etc. In the plant, they generally coexist with an enzyme called myrosinase, though glucosinolates are stored in the vacuoles cells and myrosinase exist in separate but adjacent cells. As the plant tissue is damaged, glucosinolates are released and get hydrolyzed by myrosinase. The chemical nature of the hydrolysis products depends on the structure of the glucosinolate side chain, plant species and reaction conditions. Till date, more than 130 types of glucosinolates have been identified. Biosynthesis of glucosinolates takes place in three phases: amino acid chain elongation, conversion of the amino acid moiety to the glucosinolate core structure and subsequent side chain modifications. Depending on developmental stage, tissue and photoperiod, glucosinolate pattern differs between species and ecotype as well as between and even within individual plants. The change of the glucosinolate profile by several genetic and environmental factors has brought forward different theories regarding their potential roles in the plant activities and defense. However, the most accepted theory is that the glucosinolate-myrosinase system is involved in defense against herbivores and pathogens. Among many, the main signal molecules which are recognized by the plant, are derivatives of jasmonic acid, salicylic acid and ethylene which mediate the plant response resulting in the activation of distinct sets of defense genes. This review summarizes the glucosinolate biosynthesis, degradation, organization of the myrosinase-glucosinolate system and its role in the plant defense.

Key words: Glucosinolates, myrosinase, brassicaceae, defense, metabolism

INTRODUCTION

Glucosinolates are plant secondary metabolites found commonly in the Brassicaceae family with Brassica vegetables, *Arabidopsis thaliana* etc.). The glucosinolates are found naturally and give pungent smell in many plants such as mustard, cabbage etc. The pungent smell is conferred due to mustard oils produced from glucosinolates when the plant material is cut or damaged. These natural chemicals likely contribute to plant defence against pests and diseases and it is believed to contribute to the health

promoting properties of cruciferous vegetables. Till date, more than 130 types of glucosinolates have been identified. Their structural diversity arises from side chain elongation of the amino acid and their secondary modifications including oxidation, hydroxylation, desaturation, methoxylation, sulfation and glucosylation (Wittstock et al., 2002, Halkier et al., 2006). Glucosinolates have a common core structure containing a D-thioglucose group linked to a sulfonated aldoxime moiety and a variable side chain derived from amino acids (Figure 1). Glucosinolates are primarily classified into three classes depending on the

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structure of different amino acid precursors: Aliphatic glucosinolates derived from methionine, isoleucine, leucine or valine; Aromatic glucosinolates derived from phenylalanine or tyrosine, and Indoleglucosinolates derived from tryptophan.

Along with glucosinolates, plants always possess thioglucosidase enzyme called myrosinase, which catalyzes the hydrolytic degradation of glucosinolates to numerous compounds with diverse biological functions. The enzyme only comes into contact with its glucosinolate substrates if the plant tissues are disrupted as a result of wounding, insect or pathogen attack. The chemical nature of hydrolysis products depends primarily on the structure of the glucosinolate side chain, plant species, reaction conditions etc. (Bones et al., 1996, Rask et al., 2000). Glucosinolates and their hydrolysis products are generally studied as plant defense system against insects, herbivores and pathogens. They also serve as attractants to specialist insects feeding on these plants (Wittstock et al., 2004). Mostly volatile hydrolysis products are responsible for characteristic taste and smell of cruciferous vegetables. Glucosinolate degradation products, especially isothiocyanates have been shown to have anticarcinogenic properties (Fahey et al., 2006). Thus, glucosinolates and their hydrolysis products have diverse biological properties.

Rapid development of molecular and genetic tools in combination with the availability of new data on the model plant *Arabidopsis thaliana* has greatly enhanced the gain of knowledge in recent years.

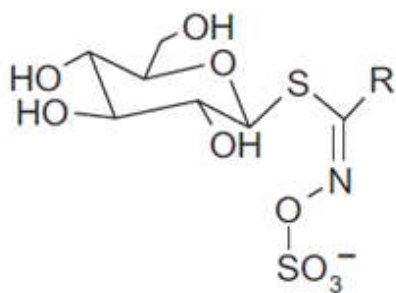


Figure 1: Glucosinolate structure. R denotes the variable side chain made up of amino acids.

Nevertheless, there are still many unanswered questions e.g. how glucosinolate diversity and accumulation are regulated in detail. A lot of detailed research is necessary to precisely regulate glucosinolate manipulation in order to exploit the potential of these compounds in improving pest

resistance and nutritional value of crop plants. This review focuses on the glucosinolate biosynthesis, degradation and their role in plant defense.

Composition of Glucosinolate

Glucosinolates are a class of organic compounds that contain sulfur and nitrogen and are synthesized from glucose and an amino acid. Glucosinolates belong to the glucosides. Every glucosinolate contains a central carbon atom, which is bound via a sulfur atom to the thioglucose group and via a nitrogen atom to a sulfate group (making a sulfated aldoxime). The central carbon is bound to a side group; different glucosinolates have different side groups, and it is variation in the side group that is responsible for the variation in the biological activities of these plant compounds. Some glucosinolates like Sinigrin is the precursor to allyl isothiocyanate, Glucotropaeolin is the precursor to benzyl isothiocyanate, Glucanasturtiin is the precursor to phenethyl isothiocyanate, Glucoraphanin is the precursor to sulforaphane etc.

Glucosinolates in Plants

In plants of the order Brassicales (Brassicaceae/Cruciferae, Caricaceae etc.), glucosinolates occur as secondary metabolites. Glucosinolates occur in cabbages (white cabbage, Chinese cabbage, broccoli), watercress, horseradish and radishes. They are typically in parts consumed, with the pungent taste of these vegetables due to breakdown products (isothiocyanates or mustard oils) of glucosinolates. The glucosinolates are also found in the seeds of these plants in significant quantity.

Biosynthesis and degradation of glucosinolates

Glucosinolates are actually the secondary compounds present in plants of the order Brassicales. This order contains the families Caricaceae (e.g. papaya), Capparaceae (e.g. caper), Cleomaceae (e.g. spiny spider-flower) and Brassicaceae (including many vegetables like cabbage, cauliflower, Brussels sprouts, turnip, radish, mustard, rapeseed, etc., and *Arabidopsis thaliana*). Glucosinolates are synthesized by a combination of proteinogenic amino acids (alanine, leucine, isoleucine, methionine, phenylalanine, tryptophan, tyrosine and valine), which undergo one to several rounds of chain elongation (especially for methionine) before the glucosinolate core structure is synthesized finally. The biosynthesis of glucosinolates comprises three phases: (i) amino acid chain

elongation, in which additional methylene groups are inserted into the side chain, (ii) conversion of the amino acid moiety to the glucosinolate core structure, (iii) and

subsequent side chain modifications (1) (Figure 2). Most of the enzymes involved in the core structure biosynthesis have been identified and cloned so far (Halkier et al., 2006).

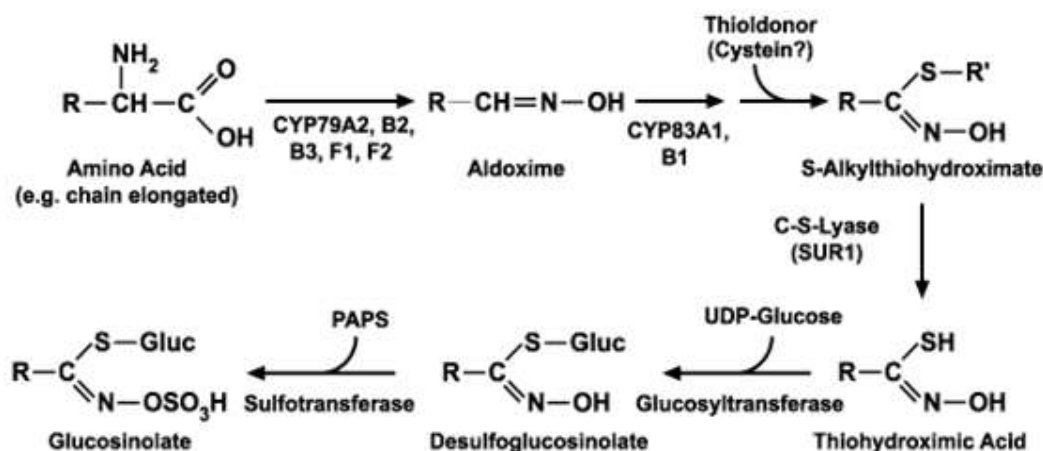


Figure 2: Steps in biosynthesis of glucosinolates in certain plants

In plants, glucosinolates are stored within the vacuoles of the specialized cells. If the plants are wounded by the attack of a pathogen or herbivore, the compounds are released from the vacuole and come in contact with the thioglucosidase enzymemyrosinase, which are localized in myrosin cells or bodies. The intermediate product rearranges to form several possible degradation products depending on the reaction conditions, the glucosinolate side chain and the presence of certain protein cofactors. Figure 3.

Relationship between glucosinolates and defense signal molecules in plants

A plant is unable to escape an attack by moving to a more favourable environment, if it is attacked by microbial pathogens and herbivores. Therefore, plants have evolved a broad range of defense mechanisms against these herbivores and pathogens. Among many, the main signal molecules which are recognized by the plant, are derivatives of jasmonic acid, salicylic acid and ethylene which mediate the plant response resulting in the activation of distinct sets of defense genes (Raymond et al., 1998, Turner et al., 2002). Several studies have indicated changes in glucosinolate pattern on treatment with signal molecules, which provide another indication for a defense related role of glucosinolates in plants.

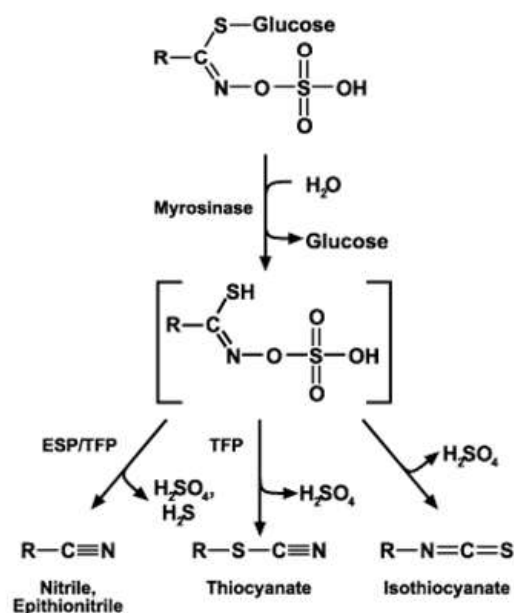


Figure 3: Glucosinolate metabolism and its degradation products

Previously it has been also studied that exogenous jasmonate application usually elicits dramatic increase of indole glucosinolates (Bodnaryk 1994, Oughty, 1995). In contrast to this, application of salicylic acid to the roots increased all classes of glucosinolates in the shoots of

oilseed rape, and the level of aromatic glucosinolate increased more than those of indole and aliphatic ones (Kiddle et al., 1994).

Concluding Remarks

Glucosinolates are very well known for their multifunctional activities ranging from plant defense systems and protection against insects, herbivores, nematodes, microbial pathogens, and in human health by reducing the risk of cancer and cardiovascular ailments. These potential benefits have established a well-deserved position for glucosinolates as a unique phytochemicals among different plant secondary metabolites studied so far. Glucosinolates exhibit certain negative effects, such as bitterness and goitre disease in animals, which caused the reduction of glucosinolate levels in crops in the past. On the contrary, their multifunctional roles have attracted the scientific arena to alleviate these problems by enhancing the accumulation of glucosinolates through metabolic engineering of their biosynthetic pathways. Studies are being done to unravel the role of glucosinolate derivatives, as well as to investigate the underlying mode of action. The process of its breakdown

is a complex process, and the outcome of the hydrolysis product depends on the glucosinolate's side chain and, more specifically, the interplay between the myrosinase and the specifier proteins, such as ESP and NSP, modifiers such as ESM1 and MVP1, and the nitrilases and glutathione transferases. Hence, regulated expression of its biosynthesis and metabolism will provide an insight for controlling insect, herbivore damage, and disease prevention. Recently, Borgen et al. developed transgenic *B. napus* plants with the seeds lacking the myrosin cells, providing a good model to study plant defense systems and other related functions. More efforts in this direction could lead us to new avenues in plant-pathogen interactions and stress tolerance studies. Earlier the research efforts on glucosinolates were mainly focused on the genes involved in its biosynthesis and their regulation; however, there is still a lack of knowledge on its transport mechanism. Therefore, the need is to pay emphasis on the study of its transport mechanism and its differential accumulation in different plant parts. Hence, the glucosinolate-myrosinase system is a potential source for engineering the plants' endogenous defense against various biotic and abiotic stresses.

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