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Role of Phenolics in Plant Defense Against Insect Herbivory

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Abstract

Several secondary metabolites synthesized in plants have significant defensive role against herbivores, pests and pathogens. The defensive role played by such secondary metabolites include deterrence/antifeedant activity, toxicity or acting as precursors to physical defence systems. Many specialist herbivores and pathogens being one step more evolved circumvent the deterrent effects of secondary metabolites but actually utilize these compounds as either host recognition cues or nutrients. Phenylpropanoids are a group of phenolics, it is a chemically diverse family of compounds ranging from simple phenolic acid to large and complex polymers such as tannins, lignin and flavonoid. Phenolics derived from amino acids and their precursors and some compounds which derived from shikimic acid pathway. This group includes metabolites derived from the condensation of acetate units (e. g., terpenoids) and produced by the modification of aromatic amino acids (e. g., phenylpropanoids; cinnamic acids, lignin, precursors, hydroxybenzoic acids, catechols and coumarins), flavonoids, isoflavonoids and tannins like dihydroxyphenols and flavonols polymerized by the action of peroxidases and polyphenoloxidases. This review present an overview of biosynthesis and role of phenolics in plants by which they protect themselves against herbivory.

Introduction

An enormous variety of secondary metabolites are derived from shikimic acid or aromatic amino acids, many of which have important roles in defense mechanism against herbivory and wounding [1]. The term, phenolics, has been used to describe a group of structurally diverse plant secondary metabolites [2]. Plants produce a high diversity of secondary metabolites having a prominent protective function against predators and microbial pathogens for having a toxic nature and repellence to herbivore and microbes. Some of these metabolites are also known for defense against abiotic stress (e. g., UV-B exposure) as well as means for the communication of the plants with other organisms [3, 4], insignificant for growth and developmental processes [5, 4]. Secondary metabolites are therefore, most important part of the plants defense system against pests and diseases including root parasitic nematodes [6]. Plants produce a large variety of secondary products that contain a phenol group, a hydroxyl functional group on an aromatic ring called phenol, a chemically heterogenous group also.

Phenolic compounds are aromatic compounds bearing one or more hydroxyl group on an aromatic ring. Phenylpropanoids are the phenolic compounds derived from phenylalanine. There are >8000 known phenolic compounds, roughly categorized into 14 compound classes based on the number of carbons and their arrangement [7]. Only some of them have been implicated in plant herbivore interactions. Amongst these are the benzoic acids, hydroxycinnamic acids (and their conjugates), furanocoumarins, coumarins, stilbenes, flavonoids (especially flavonols), hydrolysable tannins, condensed tannins and lignin [8]. The role if phenolic compounds in plant herbivore interaction has been described by different worker such as hydroxycinnamic acids may act as cell wall cross-links that fortify and protect plant cell walls against chewing damage [9,10]. Tannins accumulate in many plant species specially in trees, in response to herbivory [11,12]. In insects, tannins produced lesions in the midgut of the animals feeding on plants. Insects that normally feed on tannins have been found to have a relatively thick protective peritrophic membrane lining the midgut epithelium. It is presumed to be an

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evolutionary evidence that tannins play a role in plant insect interactions [11,12,13].

Biosynthesis of Phenolic Compounds

Phenolics are widely distributed in plants, and accumulate during normal growth and development. Thus, phenolics are constitutive products in plants and are present prior to insect or mammalian herbivory-induced damage (i. e. wounding). Indeed, roles for phenolics are pre-formed (constitutive) defense against herbivory [14, 9, 10]. The phenolics act as physical barriers present as cell wall bound phenolics, lignin suberin, and cuticle-associated phenolics as well as stored compounds that have deterring (antifeedent) or directly toxic (insecticidal) effect on herbivores [15].

Phenylpropanoid metabolism has been divided into two main stages, 'general phenylpropanoid metabolism' (i. e. biosynthesis of hydroxycinnamic acids) and 'pathway specific metabolism' (i. e. hydroxycinnamic acids as precursors to specific classes of phenylpropanoids such as flavonoids or coumarins [7]. But later, it has been found that the interconversion between hydroxycinnamic acid does not necessarily lie within a defined general pathway [16] and in fact differentiate into compound class specific pathways as early as cinnamate (or cinnamoyl-CoA), after its hydroxylation to form p-coumarate. Consequently 'general phenylpropanoid metabolism' consists of two common steps: the deamination of phenylalanine by phenylalanine ammonia lyase (PAL) and the 4-hydroxylation of cinnamate by cinnamate-4-hydroxylase (C4H) [13]. Shikmic acid pathway is a key intermediate in the synthesis of phenylpropanoids and amino acids [13] [Fig. 1].

Shikimate Pathway

The biosynthesis of most phenylpropanoid begins with amino acid phenylalanine tyrosine, and tryptophan. The first enzyme in the shikimate pathway is 3-deoxy-D-arabino-heplulosonate-7-phosphate (DAHP) synthase, which catalyses the condensation of one molecule each of phosphoenolpyruvate and erythrose-4-phosphate [13]. Both of these starting material are derived from primary metabolism. DAHP synthase has been shown to be induced, at the transcript protein, and enzymes activity levels as noted, in wounded potato tubers and tomato fruits [17].

The main classes of soluble phenolic compound involved in the response of plants to wounding and herbivory are hydrocinnamic acids (and their conjugates and derivatives) and tannins(via flavonoids)[Fig.1]. However, phenylpropanoids are derived from phenylalanine, which also has to be synthesized *de novo* as part of the overall wound/herbivory response, and it is important to consider this as an early stage of induced phenylpropanoids metabolism. Phenolic compounds generally divided into different subcompound such coumarinfurano-coumarins, lignin, isoflavonoid tannins, flavonoids, there roles in plants are described below [Fig. 1].

A. Flavonoids

Flavonoids are C_{15}compounds and form the building block of condensed tannins [13]. It is one of the largest classes of plant phenolic, perform different functions in plant system including pigmentation and defense [18]. The first key enzyme of flavonoid pathway is chalcon synthase (CHS) catalyses the first step in this pathway [19] [Fig. 1].

Isoflavonoids are derived from a flavonone intermediate, naringenin ubiquitously present in plants and play a critical role in plant developmental and defense response. The metabolic fate of naringenin is an important branch point in flavonoid biosynthesis giving rise to the flavonols (e. g. kaempferol, quercitin), dihydroflavonols, isoflavonoids (e. g. genistein) and flavones (e. g. apigenin), these all are collectively called as flavonoids [13][Fig.1].

B. Coumarins

Coumarins are simple phenolic compounds, widely distributed in vascular plants and appear to function in different capacities in various plant defense mechanism against insect herbivores and fungi. It is product of shikimic acid pathway [4] [Fig. 1]. Halogenated coumarin derivatives work very effectively *in vitro* to inhibit fungal growth. For example, 7-hydroxylated simple may play a defensive role against parasitism of *Orobanche cernua* by preventing successful germination, penetration and connection to host vascular system [20].

C. Lignin

Lignin is highly branched polymer of three simple phenolic alcohol known as monolignols, its physical toughness deter feeding by herbivorous animals and its chemical durability makes it relatively indigestible to herbivores and insects pathogens[21]. Lignifications block the growth of pathogens and are a frequent response to infection or wounding [24, 4]. But the principle function of lignin is structural, it has also been implicated as a defensive chemical. Lignin itself is not readily digested by herbivores and, because it is covalently linked to cellulose and cell wall xyloglucans, its presence decreases the digestibility of these polymers as well [23].

D. Tannins

The biological role of tannins is not clear, but tannin do appear to deter feeding by many animals when tannins free alternative are available [23]. Tannins are general toxins that significantly reduce the growth and survivorship of many herbivores and also act as feeding repellents to a great diversity of animals. They cause a sharp, astringent sensation in mouth as a result of their binding of salivary proteins. Due to this, mammalian herbivores, mammals such as cattle, dear and apes characteristically avoid plant with high tannin contents [24][Fig.1].

There are several examples of constitutive phenolics acting as feeding deterrents for herbivores and inhibitors of enzymes [25]. The evidence for the role in resistance against fungi, bacteria and nematodes is more circumstantial [26]. In this relations it appears to be the speed and duration of *de novo* biosynthesis of phenolics that is more important for resistance than the constitutive concentration.

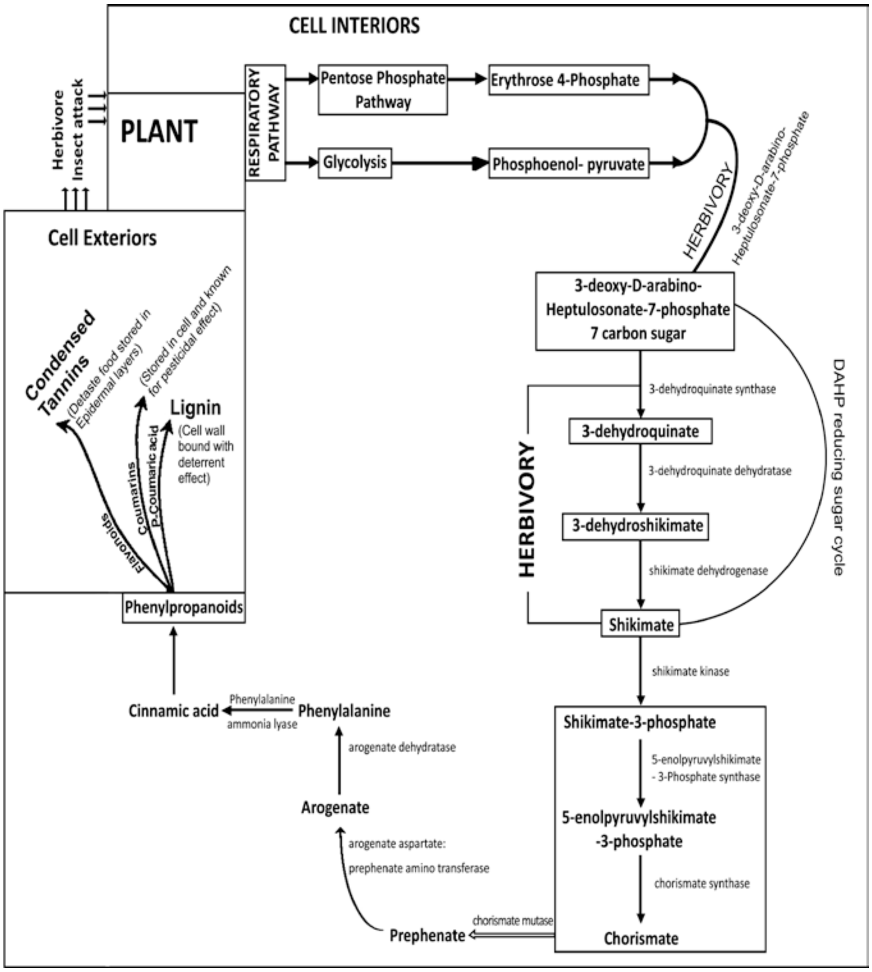

Fig. 1.: Biosynthesis, release and storage of defensive phenolics in plants attacked by herbivores. (adapted and modified in parts from Razal et al. 1996; Strack 1997, Croteau et al. 2000)

Role of Plant Phenolics and Resistance to Insects

The more complex interaction between insect pests, insect predators and phenolics in the host plant has been reported in two species of Mimosoideae [27]. Strong correlation between the constitutive concentrations of catechol based phenolics in strawberry leaves and resistance to the two spotted spider mites namely, (*Tetrancychus urticae*) [28]. A cotton phenolic pigment (gossypol) also had a deterrent effect against numerous insect pests [29]. This is strong evidence for the role of gossypol in resistance against nonspecialist insect pests, specialist feeders have developed strategies to overcome the gossypol toxicity [1]. The development of the mites on cultivars containing high concentration of phenolics was clearly suppressed, especially in cultivars with high catechol concentrations. The delayed development of the mites may be due to the phenolics covalently binding to mite digestive enzymes and inactivating them. It has also been shown that mites damage induce the *de novo* synthesis of phenolics in plants [30]. Other examples of resistance to the two spotted spider mites involving phenolics include their interaction with peppermint (monoterpenes and phenolics) [31].

The role of tannins and resistance to the larvae of the oak moth (*Opheropthera brumata*) was reported by Feeny [32]. The moth larvae feed on the young leaves of the trees in the spring but by mid-June they suddenly stop. No environmental factors or the levels of predators could account for this change in feeding. Feeny [32] found that the levels of tannins in the leaves significantly increased prior to cessation of feeding by the larvae The deterrence was thought to be because of the complexation of the tannins with the host proteins (making them indigestible) and the reaction of the tannins with digestive enzymes in the gut of the larvae.

Conclusion

The distribution of a secondary metabolite within a plant, both between tissues and during growth and development, is rarely uniform. Many compounds are synthesized by, and accumulate in, young developing tissues, particularly leaves, or in reproductive tissues such as flowers and seeds. Some secondary metabolite systems are dynamic, responding to attack, infection or stress, and that enhanced synthesis/ accumulation of secondary metabolites is part of an integrated defence mechanisms.

In this article we described the metabolism of phenylpropanoids or phenol (including coumarins, isoflavonoids, lignin and tannins in plant against herbivory. This review of induced phenylropanoids metabolism, at the transcript and/or enzyme level, is by no means exhaustive. The Figure 1 describing hydroxyl synthesis of flavonoids, coumarins and *p*-coumaric acid and condensed tannins vis-à-vis their role in plant insect interactions may serve as model.

From all of these we conclude that the study of wound and/or herbivory induced phenylpropanoid metabolism also provides the opportunity to discover novel biochemistry involved in the plant herbivore interaction and defenses.

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