Plant Secondary Metabolites Involved in Biotic Stress Tolerance

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Contributor: Jameel M. Al-Khayri, Ramakrishnan Rashmi, Varsha Toppo, Pranjali Bajrang Chole, Akshatha Banadka, Wudali Narasimha Sudheer, Praveen Nagella, Wael Fathi Shehata, Muneera Qassim Al-Mssallem, Fatima Mohammed Alessa, Mustafa Ibrahim Almaghasla, Adel Abdel-Sabour Rezk

Plant secondary metabolites are categorized into terpenoids (such as saponin), phenolics (such as flavones, lignin, isoorientin, tannin, flavonoids, and glyceollin), and nitrogen compounds (such as sinigrin and dhurrin). Different secondary metabolites show different metabolisms, which help to suppress the growth and development of herbivores. Phenolic metabolites with volatile compounds repel herbivores and protect the plant.

Keywords: biotic stress ; plant secondary metabolites ; feeding deterrents

1. Terpenes

Terpenes/terpenoids are the largest diversified chemical group of secondary metabolites, which contain more than 22,000 compounds [1]. Terpenes are present in almost all plants. Usually, 5-C isopentanoid units play an essential role in the formation of terpenes. According to the number of isoprene units, terpenes are further classified [2]. Terpenes are commonly synthesized from isomer dimethylallyl diphosphate (DMAPP) and isopentenyl diphosphate (IDP). These blocks are synthesized with two different pathways: the pyruvate-derived plastidial 2-C-methyl-D-erythritol-4-phosphate (MEP) pathway and the acetyl-CoA-derived cytosolic mevalonate (MVA) pathway [3].

In plants, terpenes have both physiological and ecological functions related to plant hormones (gibberellin, abscisic acid), insecticides, allelopathy, and insect pollination. Terpenes such as menthol, camphor, pyrethrins, artemisinins, and farnesol play an important role against protozoa, bacteria, and fungi [1]. A common example, capsaicin, which is present in pepper chilly, shows bactericidal properties. Terpenes generally perform several functions in plants. They act as a defense molecule against pathogens and herbivores, plant growth regulators, and compounds that influence (indirectly or directly) the development and growth of neighboring plants. As per a few reports, hemiterpene increases photosynthesis and thermo-tolerance in some plant species. It has been shown that when oak (*Quercus ilex*) leaves are fumigated with monoterpenes, the thermo-tolerance of the plant increases [4]. Terpene derivatives such as sterol work as an important component in cell membranes by stabilizing the interaction with phospholipids [5]. At the time of photosynthesis, volatile gas such as hydrocarbon isoprene (C_5H_8) is produced, which avoids damage to the cell membrane from extreme light or temperature conditions and protects it. Tetraterpenes such as carotenoids (orange, red, and yellow pigments) work as an accessory pigment in photosynthesis. Tetraterpenes protect photosynthetic tissues from photooxidation as well [4]. Carotenoids prevent the synthesis of singlet oxygen by extinguishing the chlorophyll molecules from the triplet state [6]. Terpenes such as plastoquinone and ubiquinone act as electron carriers. Carotenoids are precursors of abscisic acid, which regulates the stress and developmental responses in plants. Terpenes are present in almost all plants. Usually, 5-C isopentanoid units play an essential role in the formation of terpenes. According to the number of isoprene units, terpenes are further classified [2]. **Table 1** illustrates the classification of terpenes based on the number of isoprene units they contain.

Table 1. List of secondary metabolites with their category and function present in different plants.

Secondary Metabolite	Category	Plant	Function	Reference
Pyrethrins	**Monoterpenes**	***Chrysanthemum indicum***	**Neurotoxic to parasitic wasps, insects, moths, etc.**	[1]
Hemigossypol	**Sesquiterpenes**	***Gossypium hirsutum***	**Antifungal**	[7]
Gossypol	**Diterpene**	***Gossypium hirsutum***	**Antifungal and antibacterial**	[1]

Secondary Metabolite	Category	Plant	Function	Reference
Cucurbitacin-C	Triperpene	*Cucurbita* spps.	Toxic to spider mites	[8]

2. Sulfur-Containing Secondary Metabolites

Sulfur-containing metabolites protect plants from pathogenic microbes either by acting as phytoalexins or as phytoanticipants. Glucosinolates, thiosulfinates (such as allicin, which is generated from cysteine sulfoxides), and antimicrobial peptides (such as defensins and thionins) are examples of sulfur-containing secondary metabolites [1]. Most of them are volatile in nature, acrid in taste, or obnoxious in smell. These secondary metabolites are classified into two different classes according to their path of synthesis. In the first group, hydrolysis of the myrosinase enzyme results in formation of glucosinolate. Members of the cruciferae family show this pathway. Cabbage, broccoli, and nasturtium are examples of the glucosinolate–myrosinase pathway. In the second group of sulfur-containing secondary metabolites, hydrolysis of the alliinase enzyme results in the formation of alliin, which is commonly found in the genus Allium. Garlic (*Allium sativum*), leeks (*Allium porrum*), and onion (*Allium cepa*) are examples of the alliin–alliinase pathway [2]. These two pathways are evolved in herbivore defense and avoid pathogenic attack [9].

3. Lectins

Lectins are widely found in different plant species, which are bound to a specific group of sugars. Lectins are ubiquitous, carbohydrate-binding (glyco) proteins that show a protective function against various pests. In legume seeds, it is present abundantly. Lectins show the agglutinating property in a cell due to the presence of multiple binding sites. In a few lectins, a single binding site is present. Lectins such as *wheat germ* agglutinin (WGA) (wheat germ), *Phaseolus hemagglutinin* (PHA) (kidney bean seeds), and *Galanthus nivalis* (snowdrop lectin, GNA) (snowdrop) are studied widely as per their insect toxicity and chemical characteristics. GNA and PHA show specific binding with mannose and alpha-GalNAc, respectively [10]. In transgenic plants such as tobacco, when GNA is expressed in a gene, it shows more efficient protection against aphids. Their study proved that lectins could be used for crop tolerance to pests. Chitin and GlcNAc beta(1,4) GlcNAc-specific binding was observed in WGA. WGA protects against toxicity by preventing the production of peritropic membranes in lumen-rich midgut in chitin [10].

Lectins show strong insecticidal potential in herbivore digestive systems by working as an antinutritive. Lectins show stability over a large pH range, and they damage the epithelial lumen membrane, therefore, impeding the absorption and digestion of nutrients. *Galanthus nivalis* L. agglutinin (GNA) is the first plant lectin studied against hemipteran insects for its insecticidal properties. Insects such as lepidopteran, coleopteran, and homopteran work as promising agents [11]. Due to a specific interaction with carbohydrate residue present in the cell membrane, mannose-binding lectins have shown effective results against sucking insects. **Table 2** presents a comprehensive list of lectins identified in plants, along with their target insects.

Table 2. List of lectins present in plants with target insects.

Lectin	Plants	Insects	Reference
Allium sativum leaf lectin	*Cicer arietinum*, *Nicotiana* spp.	*Aphis craccivora*, Aphids	[12]
Snowdrop lectin	*Triticum aestivum*, *Oryza sativa*, *Arabidopsis* spp.	*Nilaparvata lugens*, Aphids, *Pieris rapae*, *Spodoptera littoralis*	[13]
Nictaba-related lectins NICTABA, PP2	*Nicotiana* spp.	*Manduca sexta*, *Spodoptera littoralis*, *Acyrthosiphon pisum*	[14]
Arum maculatum tuber lectin	*Arum maculatum*	*Aphis craccivora*, *Lipaphis erysimi*	[10]
Bauhinia monandra leaf lectin, Jacalin-like lectins	*Nicotiana* spp., *Triticum aestivum*	*Anagasta kuehniella*, *Mayetiola destructor*, *Callosobruchus maculates*, *Zabrotes subfasciatus*	[15]

4. Nitrogen-Containing Secondary Metabolites

Carbon elements contribute nearly 40% to the dry weight of plants, whereas nitrogen elements contribute only 2%. However, these organic substances are present in large numbers in plants. These secondary metabolites include cyanogenic glycosides, alkaloids, and some non-protein amino acids. Ammonia is the first form of nitrogen that is present in plants and produced during nitrogen fixation in plant roots. According to plant physiologists, the universal growth hormone, auxin, is an important nitrogen compound. Meanwhile, alkaloid is the largest known class in plants. These metabolites are mainly known for their anti-herbivore role in plants.

5. Phenolic Compounds

Phenolic chemicals are a large class of secondary metabolites necessary for plant development and survival. They are involved in a wide range of physiological and biochemical processes, including plant defense against biotic and abiotic stresses. These substances range in chemical complexity from simple phenolic acids to complex tannins and lignins. They are defined by the presence of one or more hydroxyl (-OH) groups connected to an aromatic benzene ring [16]. Plants can activate genes involved in the phenylpropanoid pathway in response to herbivore feeding, which results in the manufacture of different phenolic chemicals. By blocking digestive enzymes or attaching to proteins, these substances can have harmful effects on herbivores that impair their ability to grow, develop, and reproduce. The production of particular phenolic chemicals in response to herbivory can also draw the herbivores' natural predators, giving the plant additional defenses [8]. Phenolic heteropolymer lignin has a crucial role in plant defense mechanisms against pathogens by limiting their entry via increasing the toughness of leaves, reducing the feeding, and reducing the nutritional value of leaves. Polyphenol oxidase and peroxidase are enzymes that catalyze the oxidation of phenolic compounds, resulting in the formation of quinones. Quinones can bind covalently to proteins in herbivorous insects, inhibiting their function and serving as a potential defense mechanism in plants against insect damage. This process is known as phenol oxidation and is an important part of plant defense against herbivores [11].

It has been demonstrated that phenolic chemicals produced by the phenylpropanoid pathway build up in rice plants after pest infestation. Vanillic acid, syringic acid, cinnamic acid, and cinnamic acid derivatives are among the phenolic substances with increased concentrations. These phenolic acids were discovered to be prevalent in pest-infested rice plants [17]. Plant disease resistance is greatly influenced by phenolic chemicals. For instance, to ward off onion smudge disease, *Colletotrichum circinans*-infected onion scales accumulate catechol and protocatechuic acid. Similar to how tomato plants respond to being infected with *Fusarium oxysporum*, the cause of fusarium wilt, they respond by accumulating phenolic chemicals, including ferulic, caffeic, and vanillic acid in recovered leaves and roots. Additionally, the bacterium *Pseudomonas syringae* can alter the phenolic acid composition and improve extracellular phenolic accumulation in *Nicotiana tabacum* [16]. Wheat cultivars that have higher levels of cell-bound and soluble phenolics are less vulnerable to cereal aphids (*Rhopalosiphum padi*) compared with those with lower phenolic concentrations. Strawberry leaves that have a higher constitutive concentration of catechol-based phenolics are more resistant to the two-spotted spider mite (*Tetranychus urticae*), which is attributed to the high concentration of phenolics that suppress mite development in cultivars, especially those with high catechol concentrations. The concentration of phenolics in the bark of American beech trees *(Fagus grandifolia*) remained elevated even six months after being attacked by *Nectaria coccinea var. faginata* [18].

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