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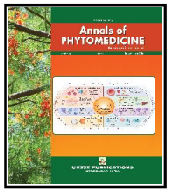

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Plant chemical defense: Synthesis, distribution and role of phytoalexins and phytoanticipins against biotic stresses

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Abstract

Biotic stresses caused by pathogens (bacteria, fungi, and nematodes) and insect herbivores significantly constrain global crop productivity and threaten food security. To recognize herbivore and pathogen attacks, plants have developed sophisticated mechanisms to defend themselves by converting those signals into appropriate biochemical and physiological responses. Plant defense mechanisms against stresses can be divided into structural (physical barriers such as trichomes, thorns, waxy or thick cuticle, *etc*.) and chemical defenses (both inducible and constitutive defenses). Phytoalexins are a part of the plant's inducible defense system. These low molecular weight antimicrobial compounds are synthesized de novo in response to a biotic attack or threat. Due to their antimicrobial activity, they disrupt the cell membrane, inhibit enzymatic activity, and interfere with the pathogen/herbivore's cellular respiration. Additionally, phytoalexins act as insect antifeedants by producing compounds unpalatable to the insects. Unlike phytoalexins, constitutive chemical defense or phytoanticipins are pre-formed and are already present in healthy plant tissue. These serve as a first line of defense against potential herbivores or pathogens. When plant tissues are damaged or under attack, phytoanticipins spring into action, directly combating threats by disrupting pathogen membranes or blocking essential enzymes needed for nutrient uptake. This paper provides a comprehensive overview of plant chemical defenses, exploring how phytoalexins and phytoanticipins are produced, stored, and deployed against pathogens and insect herbivores.

1. Introduction

Millions of years of evolution have resulted in plants developing their own set of personalized arms and ammunition against external threats. In their natural habitat, under field conditions, plants are frequently subjected to a wide range of environmental stresses. Any external factor that disrupts or blocks a plant's growth, metabolism or development is regarded as a stress condition. These are conditions that severely disrupt the normal growth and development of plants (Verma *et al.*, 2013). The various factors that cause stress in plants can be primarily divided into biotic and abiotic stress. While abiotic stress encompasses the non-living environmental factors like extreme temperatures (both hot and cold), drought, flooding, salinity, heavy metals toxicity, UV radiation, *etc.* (Gull *et al.*, 2019). On the other hand, biotic stresses are caused by other living organisms, like bacteria, fungi, virus, nematodes, insects and weeds (Gull *et al.*, 2019). Biotic stresses are a major concern, as they adversely affect the plant productivity and are responsible for both pre- and post-harvest losses. In spite of being sessile organisms, plants have developed a highly efficient and sophisticated defence mechanism to overcome biotic stresses. The plant defense mechanism is a combination of structural and chemical defenses that safeguard the plant against ongoing pathogen and insect herbivory.

When a plant is exposed to extreme stress conditions, it leads to the activation of plant defense at morphological, physiological, biochemical and molecular levels. Plant structural defense includes the morphological or physiological modifications that give the plant a fitness advantage by deterring herbivores from feeding or inhibiting the attack of a pathogen (Hanley *et al.*, 2007). Physical barriers in plants are present in the form of thick and waxy cuticle, different thorns and spines (spinescence), trichomes, toughened or hardened leaves (sclerophylly), *etc.* (Hanley *et al.*, 2007). Structural defense in plants is based on avoidance mechanism which play the role of structural deterrence. Another form of defense in plants is the production of chemical compounds, which is discussed in detail below.

The chemical defense mechanism in plants is mediated by the production of plant secondary metabolites. Secondary metabolites are often derived from primary metabolites, which have been labelled as such based on early research, where plant metabolites were divided into "primary" and "secondary", based on their role in the plant system in defense, signalling and ecological interactions (Ashraf *et al.*, 2018). Primary metabolites are involved in primary functions

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like growth, photosynthesis, reproduction and development, while secondary metabolites have no direct involvement in these roles. Secondary metabolites are synthesized by plants, specifically as a part of their defense mechanism. Plants have been reported to deploy 200,000 secondary metabolites which can be classified into different taxonomic groups (Hartmann, 2007). The concentration of these plant metabolites varies among individuals and its production is heavily influenced by the type of external stimulus/environmental factors applied. Secondary metabolites in plants can be partitioned into inducible and constitutive chemicals. Inducible chemicals are those that are produced when the plant is under attack, these are known as phytoalexins while constitutive chemicals are those that are present in the plant regardless of any stress, in an inactive form. These are termed as phytoanticipins (War *et al.*, 2012).

2. Phytoalexins

The concept of induced resistance had existed since the 1900s, when Noel Bernard found that certain chemical compounds acted as inhibitors of fungus, *Rhizoctonia repens* in *Orchis morio* and *Himantoglossum hircinum*, two types of orchids (Grayer and Kokobun, 2001). Muller *et al.* (1939) conducted a study on resistant and susceptible commercial varieties of potato against late blight, *Phytophthora infestans*. Post-inoculation with the pathogen, the induction of symptoms was observed in the inoculated tubers. Tubers belonging to resistant varieties inhibited the growth and spread of the pathogen while those belonging to susceptible varieties could not stop the spread of the infection. Following biochemical analyses, it was concluded that there were certain antimicrobial compounds found at the site of infection in case of resistant varieties, synthesized at the site of infection, which were responsible for preventing the spread of the pathogen. These compounds were either absent or were in very low amounts in susceptible varieties. These antimicrobial compounds were later named as "phytoalexins". It was also suggested that the rapidity and magnitude of phytoalexin accumulation, rather than the magnitude alone, were critical features required for providing potato tubers resistance against *P. infestans* (Ahmed and Kovinich, 2021). The word "phytoalexins" was coined by Muller and Borger (1940), "phyto" means plant and "alexin" refers to a warding off compound. Since its first report, different definitions have been formed over the years, however, the widely accepted definition is the one given by Paxton (1980), which states that phytoalexins are "low molecular weight, antimicrobial compounds that are both synthesized and accumulated in plants after exposure to microorganisms or abiotic agents".

In 1960, the first phytoalexin "pisatin" was isolated (Cruickshank and Perrin, 1960) and characterized (Perrin and Bottomley, 1962) from *Pisum sativum*. Since then, many phytoalexins have been found from plants belonging to different families (Solanaceae, Linaceae, Fabaceae, Apiaceae, Chenopodiaceae, Rosaceae, Poaceae, Euphorbiaceae, Rutaceae, Moraceae, Asteraceae, Piperaceae, *etc.*) (Tiku, 2020). Phytoalexins have generated a lot of interest in the last four decades, with huge advances in the field of biochemical and molecular basis of phytoalexin synthesis. Genes responsible for encoding of enzymes involved in biosynthetic pathways are now well studied.

2.1 Distribution of phytoalexins

Chemically, phytoalexins belong to different structural classes and are known to be species-specific. Their synthesis also depends on the type of external stress applied. Some of the common reported chemical classes of known phytoalexins are flavonoids, isoflavonoids, terpenoids, alkaloids, phenolics, indole compounds, *etc.* (Chripkova *et al.*, 2016). An estimated number of 350 phytoalexins have been chemically characterized from different plants. Although, no official classification for phytoalexins exists, they can be categorized based on their chemical classes, as done by Sharma *et al.* (2022). Some important and well-known phytoalexins are listed in Table 1.

Table 1: List of common and important classes of phytoalexins

Chemical class	Phytoalexin	Plant	References
Flavonoid	C-Glycosyl	*Cucumis sativus* L.	McNally *et al.*, 2003
	Sakuranetin	*Oryza* spp.	Wang *et al.*, 2020
Isoflavonoid	Glyceollin	*Glycine max* (L.) Merr.	Yang and Wang, 2024 Cooper *et al.*, 2024
	Genistein		
Terpenoid	Zealexin	*Zea mays* L.	Zhou *et al.*, 2024
Diterpenoids	Momilactone, Oryzalexin	*Oryza* spp.	Valletta *et al.*, 2023
Coumarin	Scopoletin, Umbelliferone	*Arabidopsis thaliana* (L.) Heyn.	Ihnatowicz *et al.*, 2024
Phenolics	Luteolinidin	*Saccharum* spp.	Vyshnavi *et al.*, 2025
Indole-derived	Camalexin	*Arabidopsis thaliana* (L.) Heyn.	Rauhut and Glawischnig, 2009
Sesquiterpenoid	α-caryophyllene, β-humulene and guaia-1(10),11-diene	*Gossypium* spp.	Yang *et al.*, 2013 Tian *et al.*, 2016
	Gossypol, Hemigossypolone		
Stilbene	Resveratrol	*Vitis vinifera* L., *Arachis hypogaea* L.	Hasan *et al.*, 2013

Some classes of phytoalexins are associated with a particular crop family. The grass family or Poaceae are one of the most important crop families, found all across the globe in a variety of terrain. Most important cereals, from a consumption point of view belong to this family (like rice, wheat, maize and barley). Poaceae are widely known to produce diterpenoid phytoalexins like kauralexins, oryzalexins,

sakuranetin, zealexins, and momilactones (Ejike *et al*., 2013; Poloni and Schirawski, 2014). Characterization of maize, barley, wheat and rice labdadienyl/copalyl diphosphate synthase (CPS) using molecular tools, show that early functional diversification of CPS gene in cereal crops (Peters, 2006). CPS is an important catalyst of labdane related diterpenoid biosynthesis. Some plants also produce flavonoid phytoalexins (Bizuneh, 2021).

Fabaceae make up the third largest plant family and hence, a considerably high number of phytoalexins have been reported from this family. Most of the phytoalexins produced by the individuals of this family belong to the isoflavonoid class (Jeandet *et al.*, 2011). The first known phytoalexin, pisatin, an isoflavonoid was isolated from *P. sativum*. Maackiain is found in many Fabaceae plants like chickpea, garden pea and alfalfa (Desjardins, 2024). Chickpeas and *Medicago trunculata* produce medicarpin reduction of medicarpin yields vestitol in *Lotus japonicus* (Masunaka *et al.*, 2011). Soyabeans are well known for their production of isoflavone, such as genistein, which has antidiabetic properties (Sharifinejad *et al.*, 2024). Three types of glyceollins, glyceollin I, glyceollin II, and glyceollin III, are produced by soybean (Yang and Wang, 2024). More than 50 non-leguminous families, including Magnoliopsida Bryopsida, Liliopsida, and Pinopsida are also known to yield isoflavonoids (Lapcýk, 2007).

2.2 Elicitation of phytoalexin biosynthesis in plants

Although, the biosynthesis of phytoalexins in plants varies drastically from species to species, the most common component in all cases is the presence of an elicitor, which are molecules produced by a pathogen or the plant itself, which are known to stimulate defense responses in plants (Hahn, 1996). Elicitors may be fatty acids, glycoproteins, peptides, polysaccharides, and pectic enzymes in nature (Dixon, 1986). More recently, studies have reported that elicitors may be general or race-specific. Structural components of pathogen cell wall like lipopolysaccharides, glucan, flagellin, and chitin also act as general elicitors (Abdul Malik *et al.*, 2020). Although, initially, elicitors were used to refer to molecules that induce the production of phytoalexins in plants, it is now used to refer to those compounds in general that play a role in induction of plant defense mechanism, including hypersensitive necrosis, production of oxidative burst (Svalheim and Robertsen, 1993). Like pathogen-host interaction, elicitors are also known to be highly species-specific, the pathogenicity of the host is and specificity of the elicitor is interrelated. According to the gene-for-gene hypothesis, the resistance of a plant against its pathogen is triggered due to the interaction between the products of the pathogen avirulence gene and the plant resistance gene (Ji *et al.*, 1998). Resistance against an oncoming pathogen is completely dependent on the plant's innate immunity and systemic signaling from the infection site (Lapin and Van den Ackerveken, 2013).

Plants have two types of immunity: plant innate and plant-induced immunity. Plant innate immunity relies on pre-existing receptor molecules in the cell, it is made up of pathogen-associated molecular patterns (PAMP)-triggered immunity (PTI) and effector-triggered immunity (ETI) (Boller and He, 2009). PTI are triggered by PAMPs while plant induced immunity, also known as just ETI, require certain effector molecules to get activated. PTI is activated when pattern recognition receptors (PRRs), present on the surface of the plant, perceive and recognize the PAMPs/microbe-associated molecular patterns (MAMP)/herbivory-associated molecular patterns (HAMPs) (considered as non-host resistance) and ETI is activated when R proteins of plants identify an effector molecule (considered as host resistance) (Abdul Malik *et al.*, 2020). This leads to Ca^{2+} signaling, activation of mitogen activated protein kinases (MAPKs) cascades, accumulation of hormones, production of reactive oxygen species (ROS) and expression of pathogenesis-related protein (PR protein) (Villena *et al.*, 2018). MAPKs perceive signals form plant receptors, then amplify and transmit the signal to tissues for defense activation (Nadarajah *et al.*, 2009). The induction of immunity in plants leads to cell death in the site of infection, finally resulting in hypersensitive response (HR) and programmed cell death (PCD) (Abdul Malik *et al.*, 2020) to prevent the spread of infection. Various signaling molecules like salicylic acid (SA), methyl salicylate, jasmonate acid (JA), and ethylene (ET) are involved in the activation of defense genes in plants, involved in plant defense (Robert-Seilaniantz *et al.*, 2011). SA signaling pathway induce plant defense against biotrophic pathogens and ET/JA signaling pathways provide defense towards necrotrophic pathogens and herbivorous pests (Bari and Jones, 2009).

During bacterial invasion, the bacterial cell secretes effectors like Type-III secreted effector (T3E) into the plant cell, detection of these by R proteins trigger the plant defense mechanism (Segonzac and Zipfel, 2011). Peptidoglycan, a bacterial cell wall component elicits defense mechanism in rice, tobacco and *Arabidopsis thaliana* (Bertsche *et al*., 2015). In case of fungal attacks, pathogenic toxins (α-picolinic acid) (Zhang *et al.*, 2004), cell membrane and cell wall components, Cerebroside (Umemura *et al.*, 2004) and β-1,3-glucan (Hahn, 1996), trigger defense related responses in plants. Plants respond to herbivory induced wounds by identifying specific salivary components of insects. fatty acid-amino acid conjugates or fatty acid amides, present in the insect saliva act as elicitors by inducing the production of 7-epi-JA (Halitschke *et al.*, 2001).

2.3 Phytoalexin biosynthesis pathways in plants

Phytoalexins are synthesized in plants *de novo* to defend the plant against various abiotic and biotic stresses. During a pathogen attack, the pathogen first comes in contact with the cell wall. Hence, it has a multi-layer defense mechanism incorporated into it which acts as a first line of defense. Pattern recognition receptors (PRRs) are ligand-receptors which initiate the signal framework of plant defense mechanism (Bacete *et al.*, 2018). The phenylpropanoid pathway in plants is responsible for producing compounds like flavonoids, lignans, and coumarins, which are essential secondary metabolites (Fraser and Chapple, 2011). The phenylpropanoid pathway gets triggered when a cell wall comes in contact with a source of biotic stress (Jaeck *et al.*, 1992). The phenylpropanoid pathway provides the lignin-building monolignols, monolignols are hydroxycinnamyl alcohols that produce lignins, lignins provide structural and vascular support along with resistance to pathogens in plants (Boerjan *et al.*, 2003).

Throughout the years, the phenylpropanoid pathway has had different iterations (Hao *et al.*, 2014). The first substrate of a general phenylpropanoid pathway is phenylalanine. Phenylalanine is an amino acid, derived as an end product from the shikimate acid pathway (Tzin and Galili, 2010). The pathway consists of a series of hydroxylation, deamination, and methylation to give the end product (Martin and Liras, 2022). Phenylalanine ammonia-lyase (PAL) catalyzes the deamination of phenylalanine to cinnamic. *p*-

coumaric acid undergoes hydroxylation in the presence of cytochrome P450-dependent monooxygenase (P450), cinnamate-4-hydroxylase (C4H) to yield cinnamic acid. The enzyme, 4-coumarate-CoA ligase or *p*-coumaroyl-CoA Ligase (4CL) attaches a helper molecule called coenzyme A (CoA) to *p*-coumaric acid, forming *p*-coumaroyl-CoA. Chalcone synthase in the presence of three molecules of malonyl-CoA catalyzes the condensation of naringenin chalcone, which is a precursor to naringenin. The end product naringenin is obtained when chalcone isomerase (CHI) converts naringenin chalcone to naringenin. Naringenin can also be synthesized with tyrosine as the first substrate amino acid. Dicotyledons use only phenylalanine as a precursor while monocotyledons use both amino acids (tyrosine and phenylalanine) as precursors of *p*-coumaroyl-CoA (Martin and Liras, 2022). Naringenin is one of the major flavonoids found in lemon, orange, grapefruit and tomato. It confers resistance against pathogens like *Pseudomonas syringae*, *Pyricularia oryzae* and *Fusarium* spp. (An *et al*., 2021). Phenylpropanoid pathways are also responsible for the synthesis of stilbenes. Branching off from the general phenylpropanoid pathway after the production of *p*-coumaroyl-CoA, the enzyme resveratrol synthase (STS) condenses one molecule of cumaryl-CoA along with three molecules of malonyl-CoA to yield resveratrol. Resveratrol is responsible for inducing resistance against pathogens in grapevine and berries (Coutos-Thévenot *et al*., 2001). Stilbenes occur naturally in fabaceae, leguminoseae, poaceae, vitaceae, *etc.* (Jeandet *et al*., 2011).

Apart from phenylpropanoid pathway, there are other major pathways involved in the production of phytoalexins in plants. Tryptophan-dependent pathway is a well-known for its role in the synthesis of indole ascetic acid (IAA), an auxin of exceeding importance which is also known as the master regulator of almost all plant processes (Cohen and Strader, 2024). Much lesser-known fact is that the pathway also synthesizes important phytoalexins like camalexin. The tryptophan derived pathway of camalexin synthesis in *A. thaliana* is probably one of the most studied pathways in phytoalexin studies (Mucha *et al*., 2019). As the name suggests, the first step of the pathway starts from tryptophan (Trp), an aromatic amino acid, is synthesized from chorismate, by two Trp synthase encoding homologous genes, through indole-3-glycerol phosphate (Liu *et al*., 2022). Cytochrome P450 enzymes are a remarkably diverse group of enzymes, around 244 cytochrome P450 enzyme-encoding genes have been identified in *Arabidopsis* spp., they play a major role in many plant development processes (Mucha *et al.,* 2019). Tryptophan is a product of the shikimate pathway. The synthesis of Trp takes place in the chloroplast of the cell. Trp is converted to indole-3-acteldoxime (IAOx), by two cytochrome P450 homologues CYP79B2 and CYP79B3, followed by its dehydration to form indole-3-acteldoxime (IAOx) by the action of CYP71A13 enzyme (Nguyen *et al*., 2022). In the presence of glutathione-*S*-transferase, IAN conjugates with glutathione to produce glutathione-indole-3-acetonitrile (GSH(IAN)) (Su *et al*., 2011). The enzymes γ-glutamyl-peptidases and phytochelatin synthase convert (GSH(IAN)) to γ-glutamyl-cysteine indole-3-acetonitrile and indole-3-acetonitrile cysteine glycine, respectively (Moldrup *et al*., 2013). CYP71B15/PAD3 catalyzes the production of indole-3-acetonitrile cysteine conjugates, which it again converts, first to dihydrocamalexic acid (DHC), and then to camalexin (Bottcher *et al*., 2009).

Terpenoid phytoalexins occur abundantly in nature, with an estimated 25,000 reported compounds. Based on the number of carbon units in their structure, they are divided into monoterpenes, diterpenes, triterpenes, tetraterpenes, sesquiterpenes and polyterpenes (Li *et al*., 2023). In plants, terpenoids are derived from two basic building substrates, isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP), these are isomers which are synthesized by the mevalonate pathway (MVA) and methylerythritol phosphate pathway (MEP). MVA consists of six enzymatic steps and takes place in the cytosol while MEP has seven enzymatic steps and takes place in the plastids (Tholl, 2015). Pyruvate along with glyceraldehyde-3-phosphate (G3P) undergoes six enzymatic steps, catalyzed by 1-deoxy-D-xylulose-5-phosphate (DXP) synthase (DXS) and DXP reductoisomerase (DXR) to yield (E)-4-hydroxy-3-methylbut-2-enyl diphosphate (HMBPP) in seven enzymatic steps and takes place in the plastids (Tholl, 2015). Pyruvate along with glyceraldehyde-3-phosphate (G3P) undergoes six enzymatic steps, catalyzed by 1-deoxy-D-xylulose-5-phosphate (DXP) synthase (DXS) and DXP reductoisomerase (DXR) to yield (E)-4-hydroxy-3-methylbut-2-enyl diphosphate (HMBPP). The enzyme (E)-4-hydroxy-3-methylbut-2-enyl diphosphate reductase (HDR) converts HMBPP to isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP). Farnesyl pyrophosphate (FPP) is synthesized by the action of farnesyl pyrophosphate synthase (FPS), which condenses two molecules of IPP and one molecule of DMAPP (Nagegowda *et al*., 2010). FPP, geranyl pyrophosphate (GPP) and geranylgeranyl pyrophosphate (GGPP) are the direct precursors for most of the terpenoids (Li *et al*., 2023). Sesquiterpene synthase converts FPP to vetispiradiene and rishitin is produced by the action of cytochrome P450 enzymes. Diterpenoid phytoalexins in rice (Momilactone, oryzalectin, *ent*-kaurene) and maize (zealexins) are also derived from terpenoid pathways (Schmelz *et al*., 2014; Li *et al*., 2022).

2.4 Action of phytoalexins against pathogens

Phytoalexins provide resistance to plants against pathogens but the type of resistance induced is extremely dependent on the host-pathogen interaction. Under natural environmental conditions, plants have to safeguard themselves against a range of microbial pathogens, these usually constitute bacteria, fungi and nematodes. As mentioned in previous sections, the plants respond to specific elicitors produced by the pathogen, which is recognized by the plant and triggers the *de novo* transcription of corresponding genes (Kaur *et al*., 2022). Phytoalexins have been reported from a number of crops. In cereal crops like rice, more than twenty phytoalexins have been reported, mostly diterpenoids (Kariya *et al*., 2023). These include 14 labdane-related diterpenes (momilactones, phytocassanes, and oryzalexins), 1 flavanone (sakuranetin), 1 casbene-related diterpene (ent-10-oxodepressin), and two amides (N-benzoyltryptamine and N-cinnamoyltryptamine) (Horie *et al.* 2016). Momilactones are a group (Momilactone A and Momilactone B) of lactone derived diterpenoids, they restrict the mycelial growth of *Colletrotrichum gloeosporioides, Botrytis cinerea*, *Fusarium solani, F. oxysporum* (Fukuta *et al*., 2007), *Pyricularia oryzae, P. infestans* and *Ustilago maydis* (Li *et al*., 2020). Apart from rice, momilactones have most notably only been reported from *Pseudoleskeella papillosa* and *Hypnum plumaeforme,* two types of moss species (Anh *et al*., 2023). Flavonoids such as quercetin and naringenin exhibited antibacterial properties against *Bacillus subtilis, Aspergillus niger*, *Pseudomonas aeruginosa, Candida albicans*, *etc.* Sakuranetin, is a derived form naringenin by naringenin 7-O-methyltransferase (NOMT) shows antifungal activity against

P. oryzae, rice blast fungus (Hasegawa *et al.*, 2014; Murata *et al.,* 2020) and rice sheath blight fungus *Rhizoctonia solani* (Katsumata *et al.*, 2018). Application of Tangeretin, a 4¹Ú,5,6,7,8-pentamethoxy flavone, extracted from citrus peel prevented appressorium formation of rice blast fungus, *Magnaporthe oryzae* (Ma *et al.*, 2024). Hordedane diterpenoids restrict the growth of *Fusarium graminearum* in barley roots (Liu *et al.*, 2023). Zealexins, a group of sesquiterpenoids, accumulate to levels greater than 800 μg g^{-1} fresh weight in response to *F. graminearum* attack in plant leaves (Huffaker *et al.*, 2011). In soybeans, daidzein are converted to glyceollins when exposed to biotic stress (Murphy *et al.*, 2002), it confers resistance against *Phytophthora sojae* (Jahan *et al.*, 2020).

Cauliflower florets produce caulilexin group (A, B and C), isalexins, 1-Methoxybrassitins and brassicanals exhibited antifungal activities against *R. solani* and *Sclerotinia sclerotiorum* to varying degrees at different concentrations (Pedras *et al.*, 2006). Cruciferous family includes some of the most economically important vegetables, like cauliflower, cabbage, rutabaga, turnip, broccoli along with mustard, horseradish and rapeseed (Pedras *et al.*, 2017). Cruciferous phytoalexins rapalexin A, brussalexin A and erucalexin have inhibitory action against the fungus, *Leptosphaeria maculans* (Pedras and *et al.*, 2012). Rishitin, phytuberin, anhydro-β-rotunol and solavetivone, found in members of Solanaceae family cause zoospores motility loss, granulation of cytoplasm, leading to bursting of the cell membrane (Harris and Dannis, 1997). Camalexin produced by *A. thaliana,* interfered with the proline upatke, caused ion and protein leakage along with serine deaminase acticity in *P. syringae* (Rogers *et al.*, 1996). Phytoalexins damage the cell membrane of the pathogen. Stilbenes like resveratrol, rhaponticin, and desoxyrhaponticin, block the oomyctes and mycelial growth of pathogenic fungi in plants (Gillmeister *et al.,* 2019). Heterologous expression of stilbene synthase genes, responsible for production of resveratrol and its derivatives endowed resistance to tobacco plants against *B. cinerea* (Hain *et al.*, 1993). In grapevines, resveratrol provides resistance against *P. viticola, Neofusicoccum parvum, Erysiphe necator* and *B. cinerea* (Liu *et al.*, 2023). Resveratrol oligomers decrease motility of bacteria and have the ability to regulate transcription of type III secretion system genes of the in bacterial species (Kang *et al.*, 2020). Papillae are physical barriers formed as cell wall thickenings at the site of infection. Presence of certain flavonoids in the papillae of barley leaves suggest that phytoalexins may play a role in prevention of fungal entry by constructing physical barriers (Friend, 2016). However, there is a lack of sufficient evidence to prove this theory. Phytoalexins restrict the growth of pathogens either in the epidermal cells or in mesophyll cells. It also interferes with bacterial multiplication in the intracellular region thus preventing its spread inside the plant (Usman *et al.*, 2018). However, much is yet to be revealed about the interaction of pathogen and phytoalexins in the plant cells.

2.5 Action of phytoalexins against insects

Insect feeding and oviposition trigger a series of biochemical, structural, and molecular reactions leading to the production of phytoalexin in plants (Xiang *et al.,* 2023). Phytoalexins present in potent amounts confers resistance to plants against insect pests (Whittaker and Feeny, 1971). Due to the differences in insect physiology, metabolism and behaviour, the mode of action of phytoalexins has to be species-specific. However, the evolutionary arms race has made phytoalexins efficient and potent enough to prevent insect herbivory. Oral secretions of insects during feeding are recognized by PRRs, which induce the production of phytoalexins (Erb *et al.*, 2012). Phytoalexins produced in response to feeding is more than those produced in response to mechanical damage. Phytoalexins have majorly been reported as having feeding deterrent properties against insects. Resistance of pasture legume, *Lotus pedunculatus* to *Costelytra zealandica* larvae has been contributed to the presence of vestitol and sativan, which are active feeding deterrents (Russell *et al.*, 1978). Adults and 4th instar larvae of *Epilachna varivestis* avoid feeding on phytoalexin-rich tissues (Hart *et al.*, 1983). Kauralexins, composed of a group of six ent-kaurene diterpenoids induce feeding resistance in young maize leaves against *Ostrinia nubilalis* (Schmelz *et al.*, 2011). Scopoletin, present in *Artemisia annua,* showed 77.1% feeding-deterrence and 116.9% growth inhibition (Tripathi *et al.*, 2010). The fall armyworm (FAW), *Spodoptera frugiperda* is a global destructive pest of economically important crops like maize and rice. Presence of (E)-β-caryophyllene in maize repels *S. frugiperda* larvae and decreases their incidence (Kumar *et al.*, 2022). Another study reported that FAW individuals reared on E-α-methylstilbene, 2, 4-dinitro-32 ,42 - (methylenedioxy) stilbene has developmental abnormalities (McComic *et al.*, 2021). In maize, C-glycosyl flavone called maysin endows the plants with resistance to maize earworm (*Helicoverpa zea*) (Casas *et al.,* 2016). Phytoalexins also disrupt the digestion process of insects by interfering with the production of their digestive enzymes like proteases and amylases (Chen *et al.,* 2008). Sakuranetin causes mortality in brown plant hopper, *Nilaparvata lugens* by inhibiting the growth of its yeast like endosymbionts (Liu *et al.*, 2023).

3. Phytoanticipins

It is important to note that not all plant antibiotics are considered as phytoalexins. Production of phytoalexins require specific conditions, *i.e.,* the plant needs to be under attack by either a biotic or abiotic stress. Phytoanticipins are those chemical compounds that are present or are pre-formed in plants (VanEtten *et al.*, 1994). It was at the symposium "phytoalexin hypothesis and beyond" held in honour of 50th year anniversary of the conception of the phytoalexin concept at Dannenfels, Germany, that the term "phytoanticipin" was proposed and defined to refer to all the pre-formed compounds in plants (Van Etten *et al.*, 1994). The etymology of the term "phytoanticipin" can be traced to "phyto" and "anticipin" which means "plant" and "to introduce something prematurely", respectively. It was defined as "low molecular weight, antimicrobial compounds that are present in plants before challenge by micro-organisms or are produced after infection solely from pre-existing constituents". The main difference between phytoalexin and phytoanticipin is made on the basis of its source rather than its structure. It is probable that a single compound can play a dual role as both phytoalexin and phytoanticipin. The isoflavonoid, maackiain is produced in response to microbial infections (Dewick, 1975) but in some instances, it occurs pre-formed as an aglycone of a glucoside and is activated during a microbial invasion (McMurchy and Higgins, 1984). Phytoanticipins are constitutive chemical compounds, as they are present in the tissue prior to microbial/herbivory incidence (Oros and Kallai, 2019).

3.1 Distribution of phytoanticipins

Pedras and Yaya (2015) merged traditional groups of phytoanticipins along with a few self-proposed chemical classes. Some of the known phytoanticipins have been listed in Table 2 based on this classification.

Table 2: List of phytoanticipins classified under different classes

Chemical class	Phytoanticipins	Plant families	References
Benzoxazinoid	DIMBOA (2,4-Dihydroxy-7-methoxy-1, 4-benzoxazin-3-one)	Poaceae, Lamiaceae, Acanthaceae,	Frey *et al.*, 2009
	DIBOA ((1,4-benzoxazin-3-one, *e.g.*, 2,4- dihydroxy-1,4-benzoxazin-3-one)	Plantaginaceae	Niculaes *et al.*, 2018
	HDMBOA (2-hydroxy-4,7-dimethoxy-1,4-benzoxazin-3-one)		
Cyanogenic glycosides	Dhurrin	Poaceae	Choi *et al.*, 2020
	Amygdalin	Rosaceae	He *et al.*, 2020
	Linamarin	Euphorbiaceae, Fabaceae, Linaceae, Compositae	Easson *et al.*, 2021
Glucosinolates	Sinigrin Glucoraphanin	Brassicaceae	Sotelo *et al.*, 2015 Shirakawa and Hara-Nishimura, 2018
	Glucotropaeolin		Bloem *et al.*, 2007
Saponins	Avenacin	Graminae	Inagaki *et al.*, 2013
	α-tomatine	Solanaceae	Liu *et al.*, 2023
Terpenoids	Azadirachtin	Meliaceae	Ashokhan *et al.*, 2020
	Artemisinin	Asteraceae	Baraldi *et al.*, 2008
Benzylisoquinoline alkaloids	Berberine	Berberidaceae Rutaceae, Annonaceae	Guo *et al.*, 2020
Pyrrolizidine alkaloids	Senecionine Retrorsine	Compositae	Tamariz *et al.*, 2018

Chemical classes like benzoxazinoids, cyanogenic glycosides, and glucosinolates are a part of the plants' two-component defense system (Easson *et al.*, 2021). They are considered as a two-component system as the glycoside and hydrolase are stored separate compartments in the plants and get activated only when they come in contact. Benzoxazinoids are an important group of phytoanticipins, found abundantly in individuals of the poaceae family (Su *et al.,* 2011). These are found in high amounts in juvenile or young plants and subsequently decline with an increase in plant age (Makowska *et al.,* 2015). Cyanogenic glycosides contain a core carbon structure attached to a -CN moiety, forming a glycosidic bond with two substituent groups and a sugar. Wounding of the plant cell due to cell damage or herbivory leads to activation of cyanogenic glycosides, which then release hydrogen cyanide by the action of endogenous β-glycosidase (Cressey and Reeve, 2019). Cyanogenic glucoside accumulates in epidermal and their glucosidases remain in the mesophyll cells (Heraud *et al.*, 2018). Likewise, glucosinolates and their glucosidases are also stored in different cells, the former accumulates in sulfur-containing cells while the latter in myrosin cells (Shirakawa and Hara-Nishimura, 2018). Almost all the plants contain terpenes. Terpenes like artemisinin and azadirachtin play a crucial role against pathogenic microbes like bacteria, fungi and virus (Tiku *et al.*, 2018).

Alkaloids represent a significant group of compounds that originate from amino acids and made up of a nitrogen atom in a heterocyclic ring (Kaur and Arora, 2015). Out of all the alkaloid secondary metabolites, benzylisoquinoline and pyrrolizidine are alkaloids are a special group of phytoanticipins, formed by the condensation of norcoclaurine synthase, forming (S)-norcoclaurine as the main intermediate (Dastmalchi *et al.*, 2018). They are found predominantly in berberidaceae and rutacea families (Guo *et al.*, 2020). Pyrrolizidine alkaloids contain two five-membered rings and are overall found in compositae, orchidaceae, fabaceae and poaceae (Kaur and Arora, 2015).

3.2 Phytoanticipin biosynthesis pathways in plants

Benzoxazinoids occur predominantly in members of the poaceae family like maize, wheat and rye. The pathway for the biosynthesis of benzoxazinoid is one of the most well-studied and elucidated. According to studies conducted on *Z. mays, Hordeum lechleri,* and *Triticum aestivum*, benzoxazinoid has a monophyletic pathway (Frey *et al.*, 2009). They are stored as glcs in the vacuole while their specific activating enzyme, glucosidases are located in the chloroplast. When the cell collapses due to damage, the glucosidase catalyzes the formation of a toxic aglucone (Sicker *et al.*, 2000). So, the whole biosynthesis pathway takes place in different in different sub-cellular structures. Based on that, the whole pathway can be divided into four sections. In the first section, the indole-3-glycerolphosphate, derived from L-tryptophan through the tryptophan biosynthesis pathway gets converted to indole in the presence of BX1 (Benzoxazineless1) in the chloroplast. Indole is the first intermediate of the pathway (Frey *et al.*, 2000). A group of cytochrome P450 monooxygenases, benzoxazineless (BX1-BX7) catalyze a chain of specific reactions in the pathway. The second portion of the pathway takes place in the microsome (endoplasmic reticulum), where indole is catalyzed to indole-2-one and then to 3-hydroxy-indolin-2-one by BX2 and BX3, respectively. Subsequently, 3-hydroxy-indolin-

2-one is converted to 2-hydroxy-2-1,4-benzoxazin-3-one (HBOA) through a ring expansion due to the action of BX4. BX5 catalyzes the N-hydroxylation of HBOA to 4-dihydroxy-1,4-benzoxazin-3-one (DIBOA) (Frey *et al.*, 2009). In the cytosol region of the cell, glucosylation of DIBOA is brought about by BX8 and BX9 (UDP-glucosyltransferases), leading to the formation of DIBOA-glucosides (DIBOA-glc) In some plants DIBOA-glc is the final product but in wheat and maize, DIBOA-glc undergoes hydroxylation in the presence of BX6 (2-oxoglutarate dependent deoxygenase) followed by O-methylation due to BX7 (O-methyltransferase) to yield TRIBOA-glc (4,7-trihydroxy-1,4-benzoxazin-3-one glucoside) and DIMBOA-glc (4-dihydroxy-7-methoxy-1,4-benzoxazin-3-one glucoside) (Jonczyk *et al.*, 2008). It has been theorized that DIMBOA is more stable than DIBOA. The glucosides are then transferred to the vacuoles to be stored. DIBOA is the predominant product of benzoxazinoid pathway in wild *Hordeum* spp. and is also found in rye leaves and roots (Copoja *et al.*, 2006).

In case of phytoanticipin glucosinolates, the glucosinolates are stored in S-cells (Koroleva *et al.*, 2010) while its activating enzyme, myrosinase is stored in specialized vacuoles called myrosin cell (Shirakawa and Hara-Nishimura, 2018). When the two compounds come in contact, hydrolysis of glucosinolates by myrosinase gives rise to unstable aglycones (Yactayo-Chang, *et al.*, 2020). Methionine serves as the main precursor for glucoraphanin, a major glucosinolate commonly present in broccoli. Methionine undergoes transamination by branched-chain aminotransferase (BCAT4), producing an α-keto acid (α-KA) intermediate. This step is initiated in the cytosol of the cell. Then, α-KA is condensed with acetyl-CoA in the presence of methylthioalkylmalate synthase (MAM) to yield a longer chain keto acid in the chloroplast. The long chain keto acid first undergoes isomerization by isopropylmalate isomerase (IPMI) followed by reduction due to isopropylmalate dehydrogenase (IPMDH) for regeneration of the elongated amino-acid (Blaževiæ *et al.*, 2020). This long chain elongation process is repeated twice, till dimethionine (DHM) is formed. In the core structure formation process, DHM is then oxidized to 4-methylthiobutyraldoxime (aldoxime) by the action of cytochrome P450 monooxygenase (CYP79F1). CYP83A1 oxidizes aldoxime to form aci-nitro intermediates. For stabilization of the compound, the aci-nitro intermediate is conjugated with UDP-glucose in the presence of Glucosyltransferase (UGT74B1) to form thiohydroximic acid glucoside. Sulfotransferase (ST5a) then transfers a sulfate group derived from 3'-phosphoadenosine-5'-phosphosulfate (PAPS) to the glucosylated intermediate to form 4-methylthiobutyl (4MTOB) glucosinolate (GLS). 4MTOB GLS is finally *S*-oxygenated to 4-methylsulinylbutyl (4MSOB) glucosinolate, also known as glucoraphanin (Crocoll *et al.*, 2016). The core glucosinolate structure is a universal scaffold in glucosinolate biosynthesis, diversified by side-chain modifications to produce various glucosinolates like glucoraphanin.

3.3 Action of phytoanticipins against pathogens

One of the major constraints that has restricted progress in the study of phytoanticipins is that for a long time, even after the proposal and establishment of the concept of "phytoanticipins", a lot of studies continued to mistakenly report phytoanticipins as phytoalexins. The fundamental difference that separates phytoanticipins from the latter is that it is found pre-formed and thus acts as the primary defense barrier against pathogens and pests as the accumulation of phytoalexins takes time. Phytoanticipins are reported to have certain antifungal and antibacterial properties. Allicin, is a phytoanticipin found in garlic, generated when alliin (*S*-allyl-l-cysteine sulphoxide) is converted by the enzyme alliin-lyase (Mansfield, 2000). It shows antagonistic activity against bacterial species, *Agrobacterium tumefaciens, Erwinia carotovora, P. syringae, Xanthomonas campestris,* fungus like *B. cinerea Magnaporthe grisea, Alternaria brassisicola, Plectosphaerella cucumerina,* and against *P. infestans* (an oomyctes) (Curtis *et al.*, 2004). Saponins isolated and characterized from banana aqueous solutions showed antifungal activity against *Mycosphaerella filiensis* (Cruz-Cruz *et al.*, 2010). Addition of fragarin, isolated from strawberry leaves, dissipated the membrane potential of phytopathogen *Clavibacter michiganensis* (Filippone *et al.*, 2001). The mode of action of phytoanticipins against various pathogens differs with respect to their chemical structure. Saponins inhibit the growth of pathogenic fungi by binding with their sterols, causing membrane disruption in the pathogenic organism (Sandrock and VanEtten, 1998). Sterols are an important component of fungal cell membrane (Der *et al.*, 2024). α-tomatine contains free 3β-hydroxyl groups, which form a complex with the fungal sterols, this results in disruption of membrane integrity, causing leakage of intracellular contents and ultimately leading to cell death (Bailly, 2021).

3.4 Action of phytoanticipins against insect pests

Phytoanticipins are secondary plant metabolites that are present in the plant tissues in an inactive form and get activated by certain plant enzymes known as hydrolases in case of tissue damage due to herbivory or microbial attack. Activating enzymes are stored separately and vary according to the type of phytoanticipin. For example, glucosinolates (β-thioglucoside-N-hydroxysulfates) are sulfur containing cells that are stored in plant cell vacuoles, separate from their activating enzyme, myrosinase. Myrosinase, a thioglucosidase, hydrolyzes glucosinolates, which leads to the production of glucose, sulphate and several toxic compounds, *viz.,* isothiocyanates, thiocyanates, nitriles and epithionitriles (Eisenschmidt-Bönn *et al.*, 2019). Over 120 distinct glucosinolates have been identified in members of the Brassicaceae family, including crops such as cabbage, broccoli, and rapeseed. Glucosinolate complex is referred to as "the mustard bomb" and is known to repel insect pests of brassicaceae family. Glucosinolates confer resistance to insect herbivores in plants both directly and indirectly. Isothiocyanate is the one of the most toxic derivatives of glucosinolate, it restricts the growth of *H. armigera* by inhibiting its gut cathepsin protease (Agnihotri *et al.*, 2018). Isothiocyanates present in the gut lumen move across cellular membranes by passive diffusion and enter the hemolymph via the gut epithelial layer. They cause loss of function in secondary and tertiary proteins (Jeschke *et al.*, 2016). Isothiocyanates have shown toxicity to neonates and final-instar larvae of many lepidopteran pests like *Trichoplusia ni* and *Anticarsia gemmatalis* (Wadleigh *et al.*, 1988). Isothiocyantes have also shown insecticidal and fumigation toxicity against *Solenopsis invicta* (Du *et al.* 2020), *Bradysia odoriphaga* (Shi *et al.*, 2017) and storage pests like *Liposcelis entomophila*, *Rhizopertha dominica*, *Sitophilus zeamais*, and *Tribolium ferrugineum* (Wu *et al.*, 2009). Isothiocyantes work as strong anti-feedants and growth inhibitors against insects and are much more toxic than other glucosinolates.

Different factors influence the effectiveness of phytoanticipins against insect herbivores. Concentration of phytoanticipin in the plant is

the main responsible factor, the concentration has to be above the toxicity threshold to be of any use against herbivore pests. It has been proved that even ancient plants had the ability to make cyanogenic glucosides. The process of synthesis of cyanides in cyanogenic plants is known as cyanogenesis. Disruption of plant tissues lead to the hydrolyzation of cyanogenic glucosides, releasing hydrogen cyanide, which inhibits respiration. Additionally, degradation of cyanogenic glucoside pathway leads to the production of defensive compounds like aldehydes, cyanohydrins, ketones, β-cyanoalanine, *etc*. Cyanogenic glucosides give off a bitter taste; hence they are classified as feeding deterrents (Zagrobelny *et al.*, 2004), β-cyanoalanine acts as a neurotoxin (Nahrstedt, 1985), while aldehydes and ketones exhibit cytotoxic properties (Naveena *et al.,* 2021).

4. Conclusion

Plants rely heavily on phytoalexins and phytoanticipins as key chemical defenses against insect pests and pathogens. These compounds act as natural barriers, suppressing microbial growth and deterring herbivores. Their diverse structures and plant-specific roles highlight their evolutionary importance in plant-pathogen battles. By decoding how plants produce these defenses and mapping their distribution, we could unlock new ways to breed hardier, pest-resistant crops, thereby promoting sustainable farming. Integrative research focusing on linking chemical defense profiles with ecological performance under field conditions, as well as exploring synergistic interactions between plant metabolites, microbiomes, and environmental factors will be crucial.

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Conflict of interest

The authors declare no conflicts of interest relevant to this article.

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