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REVIEW

Secondary metabolites as plant defensive strategy: a large role for small molecules in the near root region

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Abstract

The roles of plant roots are not merely limited to the provision of mechanical support, nutrients and water, but also include more specific roles, such as the capacity to secrete diverse chemical substances. These metabolites are actively secreted in the near root and play specific and significant functions in plant defense and communication. In this review, we detail the various preventive roles of these powerful substances in the rhizosphere with a perspective as to how plants recruit microbes as a preventive measure against other pathogenic microbes, also, briefly about how the rhizosphere can repel insect pests, and how these chemical substances alter microbial dynamics and enhance symbiotic relationships. We also highlight the need for more research in this area to detail the mode of action and quantification of these compounds in the environment and their roles in some important biological processes in microorganisms and plants.

Keywords Rhizosphere · Exudate · Bacteria · Soil · Allelopathy

Abbreviations

BXs	Benzoxazinoids
PGPB	Plant growth-promoting bacteria
ACC deaminase	1-Aminocyclopane-1-carboxylate (ACC) deaminase
PGP	Plant growth-promoting
LOCs	Lipo-chitooligosaccharides
PHB	Polyhydroxybutyrate
EPS	Exopolysaccharides

Introduction

The soil habitat is often seen as the most diverse ecological system on Earth (Amoo and Babalola 2019), inhabited by bacteria, fungi, nematodes, arthropod herbivores and plants among many other biotas (Alawiye and Babalola 2019). Organic matter is often limited in soils and this consequently results in increased competition and dynamics among the biota. To survive in the ecosystem, organisms produce variable signals to adapt and fit into rapidly changing ecological conditions. Plants interact with resident organisms by synthesizing chemical substances within the near root region. Also, plants use these metabolites to maintain soil health and other physical conditions, which allows them to withstand varied environmental stresses. Consequently, a view of the near root region (rhizosphere) presents an important perspective to improving the biological control of phyto-pathogens.

The rhizosphere, often considered to be one of the most dynamic ecosystems on earth—is the soil region directly influenced by the interactions between plant roots and microorganisms. The composition and functional diversity of the rhizosphere are dependent on an array of biotic and abiotic factors (de Boer et al. 2019; Enebe and Babalola 2018). These factors include plant species, soil types, root exudates, soil porosity, and anthropological activities (Fierer 2017). An interplay exists between plants and soil (micro)organisms that are either advantageous or detrimental (Mommer et al. 2016). These complex interactions influence biogeochemical processes such as nutrient cycling and greenhouse gas emissions. In addition, these biological interactions dictate the types and amount of metabolites produced by

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the plant, as these metabolites are produced in response to the activities within its immediate environment. The plant metabolites can shape the composition of the soil microbial community around the root region (Cotton et al. 2019). These secretions are termed exudates (primary metabolites and secondary metabolites). These exudates are composed of various low-molecular weight molecules with characteristic chemical properties that form concentration gradients in the root region (Hu et al. 2018).

Metabolites synthesized by plants play crucial roles in a myriad of activities, both good to bad. The plant rhizosphere has direct consequences on its ability to fight disease-causing organisms and make use of chemical substances produced in the root (Olanrewaju et al. 2019). Root exudates, comprised of allelochemicals, have been linked with signaling in the plant–microbe interplay and promotes communication in the rhizosphere (el Zahar Haichar et al. 2014). Exudates with potential allelopathic characteristics can help plant phytobiome selection both favorably and adversely (Sasse et al. 2018) by allowing plants to select for a rhizospheric community that could be advantageous or harmful to other microorganisms, a common biocontrol strategy often utilized by plants against pathogens (Ajilogba and Babalola 2016). The composition of secondary metabolites can change over time and are mostly impacted by various cues from the rhizosphere (De Coninck et al. 2015).

Recent studies have increased our understanding of the interplay between plant roots, resident microbes and their secondary metabolites. However, the analysis of these compounds is a major challenge and could suggest the somewhat limited number of investigations and reports on specific metabolites in the soil matrix. Moreover, there is limited understanding concerning the biocontrol functions of these compounds in the near root. In this review, we discussed secondary metabolites in the near root region with respect to how they protect plants and respond in the rhizosphere, focusing on compounds for which mechanistic information is available.

Near root microbial environment and root exudates

Microorganisms are one of the very important biotic factors that determines the growth and development of plants. Hence, they could be viewed as plant growth-promoting rhizobacteria and pathogens. Investigations have increased knowledge and our subsequent understanding of rhizosphere ecology. The microbial community in this region is impacted by root exudates which serve as vital carbon and energy sources (Yarzábal and Chica 2019). Consequently, root exudates alter the near root plant–microbe interactions. Flavonoid compounds from exudates of legumes were reported by Phillips and Tsai (1992) to improve the growth rate of bacteria, migration towards specific plants and the induction of plant nodules. It is suggested that the key reason for plant–microbe interactions is for adaptability, survival and multiplication (Zilber-Rosenberg 2013). Root exudates render nutrients to microbes and in return, the community breaks down and solubilizes complex organic compounds, thus improving the soil organic content (Canarini et al. 2019). While the influence of exudates on the rhizosphere microbial community is well known, there is still a paucity of information on the precise and chronic effects of these exudates on microbial establishment in the near root. Increased knowledge in this area could serve as the base for the development of specific biocontrol methods in the near root.

Classifications of rhizosphere metabolites

The rhizosphere is commonly viewed as the near root region of about 0–2 mm in radius, it is the region of the root with notable chemical signaling transfer and metabolite secretion by both plants and interacting microorganisms. In this region, metabolites (exudates) are released by plants and in response, microbes release varied classes of compounds to interact mutually or pathogenically. Exudates secreted are usually classified based on their molecular weights (Huang et al. 2014). Root exudate composition is determined by varying factors which include pH, plant developmental stages, soil texture, plant species and other biotic factors (de Boer et al. 2019). Root exudates can also be grouped on their biochemical nature, such as proteins, carbohydrates, peptides and glycopeptides. Although some of these, such as carbohydrates and proteins, are not found in most root exudates due to their quick degradation and uptake by microbial community in the near root (van Dam and Bouwmeester 2016). Several findings related to carbohydrates and derivatives are available as influencers of mutualistic associations between legumes and fungi (Fang and Leger 2010; Kiers et al. 2011). Amino acids also act as chemical attractants for plant growth-promoting rhizobacteria to the roots (Huang et al. 2014). Arabinogalactan proteins (AGPs) belonging to glycoprotein have been attributed to the cause of and play a significant role in the modification of near root biotic environment, by positively influencing beneficial microbes and repelling pathogens.

Though most secondary metabolites are genus and species-specific (Uarrota et al. 2011), major classes of secondary metabolites are terpenes (originating from acetyl-CoA and glycolytic intermediates), phenolics (with characteristic defensive properties, e.g. coumarin, lignin, etc.), sulphur-containing metabolites (e.g. phytoalexins, thionins, defensins, etc.), and nitrogen-containing metabolites (alkaloids, cyanogenic glucosides, etc.) (Pagare et al. 2015). Secondary metabolites play roles in defensive mechanisms, hormonal and signaling events, and in regulatory pathways. Due to the noticeable disparity and variety of these secondary metabolites, their functions are priced by humans as fragrances, drugs, inhibitors, molecular tools for profiling transcripts and metabolites, stimulants, hallucinogens, poisons, enzymes, dyes, colorants, insecticides, etc. (Pagare et al. 2015). Their usefulness in plant survival and interactions are exploited by biotechnology for the production of specific and valuable biological products for mankind. Usually, allelopathic substances are found among varied chemical classes which include benzene derivatives, hydroxamic acids, phenolics and terpenes (Fig. 1).

Root-derived specialized secondary metabolites in plant interactions

Metabolites play central roles in the interactions between plants and their microbiomes, a phenomenon which is commonly known as allelopathy. This can be either advantageous or detrimental, these association are commonly viewed as competition between plants and resident microbes (Sturz and Christie 2003). Metabolites produced during this process can either be active or passive at both interspecific and intraspecific levels (Huang et al. 2014). Allelochemicals can also be found in tissues of plants such as bark, flowers, leaves and even fruits. However, the most prominent route for substances is via root exudations into soil (Canarini et al. 2019).

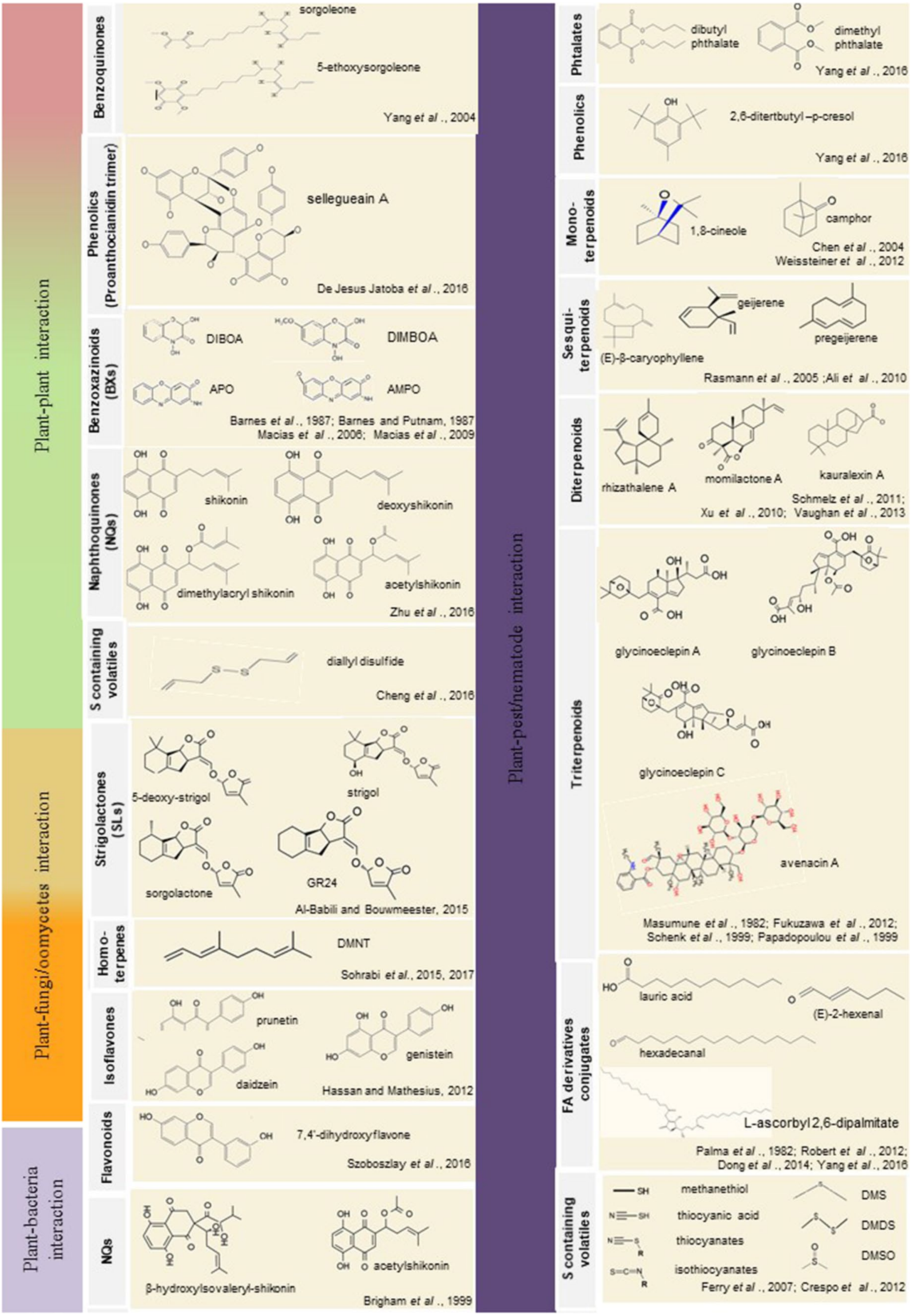
Plants synthesize metabolites through intricate biosynthetic and signaling pathways. These can be categorized as primary vs. secondary metabolites. Primary metabolites are deemed essential for functional metabolic pathways within the plant and are required by the plant at all times and under different environmental conditions. These metabolites include monomers and polymers of nucleic acids, sugars, amino acids and lipid derivatives (Pagare et al. 2015). Secondary metabolites on the other hand do not play direct roles in the functioning of the plant but rather influence its interactions with other members of the ecosystem—they determine the plant's fitness for the involved niche (Pagare et al. 2015). The variety of secondary metabolites within a particular plant species determines the complexity of its interactions with the biotic and abiotic components of its environment (Enebe and Babalola 2018). Likewise, the abiotic conditions of the soil could impact the composition and functions of metabolites in the near root (de Boer et al. 2019). For instance pH, temperature, water activity and even such texture have been reported to have great impacts by several of researchers (Raza et al. 2015; Kramshøj et al. 2019; Wang et al. 2015).

Carotenoids

Carotenoids are yellow, orange or red lipophilic organic pigments primarily composed of carotene and xanthophyll groups. They are abundant, naturally-occurring pigments on earth, second only to Chlorophyll *a*. They are mostly C_{40} terpenoids with photosynthetic, photomorphogenic, photo-protective, and developmental functions (Nisar et al. 2015). Carotenoids are produced by pathways hinged on two isoprene isomers—isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP). Production via the carotenoid pathway is regulated by phytoene synthase (PSY)—a rate-limiting enzyme in the biosynthesis of carotenoid (Nisar et al. 2015). Maize PSY3 isoform specifically expresses itself in the root (Ruiz-Sola et al. 2014), and assists in a resultant carotenoid flux during abiotic stress conditions, for example, drought and saline stress (Nisar et al. 2015; Ruiz-Sola et al. 2014). This accumulation of carotenoids within the root aids the synthesis of abscisic acid (ABA) (Nisar et al. 2015)—a plant hormone that plays a role in adaptation to stress conditions—which is synthesized from the cleavage of carotenoid precursors e.g. xanthophylls by specific dioxygenases (Ruiz-Sola et al. 2014). Carotenoids have antioxidant properties and their synthesis by maize plants; have assisted in meeting vitamin A demands in human populations. Beta-carotene, beta-cryptoxanthin, alpha-carotene lutein and zeaxanthin are common examples of carotenoids produced by maize (Uarrota et al. 2011).

Flavonoids

These nutraceuticals consist of phenolic, antioxidant, and flavone derivatives which act as pigments, colorants, and preservatives. These secondary metabolites—derivatives of 2-phenyl-benzyl-gamma-pyrone (Mierziak et al. 2014)—are common in maize grain pericarps and germs (Atanasova-Penichon et al. 2016) and play beneficial roles such as in stress tolerance (D'Amelia et al. 2018a) and pollen germination (Falcone Ferreyra et al. 2012). Some plants have been identified to synthesize sesquiterpenes commonly known as strigolactone (Fig. 1) as below-ground signals, which prompt symbiotic relationships between the roots of plants and arbuscular mycorrhizal (AM) fungi of the Glomeromycota. Furthermore, these metabolites, have been observed to influence plant–plant interactions, produce effects within mycorrhizal associations and regulate plant–microbe symbiotic interactions (Mierziak et al. 2014). Exudates are capable of inhibiting seed germination of surrounding plants, increasing the


Plant-plant interaction
Plant-fungi/oomycetes interaction
Plant-bacteria interaction
Plant-pest/nematode interaction
Benzoquinones
sorgoleone
5-ethoxysorgoleone
Yang et al., 2004
Phenolics (Proanthocianidin trimer)
sellegueain A
De Jesus Jatoba et al., 2016
Benzoxazinoids (BXs)
DIBOA
DIMBOA
APO
AMPO
Barnes et al., 1987; Barnes and Putnam, 1987
Macias et al., 2006; Macias et al., 2009
Naphthoquinones (NQs)
shikonin
deoxyshikonin
dimethylacryl shikonin
acetylshikonin
Zhu et al., 2016
S containing volatiles
diallyl disulfide
Cheng et al., 2016
Strigolactones (SLs)
5-deoxy-strigol
strigol
sorgolactone
GR24
Al-Babili and Bouwmeester, 2015
Homo-terpenes
DMNT
Sohrabi et al., 2015, 2017
Isoflavones
prunetin
genistein
daidzein
Hassan and Mathesius, 2012
Flavonoids
7,4'-dihydroxyflavone
Szoboszlay et al., 2016
NQs
β-hydroxylsovaleryl-shikonin
acetylshikonin
Brigham et al., 1999
Phtalates
dibutyl phthalate
dimethyl phthalate
Yang et al., 2016
Phenolics
2,6-ditertbutyl–p-cresol
Yang et al., 2016
Mono-terpenoids
1,8-cineole
camphor
Chen et al., 2004
Weissteiner et al., 2012
Sesqui-terpenoids
(E)-β-caryophyllene
geijerene
pregeijerene
Rasmann et al., 2005; Ali et al., 2010
Diterpenoids
rhizathalene A
momilactone A
kauralexin A
Schmelz et al., 2011;
Xu et al., 2010; Vaughan et al., 2013
Triterpenoids
glycinoeclepin A
glycinoeclepin B
glycinoeclepin C
avenacin A
Masumune et al., 1982; Fukuzawa et al., 2012;
Schenk et al., 1999; Papadopoulou et al., 1999
FA derivatives conjugates
lauric acid
(E)-2-hexenal
hexadecanal
L-ascorbyl 2,6-dipalmitate
Palma et al., 1982; Robert et al., 2012;
Dong et al., 2014; Yang et al., 2016
S containing volatiles
methanethiol
thiocyanic acid
thiocyanates
isothiocyanates
DMS
DMDS
DMSO
Ferry et al., 2007; Crespo et al., 2012

◂**Fig. 1** Specialized metabolite classes and representative compounds with functions in root-organism interactions. Strigolactones (SLs), fatty acids (FA), DIMBOA [2,4-dihydroxy-7-methoxy-2H-1,4-benzoxazin-3(4H)- one], APO [2-amino-3H-phenoxazin-3-one], AMPO [2-amino-7-methoxy-3H-phenoxazin-3-one], Benzoxazinoids (BXs), naphthoquinones (NQs), DMNT [(E)-4,8- dimethyl-1,3,7-nonatriene], dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl sulfoxide (DMSO) DIBOA [4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one]

secretion of Reactive oxygen species (ROS) in the root systems of other plants (causing death), initiate symbiosis with microbial species within the rhizosphere, influence hypersensitivities, modulating auxin activity, etc. (Mierziak et al. 2014). Additionally, flavonoids have been observed to aid resistance to metal toxicity (e.g. aluminum) in maize plants (Falcone Ferreyra et al. 2012). Environmental stress to beneficial plants such as maize has an indirect negative impact on human societies. During biotic (e.g. herbivore and pathogen attack) and abiotic (e.g. drought and UV radiation) stress, maize plants produce free radicals such as reactive oxygen species (ROS) which accumulate and educe debilitating effects on plant development (D'Amelia et al. 2018a). ROS adversely affects cell membrane components such as lipids and carbohydrates; DNA; and cellular proteins. Flavonoids assist antioxidant enzymes such as glutathione reductase, superoxide dismutase, catalase, etc. to scavenge these ROS and maintain them at a level that is not toxic to plant health (D'Amelia et al. 2018a).

Phenolics have been identified to be a key chemoattractant for plant growth-promoting rhizobacteria and defend against disease causing organisms. Flavonoids have been seen in leguminous rhizobium as a regulatory factor for nodulation and initiation of symbiosis (Abdel-Lateif et al. 2012). Antioxidant properties of flavonoids have been linked to neuroprotective, vascular protective and anti-inflammatory activities as well as ameliorating cases of cancers in humans. Flavonoids from potatoes and maize have been found to be useful in alleviating breast and prostate cancers, respectively (D'Amelia et al. 2018a).

The activity of flavonoids against human diseases is attributed to their antioxidant properties—as they are stronger scavengers of reactive oxygen and nitrogen species in the human body (D'Amelia et al. 2018b). With positive effects recorded in the health sector, flavonoids are of importance in the food industry and biotechnology. They increase shelf-life due to their antioxidant and antimicrobial properties by regulating lipid auto-oxidation and thus preventing spoilage by food-borne pathogens (D'Amelia et al. 2018b). In comparison with other cereals such as rice, wheat and oat, maize grains have been observed to contain the highest concentrations of these phenolic acids (Atanasova-Penichon et al. 2016). Common flavonoids in maize grains include flavonols–kaempferol and quercetin, flavones—luteolin and apigenin, and flavone glycosides—maysin, isoorentin, and isovitexin (Atanasova-Penichon et al. 2016). The biosynthesis of flavonoids in plant tissues relies on the activity of enzymes in the phenylpropanoid pathway (Falcone Ferreyra et al. 2012). Chalcone synthase (CHS) mediates the condensation of *p*-coumaroyl-CoA with malonyl-CoA (in a ratio of 1:3) to produce chalcone which is subsequently isomerized to flavanone by chalcone isomerase (CHI) (Mierziak et al. 2014). Being the first participant of the flavonoid synthesis pathway, CHS directs the synthesis of flavones, flavonols, and anthocyanins (D'Amelia et al. 2018b) as the flavanone produced by CHI is utilized for the production of various flavonoid products such as anthocyanins, flavonols, aurones, flavanonols, isoflavones, flavones, etc. (Mierziak et al. 2014).

Terpenoids

Terpenoids (isoprenoids) include diterpenoids (kauralexin and dolabralexin groups) and sesquiterpenoids (zealexins) (Block et al. 2019; Mafu et al. 2018). Directly implicated in plant growth and development, these molecules are essential for the phyto-physiology of maize plants. Diterpenoids are necessary for defense roles, pollination, allelopathy, repair responses to tissue damage, resistance to pests and infectious agents such as European corn borers (*Ostrinia nubilalis*), *Fusarium* spp., *Aspergillus* spp., *Rhizopus microspores*, *Cochliobolus heterostrophus,* and *Collectotrichum* spp. (Block et al. 2019; Zerbe 2015). Maize terpenoids are antimicrobial, defend the plant against insects and in some intense cases of microbial or insect infestation, act as attractants for parasitoids and predatory insects (Block et al. 2019). Diterpenoids—zealexins and kauralexins—were initially thought to be restricted to defensive roles in the aerial parts of maize; later studies show that defense pathways mediated by diterpenoids extend to belowground tissues, such as within and around root tissues (Mafu et al. 2018; Zerbe 2015). Besides biotic defense, diterpenoids also play a part in the response of plants to environmental stress such as high salinity and drought just like carotenoids (Zerbe 2015). Though kauralexins exude a negative effect on insects (biotic stress), they are also observed to accumulate in response to abiotic stress (Mafu et al. 2018).

Benzoxazinoids (1,4-benzoxazin-3(4H)-one derivatives, BXs)

These substances were first reported in an experiment that demonstrated reduced growth of weed biomass in a rye (*Secale cereale* L.) field when matched with plots without rye (Barnes and Putnam 1983). Consequently, DIBOA

[4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one] and its methoxylated analogue DIMBOA [2,4-dihydroxy-7-methoxy-2H-1,4-benzoxazin-3(4H)-one] were identified as the causative active substances (Macías et al. 2008). BXs are secondary metabolites classified as lactams, hydroxamic acids, and benzoxazolinones (Mikić and Ahmad 2018). Located in maize grains with higher concentrations in bran and germ (Atanasova-Penichon et al. 2016), they play a crucial role against insect herbivores for the survival of maize plants. The toxic nature of benzoxazinoid derivatives such as 2,4-dihydroxy-1,4-benzoxazin-3-one (DIBOA), 2,4-dihydroxy-7-methoxy-1,4-benzoxazin-3-one (DIMBOA), 2-hydroxy-1,4-benzoxazin-3-one (HBOA), 2-hydroxy-7-methoxy-1,4-benzoxazin-3-one (HMBOA), 2-hydroxy-4,7-dimethoxy-1,4-benzoxazin-3-one (HDMBOA), 6-methoxybenzoxazolin-2-one (MBOA), and 2-benzoxazolin-2(3H)-one. (BOA) are quite similar to DIBOA and its methyl derivative DIMBOA being the most extensively studied (Mikić and Ahmad 2018). The BXs are defensive and allelopathic phytochemicals with antibacterial, antifungal, insecticidal, antifeedant and phytotoxic functions (Mikić and Ahmad 2018); as major components of innate immunity and disease resistance (Liu et al. 2019). Their modes of action and toxicity vary—BOA and MBOA are breakdown products of and are less toxic than DIBOA and DIMBOA, the phytotoxicity of HBOA and HMBOA are considerably lesser than DIBOA and DIMBOA etc. (Mikić and Ahmad 2018). DIBOA and DIMBOA are very toxic indeed and hence stored in their inactive forms within cell vacuoles. Physical and chemical trauma by pathogens and pests results in the release of these BXs from the vacuoles which cause their activation by enzymes in the plastids (Mikić and Ahmad 2018). Certain plants e.g. maize, wheat and rye, utilize these secondary metabolites as induced defenses against herbivore infestation (Qi et al. 2018). The production of BXs is triggered by elicitor molecules resulting from impulses from external events such as a pathogen or pest attack (Dafoe et al. 2013). Dolman (2014); (Wang and Xie 2020), reported that host defenses in maize were unregulated concomitant from the infection of *Sporisorium reilianum*—which causes Head smut. The biosynthesis of Benzoxazinoids (BXs) via the BX biosynthesis pathway employs enzymes such as BX1 (acts on indole-3-glycerol phosphate to yield indole), cytochrome P450-dependent monooxygenases, UDP-glucosyltransferases, 2-oxoglutarate-dependent dioxygenases and *O*-methyltransferases (Qi et al. 2018). Stored as glucosides in the vacuoles of whole maize cells, these BXs are converted to unstable aglucones via hydrolytic leaf damage by herbivores (Qi et al. 2018). In maize plants, BXs occur in all plant tissues, with varying amounts in specific tissues—maize leaves and stems have a varying amount of BXs dependent on their growth and development, while maize roots show a constant composition irrespective of plant growth and development. The overall BX concentrations also vary. Some BXs are more abundant in young maize plants, while others are characteristically more associated with older maize plants (Mikić and Ahmad 2018). BXs have been observed to defend the maize plant from insect herbivores such as European corn borer (*O. nubilalis*) and Asian corn borer (*O. furnacalis*) (Qi et al. 2018). Its toxicity is due to its role in NADH oxidation of cell wall peroxidases; hydrogen peroxide accretion; lignification of the cell wall, inhibition of trypsin, cholinesterase, chymotrypsin proteases; decreased production of chlorophyll; alteration of lipid metabolism; disruption of biochemical activities during oxidative phosphorylation; and growth inhibition (Makowska-Grzyska et al. 2015). Microorganisms in the rhizosphere play a major role in the activation of BXs. Rhizosphere microbes breakdown BXs to yield more, antibacterial, antifungal and allelopathic products (Neal et al. 2012).

Due to adaptation and coevolution, plant and soil-borne fungi exhibit diverse relationships, from symbiotic, parasitic and pathogenic relationships. Several plants over the years have sustained beneficial relationships with arbuscular mychorrizal fungi (AM); however, there is more to just the chemical communications in their relationship. Strigolactones are often considered as the most common metabolite in plant- fungi relationships (Fig. 2). Akiyama et al. (2005) showed that the sesquiterpenes, 5-deoxy-strigol, sorgolactone and strigol retrieved from the exudates of *Lotus japonicus* caused an elongated hyphal branching in AM fungus. Comparable result was also seen in sorgolactone synthetic homologue (Liu et al. 2011). These plants, however, change responses to pathogens via the activation of integrates stress response. Besides the mutual relationship that exists between plant and AM fungi, plant roots are often the target of soil fungal pathogens. Before colonization, hyphae of diseases causing fungi can detect chemical communication which signals their movement towards plant host. For instance, *Fusarium oxysporum*, a plant pathogen growing towards tomato (*Solanum lycopersicum*) root was identified to have been catalyzed by the actions of class III peroxidases (Pandey et al. 2017). Although the substrate of these enzymes was not fully identified; however, it was suggested that it was synthesized from the root.

Quite a number of secondary metabolites have antifungal attributes (Palla et al. 2018; Kujur et al. 2020; Ke et al. 2020). Phenolics and flavonoids are both viewed to be a part of an extensive group of phytochemicals with high concentrations in fruits, skin, leaves and roots. These chemicals have shown some activity in plant defense against pigmentation and resistance to diseases (Table 1) (Zaynab et al. 2018). Phenolics impact cell permeability of microorganisms and deforms the function and structures of the protein membrane, consequently leading to the distraction of pH gradient, energy production,

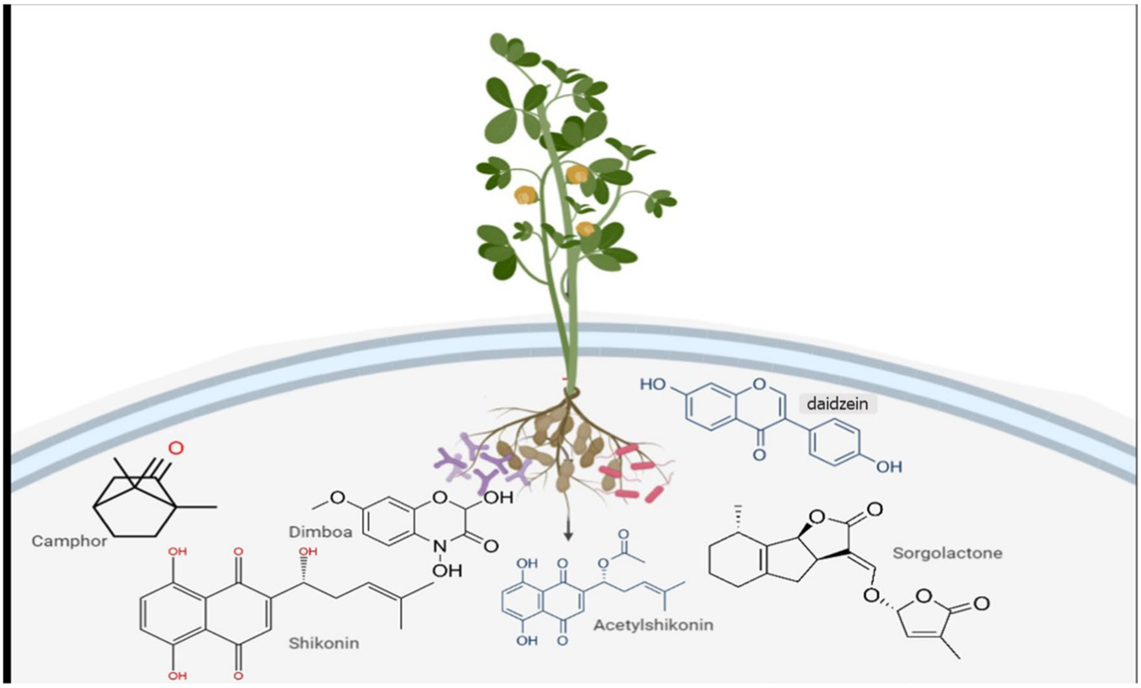


Fig. 2 Secondary metabolites involved in plant interactions in the near root (Sugiyama 2019)

Table 1 Examples of phenolic compound with anti-fungal activity

Chemical	Fungus	References
Benzaldehyde	*Botrytis cinerea*	Caruso et al. (2011)
Protocatechuic acid	*Colletotrichum circinans*	Zaynab et al. (2018)
Salicylic acid	*Eutypa lata*	Amborabé et al. (2002)
Vanillic acid	*Phytophthora infestans*	de Vries et al. (2018)
Chlorogenic acid	*Fusarium oxysporum*	Ling et al. (2013)
Naringin	*Penicillium digitatum*	Ortuño et al. (2011)
Flavones	*Aspergillus*	Wu et al. (2014)
Oleuropein	*Phytophthora*	Báidez et al. (2006)
Nobiletin	*Phoma tracheiphila*	Aboody and Mickymaray (2020), de Lamo and Takken (2020)

membrane-bounded enzymes and the use of substrate for energy generation (López-Gámez et al. 2020). Exudates with antimicrobial properties such as saponins, α-tomatine (tomato saponin) stimulate monomeric G-protein pathways and phosphotyrosine kinase that fixes to cell membranes, such that it results in the rupture and release of the cell component (Ito et al. 2007).

Secondary metabolites in plant interactions with bacteria

The rhizosphere serves as a habitat for numerous bacterial taxa (Fu et al. 2017), more so, these community members have a direct influence on plant health and its ability to fight phytopathogens. Secondary metabolite profiles and expression of genes that link with microbial colonization have been viewed to initiate significant alterations in bacteria community immediately there is biological stress (Mendes et al. 2014; Reinhold-Hurek et al. 2015). The community structure of bacteria in the rhizosphere is controlled partially by specific traits or factors exhibited by the host plant, as well as the soil dependent processes. Various root-derived metabolites are in some cases released to recruit specific bacterial taxa, as defense during stress conditions. Moreover, the investigation on *Pseudomonas syringae*-infected Arabidopsis root exudates showed the defensive attributes of selected antibacterial compounds exuded by the root against selected bacteria taxa. Specific metabolites were recovered from plants infected with pathogenic strains of bacteria and more metabolites were recovered from non-pathogenic infected plants (Pascale et al. 2020).

Studies on different plant species exudates have reported various classes of flavonoids e.g. flavonol (quercetin), flavanones (liquiritigenin), isoflavones (daidzein) (Cesco et al. 2010). An experiment by Szoboszlay et al. (2016) showed that the application of flavonoid [7,40-dihydroxyflavone (Fig. 1)] recovered from a stressed *Medicago sativa* to a neutral soil caused the recruitment and increase in the relative abundance of *Acidobacteria, Gaiella, Nocardioidaceae*, and *Thermomonosporaceae* taxa, that are recognized to associate with plant roots. These findings pinpoint the significance of such exudates in the surroundings of near root regions, especially during responses against pathogenic organisms. However, the precise mechanism of action was unknown.

Of the compounds with allopathy effects, naphthoquinones are important as they also show great influence on soil microbial community (Smith 2013). Acetyl-shikonin and β-hydroxyisovaleryl-shikonin (Fig. 1), were prominent active substances identified in the hair roots of *Lithospermum erythrorhizon* (Tatsumi et al. 2016). These substances have also been implicated as chemoattractant for the beneficial bacterium *Pseudomonas putida* in plant roots. It is commonly suggested that plant exudates attract bacterial species that have the metabolic capacity to break down the released compounds. The use of metabolites as carbon sources for such as for the catabolism of the monoterpenoid α -pinene by *P. fluorescens* and *Alcaligenes xylosoxidans* (Kleinheinz et al. 1999). Metabolites secreted in plant root can chemoselect organisms that support or hinder the growth of bacterial pathogens, but the length as to how the relationship stimulates the release of the exudates via the promotion of immune responses remain unknown.

Secondary metabolites in plant interactions with viruses

Many plant secondary metabolic compounds such as alkaloids, phenolics and flavonoids have got antiviral attributes. Commonly, alkaloids, due to its varied structures exhibit biologically active substances that could impact the existence of resident organisms in the soil. Several plants with antiviral properties have been recognized (Choudhary et al. 2020; Hassan et al. 2016; Ahmad et al. 2015). For instance, an antiviral alkaloid compound, 7-deoxytrans-dihydronarciclasine, from plantain lilies (*Hosta plantaginea*) has activity against Tobacco Mosaic Virus (Wang et al. 2007). Likewise, Bruceine-D from *Brassica javanica* inhibits the growth of potato virus and tobacco mosaic virus (Islam et al. 2018). Furthermore, quassinoids have been reported as active metabolites against TMV infections (Yan et al. 2010). Chen et al. (2009) also investigated the TMV traits of *Picarma quassioides* and identified the presence of β-carboline alkaloids.

Secondary metabolites in plant interactions with insect pest

In the root of plants, several endogenous secondary metabolites trigger behavioral changes. Townsend and Ebizuka (2010), showed that grass grubs could be hindered by isoflavonoids and other phytoalexins from legumes. The development of *Heteronychus arator* (African black beetle) larvae was also hindered by flavonoids, phaseolin, vestitol, genistein and medicarpin (Townsend and Ebizuka 2010). Emitted metabolites from the roots contribute immensely to the plants' defense systems against herbivores. For instance, a study showed that *Arabidopsis* secreted semi-volatile diterpenes against *Bradysia larvae*, an opportunistic root-pest (Vaughan et al. 2011). Myrosinases also hydrolyse precursors of glucoside to release substances that reshuffle into thiocyanates, volatile isothiocyanates and nitriles, these breakdown products have preventive effects against insect pests. A more comprehensive review of the activities of secondary metabolites in root- insect pest association has already been presented by Erb and Lu (2013). Remarkably, quite a limited number of reports of the negative impacts have been demonstrated in-situ. See Example in Table 2 for selected herbivorous plants.

Future perspective

In this review, the ability of plants to synthesize varied chemical compounds in their rhizosphere with the capacity to suppress disease-causing organisms and with recognized potential for their application in biocontrol strategies have been extrapolated. However, little is still known regarding

Table 2 List of plant secondary metabolites against insects and their link to a specific category

Secondary	Metabolites plants	Categories	Resistance against	References
Terpenoids	Tobacco	Trans-anethole and thymol, citronellal	*Spodoptera litura*	Pavela (2014)
Phenolics	Strawberry	Phenolics	*Tetranychus urticae*	Afifi et al. (2010)
Cyanogenic Glucosides	Bitter almond plants	Amygdalin and prunasin	*Capnodis tenebrionis*	Sánchez-Pérez et al. (2008)
Phenolics	Willow plant	Phenolics	*Galerucella lineola*	Larsson et al. (1986)
Phenolics	Wheat	Phenolics	*Rhopalosiphum padi*	Havlíčková et al. (1996)
Benzoic acid	Salix	Benzoic acid	*Operophtera brumata*	Zaynab et al. (2018)
Cyanogenic Glucosides	*Trifolium repens*	Amygdalin and prunasin	*Hypera postica*	Fürstenberg-Hägg et al. (2013)
Phenolics	Cotton	Gossypol	*Heliothis virescens, Heliothis zea*	Jenkins et al. (1983)
Terpenoids	Citrus	Terpenoid Limonene	*Atta cephalotes*	Bennett and Wallsgrove (1994)
Alkaloids	Nightshade potato	Alkaloid demissine	*Leptinotarsa decemlineata*	Sablon et al. (2013)
Benzoxazinoids	Gramineae	DIMBOA	*Ostrinia nubilalis*	Friebe et al. (2012)

secondary metabolites and their specific functions in the near root region. More precisely, the ones relating to allelopathic interactions, which include a comprehensive understanding of the metabolite exudation processes and the identification of transporter proteins that are specific for exudation and transport mechanisms. Studies on the regulation of transporters by abiotic and biotic near-root signals will be of significance, to better understand release rates and flux over time. Moreover, measurements of the exact concentrations of these chemical substances are still very much in need. This can be achieved by solid-phase root zone micro-extraction in selected rhizosphere points to quantify the spatial and temporal changes in exudation (Weidenhamer and Callaway 2010). With such strategy, one might be able to estimate the total amount of exudate breakdown and movement in the soil. Additionally, mutants and transgenic plants with altered exudation should be encouraged in the study of the effects of enhanced vs. suppressed secondary metabolite exudation on the rhizosphere. Characterization and quantification of metabolites by mass spectrometry can be used to monitor mutants with modified root exudation. Up to date tools are also required for such assessments. Metabolomics and proteomics investigation will assuredly improve our understanding of these metabolites. Furthermore, an enormous gap in knowledge still exists with respect to how some of these secondary metabolites act as allelopathic compounds. It will be important to know the molecular targets of these metabolites in plant species that could be hindered, consequently identifying the mode by which the activities of these beneficial metabolites can be preserved. It is yet to be determined if the exudates released are first transformed in the rhizosphere by some microbes before they become bioactive as allelochemicals.

Author contribution statement AAA and OOB conceived the idea and discussed findings. AAA developed and wrote the manuscript. OOB critically revised the manuscript did quality assurance, and made substantial contribution to the design of the review work. Final copy was read and approved by both authors.

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