

## SI EDITOR'S CHOICE

# Small molecules below-ground: the role of specialized metabolites in the rhizosphere

Hassan Massalha<sup>1</sup>, Elisa Korenblum<sup>1</sup>, Dorothea Tholl<sup>2,\*</sup> and Asaph Aharoni<sup>1,\*</sup><sup>1</sup>Department of Plant Sciences, Weizmann Institute of Science, Rehovot 76100, Israel, and<sup>2</sup>Department of Biological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

Received 1 December 2016; revised 17 March 2017; accepted 21 March 2017; published online 23 March 2017.

\*For correspondence (e-mail asaph.aharoni@weizmann.ac.il or tholl@vt.edu).

## SUMMARY

Soil communities are diverse taxonomically and functionally. This ecosystem experiences highly complex networks of interactions, but may also present functionally independent entities. Plant roots, a metabolically active hotspot in the soil, take an essential part in below-ground interactions. While plants are known to release an extremely high portion of the fixated carbon to the soil, less information is known about the composition and role of C-containing compounds in the rhizosphere, in particular those involved in chemical communication. Specialized metabolites (or secondary metabolites) produced by plants and their associated microbes have a critical role in various biological activities that modulate the behavior of neighboring organisms. Thus, elucidating the chemical composition and function of specialized metabolites in the rhizosphere is a key element in understanding interactions in this below-ground environment. Here, we review key classes of specialized metabolites that occur as mostly non-volatile compounds in root exudates or are emitted as volatile organic compounds (VOCs). The role of these metabolites in below-ground interactions and response to nutrient deficiency, as well as their tissue and cell type-specific biosynthesis and release are discussed in detail.

**Keywords:** rhizosphere, microbiome, root exudates, volatile organic compounds, specialized metabolism, allelopathy.

## INTRODUCTION

The soil domain is considered the most populated ecosystem on Earth (Gans, 2005) accommodating bacteria, fungi, nematodes, arthropod herbivores and plants to name but a few (Bonkowski *et al.*, 2009). The typically limited organic matter in soil prompts a competition between organisms leading to the development of unique relationships between them. Consequently, organisms developed a set of specific signals serving their community to achieve better fitness in dynamically changing soil conditions. The interaction of plants with soil organisms is largely driven by chemical signaling that takes place at the root vicinity. In addition, soil organisms including plants, use chemicals (i.e. metabolites) to maintain soil conditions and other physical parameters, which allow them to face abiotic stress. Hence, understanding rhizosphere interactions will likely have a great value for improving plant resistance to

both biotic and abiotic stresses, that will ultimately translate to an increase in crop yield.

Considered the richest source in organic substances in the soil environment, plants play an essential role in modulating below-ground conditions, which makes them a target for soil resident organisms. Through evolution, the nature of interactions between plants and soil organisms was shaped to be either beneficial or pathogenic. Plants use root exudates to improve fitness in soil conditions by modulating the physical and chemical conditions of the soil and enhancing nutrient uptake (Parniske, 2008; Haichar *et al.*, 2014). These exudates are rich in low-molecular-weight molecules, which exhibit varying chemical properties that form a map of concentration gradients in the rhizosphere dictated by their solubility and stability (Bais *et al.*, 2006). Apart from exudation, rhizodeposition is

an additional mechanism that impacts soil microorganisms through the release of chemical substances from dead plant tissues, i.e. leaves, roots, and detached root cells (see Dennis *et al.*, 2010). The secretion of metabolites from roots in the form of soluble exudates is complemented by the release of more hydrophobic, volatile organic compounds (VOCs) that are capable of diffusing into the rhizosphere and soil environment at an increased distance (see Peñuelas *et al.*, 2014).

The analysis of soil exudate and VOC compositions is a challenging task and this could explain the relatively limited number of reports on specialized metabolites in the soil matrix. Soil microorganisms are likely to have high impact on chemical composition. Thus, different soil types show dissimilar metabolite turnover due to microbial activity. Moreover, soil particles exhibit different affinities to diverse chemical classes, resulting in variation in metabolite quantification (Quastel, 1965). While hydroponic and aeroponic systems are often the choice for collecting root exudates, the compound mixtures collected with these methods may be different from those secreted under natural plant growth conditions (Kuijken *et al.*, 2014). These limitations have led to increased efforts to develop analytical procedures for analysing root exudates and VOCs *in situ* (e.g. Phillips *et al.*, 2011; Crespo *et al.*, 2012; Kai *et al.*, 2016).

Specialized metabolites produced and secreted by plants play a critical role in a myriad of activities. While a certain portion of specialized metabolites is released to the rhizosphere in a constitutive manner, others are induced following environmental cues (Graham, 1991; Dixon, 1995; Baetz and Martinoia, 2013). The repertoire of metabolites found to date in exudates or as VOCs cover most chemical classes including fatty acid derivatives, phenolics, benzenoids, terpenoids, alkaloids, and sulfur-containing compounds. A recent meta-analysis by Schenkel *et al.* (2015) provides a comprehensive overview of root-derived VOCs in comparison to VOCs produced by soil-borne microbes. While water and solvent soluble molecules often allow short-distance communication, VOCs are likely to be involved as long-distance messengers (Hiltpold and Turlings, 2008; Insam and Seewald, 2010). The latter can also serve as signals in interactions at multiple trophic levels (Rasmann *et al.*, 2005). Moreover, there is growing evidence for the importance of VOCs emitted from soil-borne microbes in plant–microbe chemical interactions in the rhizosphere (Kai *et al.*, 2009; Wenke *et al.*, 2010; Peñuelas *et al.*, 2014).

Root exudate and VOC compositions change over time and are stimulated by various cues from the plant above-ground and below-ground environment (Haichar *et al.*, 2008; De Coninck *et al.*, 2015). Even though the number of identified molecules released by plant roots is increasing, knowledge is limited with respect to the function of these

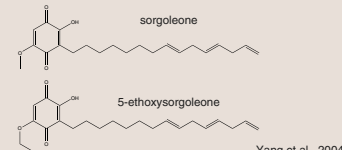
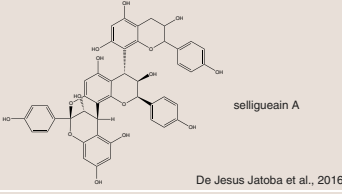
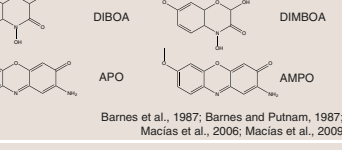
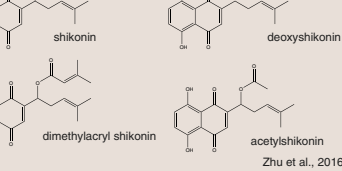
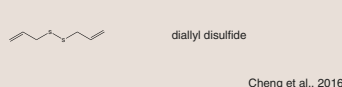
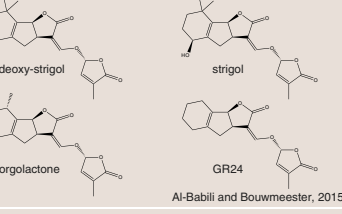

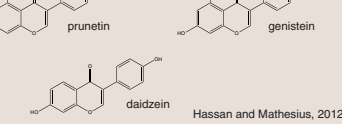
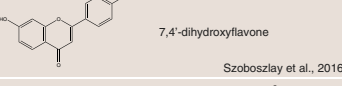
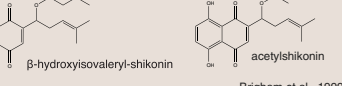
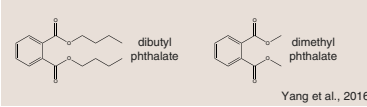
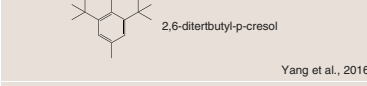
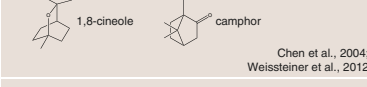
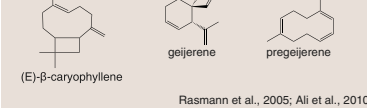
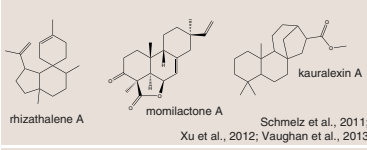
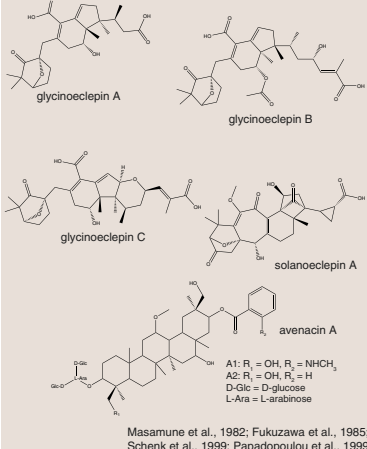
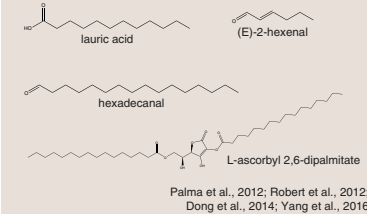
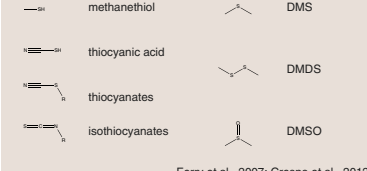
compounds in the rhizosphere. Here, we provide an overview of the recent findings with respect to specialized metabolites of root exudates and VOCs in the rhizosphere that are involved in biotic interactions. We also discuss the tissue- and cell-type-specific formation of these metabolites and their release and function in providing an optimized soil nutritional environment surrounding the root system. While this review could have been extended to many more specialized metabolites, emphasis is placed mostly on prominent compound classes and the recent mechanistic findings associated with them.

## THE ROLE OF SPECIALIZED METABOLITES IN THE BELOW-GROUND CHEMICAL COMMUNICATION

### Root-derived specialized metabolites in plant–plant interaction

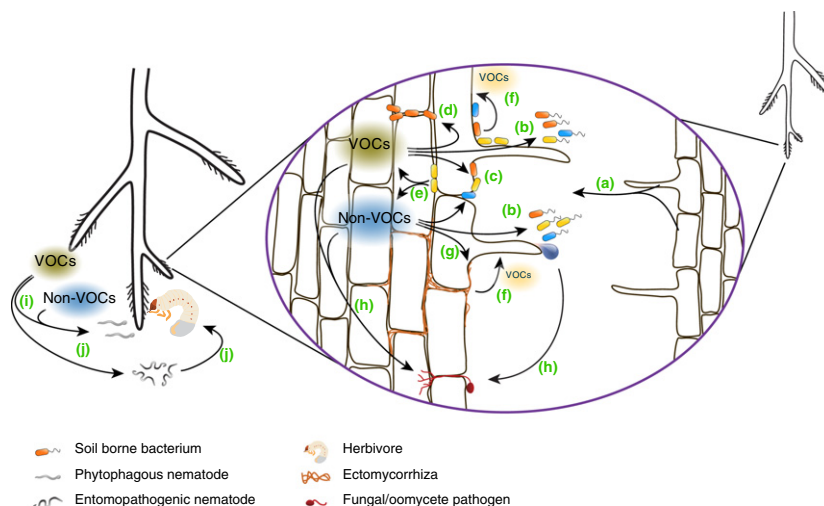
Root exudates play an important role in plant–plant interactions known as allelopathy, a phenomenon that includes both beneficial and negative interactions but is studied often in the context of competition between species and invasive plants (Turkington, 1989). Allelochemicals can be active at interspecific or intraspecific levels (Callaway *et al.*, 2004; Inderjit *et al.*, 2011) (Figures 1 and 2a). Although allelochemicals are present in several plant tissues, including leaves, bark, flowers, fruit, and roots, the major route by which these compounds reach the surrounding soil is through root exudation (Jilani *et al.*, 2008). Substances that exhibit allelopathic effects belong to several different chemical classes including benzene-derived compounds, phenolics, hydroxamic acids, and terpenes; these will be discussed here (Figure 1).

One of the most studied allelochemicals is sorgoleone, a lipophilic benzoquinone and allelotoxin from *Sorghum bicolor* (Figure 1). Sorgoleone [2-hydroxy-5-methoxy-3-[(8'Z, 11'Z)-8',11',14'-pentadecatriene]-p-benzoquinone] and the sorgoleone-like compound, 5-ethoxysorgoleone, accumulate in the form of oily droplets at the tip of *S. bicolor* root hairs, implying an important role of this root part in sorgoleone production and secretion (Chang *et al.*, 1986; Yang *et al.*, 2004a). A study by Dayan (2006) showed that sorgoleone-derived compounds can be detected in *S. bicolor* root exudates, and their concentration increases upon sensing other plants nearby, but not by most environmental changes. This factor highlighted a possible feedback sensing mechanism in regulating sorgoleone production. Sorgoleone, and other structure analogues from *Sorghum* root hair exudates, act as potent inhibitors of photosystem II (PSII) (Nimbal *et al.*, 1996; Kagan *et al.*, 2003). The compounds likely inhibit the cycling of plastoquinone B (Q<sub>B</sub>), which results in electron-transfer chain disruption leading to an impaired respiration process (Gonzalez *et al.*, 1997). In addition, sorgoleone was found to bind to hydroxyphenyl-pyruvate dioxygenase (HPPD),

Plant-plant interaction	
Benzoquinones	 <p>sorgoleone 5-ethoxysorgoleone Yang et al., 2004</p>
Phenolic (proanthocyanidin trimer)	 <p>selliguaein A De Jesus Jatoba et al., 2016</p>
Benoxazinoids (BXs)	 <p>DIBOA DIMBOA APO AMPO Barnes et al., 1987; Barnes and Putnam, 1987; Macias et al., 2006; Macias et al., 2009</p>
Naphthoquinones (NQs)	 <p>shikonin deoxyshikonin dimethylacryl shikonin acetylshikonin Zhu et al., 2016</p>
S containing volatiles	 <p>diallyl disulfide Cheng et al., 2016</p>
Plant-fungi/oomycetes interaction	
Strigolactones (SLs)	 <p>5-deoxy-strigol strigol sorgolactone GR24 Al-Babili and Bouwmeester, 2015</p>
Homo-terpenes	 <p>DMNT Sohrabi et al., 2015, 2017</p>
Isoflavones	 <p>prunetin genistein daidzein Hassan and Mathesius, 2012</p>
Plant-bacteria interaction	
Flavonoids	 <p>7,4'-dihydroxyflavone Szoboszlai et al., 2016</p>
NQs	 <p>β-hydroxyisovaleryl-shikonin acetylshikonin Brigham et al., 1999</p>
Plant-pest/nematode interaction	
Phthalates	 <p>dibutyl phthalate dimethyl phthalate Yang et al., 2016</p>
Phenolics	 <p>2,6-ditertbutyl-p-cresol Yang et al., 2016</p>
Mono-terpenoids	 <p>1,8-cineole camphor Chen et al., 2004; Weissteiner et al., 2012</p>
Sesqui-terpenoids	 <p>(E)-β-caryophyllene geijerene pregeijerene Rasmann et al., 2005; Ali et al., 2010</p>
Diterpenoids	 <p>rhizathalene A momilactone A kauralexin A Xu et al., 2012; Vaughan et al., 2013</p>
Triterpenoids	 <p>glycinolepin A glycinolepin B glycinolepin C solanolepin A avenacin A A1: R<sub>1</sub> = OH, R<sub>2</sub> = NHCH<sub>3</sub> A2: R<sub>1</sub> = OH, R<sub>2</sub> = H D-Glc = D-glucose L-Ara = L-arabinose Masamune et al., 1982; Fukuzawa et al., 1985; Schenk et al., 1999; Papadopoulou et al., 1999</p>
FA derivatives conjugates	 <p>lauric acid (E)-2-hexenal hexadecanal L-ascorbyl 2,6-dipalmitate Palma et al., 2012; Robert et al., 2012; Dong et al., 2014; Yang et al., 2016</p>
S containing volatiles	 <p>methanethiol DMS thiocyanic acid DMDS thiocyanates DMSO isothiocyanates Ferry et al., 2007; Crespo et al., 2012</p>

**Figure 1.** Specialized metabolite classes and representative compounds with functions in root-organism interactions.

Benoxazinoids (BXs), naphthoquinones (NQs), strigolactones (SLs), fatty acids (FA), DIBOA [4-dihydroxy- 2H-1,4-benzoxazin-3(4H)-one], 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], DMNT [(E)-4,8-dimethyl-1,3,7-nonatriene], dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl sulfoxide (DMSO). Strigolactones are presented in both the plant-plant interaction and plant-fungi interaction panels.



**Figure 2.** Overview of known and putative functions of volatile and non-volatile specialized metabolites in the interaction of roots with soil-borne organisms. (a) Exudates from neighboring plant roots affecting other plant roots and microbial communities in the rhizosphere. (b–d) (b) Water-soluble specialized metabolites exuded by roots or VOCs released into the rhizosphere attract soil-borne bacteria and stimulate or inhibit their growth in the (c) rhizosphere and (d) endosphere. Special functions include the role of flavonoids in the attraction of nitrogen-fixing rhizobia and root nodulation and the interference of root exudates with bacterial quorum sensing. (e) Metabolic breakdown and modification of specialized metabolites by microbes in the endosphere. (f) VOCs emitted by rhizobacteria and ectomycorrhizal fungi effecting root morphology and plant immunity. (g) Exudates (strigolactones) promote root-mycorrhizal fungi interactions (arbuscular mycorrhizal fungus not shown). (h) Attractive and growth inhibitory functions of volatile and non-volatile specialized metabolites on root microbial pathogens. (i) Direct repellent, deterrent, or attractive effects of exudates and VOCs on root herbivores and plant parasites. (j) Attraction of insect parasites (entomopathogenic nematodes) by root-derived VOCs.

causing the disruption of carotenoid biosynthesis and eventually plant death (Meazza *et al.*, 2002). While the proposed mode of action of sorgoleone was based on experiments with isolated chloroplasts, the compound is less likely to exhibit its activity in aboveground tissues because of its light sensitivity. This property might explain the evolutionary reason to release an allelotoxic metabolite to the soil (Dayan, 2006). Furthermore, a proposed activity of sorgoleone on the respiration machinery in green tissues upon root uptake and translocation to foliar tissues was not supported by labelling experiments, which demonstrated that sorgoleone is not transported to the leaves (Dayan *et al.*, 2009). Instead, Hejl and Koster (2004) proposed that sorgoleone inhibits  $H^+$ -ATPase activity in isolated maize root microsomes, which leads to an impaired uptake of water. This finding suggests an alternative mechanism of phytotoxicity that is more likely to occur in the below-ground environment.

Another group of allelopathic quinones produced by roots are the naphthoquinones (NQs) (Figure 1). Deoxyshikonin, and shikonin are the most abundant NQs in the soil, followed by acetylshikonin and dimethylacryl shikonin (Zhu *et al.*, 2016). The unique UV absorbance, autofluorescence and red coloration of shikonins assist in the experimental localization of these compounds (Yamamoto *et al.*, 2000; Tatsumi *et al.*, 2016). To prevent autotoxicity, shikonins are typically incorporated into vesicles in the periderm cells of primary and secondary roots (Zhu *et al.*, 2016). The

release of shikonins has been reported from roots of the Australian invader weed *Echium plantagineum*, where secretion occurs in the form of droplets from root hair tips of mature and young seedlings (Weston *et al.*, 2012a,b). Field observations demonstrated that *E. plantagineum* from Australia has significantly higher allelopathic activity than the same species located in Spain. Accordingly, chemical analysis of Australian *E. plantagineum* root exudates showed more shikonin accumulation than exudates obtained from plants in Spain (Grigulis *et al.*, 2001; Zhu *et al.*, 2016). Similarly, the invasive plant species *Centaurea diffusa* from Eurasia has strong inhibitory effects on bunchgrass species from North America, but mild effects on bunchgrass species from Eurasia (Callaway and Aschehoug, 2000). Although the active compound from *C. diffusa* is not well characterized yet, this observation suggests a possible change in the target plant sensitivity dictated by the neighbors found in the new geographic location. Together, these findings indicate that geographic relationships play an essential role in plant–plant communication and that both allelochemical plant-producers and target plants may show different susceptibility depending on their geographical location.

Phenolic substances have been reported to possess toxic effects towards other plants at different growth stages. Several phenolic compounds found in the soil were shown to inhibit seed germination under lab conditions (Muscolo *et al.*, 2001; Li *et al.*, 2010). Vanillic, *p*-coumaric,

*p*-hydroxybenzoic and protocatechuic acids inhibit different glycolytic enzymes and, as a result, reduce the net ATP and carbon production required for developing new tissues at the seed stage (Muscolo *et al.*, 2001). De Jesus Jatoba *et al.* (2016), showed that selligueain A, a proanthocyanidin trimer derived from the invasive fern species *Pteridium arachnoideum*, is found in soil through absorption from dead plant tissues (Figure 1). The compound showed phytotoxic activity against *Sesamum indicum*, largely by inhibiting root and stem growth and affecting chlorophyll content.

Flavonoids, which are specialized metabolites derived from the phenylpropanoid pathway (Vogt, 2010), have been described more recently for their allelopathic activity on parasitic weeds (Hooper *et al.*, 2015). Controlling parasitic plants by phytotoxic compounds has been subject to studies over many years due to severe crop losses inflicted by these plant species. Plants release sesquiterpene lactones named strigolactones (Figure 1) as below-ground signals to induce symbiosis between plant roots and arbuscular mycorrhizal (AM) fungi of the Glomeromycota. This interaction is based on the bidirectional transfer of organic carbon and soil nutrients (Smith and Smith, 2011). Parasitic weeds, which are completely dependent on their host for survival and development, hijack these signals to find a living root nearby (Al-Babili and Bouwmeester, 2015). Application of exudates collected from the drought tolerant species *Desmodium uncinatum* was able to significantly inhibit parasitism of maize roots by *Striga hermonthica* under field conditions (Hooper *et al.*, 2015). Chemical analysis of the collected exudates revealed that they were dominated by *C*-glycosyl flavonoids, which showed allelopathic effects on parasitic weeds (Hooper *et al.*, 2015).

Another important group of aromatic compounds possessing allelopathic activity are cyclic hydroxamic acids [e.g., benzoxazinoids (BXs) or benzoxazinones]. These substances were first discovered in experiments showing a 93% reduction in weed biomass growth in plots cultivated with rye (*Secale cereale* L.) as compared with plots without rye (Barnes and Putnam, 1983). The active molecules responsible for biomass reduction were identified as 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] (Barnes and Putnam, 1987; Barnes *et al.*, 1987; Macías *et al.*, 2006) (Figure 1). In the plant tissue, DIBOA and DIMBOA undergo degradation to give more stable metabolites. In particular, the aminophenoxazinone compounds APO [2-amino-3H-phenoxazin-3-one] and AMPO [2-amino-7-methoxy-3H-phenoxazin-3-one] are two highly potent phytotoxins (Macías *et al.*, 2004, 2006, 2009) (Figure 1). These degradation products were detected together with their precursors, DIBOA and DIMBOA, in roots of *Sinapis alba* cultivated with Triticeae species (Belz and Hurle, 2005). The different

cyclic hydroxamic acids are physiologically active on various plant species suggesting a conserved mode of action on cellular processes (Dayan *et al.*, 2009). Indeed, these compounds inhibit histone acetyltransferases and histone deacetylases (HDACs), which cause a wide range of chromatin rearrangements in the target plants. When growth inhibition activity of the more stable aminophenoxazinones, APO and AMPO, was tested *in vivo* on *Arabidopsis* and lettuce (*Lactuca sativa*) seedlings, they had a similar and even lower EC<sub>50</sub> values as compared to those of a commercial phytotoxic HDAC inhibitor, demonstrating the potency of these metabolites (Venturelli *et al.*, 2015). Interestingly, the target plants showed differences in sensitivity to these allelochemicals. Sicker *et al.* (2001) showed that maize (*Zea mays*) and other plants are able to detoxify BOA in several ways. In particular, transformation of the active functional groups in BOA to carbamate occurs through formation of BOA-6-*O*-glucosylation and *N*-glucosylation to form nontoxic compounds. Accumulation of the BXs detoxification products has, however, only been reported from maize roots (Sicker *et al.*, 2001; Sirikantaramas *et al.*, 2008). Interestingly, DIMBOA in maize functions as an inducer of innate immunity against fungi and insects in above ground tissues, thus indicating a potential role of BXs in the interaction with other organisms apart from plants (Ahmad *et al.*, 2011).

Apart from non-volatile exudates, root-derived VOCs have been implicated in below-ground plant–plant interactions. Jassbi *et al.* (2010) associated blends of monoterpene and sesquiterpene volatiles from roots of sagebrush (*Artemisia tridentata*) with phytotoxic effects on seedlings of the naturally co-occurring tobacco species, *Nicotiana attenuata*. In a recent study, Cheng *et al.* (2016) tested growth inhibitory effects of the sulfur-containing volatile diallyl disulfide from garlic, which is known for its strong allelochemical potential. Diallyl disulfide either stimulated or inhibited the growth of tomato seedlings in a dose-dependent manner by affecting cell division, phytohormone balance, and the expression of expansin genes. Similar mechanisms of phytotoxicity have been examined for a variety of volatile terpenoids. Treatment of *Arabidopsis* roots with the sesquiterpene farnesene leads to a loss of gravitropism, which is related to microtubule disorganization (Araniti *et al.*, 2016). The authors associated this alteration of microtubules with hormonal imbalance (increase in ethylene and auxin) and elevated levels of reactive oxygen species (Araniti *et al.*, 2016). Disruption of microtubules of *Arabidopsis* seedlings has also been described previously upon treatments with the monoterpene aldehyde citral (Chaimovitsh *et al.*, 2010). Many other studies have demonstrated *in vitro* growth inhibitory effects of essential oils collected from above and below-ground tissues; however, there is often little evidence for the activity of these compounds in a natural soil environment.

In general, studies on the function of root-derived metabolites in plant–plant interactions need to consider the likely degradation of compounds by soil microbes. For instance, allelopathic effects of meta-tyrosine were documented in sterilized soil but significantly diminished when non-sterile soil was used, raising the possibility that m-tyrosine might be altered by the soil microbial community (Kaur *et al.*, 2009). Conversely, soil microbes can play an intermediary role in plant–plant interactions by converting chemicals in the rhizosphere to more potent substances. For example, *Acinetobacter calcoaceticus* can convert the BXs 2(3H)-benzoxazolinone (BOA) to 2,2'-oxo-1,1'-azobenzene (AZOB), the latter of which possesses a more inhibitory effect on some plant species (Jilani *et al.*, 2008). A rather elegant but still underutilized way to gain a better understanding of the allelopathic effects or other functions of root exudates and their possible conversion products *in situ*, is the use of genetic approaches. In this way, allelopathic effects have been documented for momilactones (Figure 1), which are labdane-derived diterpenoids produced by rice. By using momilactone biosynthetic mutants, Xu *et al.* (2012) provided convincing evidence for a role of these compounds in suppressing the growth of the rice paddy weed, barnyard grass (*Echinochloa crus-galli*).

## ROOT–BACTERIA INTERACTIONS MEDIATED BY SPECIALIZED METABOLITES

### The function of plant-derived specialized metabolites

The rhizosphere microbiome has a direct effect on plant health and resistance to pathogens (Pieterse *et al.*, 2014). Root metabolite profiles and gene expression associated with microbial colonization were shown multiple times to undergo major changes once above- or below-ground biotic stresses are imposed (Brigham *et al.*, 1999; Haichar *et al.*, 2008; Lundberg *et al.*, 2012; Gulati *et al.*, 2014; Mendes *et al.*, 2014; Reinhold-Hurek *et al.*, 2015). The assembly of root-associated microbial communities from soil microbiomes is driven, in part, by host-specific factors as well as soil-dependent influences. Bulgarelli *et al.* (2013) developed a two-step selection model for the differentiation of root microbiota. According to this model, the recruitment of microbes from the soil and the first shift in the soil microbiome community is caused by the release of nutrient-containing rhizodeposits. In a second step, additional selective factors dependent on the host plant genotype, generate a more distinct microbial community on the immediate root surface and within the root. It can be assumed that various root-derived specialized metabolites that promote or inhibit bacterial growth are involved in this selective process (Figure 2b–d).

A classic example for phenylpropanoid type compounds that are released from wounded plants and serve as chemoattractants of a soil-borne pathogen are

3,5-dimethoxyacetophenone (acetosyringone) and hydroxyacetosyringone. These compounds attract *Agrobacterium tumefaciens*, which causes crown gall disease (Stachel *et al.*, 1985; Hess *et al.*, 1991; Dixon, 1995). The by-far most studied phenylpropanoids and plant specialized metabolites in the rhizosphere with respect to their role in plant–microbe interactions are the flavonoids. Different classes of flavonoids including flavonol (e.g. quercetin and kaempferol), flavanones (e.g. naringenin and liquiritigenin), isoflavones (e.g. genistein and daidzein) and flavanols (e.g. catechin) have been detected in root exudates of different plant species (Cesco *et al.*, 2010). Flavonoids have been associated with the regulation of nodulation genes in nitrogen-fixing rhizobia (Hassan and Mathesius, 2012) as well as quorum-sensing (QS) signals of *Pseudomonas aeruginosa* PAO1 (Vandeputte *et al.*, 2010, 2011). Application of the most abundant flavonoid in the root exudate of *Medicago sativa*, 7,4'-dihydroxyflavone (Figure 1), to bulk soil resulted in significant changes in the relative richness of *Acidobacteria*, *Gaiella*, *Nocardioideae*, and *Thermomonosporaceae* taxa, that are known to interact with plant roots (Szoboszlay *et al.*, 2016). As compared with bulk soil, the rhizosphere harbors a high number of bacterial taxa that employ QS (Elasri *et al.*, 2001). This finding highlights the importance of such signaling mechanisms in the vicinity of plant roots. Exudate blends from pea (*Pisum sativum*), crown vetch (*Coronilla varia*), *Medicago truncatula*, rice (*Oryza sativa*), soybean (*Glycine max*) and tomato (*Lycopersicon lycopersicon*) showed a QS mimicking activity when tested with bacterial sensors of the N-acyl-homoserine lactones (AHLs) system (Teplitski *et al.*, 2000; Rasmussen *et al.*, 2005). The exact mode of action of the applied exudate blends is still unknown, yet, it is likely that such QS mimicry activity is mediated through specialized metabolites found in plant exudates.

Naphthoquinones are not only compounds that exhibit allelopathic activities (see above) but also have a strong impact on soil microorganisms as was shown for derivatives of NQs isolated from roots of *Lithospermum erythrorhizon* (Brigham *et al.*, 1999). The two derivatives, acetyl-shikonin and  $\beta$ -hydroxyisovaleryl-shikonin (Figure 1), were the most biologically active compounds detected in hairy root culture of *L. erythrorhizon* (Tatsumi *et al.*, 2016). Dual functions have also been described for BXs secreted from maize roots, which act as allelochemicals but also function as chemoattractants for the plant-beneficial bacterium *Pseudomonas putida* in the rhizosphere. Moreover, BXs were found to induce *P. putida* root colonization, a response that was not observed in the DIMBOA-deficient *bx1* mutant (Neal *et al.*, 2012).

The phytohormone salicylic acid (SA) is primarily known for mediating systemic acquired resistance (SAR) in above-ground tissues. Recently, Lebeis *et al.* (2015) examined the effect of SA on root–microbial community composition.

Interestingly, the authors showed that in *Arabidopsis* SA is involved with shaping the root microbiome by analysing a set of immune-compromised mutants including *jar1 ein2 npr1*, *ein2 npr1*, and *npr1 jar1*, which all lack a response to SA. Those plants presented a much lower abundance of certain bacterial phyla, e.g. *Firmicutes*, as part of the endophytic microbiome, which is a sub-population of the rhizosphere microbial community (Turner *et al.*, 2013). The selectivity of the microbes that colonize this plant compartment is still not fully understood and phytohormone secretion through exudates not yet proved; thus, there is still a critical gap of information in this emerging research field.

The effect of root-derived VOCs on epiphytic and endophytic microbes is largely unknown. A critical role of VOCs in defining microbial communities has been demonstrated in the phyllosphere (leaf surface) and anthosphere (surface of floral tissues) (Farré-Armengol *et al.*, 2016). VOCs emitted from flowers are involved in protecting floral reproductive tissues from phytopathogenic bacteria that reduce plant fitness (Huang *et al.*, 2012). An analysis by Junker *et al.* (2011) of entire bacterial communities on flower petals revealed that the community composition on these tissues was different and less diverse than that found on leaves. A follow up statistical approach correlated the distribution of bacterial taxa with different profiles of VOCs and clearly indicated that bacterial genera occupy strongly divergent niches based on scent emissions (Junker *et al.*, 2013). In line with these findings, a study of the composition of microbial communities in the essential oil producing roots of *Vetiver* grass (*Vetiveria zizanioides*) has given some important insights into the role of VOCs as host-specific chemical selective factors (Del Giudice *et al.*, 2008). Bacterial endophytes of the *Pseudomonadaceae* and *Enterobacteriaceae* families were shown to use sesquiterpenes in *Vetiver* roots as sole C source (Figure 2e). These bacteria appear to specifically reside in the vicinity of oil accumulating cells in the cortex. The association with terpene metabolizing bacteria seems to be important for stimulating VOC production in *Vetiver* roots since plants grown under sterile conditions do not accumulate terpenoids. These findings suggest a mutualistic interaction in which the plant provides VOC based nutrients and at the same time benefits from the stimulated production of these compounds by using them for defense against pathogens and pests.

It can be assumed that VOCs released by plant roots function as chemoattractants to recruit VOC metabolizing bacteria from the soil environment (Figure 2a). The use of VOCs as carbon source of soil-borne microbes has been described in other cases such as for the catabolism of the monoterpene  $\alpha$ -pinene by *Pseudomonas fluorescens* and *Alcaligenes xylosoxidans* (Kleinheinz *et al.*, 1999) and the multi-step conversion of camphor to isobutanoyl-CoA by soil-borne *Pseudomonas putida* strains carrying a pCAM plasmid for camphor breakdown (Rheinwald *et al.*, 1973;

Kadow *et al.*, 2011). Together, these findings suggest that VOCs and likewise non-volatile specialized metabolites produced by roots have the ability to function as host plant specific chemo-selective 'filters' that support and/or inhibit microbial growth. To what extent root-associated microbes stimulate the formation of these compounds by eliciting immune responses remains to be determined.

### Specialized metabolites from the 'other' side – volatile signals from microbes

A growing agronomic interest in root-associated microbes that benefit plant growth and health, has led to efforts to identify possible microbial elicitors in this process. Many studies have provided evidence for a possible role of VOCs released by rhizobacteria of the genus *Pseudomonas* and *Bacillus* in promoting plant growth and mediating biotic and abiotic stress resistance, e.g. Ryu *et al.* (2003, 2004a), Farag *et al.* (2006), Hernández-León *et al.* (2015), Asari *et al.* (2016) (Figure 2f). Root-colonizing bacteria produce a diverse array of volatiles that are rich in alkenes, alcohols, ketones, and terpenes (Peñuelas *et al.*, 2014; Schenkel *et al.*, 2015). While the effects of VOC blends on plant performance were examined mostly *in vitro*, relatively few experiments have verified these functions *in situ* by using bacterial mutants that are impaired in the biosynthesis of distinct compounds. For example, Cho *et al.* (2008) showed that *Arabidopsis* plants inoculated with *Pseudomonas chlororaphis* mutants that are unable to produce 2*R*,3*R*-butanediol, did not exhibit drought tolerance in contrast to plants being colonized with wild type bacteria.

Root responses to bacterial VOCs depend on different signaling pathways. Blends of VOCs released by different *Bacillus subtilis* strains have been shown to differentially upregulate ethylene, jasmonate, and salicylate defense signaling pathways (Ping and Boland, 2004; Ryu *et al.*, 2004b; Kwon *et al.*, 2010). Notably, rhizobacterial VOCs have been implicated in facilitating the well known response of induced-systemic resistance (ISR) (Ryu *et al.*, 2004a). Recently, Zamioudis *et al.* (2015) demonstrated in *Arabidopsis* that VOCs of ISR-inducing *Pseudomonas* bacteria enhance the expression of the transcription factor MYB72, which plays a role in systemic immunity as well as in activating iron acquisition. That VOCs modify the expression of specific transcription factors was also apparent from a study by Wenke *et al.* (2012), which investigated volatiles emitted by plant growth-inhibiting bacteria.

Besides their role in plant immunity, bacterial VOCs can have distinct effects on root architecture. Such modifications of roots include increased length and branching and have been observed in both dicots and monocots (Delaplace *et al.*, 2015; Gutiérrez-Barranquero *et al.*, 2015) (Figure 2f). VOCs produced by root-colonizing mycorrhizal fungi were suggested to play equally important roles on root morphology (see below) (Figure 2f). How microbial

VOCs elicit changes in root architecture is largely unknown. However, it appears that various different genes involved in plant growth are targeted in response to VOCs as has been revealed recently by genome-wide association studies using different *Arabidopsis* accessions in exposure to VOC blends from the plant growth-promoting rhizobacterium *Pseudomonas simiae* (Wintermans *et al.*, 2016).

## SPECIALIZED METABOLITES AND ROOT-FUNGI/OOMYCETE INTERACTIONS

### Interactions with mycorrhizal fungi

Plants and soil-borne fungi or oomycetes have developed symbiotic, parasitic, and pathogenic relationships through adaptation and co-evolution. Many plants sustain beneficial interactions with AM fungi; however, still relatively little is known with respect to the chemical communication between the two organisms. The best studied chemical signals associated with root-AM interactions are the strigolactones (Figures 1 and 2g). Akiyama *et al.* (2005) reported that the sesquiterpenes, 5-deoxy-strigol, sorgolactone and strigol, when collected from root exudates of *Lotus japonicas*, induced extensive hyphal branching in the AM fungus *Gigaspora margarita* at nanomolar concentrations. This effect was also detected with the sorgolactone synthetic homologue, GR24 (Dor *et al.*, 2011). In fact, sorgolactones showed the same effect on additional AM strains, i.e. *Gigaspora rosea* and *Glomus intraradices* (Akiyama and Hayashi, 2006). AM-colonized plants were found to change their response to pathogens through activation of ISR (Watts-Williams *et al.*, 2015). Other studies have demonstrated that AM-colonized plants have altered metabolic profiles of exudates (Scheffknecht *et al.*, 2006), which suggests that AM fungi could indirectly induce major changes in soil microbiome composition.

As has been observed with root-colonizing bacteria, there is growing evidence that specialized metabolites released by mycorrhizal fungi affect root architecture (Figure 2f). A study by Ditengou *et al.* (2015), demonstrated that volatile sesquiterpenes released by the ectomycorrhizal fungus *Laccaria bicolor* promote the formation of lateral roots in poplar and *Arabidopsis*, thereby enhancing the root surface area for improved nutrient uptake and fungal access. Similarly, the volatile compound 6-pentyl-2H-pyran-2-one derived from a root-associate fungus in the genus *Trichoderma* inhibits primary root growth and induces lateral root formation (Garnica-Vergara *et al.*, 2016).

### Interactions with pathogenic fungi/oomycetes

Besides mutualistic interactions, plant roots are frequent targets of soil-borne fungal or oomycete pathogens. Prior to colonization, hyphae of fungal pathogens can detect chemical stimuli to orient their growth towards the plant

host (Figure 2h). For example, directed growth of the plant pathogen *Fusarium oxysporum* towards tomato (*Solanum lycopersicum*) roots was characterized recently and involves the catalytic activity of root-secreted class III peroxidases (Turrà *et al.*, 2015). The substrates of these enzymes remain unknown but were proposed to be secreted from the plant roots. Conversely, *F. oxysporum* chemotrophic sensing was found in this study to be mediated through a distinct MAPK signaling cascade activated by a protein with homology to the *Saccharomyces cerevisiae* Ste2 sex pheromone receptor, which binds to a  $\alpha$ -pheromone peptide. This finding suggests that root signals sensed by the fungus may be peptides as well (Turrà *et al.*, 2015).

A similar eavesdropping has been described in legumes for root-secreted isoflavones (i.e. prunetin, genistein, and daidzein) (Figure 1), which play an important role in *Rhizobium*-legume symbiosis as chemoattractants, inducers for nodulation genes, and regulators of phytoalexin resistance (Hassan and Mathesius, 2012). The chemotactic oomycete pathogens, *Phytophthora niederhauserii*, *P. pisi*, *P. sojae* and *P. vignae*, have evolved reception mechanisms to recognize the same chemical signals released by legume roots, which highlights an evolutionary change to hijack a beneficial plant-microbe symbiosis (Hosseini *et al.*, 2014).

Plants, which successfully combat root fungal pathogen attack, often exude specialized metabolites with direct defensive activities (Figure 2h). In *Arabidopsis*, tryptophan-derived compounds including the phytoalexin camalexin, accumulate upon infection by the fungal pathogen *Verticillium longisporum* (Iven *et al.*, 2012). Double mutants impaired in the biosynthesis of these compounds show higher susceptibility to the pathogen (Iven *et al.*, 2012). Triterpenoids (Figure 1) are among the most potent antifungal defense compounds released by plant roots. Specifically, saponins, glycosylated triterpenoids produced by cereals, represent well known constitutive defense chemicals against fungal pathogens as has been demonstrated for the antifungal effects of avenacin secreted by oat roots (Papadopoulou *et al.*, 1999; Osbourn, 2003). Other more recently detected terpenoids with activities as phytoalexins are the sesquiterpene zealexins and the diterpene kauralexins (Huffaker *et al.*, 2011; Schmelz *et al.*, 2011) (Figure 1). The accumulation of these compounds is induced in the roots of maize upon fungal pathogen infection and abiotic stresses such as drought and salt stress (Vaughan *et al.*, 2015). Mutants deficient in kauralexin production are more sensitive to drought. Whether these diterpenoids protect against drought in a direct or indirect manner will require further analysis.

Several studies have, furthermore, suggested that VOCs emitted by roots inhibit the growth of pathogens (Figure 2h), as was shown, for example, for oxygenated fatty acid derivatives and their effects on *Fusarium* (Cruz *et al.*,



2012). Similar activities have been suggested for root-derived volatile terpenoids, such as the common below-ground VOC 1,8-cineole (Wenke *et al.*, 2010) (Figure 1). Moreover, studies in *Arabidopsis* indicated defensive functions of the common volatile homoterpene (*E*)-4,8-dimethyl-1,3,7-nonatriene (DMNT) against infection by the root rot pathogen *Pythium irregulare* (Sohrabi *et al.*, 2015, 2017). DMNT is released as a breakdown product of the triterpenoid precursor, arabidiol, in response to physical contact of *Arabidopsis* roots with *Pythium* oospores. It may contribute to reducing oospore germination at the early stage of infection as was suggested by *in vitro* experiments (Sohrabi *et al.*, 2015).

### SPECIALIZED METABOLITES IN THE INTERACTION OF ROOTS WITH INSECT HERBIVORES AND PLANT-PARASITIC NEMATODES

#### Interactions with phytophagous nematodes

Several specialized metabolites released by plant roots have been implicated in defensive roles to combat root-attacking arthropods or nematodes (Figure 2i). Soil nematodes are among the most abundant and species-rich organisms in the soil. Many soil nematodes are phytophagous and feed on below-ground plant tissues, predominantly roots (Bohmann, 2015). Recruitment of nematodes to plant roots can be through specific signals secreted as a result of insect herbivory (Rasmann and Turlings, 2008), or root mechanical damage (Laznik and Trdan, 2013). Nematode–plant interactions display specificity, which is likely driven by chemical signals. For example, *in vitro* assays showed that *Ditylenchus destructor* was attracted to sweet potato crude root exudates (Xu *et al.*, 2015). In addition, water-soluble metabolites exuded from the root tip of green pea (*Pisum sativum* L.) and maize resulted in a dormancy-like state in nematodes and reduced their infectability (Zhao *et al.*, 2000; Hawes *et al.*, 2005).

Plant-exuded specialized metabolites can affect various stages of the nematode life cycle such as egg hatching, chemotaxis toward root hosts, and mortality. The root-knot nematode *Meloidogyne incognita* is well known for its devastating effect on tomato. Compositional analysis of tomato cultivars with varying susceptibility to *M. incognita* showed a significant increase in L-ascorbyl 2,6-dipalmitate, dibutyl phthalate, dimethyl phthalate (Figure 1) and 2,6-ditertbutyl-*p*-cresol when inoculated with *M. incognita*. Each of these compounds suppresses *M. incognita* egg hatching and increases the mortality rate of second stage juvenile nematodes (Yang *et al.*, 2016). By contrast, both tomato and potato roots were found to stimulate egg hatching of cyst nematodes of the genera *Heterodera* and *Globodera* by secretion of the nortriterpene solanoelepin A (Schenk *et al.*, 1999). Similarly, soybean (*Glycine max*)

and kidney bean (*Phaseolus vulgaris*) secrete eclepins, glycinoelepin A and glycinoelepin B/C, respectively (Masamune *et al.*, 1982; Fukuzawa *et al.*, 1985) (Figure 1). Intercropping of tomato and crown daisy plants resulted in significant reduction of tomato root infestation by *M. incognita*. Interestingly, the crown daisy plant (*Chrysanthemum coronarium*) was found to secrete lauric acid (Figure 1) from the roots to reduce *M. incognita* root infestation, by disturbing the transcript level of Mi-flp-18, a neuromodulator that regulates nematode chemotaxis (Dong *et al.*, 2014). The release of chemicals that affect root parasitic nematodes can also be mediated by microorganisms in the soil. For instance, Vos *et al.* (2012) observed that the presence of AM fungi reduces the penetration by *M. incognita* through an alteration of the root exudate profile of the host plant (Vos *et al.*, 2012). These examples highlight the importance of experimenting in a soil matrix, as it accommodates several types of organisms that are involved in integrating plant response.

#### Interactions with insect herbivores

Besides reducing infections by plant-parasitic nematodes, root-derived specialized metabolites may mitigate or inhibit feeding by soil-dwelling arthropod herbivores (Figure 2i). Erb *et al.* (2013) presented an excellent overview of the activities of different specialized metabolites in root–herbivore interactions. Surprisingly, few negative effects of specialized compounds on root herbivores have so far been demonstrated *in situ*. Examples include cardenolides produced by milkweed (Rasmann *et al.*, 2011) and hydroxycinnamic acids in sweet potato (Stevenson *et al.*, 2009).

Volatile organic compounds emitted by plant roots contribute to the defense against root-attacking herbivores. For example, studies in *Arabidopsis* demonstrated anti-feedant activities of constitutively produced semi-volatile diterpenes named rhizathalenes against opportunistic root herbivores such as *Bradysia* larvae (Vaughan *et al.*, 2013) (Figure 1). Sulfur-containing volatiles that are considered direct defenses of crucifers against below-ground herbivores are the enzymatic breakdown products of glucosinolates (Halkier and Gershenzon, 2006; Xu *et al.*, 2016). Endogenous thioglucosidases called myrosinases hydrolyze the glycoside precursors to release glucose and an aglycone that is further rearranged into volatile isothiocyanates (ITC), thiocyanates (TC) and nitriles (Halkier and Gershenzon, 2006; Xu *et al.*, 2016) (Figure 1). The breakdown products have toxic or deterrent effects on insects and exhibit nematocidal activities (Buskov *et al.*, 2002). Herbivory can stimulate an increase in root glucosinolate levels, as was, for instance, observed for indole glucosinolates in *B. nigra* roots upon feeding by the cabbage root fly, *Delia radicum* (Van Dam and Raaijmakers, 2006). Emissions of the corresponding volatile breakdown products have been monitored directly by the use of proton transfer

reaction mass spectrometry (PTR-MS) (Crespo *et al.*, 2012). This study also demonstrated dynamic changes in the profiles of sulfur-containing compounds upon *Delia radicum* feeding. While thiocyanates and isothiocyanates accumulated during the first 1–6 h after infestation, methanethiol, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) (Figure 1) levels increased 6–12 h post larval application.

As a consequence of evolutionary adaptation, root-derived volatile and non-volatile specialized metabolites with repellent or deterrent activities may also serve as chemical cues to attract herbivorous insects or plant-parasitic nematodes and stimulate feeding (Farnier *et al.*, 2012) (Figure 2i). MBOA, a breakdown product of BXs in maize roots, enhances feeding by western corn rootworm larvae (Robert *et al.*, 2012b). Another example are isoflavonoids that are exuded by root nodules of clover and serve as attractants to the clover root weevil, *Sitona Lepidus* (Johnson *et al.*, 2005). In terms of volatile cues that function at longer distance, Palma *et al.* (2012) found that females of the clover root borer, *Hylastinus obscurus*, are particularly attracted to the C6 volatile (*E*)-2 hexenal (Figure 1), which is emitted among other volatile compounds from roots of red clover plants (*Trifolium pratense* L.). Among volatile terpenoids, 1,8-cineole emitted from damaged roots of oak attract larvae of the cockchafer *Melolontha hippocastani* (Weissteiner *et al.*, 2012) (Figure 1). Similarly,  $\beta$ -pinene has been recognized as a volatile attractant for root-feeding larvae of the cochineal scale, *Porphyrophora sophorae*, an oligophagous pest of Chinese liquorice, *Glycyrrhiza uralensis* (Liu *et al.*, 2016). Interestingly, the attractiveness of these root-specific volatile cues can be compromised in the presence of endophytic mutualists of the host plant. Rostás *et al.* (2015) found that the endophytic fungus *Neotyphodium uncinatum*, which colonizes the aerial parts of the grass hybrid *Festuca pratensis*  $\times$  *Lolium perenne*, reduced VOC emission levels from the roots and thereby made below-ground tissues less apparent for grubs (*Costelytra zealandica*).

Volatile organic compounds that are emitted in response to herbivore feeding typically attract parasites or predators at higher trophic levels. In the below-ground environment, VOC emissions induced by root feeders often represent chemical cues for insect-parasitizing (entomopathogenic) nematodes (Choo *et al.*, 1989) (Figure 2j). Many studies have documented the existence of such tritrophic interactions following the pioneering work by Turlings and colleagues on the attraction of entomopathogenic nematodes by the herbivore-induced release of the sesquiterpene (*E*)- $\beta$ -caryophyllene (Figure 1) from the roots of maize (Rasmann *et al.*, 2005; Rasmann and Turlings, 2008). Similar interactions have since then been described, for example, for the role of volatile terpenes emitted from citrus roots in response to the attack by the root weevil, *Diaprepes abbreviatus* (Ali *et al.*, 2011). Geijerene (2-isopropenyl-1-methyl-

1-vinyl-3-cyclohexane) and pregeijerene (1,5-dimethylcyclohexa-1,5,7-triene) (Figure 1) are the major two volatiles found in the solvent extract of *Diaprepes abbreviatus*-infested plants but not in mechanically damaged roots or undamaged roots (Ali *et al.*, 2010). Other examples include the function of S-containing VOCs such as DMDS (Figure 1) as attractants of soil-dwelling beetle predators of root fly larvae (Ferry *et al.*, 2007), or VOCs emitted by the roots of sugar cane in response to feeding by the sugarcane spittlebug (*Mahanarva fimbriolata*) (Tonelli *et al.*, 2016).

Knowledge of these indirect defense mechanisms have spurred efforts for their application in sustainable pest management. However, engineering VOCs that attract entomopathogenic nematodes requires a comprehensive understanding of 'who else' might be eavesdropping on these compounds. In the case of citrus, the control of root weevil pests via the attraction of parasitizing nematodes is hampered by the fact that the root-emitted VOCs also attract plant-parasitic nematodes (Ali *et al.*, 2011). In maize, the release of (*E*)- $\beta$ -caryophyllene induced by larvae of the western corn rootworm *Diabrotica virgifera virgifera* can attract 2nd instar larvae in a dose-dependent manner (Robert *et al.*, 2012a,c) although neonate larvae do not seem to follow this cue and instead use CO<sub>2</sub> as a general primary attractant (Reinecke *et al.*, 2008; Hiltbold and Hibbard, 2016). Notably, transgenic maize cultivars that constitutively produce (*E*)- $\beta$ -caryophyllene were found to be more susceptible to infection by the major fungal pathogens *Colletotrichum graminicola* and *Fusarium graminearum*, whose growth is stimulated in the presence of the volatile compound (Fantaye *et al.*, 2015). A similar case was observed in *Arabidopsis* lines overexpressing the 1,8-cineole synthases TPS23 and TPS27. Enhanced levels of 1,8 cineole in these transgenic lines in comparison to wild type plants had a stimulatory effect on conidial germination and hyphal growth of the soil-borne fungal pathogen *Verticillium longisporum* (Roos *et al.*, 2015). Overall, these results exemplify the complexity of dose-dependent beneficial and harmful interactions mediated by VOCs in the root environment.

#### TISSUE-SPECIFICITY, SUBCELLULAR LOCALIZATION AND RELEASE OF SPECIALIZED METABOLITES FROM ROOTS

Root-secreted specialized metabolites should be produced, stored and released to the rhizosphere at the correct time and place. Secretion of defense chemicals is tightly regulated, particularly for toxic metabolites, and plants employ various mechanisms to prevent autotoxicity. The chemical nature of exuded specialized metabolites remains too polar to simply diffuse through a lipid membrane, especially if modified by glycosylation, acylation, or hydroxylation reactions (Sirikantaramas *et al.*, 2008). Such modifications imply the involvement of transport pathways for root

efflux. Weston *et al.* (2012a) and Yazaki (2005) reviewed the major transport mechanisms utilized by plant roots to transport biologically active molecule to the rhizosphere, covering facilitated transports and vesicles.

Plants often store different metabolites in dissimilar tissues and cell types depending on their functionalities (Table 1). Direct metabolite measurements from a specific root tissue is technically laborious. Moussaieff *et al.* (2013) were able to localize more than fifty metabolites in defined *Arabidopsis* root cell types, with the most predominant classes detected being glucosinolates (GSLs), phenylpropanoids (PPs) and dipeptides (DPs). GSLs and PPs were found to accumulate in the inner cell layer, the cortex, while the downstream products of these two pathways were reported to be secreted to the rhizosphere (Muscolo *et al.*, 2001; Halkier and Gershenzon, 2006; Cesco *et al.*, 2010; De Jesus Jatoba *et al.*, 2016). Similarly, studies by Sohrabi *et al.* (2015, 2017) indicated that the triterpenoid arabidiol undergoes enzymatic oxidative cleavage in the stele of the *Arabidopsis* root, but derivatives of the non-volatile breakdown product, apo-arabidiol, are partly secreted in the rhizosphere. Such results, raise the possibility for metabolite transport between different root layers, especially in cases when the expression level of genes encoding key biosynthetic proteins is not in accordance

with metabolite accumulation in the roots cell layers (Brady *et al.*, 2007; Rogers *et al.*, 2012). DPs showed an interesting accumulation pattern. They were highly abundant in both endodermis and epidermis root layers, highlighting the possibility of their exudation and function as a chemotactic signal for fungal hyphae growth (Turrà *et al.*, 2015).

Root hairs are specialized cells extended from the main root epidermal layer. These cells are important for nutrient acquisition, plant anchoring, and production of specialized metabolites for defense purposes, as they are covering most of the root surface (Grierson *et al.*, 2014). Sorgoleone and related long chain hydroquinones (i.e. shikonins) are produced in copious quantities at the *Sorghum* spp. root hairs and are secreted from the root forming visible golden-colored droplets (Dayan *et al.*, 2009). Using light and electron microscopy, Czarnota *et al.* (2001, 2003) showed that sorgoleone synthesis is associated with the smooth endoplasmic reticulum and separated from the cytosol in vesicles, allowing safe transport out of root hair cells. In line with these observations, transcripts corresponding to the key enzyme in sorgoleone biosynthesis, the desaturase SOR1, were found exclusively in root hairs (Yang *et al.*, 2004b). Other lipophilic specialized metabolites such as shikonins are also transported in the cell via

**Table 1** Summary of tissue and cell type-specific accumulation and export mechanisms for plant root exudates

Compound class	Cell-specific site of storage <sup>a,b</sup>	Mechanism of transport/exudation	References
Glucosinolates	Cortex (t) (m)	–	Moussaieff <i>et al.</i> (2013), Brady <i>et al.</i> (2007)
Phenylpropanoids	Vacuoles of cortical cells, root hairs, cell wall, root tip and border cells (t) (m) (s)	PDR2; PDR7	Moussaieff <i>et al.</i> (2013), Brady <i>et al.</i> (2007), Badri <i>et al.</i> (2009, 2008), Hassan and Mathesius (2012), Hawes <i>et al.</i> (1998)
Dipeptides	Cortex (m)	–	Moussaieff <i>et al.</i> (2013)
Shikonins	Border cells. Lipid bodies of epidermal cells, later accumulated at the apoplast of the mature part of the root (t) (m) (s)	Exocytosis vesicles	Brigham <i>et al.</i> (1999), Yamamoto <i>et al.</i> (2000), Tatsumi <i>et al.</i> (2016), Zhu <i>et al.</i> (2016)
Sorgoleone	Root hair (t) (m) (s)	Exocytosis vesicles	Dayan <i>et al.</i> (2009), Czarnota <i>et al.</i> (2001, 2003), Yang <i>et al.</i> (2004b)
Coumarins	Root tip (t) (m) (s)	PDR9 (lateral root cap)	Fourcroy <i>et al.</i> (2014), Ružička <i>et al.</i> (2010)
Triterpenoids	Epidermis, mainly in the vacuoles (t) (m) (s)	–	Osborn <i>et al.</i> (1994), Osborn (1996), Papadopoulou <i>et al.</i> (1999), Field and Osborn (2008), Thimmappa <i>et al.</i> (2014)
Strigolactones	Root tips, styles, vascular (MZ) (t)	PDR1 (lateral root cap)	Kretschmar <i>et al.</i> (2012), Bainbridge <i>et al.</i> (2005), Booker <i>et al.</i> (2014), Arite <i>et al.</i> (2007)
Monoterpenoids, sesquiterpenoids	Epidermis, cortex (t) (m)	–	Chen <i>et al.</i> (2004), Ro <i>et al.</i> (2006)
Semi-volatile diterpenoids	Stele (t) (m)	–	Vaughan <i>et al.</i> (2013)
Homoterpene	Stele (MZ); Quiescent center (t) (m)	–	Sohrabi <i>et al.</i> (2015)

<sup>a</sup>Cell-specific site of biosynthesis and/or storage based on transcriptome and/or gene promoter activity data (t) or metabolomics data (m) or cell-specific detection of the compound (e.g. fluorescence) (s).

<sup>b</sup>Root elongation zone (EZ), root mature zone (MZ).

vesicles. These metabolites were found to accumulate in the sloughed border cells at the root tip and in lipid bodies in the epidermal cells of the young root. By contrast, in mature roots, shikonins are deposited in the apoplast (Brigham *et al.*, 1999; Yamamoto *et al.*, 2000; Tatsumi *et al.*, 2016).

Phenylpropanoids and flavonoids are largely considered as response molecules secreted under biotic and abiotic stress conditions. This group of molecules typically accumulates in vacuoles and the cell wall (Lin *et al.*, 2003). Along the length of a root, flavonoids are often found at the root tip region (Hawes *et al.*, 1998). A large number of studies examined the site of phenylpropanoid accumulation mostly using autofluorescence and abundance of transcripts corresponding to enzymes involved in their production and transport (Brady *et al.*, 2007; Badri *et al.*, 2008, 2009; Hassan and Mathesius, 2012; Moussaieff *et al.*, 2013). For instance, coumarins were localized to the *Arabidopsis* root tip based on the high transcript levels of the key biosynthetic enzyme Feruloyl Coenzyme A 6'-Hydroxylase 1 (F6'H1) (Schmid *et al.*, 2014) and the localization of their putative transporter to the outer cellular side of the lateral root cap and epidermis (Ružička *et al.*, 2010; Fourcroy *et al.*, 2014).

Direct localization of triterpenes in plant tissues is often facilitated by the fluorescent signal of their aromatic backbone. For example, the antifungal saponin avenacin discovered in oat roots tips has been localized to the root epidermal cells, mainly in vacuoles, by using fluorescence microscopy (Osborn *et al.*, 1994; Osborn, 1996; Morrissey and Osborn, 1999). The presence of antifungal compounds in the epidermal cells is likely an evolutionary process to prevent penetration by avenacin-sensitive fungi. Additional studies by Osborn and colleagues over the past years have demonstrated that the enzymes producing avenacins are co-expressed in the epidermis and encoded by genes organized in a metabolic gene clusters (Field and Osborn, 2008; Thimmappa *et al.*, 2014). Interestingly, the same authors revealed that simple triterpenoids such as  $\beta$ -amyrin impact root epidermal cell patterning and thus bear additional functions in root growth and development (Kemen *et al.*, 2014). Transport of terpenoids to the rhizosphere was so far studied with relation to strigolactones (SLs). SLs are actively secreted to the rhizosphere through the ABC transporter PDR1, which was found to be localized to the plasma membrane of root cells (Kretschmar *et al.*, 2012; Smith and Waters, 2012).

Volatile specialized metabolites produced in roots can accumulate inside the tissue when confined to oil ducts. In carrot roots, terpenes are synthesized in an interconnected network of oil ducts located in the phloem (Senalik and Simon, 1986). As another example, essential oils produced by roots of *Vetiver* grass accumulate in cortical parenchymatous secretory cells (Del Giudice *et al.*, 2008). Herbivory

or pathogen infection likely release these VOCs from their storage pools. Even in the absence of distinct secretory structures, the biosynthesis of VOCs can be confined to distinct root cell types. According to fine scale transcriptome maps in *Arabidopsis* (Brady *et al.*, 2007), terpene synthases that make monoterpenes, sesquiterpenes and semi-volatile diterpenes, are expressed in distinct tissues. For example, *TPS23* encoding a 1,8-cineole synthase is predominantly expressed in the epidermal layer, while *TPS08* produces semi-volatile diterpenes named rhizathalenes mostly in the stele (Chen *et al.*, 2004; Vaughan *et al.*, 2013). While the diffusion of VOCs might seem to compromise any tissue-specific function, it is possible that, given the radial nature of root tissues, overlapping chemical gradients of different VOCs might establish distinct concentration dependent zones in the endosphere and rhizosphere in interaction with microbes and herbivores. In fact, rhizathalenes, when produced in the center of the root, function as local antifeedants that protect surrounding cell layers against damage by below-ground herbivores (Vaughan *et al.*, 2013).

A stele-specific production in *Arabidopsis* roots has also been observed for the common volatile homoterpene DMNT, which is released as a breakdown product of the triterpenoid precursor, arabidiol (Sohrabi *et al.*, 2015). Interestingly, expression of the DMNT synthase gene, *CYP705A1*, occurs also specifically in the stem cell niche of *Arabidopsis* roots but the potential consequences of this cell type specificity are currently not well understood (Sohrabi *et al.*, 2015). It should be noted that the cell-specific formation of VOCs can change depending on the root developmental zone since expression of *Arabidopsis* terpene synthase genes for 1,8-cineole synthase and (*Z*)- $\gamma$ -bisabolene synthase convert from stele-specific expression in the elongation zone to epidermal and cortex-specific expression in more mature roots (Chen *et al.*, 2004; Ro *et al.*, 2006).

The exact mechanism of how VOCs are released from their site of biosynthesis and the root surface is poorly understood. It is possible that VOCs do not depart from root surfaces only by simple diffusion. Recently, Widhalm *et al.* (2015) suggested that mechanisms such as membrane trafficking contribute to VOC emission. Moreover, it is conceivable that semi-volatile compounds such as diterpene olefins could be transported in association with lipid-binding proteins via symplastic routes or depend on active transporters when passing the intercellular space. A major advantage of VOCs is their ability to function as long distance diffusible cues to attract or repel other organisms. While this role appears to be limited in the soil environment and dependent on soil moisture, olefinic sesquiterpenes such as (*E*)- $\beta$ -caryophyllene have been detected in sand and soil substrate as far as 10 cm from their source of release in contrast to more polar compounds such as

*trans*-nerolidol with comparatively poor ability to migrate at longer distance (Hiltpold and Turlings, 2008; Insam and Seewald, 2010). Likewise, the bicyclic monoterpene camphor, which is released from the roots of oak, can diffuse through soil at a distance of at least 10 cm from its source of emission (Weissteiner *et al.*, 2012), which supports the potential role of this molecule as a repellent or chemoattractant.

### THE ROLE OF EXUDATED SPECIALIZED METABOLITES IN PLANT NUTRITIONAL STRESS

Bioavailability of minerals and trace elements is essential for plant development as they serve as cofactors for a wide range of cellular processes (White *et al.*, 2014). The main source of minerals for plants is restricted to active acquisition through the root tissue (Aibara and Miwa, 2014). Hence, availability of minerals is strongly dictated by soil chemistry. Recent studies showed that specialized metabolites produced in roots and secreted to the rhizosphere play a major role in making several essential elements available (Rodríguez-Celma *et al.*, 2013). Hitherto, iron (Fe) and phosphate (P) deficiency are the two most studied processes in this respect; they are discussed in detail below (Figure 3).

#### The role of specialized metabolites in plants under iron deficiency

Iron (Fe) bioavailability is highly affected by soil acidity. In alkaline conditions, such as calcareous soil, iron ions exist in an insoluble form ( $\text{Fe}^{+3}$ , ferric ions) and cannot be utilized by plants. Plants grown under iron-deficiency display inter-veinal chlorosis (Vose, 1982) and are typically characterized by a reduction in leaf area, shoot and root dry weight, growth retardation and eventually a drop in crop yield (Roriz *et al.*, 2014). The common strategy used by plants to combat iron deficiency is mainly based on acidification of the soil at the root vicinity. In *Arabidopsis*, this involves a complex set of membrane proteins regulated by the master regulator FE-LIKE IRON-DEFICIENCY INDUCED TRANSCRIPTION FACTOR (FIT) protein (Colangelo and Guerinot, 2004). Rhizosphere acidification is mainly carried out by exporting protons catalyzed by the activity of H(+)-ATPASE 2 (AHA2) ATPase (Santi and Schmidt, 2009). The acidification process facilitates ferric ions solubility that can be later reduced by the ferric-chelate reductase FERRIC REDUCTION OXIDASE 2 (FRO2) to generate ferrous ions ( $\text{Fe}^{+2}$ ) (Robinson *et al.*, 1999), which are eventually transported to the internal root tissues by IRON-REGULATED TRANSPORTER1 (IRT1) (Eide *et al.*, 1996; Vert *et al.*, 2002).

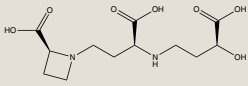
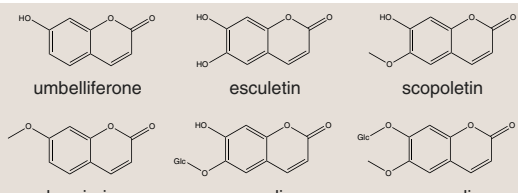
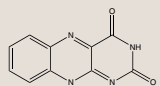
To make iron bioavailable, plants deploy either chelation- or reduction- based strategies. The chelation-based strategy is mainly found in *Graminaceae* species; renowned examples include mugineic acids (MAs) and polyaminocarboxylic chelators (so called phytosiderophores; PS) derived from

S-adenosyl-L-methionine (Kobayashi and Nishizawa, 2012). All MAs are synthesized from L-methionine sharing the same pathway to 2'-deoxymugineic acid while the subsequent steps may differ depending on plant species and cultivars (Suzuki *et al.*, 2006). In maize, these chelators are secreted to the rhizosphere and bind iron in the form of  $\text{Fe}^{+3}$ -PS complexes that are taken up by Yellow strip 1 (YS1) transporter (Curie *et al.*, 2001). Reduction-based strategies are less characterized and involve the secretion of specialized metabolites acting as reductants of ferric ions.

Coumarins synthesized from the phenylpropanoid pathway play an important role in assisting plants tolerate iron deficiency (Clemens and Weber, 2016). They are the most abundant compounds in *Arabidopsis* roots and actively secreted upon sensing low iron concentration (Fourcroy *et al.*, 2014). FERULOYL COENZYME A 6'-HYDROXYLASE 1 (F6'H1) (Schmid *et al.*, 2014) is a key enzyme in coumarin biosynthesis which are secreted to the rhizosphere by the ATP-BINDING CASSETTE 37 transporter (subclass G) ABCG37 (also named PDR9) (Fourcroy *et al.*, 2014). Both *F6'H1* and *ABCG37* transcript levels were shown to be highly induced under low iron conditions. Mutant plants of *f6'h1* have a severe phenotype in iron-deficient medium, which emphasizes the important role of coumarins to plant fitness (Fourcroy *et al.*, 2014). While their mode of action is still to be discovered, *in vitro* studies demonstrated the ability of coumarins to bind insoluble iron ( $\text{Fe}^{+3}$ ) and catalyze the conversion to  $\text{Fe}^{+2}$ , the iron soluble form (Mladěnka *et al.*, 2010). Other studies propose that  $\text{Fe}^{+3}$ -coumarin complexes are transported to the internal root tissues through an unknown transporter located at the plasma membrane of the epidermal layer. As an additional possibility, the  $\text{Fe}^{+3}$ -coumarin complex may facilitate the conversion of ferric ion to ferrous ion through the activity of FRO2 activity (Tsai and Schmidt, 2017). Furthermore, the canonical iron-acquisition machineries (reduction-based strategy) were found to be regulated by the activity of the MYB72 transcription factor (Palmer *et al.*, 2013). Recently, Zamioudis *et al.* (2015) showed that VOCs released from the rhizobacteria *Pseudomonas fluorescens* are important elicitors of MYB72, resulting in ISR activation and the secretion of iron-acquisition molecules (i.e. phenols, coumarins, and nicotianamines) independently of iron availability in the root vicinity (Zamioudis *et al.*, 2014, 2015). These results shed new light with respect to a possible link between plant perception of nutrition deficiency and ISR.

Finally, in some cases, flavins [i.e. riboflavin (Rbfl)] are also secreted to the rhizosphere and reported to facilitate ferric ions uptake. *Beta vulgaris* flavins act as reductant substances secreted to the soil in iron-deficient conditions (Sisó-Terraza *et al.*, 2016). They were proposed to act as a soluble redox shuttle released from the roots to facilitate the reduction of ferric ions in  $\text{Fe}^{+3}$ -flavin complexes. Together, these studies demonstrate that specialized

**Figure 3.** Structural information and chemical classes of exuded root metabolites involved in the plant response to mineral deficiency.

<b>Fe deficient conditions</b>	Polyamino-carboxylic acid	 2'-deoxymugineic acid Suzuki et al., 2006; Kobayashi and Nishizawa, 2012
	Coumarins	 umbelliferone      esculetin      scopoletin herniarin      esculin      scopolin Mladěnka et al., 2010; Fourcroy et al., 2014; Schmid et al., 2014
	Flavins	 flavin group Sisó-Terraza et al., 2016
<b>P deficient conditions</b>	SLs	see Figure 1

metabolites exuded by roots are able to support nutrient acquisition directly or indirectly, which represents yet another function among the multiple roles of specialized compounds in the complex soil environment.

#### Phosphorus deficiency and specialized metabolites

Inorganic phosphorus (P) present in soils is mostly found in the form of insoluble complexes making it almost inaccessible and, thus, a limiting factor for plant development (Péret *et al.*, 2011; Smith and Waters, 2012). P starvation conditions increase the elongation and branching of roots and plants are induced to secrete SLs to the rhizosphere (Yoneyama *et al.*, 2007; López-Ráez *et al.*, 2008; Kohlen *et al.*, 2013). Various SLs have been detected in root exudates, e.g. orobanchol, didehydroorobanchol, solanacol, orobanchyl acetate. A detailed identification of SL species in tomato exudates was reported by Kohlen *et al.* (2013). The chemical structure of these SLs consists of a tricyclic lactone (A, B, C rings) and a butenolide group (D-ring). Despite being highly similar, the A- and B-rings of SLs vary in different plants, which might define different biological functions in soil (Xie *et al.*, 2010; Al-Babili and Bouwmeester, 2015).

Under low P conditions, one of the remarkable roles of SLs, when exuded into the rhizosphere, is to initiate the symbiosis between plant roots and AM fungi of the *Glomeromycota* (Cheng *et al.*, 2013). AM fungi perceive SLs through a calcium-mediated pathway, which activates cell

wall-related metabolism (hyphal branching and chitin oligosaccharides production), mitochondrial function, and spore germination. SLs also induce a series of molecular events that are crucial for fungal infectivity. Thereafter, AM fungi provide water and nutrients (P and N) from the soil to the plant host. In addition, plants become more tolerant to biotic and abiotic stresses, while the host supplies the fungal counterpart with a C source (Bonfante and Genre, 2015). A recent study showed that plants colonized by AM accumulate higher levels of the P transporter PHT1 for efficient P uptake, thus highlighting that the information exchanged between AM and the host plant includes more than merely minerals (Sawers *et al.*, 2017). Interestingly, the response of AM fungi to SLs is unselective to the chemical structure, which allows the fungi to establish symbiotic associations with most land plants. However, differences in SL structure are perceived by parasitic plants such as those of the *Striga*, *Orobanche* and *Phelipanche* genera (Ruyter-Spira *et al.*, 2013). Consequently, engineering plants to secrete specific SLs into the rhizosphere may allow AM colonization but evade the germination of parasitic weed seeds (Kohlen *et al.*, 2013).

#### CONCLUSIONS

Regardless of the great complexity of metabolites secreted by plant roots to the rhizosphere, it is technically difficult to probe the metabolic profiles of native soil exudates in a sensitive, reproducible and comprehensive manner. Even

more limited is our capability to examine metabolites in a spatial resolution at varying distances from root systems (Massalha *et al.*, 2017). Novel technologies for sampling soil root exudates are thus likely to be employed in the coming years to overcome these limitations. One such method could be based on the use of Mass Spectrometry Imaging (MSI), a technology allowing high-resolution spatial mapping of metabolites, possibly soil sections surrounding the roots (Dong *et al.*, 2016). Besides, we also lack information with respect to which root parts and cell types synthesize and exude specialized metabolites. Together with the mode of particular metabolite secretion and the associated transporters, these represent key questions for rhizosphere research in the coming years.

Our major gap however still remains the role of particular classes or individual specialized metabolites in below-ground interactions. More than a few studies provided evidence that a single class of specialized metabolites or even the same metabolite could affect more than one organism. The case of SLs is one of the best examples for such multi-functionality of a particular metabolite class. Thus, once a rhizosphere 'active' metabolite class is identified it should be examined for its role in other types of interactions. Metabolites produced and exuded by other rhizosphere residents (e.g. bacteria) might also impact interactions in the rhizosphere. Genetic approaches based on natural metabolic variation or mutants of metabolic pathways are likely to complement the efforts for elucidating these underground mechanisms. The discovery of additional roles of specialized metabolites in soil will consequently impact our future capacity to develop novel solutions to combat soil pathogens and bio-stimulate growth and productivity of crops.

## ACKNOWLEDGEMENTS

We are grateful to Uwe Heinig for helpful discussions regarding specialized metabolites. We also thank the Adelis Foundation, Leona M. and Harry B. Helmsley Charitable Trust, Jeanne and Joseph Nissim Foundation for Life Sciences, Tom and Sondra Rykoff Family Foundation Research and the Raymond Burton Plant Genome Research Fund for supporting the A.A. lab activity. A.A. is the incumbent of the Peter J. Cohn Professorial Chair. H.M PhD is funded by the Planning & Budgeting Committee of the Council of Higher Education of Israel. D.T. has been supported by the National Science Foundation (MCB-0950865) and the Binational Agricultural Research and Development Fund (IS-4745-14R).

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

## REFERENCES

- Ahmad, S., Veyrat, N., Gordon-Weeks, R. *et al.* (2011) Benzoxazinoid metabolites regulate innate immunity against aphids and fungi in maize. *Plant Physiol.* **157**, 317–327.
- Aibara, I. and Miwa, K. (2014) Strategies for optimization of mineral nutrient transport in plants: multilevel regulation of nutrient-dependent dynamics of root architecture and transporter activity. *Plant Cell Physiol.* **55**, 2027–2036.
- Akiyama, K. and Hayashi, H. (2006) Strigolactones: chemical signals for fungal symbionts and parasitic weeds in plant roots. *Ann. Bot.* **97**, 925–931.
- Akiyama, K., Matsuzaki, K. and Hayashi, H. (2005) Plant sesquiterpenes induce hyphal branching in arbuscular mycorrhizal fungi. *Nature*, **435**, 824–827.
- Al-Babili, S. and Bouwmeester, H.J. (2015) Strigolactones, a novel carotenoid-derived plant hormone. *Annu. Rev. Plant Biol.* **66**, 161–186.
- Ali, J.G., Alborn, H.T. and Stelinski, L.L. (2010) Subterranean herbivore-induced volatiles released by citrus roots upon feeding by *Diaprepes abbreviatus* recruit entomopathogenic nematodes. *J. Chem. Ecol.* **36**, 361–368.
- Ali, J.G., Alborn, H.T. and Stelinski, L.L. (2011) Constitutive and induced subterranean plant volatiles attract both entomopathogenic and plant parasitic nematodes. *J. Ecol.* **99**, 26–35.
- Araniti, F., Graña, E., Krasuska, U., Bogatek, R., Reigosa, M.J., Abenavoli, M.R. and Sánchez-Moreiras, A.M. (2016) Loss of gravitropism in farne-sene-treated Arabidopsis is due to microtubule malformations related to hormonal and ROS unbalance. *PLoS ONE*, **11**, 1–26.
- Arite, T., Iwata, H., Ohshima, K., Maekawa, M., Nakajima, M., Kojima, M., Sakakibara, H. and Kyo-zuka, J. (2007) DWARF10, an RMS1/MAX4/DAD1 ortholog, controls lateral bud outgrowth in rice. *Plant J.* **51**, 1019–1029.
- Asari, S., Matzén, S., Petersen, M.A., Bejai, S. and Meijer, J. (2016) Multiple effects of *Bacillus amyloliquefaciens* volatile compounds: plant growth promotion and growth inhibition of phytopathogens. *FEMS Microbiol. Ecol.* **92**, fiw070.
- Badri, D.V., Loyola-vargas, V.M., Broeckling, C.D. *et al.* (2008) Altered profile of secondary metabolites in the root exudates of Arabidopsis ATP-binding cassette transporter mutants. *Plant Physiol.* **146**, 762–771.
- Badri, D.V., Quintana, N., El Kassisi, E.G., Kim, H.K., Choi, Y.H., Sugiyama, A., Verpoorte, R., Martinoia, E., Manter, D.K. and Vivanco, J.M. (2009) An ABC transporter mutation alters root exudation of phytochemicals that provoke an overhaul of natural soil microbiota. *Plant Physiol.* **151**, 2006–2017.
- Baetz, U. and Martinoia, E. (2013) Root exudates: the hidden part of plant defense. *Trends Plant Sci.* **19**, 90–98.
- Bainbridge, K., Sorefan, K., Ward, S. and Leyser, O. (2005) Hormonally controlled expression of the Arabidopsis MAX4 shoot branching regulatory gene. *Plant J.* **44**, 569–580.
- Bais, H.P., Weir, T.L., Perry, L.G., Gilroy, S. and Vivanco, J.M. (2006) The role of root exudates in rhizosphere interactions with plants and other organisms. *Annu. Rev. Plant Biol.* **57**, 233–266.
- Barnes, J.P. and Putnam, A.R. (1983) Rye residues contribute weed suppression in no-tillage cropping systems. *J. Chem. Ecol.* **9**, 1045–1057.
- Barnes, J.P. and Putnam, A.R. (1987) Role of benzoxazinones in allelopathy by rye (*Secale cereale* L.). *J. Chem. Ecol.* **13**, 889–906.
- Barnes, J.P., Putnam, A.R., Burke, B.A. and Aasen, A.J. (1987) Isolation and characterization of allelochemicals in rye herbage. *Phytochemistry*, **26**, 1385–1390.
- Belz, R.G. and Hurlé, K. (2005) Differential exudation of two benzoxazinoids – one of the determining factors for seedling allelopathy of Triticeae species. *J. Agric. Food Chem.* **53**, 250–261.
- Bohlmann, H. (2015) Introductory chapter on the basic biology of cyst nematodes. *Adv. Bot. Res.* 33–59.
- Bonfante, P. and Genre, A. (2015) Arbuscular mycorrhizal dialogues: do you speak “plantish” or “fungish”? *Trends Plant Sci.* **20**, 150–154.
- Bonkowski, M., Villenave, C. and Griffiths, B. (2009) Rhizosphere fauna: the functional and structural diversity of intimate interactions of soil fauna with plant roots. *Plant Soil*, **321**, 213–233.
- Booker, J., Aldridge, M., Wills, S., McCarty, D., Klee, H. and Leyser, O. (2014) MAX3/CCD7 is a carotenoid cleavage dioxygenase required for the synthesis of a novel plant signaling molecule. *Can. Field Nat.* **128**, 189–190.
- Brady, S.M., Orlando, D.A., Lee, J.-Y., Wang, J.Y., Koch, J., Dinneny, J.R., Mace, D., Ohler, U. and Benfey, P.N. (2007) A high-resolution root spatiotemporal map reveals dominant expression patterns. *Science*, **318**, 801–806.
- Brigham, L., Michaels, P. and Flores, H. (1999) Cell-specific production and antimicrobial activity of naphthoquinones in roots of lithospermum erythrorhizon. *Plant Physiol.* **119**, 417–428.

- Bulgarelli, D., Schlaeppi, K., Spaepen, S., van Themaat, E. and Schulze-Lefert, P. (2013) Structure and functions of the bacterial microbiota of plants. *Annu. Rev. Plant Biol.* **64**, 807–838.
- Buskov, S., Serra, B., Rosa, E., Sørensen, H. and Sørensen, J.C. (2002) Effects of intact glucosinolates and products produced from glucosinolates in myrosinase-catalyzed hydrolysis on the potato cyst nematode (*Globodera rostochiensis* cv. Woll). *J. Agric. Food Chem.* **50**, 690–695.
- Callaway, R.M. and Aschehoug, E.T. (2000) Invasive plants versus their new and old neighbors: a mechanism for exotic invasion. *Science*, **290**, 521–523.
- Callaway, R.M., Thelen, G.C., Rodriguez, A. and Holben, W.E. (2004) Soil biota and exotic plant invasion. *Nature*, **427**, 731–733.
- Cesco, S., Neumann, G., Tomasi, N., Pinton, R. and Weiskopf, L. (2010) Release of plant-borne flavonoids into the rhizosphere and their role in plant nutrition. *Plant Soil*, **329**, 1–25.
- Chaimovitch, D., Abu-Abied, M., Belausov, E., Rubin, B., Dudai, N. and Sadot, E. (2010) Microtubules are an intracellular target of the plant terpene citral. *Plant J.* **61**, 399–408.
- Chang, M., Netzly, D.H., Butler, L.G. and Lynn, D.G. (1986) Chemical regulation of distance: characterization of the first natural host germination stimulant for *Striga asiatica*. *J. Am. Chem. Soc.* **108**, 7858–7860.
- Chen, F., Pichersky, E., Ro, D., Petri, J., Gershenzon, J. and Tholl, D. (2004) Characterization of a root-specific Arabidopsis terpene synthase responsible for the formation of the volatile. *Plant Physiol.* **135**, 1956–1966.
- Cheng, X., Ruyter-Spira, C. and Bouwmeester, H. (2013) The interaction between strigolactones and other plant hormones in the regulation of plant development. *Front. Plant Sci.* **4**, 199.
- Cheng, F., Cheng, Z. and Meng, H. (2016) Transcriptomic insights into the allelopathic effects of the garlic allelochemical diallyl disulfide on tomato roots. *Sci. Rep.* **6**, 38902.
- Cho, S.M., Kang, B.R., Han, S.H., Anderson, A.J., Park, J.Y., Lee, Y.H., Cho, B.H., Yang, K.Y., Ryu, C.M. and Kim, Y.C. (2008) 2R,3R-butanediol, a bacterial volatile produced by *Pseudomonas chlororaphis* O6, is involved in induction of systemic tolerance to drought in *Arabidopsis thaliana*. *Mol. Plant Microbe Interact.* **21**, 1067–1075.
- Choo, H.Y., Kaya, H.K., Burlando, T.M. and Gaugler, R. (1989) Entomopathogenic nematodes: host-finding ability in the presence of plant roots. *Environ. Entomol.* **18**, 5.
- Clemens, S. and Weber, M. (2016) The essential role of coumarin secretion for Fe acquisition from alkaline soil. *Plant Signal. Behav.* **11**, e1114197.
- Colangelo, E.P. and Gueriot, M.L. (2004) The essential basic helix-loop-helix protein FIT1 is required for the iron-deficiency response. *Plant Cell*, **16**, 3400–3412.
- Crespo, E., Hordijk, C.A., de Graaf, R.M., Samudrala, D., Cristescu, S.M., Harren, F.J.M. and van Dam, N.M. (2012) On-line detection of root-induced volatiles in *Brassica nigra* plants infested with *Delia radicum* L. root fly larvae. *Phytochemistry*, **84**, 68–77.
- Cruz, A.F., Hamel, C., Yang, C., Matsubara, T., Gan, Y., Singh, A.K., Kuwada, K. and Ishii, T. (2012) Phytochemicals to suppress Fusarium head blight in wheat-chickpea rotation. *Phytochemistry*, **78**, 72–80.
- Curie, C., Panaviene, Z., Loulergue, C., Dellaporta, S.L., Briat, J.F. and Walker, E.L. (2001) Maize yellow stripe1 encodes a membrane protein directly involved in Fe(III) uptake. *Nature*, **409**, 346–349.
- Czarnota, M.A., Paul, R.N., Dayan, F.E., Nimbale, C.I. and Weston, L.A. (2001) Mode of action, localization of production, chemical nature, and activity of sorgoleone: a potent PSII inhibitor in Sorghum spp. root exudates. *Weed Technol.* **15**, 813–825.
- Czarnota, M.A., Paul, R.N., Weston, L.A. and Duke, S.O. (2003) Anatomy of sorgoleone-secreting root hairs of Sorghum species. *Int. J. Plant Sci.* **164**, 861–866.
- Dayan, F.E. (2006) Factors modulating the levels of the allelochemical sorgoleone in *Sorghum bicolor*. *Planta*, **224**, 339–346.
- Dayan, F.E., Howell, J. and Weidenhamer, J.D. (2009) Dynamic root exudation of sorgoleone and its in planta mechanism of action. *J. Exp. Bot.* **60**, 2107–2117.
- De Coninck, B., Timmermans, P., Vos, C., Cammue, B.P.A. and Kazan, K. (2015) What lies beneath: belowground defense strategies in plants. *Trends Plant Sci.* **20**, 91–101.
- De Jesus Jatoba, L., Varela, R.M., Molinillo, J.M.G., Din, Z.U., Gualtieri, S.C.J., Rodrigues-Filho, E. and Macias, F.A. (2016) Allelopathy of bracken fern (*Pteridium arachnoideum*): new evidence from green fronds, litter, and soil. *PLoS ONE*, **11**, 1–16.
- Del Giudice, L., Massardo, D.R., Pontieri, P. et al. (2008) The microbial community of Vetiver root and its involvement into essential oil biogenesis. *Environ. Microbiol.* **10**, 2824–2841.
- Delaplace, P., Delory, B.M., Baudson, C., Mendaluk-Saunier de Cazenave, M., Spaepen, S., Varin, S., Brostaux, Y. and du Jardin, P. (2015) Influence of rhizobacterial volatiles on the root system architecture and the production and allocation of biomass in the model grass *Brachypodium distachyon* (L.) P. Beauv. *BMC Plant Biol.* **15**, 195.
- Dennis, P.G., Miller, A.J. and Hirsch, P.R. (2010) Are root exudates more important than other sources of rhizodeposits in structuring rhizosphere bacterial communities? *FEMS Microbiol. Ecol.* **72**, 313–327.
- Ditengou, F.A., Müller, A., Rosenkranz, M., Felten, J., Lasok, H., van Doorn, M.M., Legué, V., Palme, K., Schnitzler, J.-P. and Polle, A. (2015) Volatile signalling by sesquiterpenes from ectomycorrhizal fungi reprogrammes root architecture. *Nat. Commun.* **6**, 6279.
- Dixon, R.A. (1995) Stress-induced phenylpropanoid metabolism. *Plant Cell*, **7**, 1085–1097.
- Dong, L., Li, X., Huang, L., Gao, Y., Zhong, L., Zheng, Y. and Zuo, Y. (2014) Lauric acid in crown daisy root exudate potentially regulates root-knot nematode chemotaxis and disrupts Mi-flp-18 expression to block infection. *J. Exp. Bot.* **65**, 131–141.
- Dong, Y., Li, B. and Aharoni, A. (2016) More than pictures: when MS imaging meets histology. *Trends Plant Sci.* **21**, 686–698.
- Dor, E., Joel, D.M., Kapulnik, Y., Koltai, H. and Hershenhorn, J. (2011) The synthetic strigolactone GR24 influences the growth pattern of phytopathogenic fungi. *Planta*, **234**, 419–427.
- Eide, D., Broderius, M., Fett, J. and Gueriot, M.L. (1996) A novel iron-regulated metal transporter from plants identified by functional expression in yeast. *Proc. Natl Acad. Sci. USA*, **93**, 5624–5628.
- Elasri, M., Delorme, S., Lemanceau, P., Stewart, G., Laue, B., Glickmann, E., Oger, P.M. and Dessaux, Y. (2001) Acyl-homoserine lactone production is more common among plant-associated *Pseudomonas* spp. than among soilborne *Pseudomonas* spp. *Appl. Environ. Microbiol.* **67**, 1198–1209.
- Erb, M., Huber, M., Robert, C.A.M., Ferrieri, A.P., Machado, R.A.R. and Arce, C.C.M. (2013) The role of plant primary and secondary metabolites in root-herbivore behaviour, nutrition and physiology. In *Advances in Insect Physiology* (Johnson, S.N., Hiltbold, I. and Turlings, T.C.J., eds). USA: Elsevier Ltd., pp. 53–95.
- Fantaye, C.A., Köpke, D., Gershenzon, J. and Degenhardt, J. (2015) Restoring (*E*)- $\beta$ -caryophyllene production in a non-producing maize line compromises its resistance against the fungus *Colletotrichum graminicola*. *J. Chem. Ecol.* **41**, 213–223.
- Farag, M.A., Ryu, C.M., Sumner, L.W. and Paré, P.W. (2006) GC-MS SPME profiling of rhizobacterial volatiles reveals prospective inducers of growth promotion and induced systemic resistance in plants. *Phytochemistry*, **67**, 2262–2268.
- Farnier, K., Bengtsson, M., Becher, P.G., Witzell, J., Witzgall, P. and Manduric, S. (2012) Novel bioassay demonstrates attraction of the white potato cyst nematode *Globodera pallida* (stone) to non-volatile and volatile host plant cues. *J. Chem. Ecol.* **38**, 795–801.
- Farré-Armengol, G., Filella, I., Llusia, J. and Penuelas, J. (2016) Bidirectional interaction between phyllospheric microbiotas and plant volatile emissions. *Trends Plant Sci.* **21**, 854–860.
- Ferry, A., Dugravot, S., Delattre, T., Christides, J.P., Auger, J., Bagnères, A.G., Poinot, D. and Cortesero, A.M. (2007) Identification of a widespread monomolecular odor differentially attractive to several *Delia radicum* ground-dwelling predators in the field. *J. Chem. Ecol.* **33**, 2064–2077.
- Field, B. and Osbourn, A.E. (2008) Metabolic diversification – independent assembly of operon-like gene clusters in different plants. *Science*, **320**, 543–547.
- Fourcroy, P., Sisó-Terraza, P., Sudre, D., Savirón, M., Rey, G., Gaymard, F., Abadía, A., Abadía, J., Álvarez-Fernández, A. and Briat, J.-F. (2014) Involvement of the ABCG37 transporter in secretion of scopoletin and derivatives by Arabidopsis roots in response to iron deficiency. *New Phytol.* **201**, 155–167.
- Fukuzawa, A., Matsue, H., Ikura, M. and Masamune, T. (1985) Glycinoclepins B and C, nortriterpenes related to glycinoclepin A. *Tetrahedron Lett.* **26**, 5539–5542.



- Gans, J. (2005) Computational improvements reveal great bacterial diversity and high metal toxicity in soil. *Science*, **309**, 1387–1390.
- Garnica-Vergara, A., Barrera-Ortiz, S., Muñoz-Parra, E., Raya-González, J., Méndez-Bravo, A., Macías-Rodríguez, L., Ruiz-Herrera, L.F. and López-Bucio, J. (2016) The volatile 6-pentyl-2H-pyran-2-one from *Trichoderma atroviride* regulates *Arabidopsis thaliana* root morphogenesis via auxin signaling and ETHYLENE INSENSITIVE 2 functioning. *New Phytol.* **209**, 1496–1512.
- Gonzalez, V.M., Kazimir, J., Nimbale, C., Weston, L.A. and Cheniae, G.M. (1997) Inhibition of a photosystem II electron transfer reaction by the natural product sorgoleone. *J. Agric. Food Chem.* **45**, 1415–1421.
- Graham, T.L. (1991) Flavonoid and isoflavonoid distribution in developing soybean seedling tissues and in seed and root exudates. *Plant Physiol.* **95**, 594–603.
- Grierson, C., Nielsen, E., Ketelaarc, T. and Schiefelbein, J. (2014) Root hairs. *Arabidopsis Book*, **12**, e0172.
- Grigulis, K., Sheppard, A.W., Ash, J.E. and Groves, R.H. (2001) The comparative demography of the pasture weed *Echium plantagineum* between its native and invaded ranges. *J. Appl. Ecol.* **38**, 281–290.
- Gulati, J., Baldwin, I.T. and Gaquerel, E. (2014) The roots of plant defenses: integrative multivariate analyses uncover dynamic behaviors of gene and metabolic networks of roots elicited by leaf herbivory. *Plant J.* **77**, 880–892.
- Gutiérrez-Barranquero, J.A., Jerry Reen, F., McCarthy, R.R. and O'Gara, F. (2015) Deciphering the role of coumarin as a novel quorum sensing inhibitor suppressing virulence phenotypes in bacterial pathogens. *Appl. Microbiol. Biotechnol.* **99**, 3303–3316.
- Haichar, F.E.Z., Marol, C., Berge, O., Rangel-Castro, J.I., Prosser, J.I., Balesdent, J., Heulin, T. and Achouak, W. (2008) Plant host habitat and root exudates shape soil bacterial community structure. *ISME J.* **2**, 1221–1230.
- Haichar, F.Z., Santaella, C., Heulin, T. and Achouak, W. (2014) Root exudates mediated interactions belowground. *Soil Biol. Biochem.* **77**, 69–80.
- Halkier, B.A. and Gershenzon, J. (2006) Biology and biochemistry of glucosinolates. *Annu. Rev. Plant Biol.* **57**, 303–333.
- Hassan, S. and Mathesius, U. (2012) The role of flavonoids in root-rhizosphere signalling: opportunities and challenges for improving plant-microbe interactions. *J. Exp. Bot.* **63**, 3429–3444.
- Haves, M.C., Brigham, L.A., Wen, F., Woo, H.H. and Zhu, Y. (1998) Function of root border cells in plant health: pioneers in the rhizosphere. *Annu. Rev. Phytopathol.* **36**, 311–327.
- Haves, M., Flores-Lara, Y., McClure, M., Hubbard, J., Schmitt, M. and Stock, S.P. (2005) Increased penetration of host roots by nematodes after recovery from quiescence induced by root cap exudate. *Nematology*, **7**, 321–331.
- Hejl, A.M. and Koster, K.L. (2004) The allelochemical sorgoleone inhibits root H<sup>+</sup>-ATPase and water uptake. *J. Chem. Ecol.* **30**, 2181–2191.
- Hernández-León, R., Rojas-Solís, D., Contreras-Pérez, M., Orozco-Mosqueda, M. del C., Macías-Rodríguez, L.I., deReyes-la Cruz, H., Valencia-Cantero, E. and Santoyo, G. (2015) Characterization of the antifungal and plant growth-promoting effects of diffusible and volatile organic compounds produced by *Pseudomonas fluorescens* strains. *Biol. Control* **81**, 83–92.
- Hess, K.M., Dudley, M.W., Lynn, D.G., Joerger, R.D. and Binns, A.N. (1991) Mechanism of phenolic activation of *Agrobacterium* virulence genes: development of a specific inhibitor of bacterial sensor/response systems. *Proc. Natl Acad. Sci. USA*, **88**, 7854–7858.
- Hiltbold, I. and Hibbard, B.E. (2016) Neonate larvae of the specialist herbivore *Diabrotica virgifera virgifera* do not exploit the defensive volatile (E)- $\beta$ -caryophyllene in locating maize roots. *J. Pest Sci.* (2004), **89**, 1–6.
- Hiltbold, I. and Turlings, T.C.J. (2008) Belowground chemical signaling in maize: when simplicity rhymes with efficiency. *J. Chem. Ecol.* **34**, 628–635.
- Hooper, A.M., Caulfield, J.C., Hao, B., Pickett, J.A., Midega, C.A.O. and Khan, Z.R. (2015) Isolation and identification of *Desmodium* root exudates from drought tolerant species used as intercrops against *Striga hermonthica*. *Phytochemistry*, **117**, 380–387.
- Hosseini, S., Heyman, F., Olsson, U., Broberg, A., Funck Jensen, D. and Karlsson, M. (2014) Zoospore chemotaxis of closely related legume-root infecting Phytophthora species towards host isoflavones. *Plant. Pathol.* **63**, 708–714.
- Huang, M., Sanchez-Moreiras, A.M., Abel, C., Sohrabi, R., Lee, S., Gershenzon, J. and Tholl, D. (2012) The major volatile organic compound emitted from *Arabidopsis thaliana* flowers, the sesquiterpene (E)- $\beta$ -caryophyllene, is a defense against a bacterial pathogen. *New Phytol.* **193**, 997–1008.
- Huffaker, A., Kaplan, F., Vaughan, M.M., Dafoe, N.J., Ni, X., Rocca, J.R., Alborn, H.T., Teal, P.E.A. and Schmelz, E.A. (2011) Novel acidic sesquiterpenoids constitute a dominant class of pathogen-induced phytoalexins in maize. *Plant Physiol.* **156**, 2082–2097.
- Inderjit, Wardle, D.A., Karban, R. and Callaway, R.M. (2011) The ecosystem and evolutionary contexts of allelopathy. *Trends Ecol. Evol.* **26**, 655–662.
- Insam, H. and Seewald, M. (2010) Volatile organic compounds (VOCs) in soils. *Biol. Fertil. Soils*, **46**, 199–213.
- Iven, T., König, S., Singh, S., Braus-Stromeier, S.A., Bischoff, M., Tietze, L.F., Braus, G.H., Lipka, V., Feussner, I. and Dröge-Laser, W. (2012) Transcriptional activation and production of tryptophan-derived secondary metabolites in *Arabidopsis* roots contributes to the defense against the fungal vascular pathogen *Verticillium longisporum*. *Mol. Plant*, **5**, 1389–1402.
- Jassbi, A.R., Zamanizadehnajari, S. and Baldwin, I.T. (2010) Phytotoxic volatiles in the roots and shoots of *Artemisia tridentata* as detected by headspace solid-phase microextraction and gas chromatographic-mass spectrometry analysis. *J. Chem. Ecol.* **36**, 1398–1407.
- Jilani, G., Mahmood, S., Chaudhry, A.N., Hassan, I. and Akram, M. (2008) Allelochemicals: sources, toxicity and microbial transformation in soil. *Ann. Microbiol.* **58**, 351–357.
- Johnson, S.N., Gregory, P.J., Greenham, J.R., Zhang, X. and Murray, P.J. (2005) Attractive properties of an isoflavonoid found in white clover root nodules on the clover root weevil. *J. Chem. Ecol.* **31**, 2223–2229.
- Junker, R.R., Loewel, C., Gross, R., Dötterl, S., Keller, A. and Blüthgen, N. (2011) Composition of epiphytic bacterial communities differs on petals and leaves. *Plant Biol.* **13**, 918–924.
- Junker, R.R., Blüthgen, N., Brehm, T., Binkenstein, J., Paulus, J., Martin Schaefer, H. and Stang, M. (2013) Specialization on traits as basis for the niche-breadth of flower visitors and as structuring mechanism of ecological networks. *Funct. Ecol.* **27**, 329–341.
- Kadow, M., Saß, S., Schmidt, M. and Bornscheuer, U.T. (2011) Recombinant expression and purification of the 2,5-diketocamphane 1,2-monooxygenase from the camphor metabolizing *Pseudomonas putida* strain NCIMB 10007. *AMB Express*, **1**, 13.
- Kagan, I.A., Rimando, A.M. and Dayan, F.E. (2003) Chromatographic separation and in vitro activity of sorgoleone congeners from the roots of *Sorghum bicolor*. *J. Agric. Food Chem.* **51**, 7589–7595.
- Kai, M., Hausteiner, M., Molina, F., Petri, A., Scholz, B. and Piechulla, B. (2009) Bacterial volatiles and their action potential. *Appl. Microbiol. Biotechnol.* **81**, 1001–1012.
- Kai, M., Effmert, U. and Piechulla, B. (2016) Bacterial-plant-interactions: approaches to unravel the biological function of bacterial volatiles in the rhizosphere. *Front. Microbiol.* **7**, 108.
- Kaur, H., Kaur, R., Kaur, S., Baldwin, I.T., and Inderjit (2009) Taking ecological function seriously: soil microbial communities can obviate allelopathic effects of released metabolites. *PLoS ONE*, **4**, 1–6.
- Kemen, A.C., Honkanen, S., Melton, R.E., Findlay, K.C., Mugford, S.T., Hayaishi, K., Haralampidis, K., Rosser, S.J. and Osbourn, A. (2014) Investigation of triterpene synthesis and regulation in oats reveals a role for  $\beta$ -amyryn in determining root epidermal cell patterning. *Proc. Natl Acad. Sci. USA*, **111**, 8679–8684.
- Kleinheinz, G.T., Bagley, S.T., St. John, W.P., Rughani, J.R. and McGinnis, G.D. (1999) Characterization of alpha-pinene-degrading microorganisms and application to a bench-scale biofiltration system for VOC degradation. *Arch. Environ. Contam. Toxicol.* **37**, 151–157.
- Kobayashi, T. and Nishizawa, N.K. (2012) Iron uptake, translocation, and regulation in higher plants. *Annu. Rev. Plant Biol.* **63**, 131–152.
- Kohlen, W., Charnikhova, T., Bours, R., López-Ráez, J.A. and Bouwmeester, H. (2013) Tomato strigolactones: a more detailed look. *Plant Signal. Behav.* **8**, e22785.
- Kretschmar, T., Kohlen, W., Sasse, J., Borghi, L., Schlegel, M., Bachelier, J.B., Reinhardt, D., Bours, R., Bouwmeester, H.J. and Martinoia, E. (2012) A petunia ABC protein controls strigolactone-dependent symbiotic signalling and branching. *Nature*, **483**, 341–344.

- Kuijken, R.C.P., Snel, J.F.H., Heddes, M.M., Bouwmeester, H.J. and Marcelis, L.F.M. (2014) The importance of a sterile rhizosphere when phenotyping for root exudation. *Plant Soil*, **387**, 131–142.
- Kwon, Y.S., Ryu, C.M., Lee, S. *et al.* (2010) Proteome analysis of *Arabidopsis* seedlings exposed to bacterial volatiles. *Planta*, **232**, 1355–1370.
- Laznik, Z. and Trdan, S. (2013) An investigation on the chemotactic responses of different entomopathogenic nematode strains to mechanically damaged maize root volatile compounds. *Exp. Parasitol.* **134**, 349–355.
- Lebeis, S.L., Paredes, S.H., Lundberg, D.S. *et al.* (2015) Salicylic acid modulates colonization of the root microbiome by specific bacterial taxa. *Science*, **349**, 860–864.
- Li, Z.H., Wang, Q., Ruan, X., Pan, C.De and Jiang, D.A. (2010) Phenolics and plant allelopathy. *Molecules*, **15**, 8933–8952.
- Lin, Y., Irani, N.G. and Grotewold, E. (2003) Sub-cellular trafficking of phytochemicals explored using auto-fluorescent compounds in maize cells. *BMC Plant Biol.* **3**, 10.
- Liu, X.F., Chen, H.H., Li, J.K., Zhang, R., Turlings, T.C.J. and Chen, L. (2016) Volatiles released by Chinese liquorice roots mediate host location behaviour by neonate *Porphyrophora sophorae* (Hemiptera: Margarodidae). *Pest Manag. Sci.* **72**, 1959–1964.
- López-Ráez, J.A., Charnikhova, T., Gómez-Roldán, V. *et al.* (2008) Tomato strigolactones are derived from carotenoids and their biosynthesis is promoted by phosphate starvation. *New Phytol.* **178**, 863–874.
- Lundberg, D.S. *et al.* (2012) Defining the core *Arabidopsis thaliana* root microbiome. *Nature*, **488**, 86–90.
- Macías, F.A., Oliveros-Bastidas, A., Marín, D., Castellano, D., Simonet, S.M. and Molinillo, J.M.G. (2004) Degradation studies on benzoxazinoids. Soil degradation dynamics of 2,4-Dihydroxy-7-methoxy-(2H)-1,4-benzoxazin-3(4H)-one (DIMBOA) and its degradation products, phytotoxic allelochemicals from Gramineae. *J. Agric. Food Chem.* **52**, 6402–6413.
- Macías, F.A., Marín, D., Oliveros-Bastidas, A., Chinchilla, D., Simonet, M. and Molinillo, J.M.G. (2006) Isolation and synthesis of allelochemicals from Gramineae: benzoxazinones and related compounds. *J. Agric. Food Chem.* **54**, 991–1000.
- Macías, F.A., Marín, D., Oliveros-Bastidas, A. and Molinillo, J.M.G. (2009) Rediscovering the bioactivity and ecological role of 1,4-benzoxazinones. *Nat. Prod. Rep.* **26**, 478–489.
- Masamune, T., Anetai, M., Takasugi, M. and Katsui, N. (1982) Isolation of a natural hatching stimulus, glycinolecypin A, for the soybean cyst nematode. *Nature*, **297**, 495–496.
- Massalha, H., Korenblum, E., Malitsky, S., Shapiro, O.H. and Aharoni, A. (2017). Live imaging of root–bacteria interactions in a microfluidics setup. *Proc. Natl Acad. Sci. USA*. pii: 201618584.
- Meazza, G., Scheffler, B.E., Tellez, M.R., Rimando, A.M., Romagni, J.G., Duke, S.O., Nanayakkara, D., Khan, I.A., Abourashed, E.A. and Dayan, F.E. (2002) The inhibitory activity of natural products on plant p-hydroxyphenylpyruvate dioxygenase. *Phytochemistry*, **60**, 281–288.
- Mendes, L.W., Kuramae, E.E., Navarrete, A.A., van Veen, J.A. and Tsai, S.M. (2014) Taxonomical and functional microbial community selection in soybean rhizosphere. *ISME J.* **8**, 1577–1587.
- Mladenka, P., Macáková, K., Zatloukalová, L., Reháková, Z., Singh, B.K., Prasad, A.K., Parmar, V.S., Jahodár, L., Hrdina, R. and Saso, L. (2010) In vitro interactions of coumarins with iron. *Biochimie*, **92**, 1108–1114.
- Morrissey, J.P. and Osbourn, A.E. (1999) Fungal resistance to plant antibiotics as a mechanism of pathogenesis. *Microbiol. Mol. Biol. Rev.* **63**, 708–724.
- Moussaieff, A., Rogachev, I., Brodsky, L., Malitsky, S., Toal, T.W., Belcher, H., Yativ, M., Brady, S.M., Benfey, P.N. and Aharoni, A. (2013) High-resolution metabolic mapping of cell types in plant roots. *Proc. Natl Acad. Sci. USA*, **110**, E1232–E1241.
- Muscolo, A., Panuccio, M.R. and Sidari, M. (2001) The effect of phenols on respiratory enzymes in seed germination. *Plant Growth Regul.* **35**, 31–35.
- Neal, A.L., Ahmad, S., Gordon-Weeks, R. and Ton, J. (2012) Benzoxazinoids in root exudates of maize attract *Pseudomonas putida* to the rhizosphere. *PLoS ONE*, **7**, e35498.
- Nimbal, C.I., Yerkes, C.N., Weston, L.A. and Weller, S.C. (1996) Herbicidal activity and site of action of the natural product sorgoleone. *Pestic. Biochem. Physiol.* **54**, 73–83.
- Osbourn, A. (1996) Preformed antimicrobial compounds and plant defense against fungal attack. *Plant Cell*, **8**, 1821–1831.
- Osbourn, A.E. (2003) Saponins in cereals. *Phytochemistry*, **62**, 1–4.
- Osbourn, A.E., Clarke, B.R., Lunness, P., Scott, P.R. and Daniels, M.J. (1994) An oat species lacking avenacin is susceptible to infection by *Gaeumannomyces graminis* var. *tritici*. *Physiol. Mol. Plant Pathol.* **45**, 457–467.
- Palma, R., Mutis, A., Manosalva, L., Ceballos, R. and Quiroz, A. (2012) Behavioral and electrophysiological responses of *Hylastinus obscurus* to volatiles released from the roots of *Trifolium pratense* L. *J. Soil Sci. Plant Nutr.* **12**, 183–193.
- Palmer, C.M., Hindt, M.N., Schmidt, H., Clemens, S. and Gueriot, M.L. (2013) MYB10 and MYB72 are required for growth under iron-limiting conditions. *PLoS Genet.* **9**, e1003953.
- Papadopoulou, K., Melton, R.E., Leggett, M., Daniels, M.J. and Osbourn, A.E. (1999) Compromised disease resistance in saponin-deficient plants. *Proc. Natl Acad. Sci. USA*, **96**, 12923–12928.
- Parniske, M. (2008) Arbuscular mycorrhiza: the mother of plant root endosymbioses. *Nat. Rev. Microbiol.* **6**, 763–775.
- Peñuelas, J., Asensio, D., Tholl, D., Wenke, K., Rosenkranz, M., Piechulla, B. and Schnitzler, J.P. (2014) Biogenic volatile emissions from the soil. *Plant Cell Environ.* **37**, 1866–1891.
- Péret, B., Clément, M., Nussaume, L. and Desnos, T. (2011) Root developmental adaptation to phosphate starvation: better safe than sorry. *Trends Plant Sci.* **16**, 442–450.
- Phillips, R.P., Finzi, A.C. and Bernhardt, E.S. (2011) Enhanced root exudation induces microbial feedbacks to N cycling in a pine forest under long-term CO<sub>2</sub> fumigation. *Ecol. Lett.* **14**, 187–194.
- Pieterse, C.M.J., Zamioudis, C., Berendsen, R.L., Weller, D.M., van Wees, S.C.M. and Bakker, P.A.H.M. (2014) Induced systemic resistance by beneficial microbes. *Annu. Rev. Phytopathol.* **52**, 347–375.
- Ping, L. and Boland, W. (2004) Signals from the underground: bacterial volatiles promote growth in *Arabidopsis*. *Trends Plant Sci.* **9**, 263–266.
- Quastel, J.H. (1965) Soil metabolism. *Annu. Rev. Plant Physiol.* **16**, 217–240.
- Rasmann, S. and Turlings, T.C.J. (2008) First insights into specificity of belowground tritrophic interactions. *Oikos*, **117**, 362–369.
- Rasmann, S., Köllner, T.G., Degenhardt, J., Hiltbold, I., Toepfer, S., Kuhlmann, U., Gershenson, J. and Turlings, T.C. (2005) Recruitment of entomopathogenic nematodes by insect-damaged maize roots. *Nature*, **434**, 732–737.
- Rasmann, S., Erwin, A.C., Halitschke, R. and Agrawal, A.A. (2011) Direct and indirect root defences of milkweed (*Asclepias syriaca*): trophic cascades, trade-offs and novel methods for studying subterranean herbivory. *J. Ecol.* **99**, 16–25.
- Rasmussen, T.B. *et al.* (2005) Screening for quorum-sensing inhibitors (QSI) by use of a novel genetic system, the QSI selector. *J. Bacteriol.* **187**, 1799–1814.
- Reinecke, A., Müller, F. and Hilker, M. (2008) Attractiveness of CO<sub>2</sub> released by root respiration fades on the background of root exudates. *Basic Appl. Ecol.* **9**, 568–576.
- Reinhold-Hurek, B., Bünge, W., Burbano, C.S., Sabale, M. and Hurek, T. (2015) Roots shaping their microbiome: global hotspots for microbial activity. *Annu. Rev. Phytopathol.* **53**, 403–424.
- Rheinwald, J.G., Chakrabarty, A.M. and Gunsalus, I.C. (1973) A transmissible plasmid controlling camphor oxidation in *Pseudomonas putida*. *Proc. Natl Acad. Sci. USA*, **70**, 885–889.
- Ro, D.K., Ehltng, J., Keeling, C.I., Lin, R., Mattheus, N. and Bohlmann, J. (2006) Microarray expression profiling and functional characterization of AtTPS genes: duplicated *Arabidopsis thaliana* sesquiterpene synthase genes At4g13280 and At4g13300 encode root-specific and wound-inducible (Z)-gamma-bisabolene synthases. *Arch. Biochem. Biophys.* **448**, 104–116.
- Robert, C.A.M. *et al.* (2012a) A specialist root herbivore exploits defensive metabolites to locate nutritious tissues. *Ecol. Lett.* **15**, 55–64.
- Robert, C.A.M., Erb, M., Duployer, M., Zwahlen, C., Doyen, G.R. and Turlings, T.C.J. (2012b) Herbivore-induced plant volatiles mediate host selection by a root herbivore. *New Phytol.* **194**, 1061–1069.
- Robert, C.A.M., Erb, M., Hibbard, B.E., Wade French, B., Zwahlen, C. and Turlings, T.C.J. (2012c) A specialist root herbivore reduces plant resistance and uses an induced plant volatile to aggregate in a density-dependent manner. *Funct. Ecol.* **26**, 1429–1440.
- Robinson, N.J., Procter, C.M., Connolly, E.L. and Gueriot, M.L. (1999) A ferric-chelate reductase for iron uptake from soils. *Nature*, **397**, 694–697.

- Rodríguez-Celma, J., Lin, W.-D., Fu, G.-M., Abadía, J., López-Millán, A.-F. and Schmidt, W. (2013) Mutually exclusive alterations in secondary metabolism are critical for the uptake of insoluble iron compounds by *Arabidopsis* and *Medicago truncatula*. *Plant Physiol.* **162**, 1473–1485.
- Rogers, E.D., Jackson, T., Moussaieff, A., Aharoni, A. and Benfey, P.N. (2012) Cell type-specific transcriptional profiling: implications for metabolite profiling. *Plant J.* **70**, 5–17.
- Roos, J., Bejai, S., Mozurkai, R. and Dixelius, C. (2015) Susceptibility to *Verticillium longisporum* is linked to monoterpene production by TPS23/27 in *Arabidopsis*. *Plant J.* **81**, 572–585.
- Roriz, M., Carvalho, S.M.P., Vasconcelos, M.W. et al. (2014) High relative air humidity influences mineral accumulation and growth in iron deficient soybean plants. *Front. Plant Sci.* **44**, 189–198.
- Rostás, M., Cripps, M.G. and Silcock, P. (2015) Aboveground endophyte affects root volatile emission and host plant selection of a belowground insect. *Oecologia*, **177**, 487–497.
- Ruyter-Spira, C., Al-Babili, S., Van Der Krol, S. and Bouwmeester, H. (2013) The biology of strigolactones. *Trends Plant Sci.* **18**, 72–83.
- Ruzicka, K. et al. (2010) *Arabidopsis* PIS1 encodes the ABCG37 transporter of auxinic compounds including the auxin precursor indole-3-butyric acid. *Proc. Natl Acad. Sci. USA*, **107**, 10749–10753.
- Ryu, C.M., Farag, M.A., Hu, C.H., Reddy, M.S., Wei, H.-X., Paré, P.W. and Kloepper, J.W. (2003) Bacterial volatiles promote growth in *Arabidopsis*. *Proc. Natl Acad. Sci. USA*, **100**, 4927–4932.
- Ryu, C.M., Farag, M.A., Hu, C.H., Reddy, M.S., Kloepper, J.W. and Paré, P.W. (2004a) Bacterial volatiles induce systemic resistance in *Arabidopsis*. *Plant Physiol.* **134**, 1017–1026.
- Ryu, C.M., Murphy, J.F., Mysore, K.S. and Kloepper, J.W. (2004b) Plant growth-promoting rhizobacteria systemically protect *Arabidopsis thaliana* against Cucumber mosaic virus by a salicylic acid and NPR1-independent and jasmonic acid-dependent signaling pathway. *Plant J.* **39**, 381–392.
- Santi, S. and Schmidt, W. (2009) Dissecting iron deficiency-induced proton extrusion in *Arabidopsis* roots. *New Phytol.* **183**, 1072–1084.
- Sawers, R.J.H., Svane, S.F., Quan, C. et al. (2017) Phosphorus acquisition efficiency in arbuscular mycorrhizal maize is correlated with the abundance of root-external hyphae and the accumulation of transcripts encoding PHT1 phosphate transporters. *New Phytol.* **214**, 632–643.
- Scheffknecht, S., Mammerer, R., Steinkellner, S. and Vierheilig, H. (2006) Root exudates of mycorrhizal tomato plants exhibit a different effect on microconidia germination of *Fusarium oxysporum* f. sp. lycopersici than root exudates from non-mycorrhizal tomato plants. *Mycorrhiza*, **16**, 365–370.
- Schenk, H., Driessen, R.A.J. and De Gelder, R. (1999) Elucidation of the structure of solanoclepin A, a natural hatching factor of potato and tomato cyst nematodes, by Single-crystal X-ray diffraction. *Croat. Chem. Acta*, **72**, 593–606.
- Schenkel, D., Lemfack, M.C., Piechulla, B. and Spillvallo, R. (2015) A meta-analysis approach for assessing the diversity and specificity of belowground root and microbial volatiles. *Front. Plant Sci.* **6**, 707.
- Schmelz, E.A., Kaplan, F., Huffaker, A., Dafoe, N.J., Vaughan, M.M., Ni, X., Rocca, J.R., Alborn, H.T. and Teal, P.E. (2011) Identity, regulation, and activity of inducible diterpenoid phytoalexins in maize. *Proc. Natl Acad. Sci. USA*, **108**, 5455–5460.
- Schmid, N.B., Giehl, R.F.H., Döll, S., Mock, H.-P., Strehmel, N., Scheel, D., Kong, X., Hider, R.C. and von Wirén, N. (2014) Feruloyl-CoA 6'-Hydroxylase1-dependent coumarins mediate iron acquisition from alkaline substrates in *Arabidopsis*. *Plant Physiol.* **164**, 160–172.
- Senalik, D. and Simon, P.W. (1986) Relationship between oil ducts and volatile terpenoid content in carrot root. *Am. J. Bot.* **73**, 60–63.
- Sicker, D., Schneider, B., Hennig, L., Knop, M. and Schulz, M. (2001) Glycoside carbamates from benzoxazolin-2(3H)-one detoxification in extracts and exudates of corn roots. *Phytochemistry*, **58**, 819–825.
- Sirikantaramas, S., Yamazaki, M. and Saito, K. (2008) Mechanisms of resistance to self-produced toxic secondary metabolites in plants. *Phytochem. Rev.* **7**, 467–477.
- Sisó-Terraza, P., Rios, J.J., Abadía, J., Abadía, A. and Álvarez-Fernández, A. (2016) Flavins secreted by roots of iron-deficient *Beta vulgaris* enable mining of ferric oxide via reductive mechanisms. *New Phytol.* **209**, 733–745.
- Smith, S.E. and Smith, F.A. (2011) Roles of arbuscular mycorrhizas in plant nutrition and growth: new paradigms from cellular to ecosystem scales. *Annu. Rev. Plant Biol.* **62**, 227–250.
- Smith, S.M. and Waters, M.T. (2012) Strigolactones: destruction-dependent perception? *Curr. Biol.* **22**, R924–R927.
- Sohrabi, R., Huh, J.-H., Badieyan, S., Rakotondraibe, L.H., Kliebenstein, D.J., Sobrado, P. and Tholl, D. (2015) In planta variation of volatile biosynthesis: an alternative biosynthetic route to the formation of the pathogen-induced volatile homoterpene DMNT via triterpene degradation in *Arabidopsis* roots. *Plant Cell Online*, **27**, 874–890.
- Sohrabi, R., Ali, T., Harinantenaina Rakotondraibe, L. and Tholl, D. (2017) Formation and exudation of non-volatile products of the arabioidol triterpenoid degradation pathway in *Arabidopsis* roots. *Plant Signal. Behav.* **12**, e1265722.
- Stachel, S.E., Messens, E., Van Montagu, M. and Zambryski, P. (1985) Identification of the signal molecules produced by wounded plant cells that activate T-DNA transfer in *Agrobacterium tumefaciens*. *Nature*, **318**, 624–629.
- Stevenson, P.C., Muyinza, H., Hall, D.R., Porter, E.A., Farman, D.I., Talwana, H. and Mwanga, R.O.M. (2009) Chemical basis for resistance in sweet-potato *Ipomoea batatas* to the sweetpotato weevil *Cylas puncticollis*. *Pure Appl. Chem.* **81**, 141–151.
- Suzuki, M., Takahashi, M., Tsukamoto, T. et al. (2006) Biosynthesis and secretion of mugineic acid family phytosiderophores in zinc-deficient barley. *Plant J.* **48**, 85–97.
- Szoboszlai, M., White-Monsant, A. and Moe, L.A. (2016) The effect of root exudate 7,4'-dihydroxyflavone and naringenin on soil bacterial community structure. *PLoS ONE*, **11**, e0146555.
- Tatsumi, K., Yano, M., Kaminade, K., Sugiyama, A., Sato, M., Toyooka, K., Aoyama, T., Sato, F. and Yazaki, K. (2016) Characterization of shikonin derivative secretion in *Lithospermum erythrorhizon* hairy roots as a model of lipid-soluble metabolite secretion from plants. *Front. Plant Sci.* **7**, 1–11.
- Teplitski, M., Robinson, J.B. and Bauer, W.D. (2000) Plants secrete substances that mimic bacterial N-acyl homoserine lactone signal activities and affect population density-dependent behaviors in associated bacteria. *Mol. Plant Microbe Interact.* **13**, 637–648.
- Thimmappa, R., Geisler, K., Louveau, T., O'Maille, P. and Osbourn, A. (2014) Triterpene biosynthesis in plants. *Annu. Rev. Plant Biol.* **65**, 225–257.
- Tonelli, M., Peanflor, M.F.G.V., Leite, L.G., Silva, W.D., Martins, F. and Bento, J.M.S. (2016) Attraction of entomopathogenic nematodes to sugarcane root volatiles under herbivory by a sap-sucking insect. *Chemoecology*, **26**, 59–66.
- Tsai, H.-H. and Schmidt, W. (2017) One way. Or another? Iron uptake in plants. *New Phytol.* **214**, 500–505.
- Turkington, R. (1989) The growth, distribution and neighbour relationships of *Trifolium repens* in a permanent pasture. V. The coevolution of competitors. *J. Ecol.* **77**, 717–733.
- Turner, T.R. et al. (2013) The plant microbiome. *Genome Biol.* **14**, 209.
- Turrà, D., El Ghalid, M., Rossi, F. and Di Pietro, A. (2015) Fungal pathogen uses sex pheromone receptor for chemotropic sensing of host plant signals. *Nature*, **527**, 521–524.
- Van Dam, N.M. and Raaijmakers, C.E. (2006) Local and systemic induced responses to cabbage root fly larvae (*Delia radicum*) in *Brassica nigra* and *B. oleracea*. *Chemoecology*, **16**, 17–24.
- Vandeputte, O.M., Kiendrebeogo, M., Rajaonson, S., Diallo, B., Mol, A., El Jaziri, M. and Baucher, M. (2010) Identification of catechin as one of the flavonoids from *Combretum albiglorum* bark extract that reduces the production of quorum-sensing-controlled virulence factors in *Pseudomonas aeruginosa* PAO1. *Appl. Environ. Microbiol.* **76**, 243–253.
- Vandeputte, O.M., Kiendrebeogo, M., Rasamiravaka, T., Stévigny, C., Duez, P., Rajaonson, S., Diallo, B., Mol, A., Baucher, M. and el Jaziri, M. (2011) The flavanone naringenin reduces the production of quorum sensing-controlled virulence factors in *Pseudomonas aeruginosa* PAO1. *Microbiology*, **157**, 2120–2132.
- Vaughan, M.M., Wang, Q., Webster, F.X. et al. (2013) Formation of the unusual semivolatile diterpene rhizathalene by the *Arabidopsis* class I terpene synthase TPS08 in the root stele is involved in defense against belowground herbivory. *Plant Cell*, **25**, 1108–1125.

- Vaughan, M.M., Christensen, S., Schmelz, E.A., Huffaker, A., Mcaulane, H.J., Alborn, H.T., Romero, M., Allen, L.H. and Teal, P.E.A. (2015) Accumulation of terpenoid phytoalexins in maize roots is associated with drought tolerance. *Plant Cell Environ.* **38**, 2195–2207.
- Venturelli, S. *et al.* (2015) Plants release precursors of histone deacetylase inhibitors to suppress growth of competitors. *Plant Cell*, **27**, 3175–3189.
- Vert, G., Grotz, N., Dédaldéchamp, F., Gaymard, F., Guerinot, M.L., Briat, J.-F. and Curie, C. (2002) IRT1, an Arabidopsis transporter essential for iron uptake from the soil and for plant growth. *Plant Cell*, **14**, 1223–1233.
- Vogt, T. (2010) Phenylpropanoid biosynthesis. *Mol. Plant*, **3**, 2–20.
- Vos, C., Claerhout, S., Mkandawire, R., Panis, B., de Waele, D. and Elsen, A. (2012) Arbuscular mycorrhizal fungi reduce root-knot nematode penetration through altered root exudation of their host. *Plant Soil*, **354**, 335–345.
- Vose, P.B. (1982) Iron nutrition in plants: a world overview. *J. Plant Nutr.* **5**, 233–249.
- Watts-Williams, S.J., Jakobsen, I., Cavagnaro, T.R., Gronlund, M. and Gronlund, M. (2015) Local and distal effects of arbuscular mycorrhizal colonization on direct pathway Pi uptake and root growth in *Medicago truncatula*. *J. Exp. Bot.* **66**, 4061–4073.
- Weissteiner, S., Huetteroth, W., Kollmann, M., Weißbecker, B., Romani, R., Schachtner, J. and Schütz, S. (2012) Cockchafer larvae smell host root scents in soil. *PLoS ONE*, **7**, e45827.
- Wenke, K., Kai, M. and Piechulla, B. (2010) Belowground volatiles facilitate interactions between plant roots and soil organisms. *Planta*, **231**, 499–506.
- Wenke, K., Wanke, D., Kilian, J., Berendzen, K., Harter, K. and Piechulla, B. (2012) Volatiles of two growth-inhibiting rhizobacteria commonly engage AtWRKY18 function. *Plant J.* **70**, 445–459.
- Weston, L.A., Ryan, P.R. and Watt, M. (2012a) Mechanisms for cellular transport and release of allelochemicals from plant roots into the rhizosphere. *J. Exp. Bot.* **63**, 3445–3454.
- Weston, L.A., Weston, P.A. and McCully, M. (2012b) Production of bioactive naphthoquinones by roots of paterson's curse (*Echium plantagineum*) – implications for invasion success? *Pak. J. Weed Sci. Res.* **18**, 677–686.
- White, P.J., George, T.S., Hammond, J.P. and James, E.K. (2014) Improving crop mineral nutrition. *Plant Soil*, **384**, 1–5.
- Widhalm, J.R., Jaini, R., Morgan, J.A. and Dudareva, N. (2015) Rethinking how volatiles are released from plant cells. *Trends Plant Sci.* **20**, 545–550.
- Wintermans, P.C.A., Bakker, P. and Pieterse, C.M.J. (2016) Natural genetic variation in Arabidopsis for responsiveness to plant growth-promoting rhizobacteria. *Plant Mol. Biol.* **90**, 623–634.
- Xie, X., Yoneyama, K. and Yoneyama, K. (2010) The strigolactone story. *Annu. Rev. Phytopathol.* **48**, 93–117.
- Xu, D., Hanschen, F.S., Witzel, K., Nintemann, S.J., Nour-Eldin, H.H., Schreiner, M. and Halkier, B.A. (2016) Rhizosecretion of stele-synthesized glucosinolates and their catabolites requires GTR-mediated import in Arabidopsis. *J. Exp. Bot.*: erw355.
- Xu, M., Galhano, R., Wiemann, P. *et al.* (2012) Genetic evidence for natural product-mediated plant–plant allelopathy in rice (*Oryza sativa*). *New Phytol.* **193**, 570–575.
- Xu, Z., Zhao, Y.-Q., Yang, D.-J., Sun, H.-J., Zhang, C.-L. and Xie, Y.-P. (2015) Attractant and repellent effects of sweet potato root exudates on the potato rot nematode, *Ditylenchus destructor*. *Nematology*, **17**, 117–124.
- Yamamoto, H., Yazaki, K. and Inoue, K. (2000) Simultaneous analysis of shikimate-derived secondary metabolites in *Lithospermum erythrorhizon* cell suspension cultures by high-performance liquid chromatography. *J. Chromatogr. B Biomed. Sci. Appl.* **738**, 3–15.
- Yang, X., Owens, T.G., Scheffler, B.E. and Westoni, L.A. (2004a) Manipulation of root hair development and sorgoleone production in Sorghum seedlings. *J. Chem. Ecol.* **30**, 199–213.
- Yang, X., Scheffler, B.E. and Weston, L.A. (2004b) SOR1, a gene associated with bioherbicide production in Sorghum root hairs. *J. Exp. Bot.* **55**, 2251–2259.
- Yang, G., Zhou, B., Zhang, X., Zhang, Z., Wu, Y., Zhang, Y., Lü, S., Zou, Q., Gao, Y. and Teng, L. (2016) Effects of tomato root exudates on *Meloidogyne incognita*. *PLoS ONE*, **11**, 1–16.
- Yazaki, K. (2005) Transporters of secondary metabolites. *Curr. Opin. Plant Biol.* **8**, 301–307.
- Yoneyama, K., Yoneyama, K., Takeuchi, Y. and Sekimoto, H. (2007) Phosphorus deficiency in red clover promotes exudation of orobanchol, the signal for mycorrhizal symbionts and germination stimulant for root parasites. *Planta*, **225**, 1031–1038.
- Zamioudis, C., Hanson, J. and Pieterse, C.M.J. (2014)  $\beta$ -Glucosidase BGLU42 is a MYB72-dependent key regulator of rhizobacteria-induced systemic resistance and modulates iron deficiency responses in Arabidopsis roots. *New Phytol.* **204**, 368–379.
- Zamioudis, C., Korteland, J., Van Pelt, J.A. *et al.* (2015) Rhizobacterial volatiles and photosynthesis-related signals coordinate MYB72 expression in Arabidopsis roots during onset of induced systemic resistance and iron-deficiency responses. *Plant J.* **84**, 309–322.
- Zhao, X., Schmitt, M. and Hawes, M.C. (2000) Species-dependent effects of border cell and root tip exudates on nematode behavior. *Phytopathology*, **90**, 1239–1245.
- Zhu, X., Skoneczny, D., Weidenhamer, J.D., Mwendwa, J.M., Weston, P.A., Gurr, G.M., Callaway, R.M. and Weston, L.A. (2016) Identification and localization of bioactive naphthoquinones in the roots and rhizosphere of Paterson's curse (*Echium plantagineum*), a noxious invader. *J. Exp. Bot.* **67**, 3777–3788.