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REVIEW

Plant-borne flavonoids released into the rhizosphere: impact on soil bio-activities related to plant nutrition. A review

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Abstract Plants produce and release in the surrounding soil, the so-called rhizosphere, a vast variety of secondary metabolites. Among them, flavonoids are the most studied, mainly for their role in the establishment of rhizobium–legume symbiosis; on the other hand, some studies highlight that they are also important in the plant strategies to acquire nutrients from the soil, for example, by acting on its chemistry. The scope of this review is to give a quick overview on the types and amounts of plant-released flavonoids in order to focus on their effects on soil activities that in turn can influence nutrient availability and so plant mineral nutrition; emphasis is given to the different nutrient cycles, soil enzyme, and soil bacteria activities, and their influence on soil macrofauna and roots of other plants. Finally, the possible outcome of the climate change on these processes is discussed.

Keywords Nutrient cycle · Nutrient availability · Rhizosphere · Soil enzyme · Climate change · Allelopathy · Soil bacteria · Soil macrofauna · Soil fungi · Carbon · Nitrogen · Phosphorus · Sulfur · Micronutrients

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Introduction

Flavonoids are polyphenolic compounds synthesized via the shikimic acid/phenylpropanoid pathways. These plant metabolites, which include chalcones, flavones, isoflavones, flavonols, flavanones, and isoflavonoids (Fig. 1), can be released by plant roots into the rhizosphere as a result of root turnover, root injury, and root decomposition (passive release) or through root exudation (active release) (Shaw et al. 2006). In the rhizosphere, the released flavonoids can have multifunctional roles, such as protect plants against pests and diseases (Dakora 2003; Dakora and Phillips 2002), regulate root growth and functions (Rao 1990; Buer et al. 2010), influence nutrient cycles such as N cycle (Kuiters 1990; Rao 1990; Garg and Geetanjali 2007), interact with proteins and make protein N more resistant to microbial degradation (Hättenschwiler and Vitousek 2000), and induce allelopathic growth effects (Chaves et al. 2001). Although flavonoids play a dominant role in controlling some of plant–soil interactions related to soil organic matter

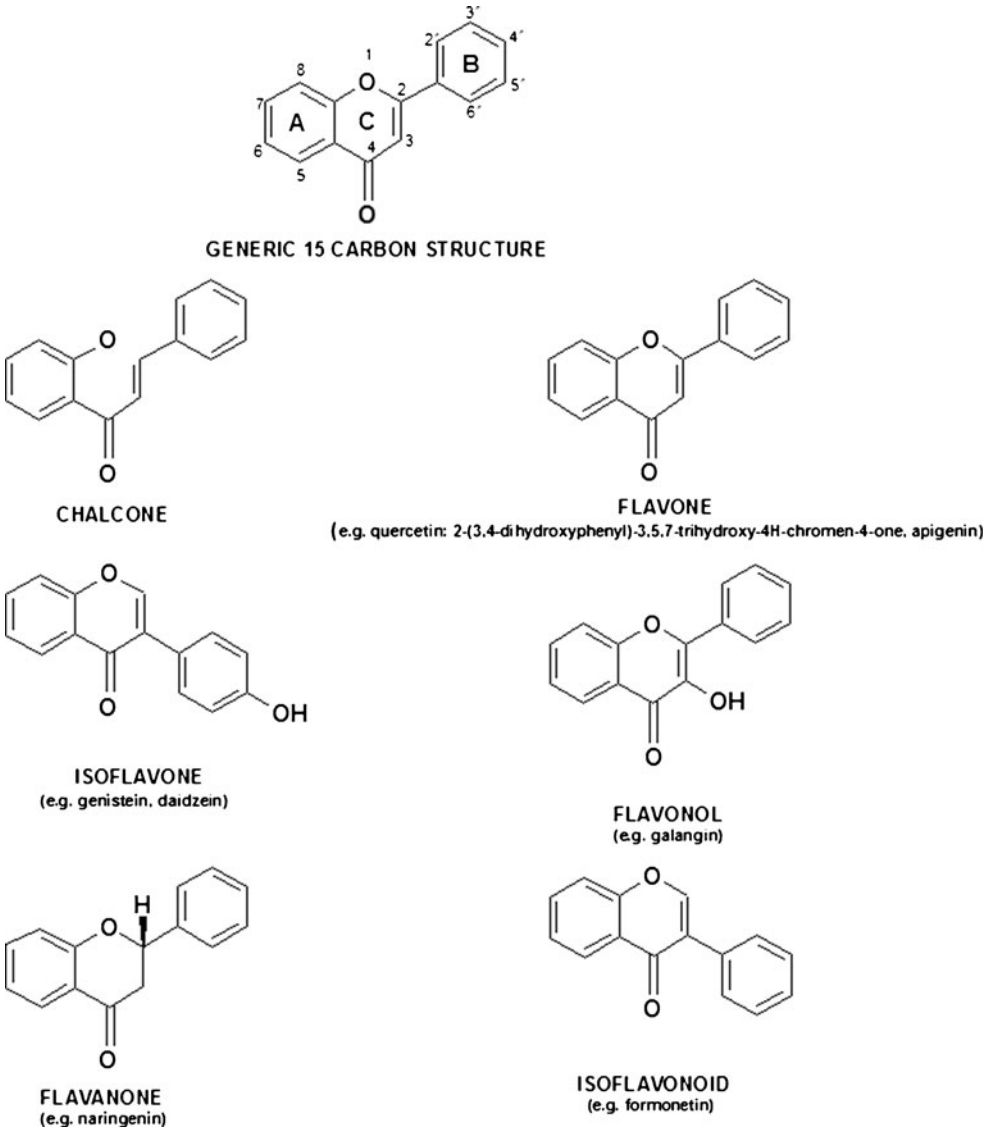

Fig. 1 Chemical structure of flavonoids and their subgroups

dynamics and nutrient cycling (Kuiters 1990), there is not any comprehensive discussion on their origin, composition, and persistence in the rhizosphere soil and their effects on biological activities of soil and how, in turn, they affect plant nutrition. Therefore, the main aim of this review is to discuss the effects of flavonoids on bio-activities of rhizosphere soil and the role of these effects on plant nutrition. Since these effects depend on either the type of flavonoids and on the bio-available amounts in situ, we shall also discuss origin, composition, and persistence of flavonoids in the rhizosphere soil. Information about concentration of flavonoids in the rhizosphere as well as their persistence and degradation/turnover, once released by the roots, is still largely lacking and often contrasting. This knowledge is crucial to define the mobility, bioavailability, as well as the effects of flavonoids, which is needed to understand their role in the rhizosphere. We shall not discuss in detail the effect of flavonoids on N fixation because the topic has already been reviewed (Cooper 2007; Schultze and Kondorosi 1998)

Types, amounts, and persistence of plant-borne flavonoids released into the rhizosphere

Plants can release different types and amounts of flavonoids into the rhizosphere (Cesco et al. 2010). Both types and amounts depend on the plant species and cultivar, cultivation system, biotic stresses, and/or environmental conditions affecting plant physiology, nutrient availability, and plant development. It is widely accepted that chemical composition and concentration are key factors in determining the biotic and abiotic activity of flavonoids. However, most knowledge derive from studies in systems such as hydroponic

culture, sand, water-agar, etc. (Cesco et al. 2010), and it is reasonable to hypothesize that the flavonoid concentrations in the rhizosphere soil are lower than those released by plants under in vitro conditions due to flavonoids adsorption by surface-reactive soil particles, biotic or abiotic degradation, and variable in situ release. Therefore, the residence time of the flavonoid (the period in which it is active) in the rhizosphere can be significantly affected by the experimental conditions. Determination of the amount and residence time of the target flavonoid in the rhizosphere is difficult due to soil heterogeneity (e.g., variable pH and redox potential values, different surface-reactive solid phases), chemical structure, and reactivity of the various flavonoid molecules (Inderjit and Dakshini 1992a; Perry et al. 2007a, b; Alford et al. 2007; Barto and Cipollini 2009; Chaves et al. 2001) and also by the temporal variations of the exudation process (Alford et al. 2007). Consequently, concentrations, types, degradation, and turnover of flavonoids in the rhizosphere are poorly understood, and their knowledge is essential to define their mobility, bioavailability, and role in the rhizosphere.

Phenols, which also include flavonoids, undergo various biotic and abiotic processes in soil, such as use by microorganisms as C source (Blum and Shafer 1988; Blum 1998; Blum et al. 1999; Hättenschwiler and Vitousek 2000), sorption by soil organic matter (Makino et al. 1996) and by clay minerals (Huang et al. 1999), polymerization into insoluble and recalcitrant humic substances (Wang et al. 1986; Hättenschwiler and Vitousek 2000), and chemical transformation into other toxic or nontoxic compounds (Blum 1998; Okumura et al. 1999). These processes depend on the phenol type and on chemical, physical, and biological properties of the rhizosphere soil. According to Hättenschwiler and Vitousek (2000), soluble polyphenols in soil may also form chelates with Al or Fe ions or remain soluble, being leached by percolating water as dissolved organic carbon. The diagram showing a simplified overview of the polyphenols fate in the rhizosphere soil is reported in Fig. 2.

Flavonoids can be aerobically broken down by flavonoid-degrading bacterial strains as discussed by Cooper (2004a) and Shaw et al. (2006). It has also been shown that flavonoids can stimulate the biodegradation of xenobiotics (Shaw et al. 2006) and reduce the degradation of organic acids in the rhizosphere (Tomasi et al. 2008). Both concentration and type of flavonoids in the rhizosphere soil are affected by soil microorganisms through modification of root exudation patterns and microbial catabolisms (Shaw et al. 2006). Also, the plant age affects root exudation of flavonoids. In vitro studies have shown that exudation rates of catechin from seedlings and mature plants of spotted knapweed are different. It is still unknown whether each flavonoid requires a specific enzymatic system for its biodegradation or if the same enzymatic system can degrade different flavonoid molecules. Shaw and Hooker (2008) showed that naringenin (flavone) and formononetin (isoflavonoid) were degraded in 4 and 24 h, respectively. The different lag times may indicate the requirement of different catabolic enzymes for degrading isoflavonoids or flavonones.

Half-lives of the flavonoid glycosides produced by *Alliaria petiolata* (M.Bieb) Cavara & Grande were longer in sterile than in non-sterile soils (Barto and Cipollini 2009). Aglycone flavonoids from *Cistus ladanifer* were partly degraded because molecules were partly trapped in the solid organic phase or in aggregates within soil micropores (Sosa et al. 2010), being thus inaccessible to microorganisms (Pignatello 1989; Pignatello and Xing 1996). It is likely that the rate of flavonoid biodegradation by microbial communities of the rhizosphere may increase by ageing plant, due to the enrichment with flavonoid-degrading microbial communities in response to the prolonged flavonoid release (Shaw et al. 2006). On the other hand, microbial activity can increase the level of free flavonoids in the soil solution, since microbial glycosidases hydrolyze the flavonol glycosides stored within roots to produce unconjugated aglycones (Hartwig and Phillips 1991), which can be further metabolized in the rhizosphere soil to produce new flavonoid structures. Shaw et al. (2006) showed that naringenin and chalcone intermediates are produced during quercetin biodegradation. Furthermore, glycoside forms are more water-soluble than the free aglycone, and the conjugated forms are expected to be less adsorbed to the soil matrix and thus more mobile and more bio-available than the respective free aglycone molecule. However, the conjugated form is likely short-lived, because hydrolysis by glycosidase enzymes of both plant and microbial origin can occur shortly after root exudation (Hartwig and Phillips 1991) even if Leon-Barrios et al. (1993) described unexpected stability of formononetin-7-*O*-glycoside in the rhizosphere soil.

As mentioned above, microbial degradation of free flavonoids in soil is also affected by their high reactivity towards the organo-mineral matrix; this interaction may make the flavonoids more resistant to microbial degradation, but it may also contribute to the rapid decrease of flavonoid concentration in the soil solution. Gallet and Lebreton (1995) did not detect flavonoids in the humus of a forest soil by monitoring the fate of phenolics of *Picea abies* L. and *Vaccinium myrtillus* L. from the foliage to soil, suggesting that phenolics were degraded to monocyclic acids such as protocatechuic acid, as reported by Barz and Höesel (1975), or incorporated into organic matter during the humification process (Bollag et al. 1997; Dec et al. 2001; Dec and Bollag 2000). Wallstedt et al. (2005) suggested that a proportion of phenols released as root exudates, probably reacted with soil components or became physically trapped by soil organic matter.

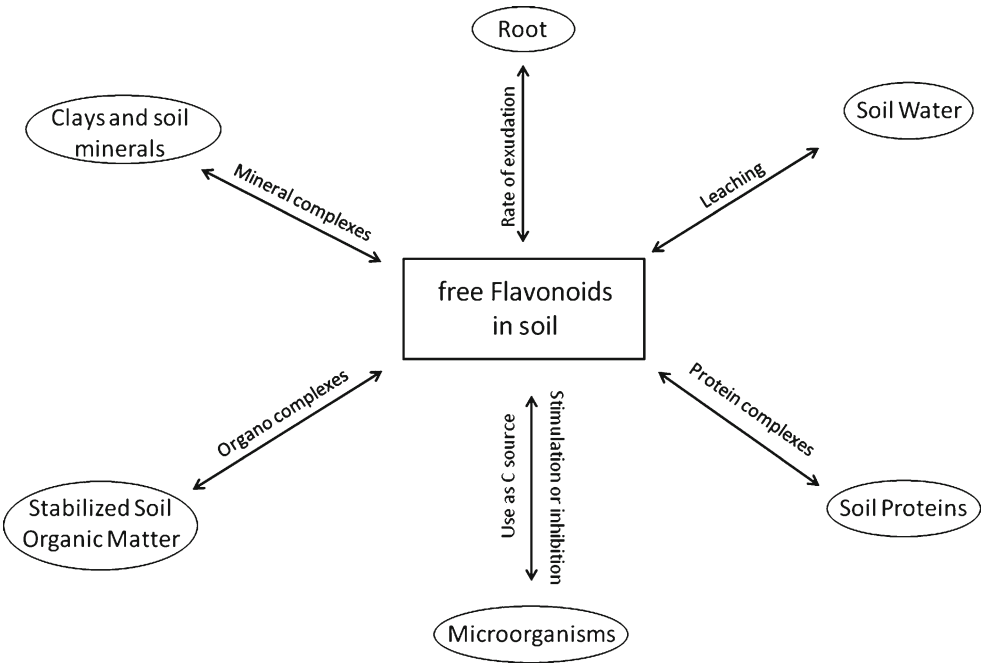

Fig. 2 Flavonoids released by roots into the rhizosphere and their interaction with the soil components

As already discussed, the flavonoid concentration in the soil solution depends on several processes and interactions with the soil solid phase, and this makes its determination and thus the evaluation of flavonoid availability quite difficult; consequently, only little quantitative information on concentrations of flavonoids in soil is present in literature. Generally, phenolics are found in very small concentrations (<1 μM) in the soil solution (Gallet and Keller 1999). Catechin concentration in three different soils infested by *Centaurea maculosa* (spotted knapweed) was very low ranging from less than 0.1 to 1.3 μg g^{-1} soil (Blair et al. 2006). Analysis of *C. ladanifer* L. soils showed five aglycone flavonoids: apigenin, 4′(*O*)methyl apigenin, 7(*O*)methyl apigenin, 3(*O*)methyl kaempferol, and 3,7di(*O*) methyl kaempferol (Sosa et al. 2010). The highest amount of total flavonoids was observed in autumn and spring samples (11.13 and 8.68 μg g^{-1}, respectively). Flavonoids such as 4′,7-dihydroxyflavanone, 4′,7-dihydroxyflavone, and medicarpin glycoside were detected in the rhizosphere soil of *Medicago sativa* L. (Phillips 1997; Shaw et al. 2006) while kaempferol and quercetin glycosides were the main flavonoids produced by wild-type *Arabidopsis* (Saslowsky et al. 2000). However, experimental conditions can markedly affect the concentration of the bio-available fraction of flavonoids. This has been found to range from 0 to 2.4 (Blair et al. 2005), 5 to 35 (Weir et al. 2003), 0 to 113 (Ridenour et al. 2008), and 83 to 185 μg ml^{-1} (Bais et al. 2002). These variable data are likely due to the efficiency of the extraction method and soil type. The extraction yield of catechin was 100% with methanol (Bais et al. 2002; Thelen et al. 2005) but was also lower from 0 to 17% depending on the soil types (Blair et al. 2005). Blair et al. (2005) showed that 75:25% acetone/water solution containing 0.1% H_3PO_4 was the most efficient extractant among nine different solutions tested to extract catechin from soil. However, methanol extraction is the most used extractant for flavonoids from soil (Bardo and Cipollini 2009; Ozan et al. 1997; Perry et al. 2007a, b; Sosa et al. 2010). Recently, a biomimetic extraction procedure has also been proposed which is based on the insertion of a polydimethylsiloxane tubing (0.30 mm ID, 0.64 mm OD) into the rhizosphere; this extraction procedure allowed the estimation of the flavonoids released in the rhizosphere solution of *A. petiolata* (M.Bieb) Cavara and Grande in 3 months (Barto and Cipollini 2009).

There are contradictory reports about the residence time of flavonoids in soil. Relatively great stability of catechin in soil has been reported (Bais et al. 2002, 2003; He et al. 2009; Inderjit et al. 2008; Pollock et al. 2009; Weidenhamer and Callaway 2010), but also showed no presence of this flavonoid probably due to its instability in the soil solution (Blair et al. 2006; Duke et al. 2009a, b; Perry et al. 2007a, b; Stermitz et al. 2009). Sosa et al. (2010) have shown that the residence time of apigenin, 4′(*O*)methyl apigenin, 3(*O*) methyl kaempferol, and 3,7di(*O*) methyl kaempferol) in soil under *C. ladanifer* L. was rather long since their half-lives in autumn were 5.75, 4.36, 9.74, and 8.3 months, respectively, with values even higher in winter and summer. The seasonal variation in the persistence of flavonoids in soil is due to changes in microbial activities which are generally lower in winter and summer than in autumn and spring. The residence times of flavonoids found by Sosa et al. (2010) differ from those obtained by Shaw and Hooker (2008), Weidenhamer and Romeo (2004), and Barto and Cipollini (2009) for formonentin, naringenin,

hydroquinone, benzoquinone, gallic acid, arbutin, and isovitexin-6′-*O*-β-D-glucopyranoside, since these latter, when added to different types of soils, disappeared over a period of several hours or days. On the other hand, the results by Sosa et al. (2010) are similar to those by Wallstedt et al. (2005) with batatasin III, which persisted at 2–5 μg g^{-1} in soils of *Empetrum nigrum* L. ssp. *hermaphroditum* (Lange ex Hagerup) because phenols probably reacted with soil components and/or were physically trapped by soil organic matter. The flavonoids strongly bound to the soil organic matter (2–5 μg/g of total flavonoids) can be extracted by organic solvents and represent the stable fraction, not available to soil organisms (Bhandari et al. 1998). The persistence of flavonoids in soils depends not only on soil type but also on flavonoid structure. For example, naringenin and formononetin showed different lag phases (<4 h for naringenin and ca. 24 h for formononetin) prior to onset of rapid biodegradation (after 96 h, 0.26% of the added naringenin was present whereas formononetin was reduced of ca. 95% after 72 h) in an acidic soil (pH 5.6) with 1.1% organic C (Shaw and Hooker 2008). In addition to the organic fractions, other chemical soil properties, such as pH and mineral constituents, may affect flavonoid availability. Flavonoids with a catechol moiety as catechin are quickly degraded and adsorbed in soils with a high pH value. Furubayashi et al. (2007) found that, after 4 h, 0.013 and 0.054 mol of chatechin kg^{-1} soil added at 0.2 mol kg^{-1} to a volcanic ash and an alluvial soil were adsorbed at an equilibrium pH of 4 and 7, respectively. The decrease in the flavonoid concentration was similar than that observed by Blair et al. (2005) for catechol incubated in a loamy sand/sand soil at pH 5.2 These authors observed a decrease of 75% extractable catechin after 1 h and a complete disappearance after 24 h in soil samples initially treated with 10 μg g^{-1} catechin. According to Blair et al. (2005), the complete disappearance of catechin was mainly due to microbial degradation and binding reactions to organic matter. Forty percent and 80% of formononetin and biochanin were degraded, respectively, over a 15-day period (Shaw et al. 2006) in a soil (pH 7.5)/sand mixture (1:1) (Ozan et al. 1997). Pollock et al. (2009) observed that redox-active metals such as Fe and Cu rapidly degraded catechin whereas less redox-active metals as Mg and Pb also decreased the catechin concentration but to a lesser extent. Interestingly, Ca had the opposite effect of protecting the flavonoid from auto-oxidation. These results suggest the importance of cationic species distribution within the rhizosphere soil and their effect on the stability of flavonoids.

Soil (bio)activities and nutrient cycles within the rhizosphere

Flavonoids may affect soil biological processes, but this paragraph focuses on their effects on nutrient biogeocycles.

The influence on C cycle

The decomposition of plant, animal, and microbial remains in soil is carried out by fauna and microorganisms with release of CO_2 into the atmosphere. In general, degradation of more recalcitrant compounds takes more time than that for degradable compounds (Nannipieri and Badalucco 2003), and intermediate residues may enter into formation of humic substances (Stevenson 1994).

Flavonoids, as other plant phenols, can indirectly affect the C cycle through direct effects on the composition and activity of decomposer communities, thus influencing the decomposition rate (Hättenschwiler and Vitousek 2000). Soil organic matter is the major storehouse in soil not only for C but also for other plant nutrients, such as N, P, S, Ca, Mg, and several micronutrients. Therefore, any effect on the mineralization/immobilization of C may affect the availability of the other nutrients.

Considering the composition of the plant organic-C pool, tannins represent a significant C portion of terrestrial biomass in addition to cellulose, hemicelluloses, and lignin (Hernes and Hedges 2000). Such compounds can be considered polymers of flavonoids such as catechins, and in leaves and bark, they can represent up to 40% of the dry weight (Kuiters 1990; Matthews et al. 1997). The biodegradation of tannins to CO_2 (mineralization) may be the rate-limiting step in recycling biological C (Lattanzio et al. 2008). Various tannins may largely vary in their structures, but all bind and precipitate proteins. In particular, condensed tannins, also referred as proanthocyanidins, are polymers of the flavonoid skeleton flavan-3-ols (catechins) or flavan-3,4-diols or combination of both (Lattanzio et al. 2008). In plant roots, tannins are mainly accumulated into the hypodermis, below the suberized epidermal layer, where they can protect plant against pathogens. They can be released into the rhizosphere after cell death, senescence, or root injury also provoked by plant pathogens (Dakora and Phillips 1996; Ndakidemi and Dakora 2003). These polyphenols may be important substrates for the formation of humic substances via the formation of protein–tannin complexes and, once oxidized to quinones, of stable polymers by copolimerization with other phenolics, amino acids, and amino sugars (Schnitzer et al. 1984; Stevenson 1994). The protection of important biological molecules, such as proteins, against decomposition (Lorenz et al. 2007) is due to the intrinsic toxicity of tannins, against which organisms can secrete a variety of compounds (Scalbert 1991; Schultz et al. 1992) and to the potentially recalcitrant characteristics of their complexes and polymers (de Leeuw and Largeau 1993; Kolattukudy 2001; de Leeuw et al. 2006). On the other hand, the formation of humic substances by tannins could be mined by the presence of specific bacterial species, which can use these phenolic compounds as a sole carbon

source (Bhat et al. 1998; Scalbert 1991 and references therein). For example, catechin, a building unit of condensed tannins, and other flavonoids can be degraded in the rhizosphere by bacteria or fungi such as *Aspergillus*, *Fusarium*, *Penicillium*, *Rhizobia*, *Pseudomonas*, *Bacillus*, and *Rhodococcus* spp. The relative degradation pathways depend on substrate molecule and microbial species (Barz 1970; Barz et al. 1970; Barz and Hoesel 1975; Pillai and Swarup 2002; Schoefer et al. 2003).

A survey of flavonoid-degrading rhizobial strains revealed that flavonoids were generally cleaved via C-ring fission (chalcone intermediate) yielding phloroglucinol (ring A) and protocatechuic acid (ring B) (Fig. 3). Protocatechuic acid originates from the corresponding cinnamic acid derivative after the shortening of the side-chain by β-oxidation. For example, *Alternaria* sp. isolated from soil can shorten the cinnamic acid derivatives side-chain by β-oxidation, thus converting these compounds to corresponding benzoic acids (Nambudiri et al. 1970; Rao et al. 1991; Rao and Cooper 1994; Shultz et al. 1974). Phloroglucinol and protocatechuic acid can, in turn, undergo intradiol ring cleavage by specific oxygenase activities to give aliphatic products or CO_2. β-Ketoadipic acid can be a product of ring cleavage in the case of protocatechuic acid. Phloroglucinol, after cleavage of the aromatic ring by various oxigenases, is also converted to β-ketoadipate (Nambudiri et al. 1970; Bhat et al. 1998), which is converted to acetyl-CoA.

The influence on N cycle

Nitrogen (N), one of the most limiting nutrients in plant growth and production, occurs in soil both in organic and inorganic (nitrate, ammonium, and under certain conditions nitrite) forms, and it is characterized by a dynamic and complex cycle. Organic N is generally the largest N pool in soil (about 98%) and is mineralized to inorganic N, which is the N form generally taken up by plants. In soils with high content of micaceous clays, the fixed ammonium content may be higher than that of organic N. Net N mineralization indicates N available to plants since N immobilization (transformation of ammonium to organic N) occurs concurrently with gross N mineralization (Nannipieri and Paul 2009). It has been suggested that flavonoids can have positive or negative effects on soil N processes depending on

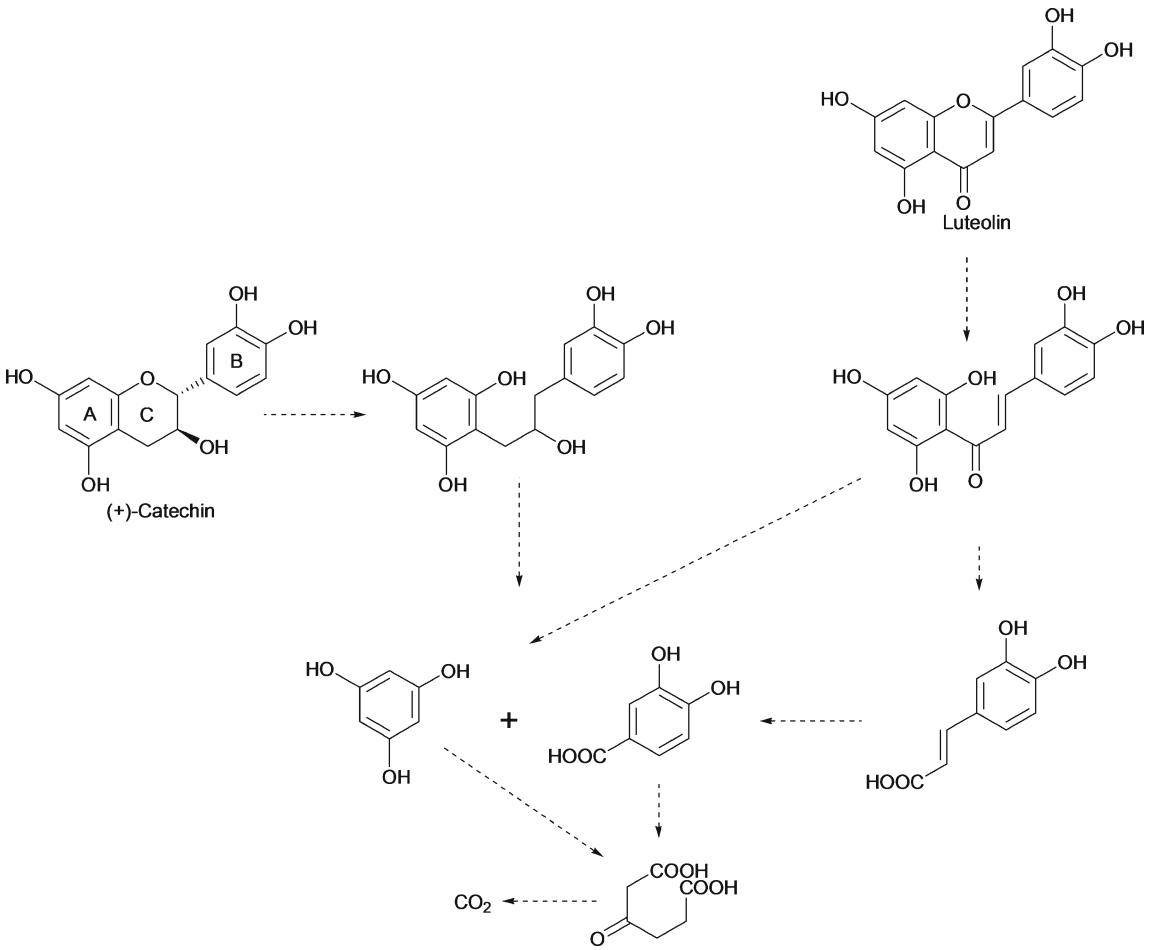

Fig. 3 Schematic pattern of flavonoid degradation by soil microorganisms

type of phenolic compound and on the microbial activity involved as observed for saprotrophic fungi (Tsai and Phillips 1991), nitrifiers (Baldwin et al. 1983), and symbiotic N-fixing bacteria *Frankia* and *Rhizobium* (Hättenschwiler and Vitousek 2000). In addition, flavonoids can act as chemo-attractants (Hartwig et al. 1991), *nod* gene inducers for rhizobia (Phillips and Tsai 1992), inhibitors of nitrification (Erickson et al. 2000), and also be involved in pathogen and allelopathic interactions (Rao 1990). All these effects exherted by flavonoids can indirectly affect N immobilization or mineralization rates in soil.

As already mentioned, when released into the rhizosphere, phenols, like flavonoids, may form stable complexes with proteins from litter and/or with extracellular enzymes from microorganisms, producing the so-called polyphenol–protein complexes (PP-complexes) (Northup et al. 1995; Oades 1988). These complexes can also be formed during senescence of plant tissues directly within the plant cells when polyphenols, stored in the vacuole, come into contact with cytoplasmatic proteins (Northup et al. 1995). The formation of PP-complexes might be important in N-poor soils, where their formation enhance N immobilization, limits N mineralization and thus the possibility to produce nitrate which can be easily leached and thus lost from soil; in these soils, mineralization usually produces organic N-compounds of low molecular weight (for example, aminoacids), which can be taken up by plants (Hättenschwiler and Vitousek 2000; Northup et al. 1998). In N-rich soils, high N concentrations might inhibit the production and release of isoflavonoids as signals for rhizobia (Cho and Harper 1991; Dakora and Phillips 2002). However, NH_4^+ application might enhance flavonoid exudation by roots (Wojtaszek et al. 1993) as a consequence of either an increased electrochemical trans-membrane gradient or an acid-induced impairment of membrane integrity (Römheld and Marschner 1983).

The influence on P cycle

The biological P cycle in soil is mainly controlled by bacterial and fungal decomposition, immobilization, mineralization, and plant uptake (Cross and Schlesinger 1995). As previously described for the C and N cycles, flavonoids, through their effect on the biotic activities of soil, can indirectly affect biological P cycle in soil. Phosphorus (P) can be taken up by plants as HPO_4^{2-} or $H_2PO_4^-$ depending on soil pH, besides having a very low mobility. Organic P is mainly of microbial origin, including phytates, nucleic acids, phospholipids, and inositol phosphates, and has to be prior mineralized to be taken up by plants. As for N in soil, mineralization is carried out by microbes, and the released P, besides being absorbed by roots, can be adsorbed by soil minerals or taken up by microbes, which can transform inorganic P into stable organic forms. Concentration of the inorganic P available to plants in the soil solution is often below 1 μM (Nye 1979).

Flavonoids as polyphenols can indirectly contribute to P availability via competition with phosphate ions for sorption sites (Nannipieri et al. 2008; Northup et al. 1998). They can also desorb phosphates from soil–mineral surfaces, and, once released by roots into the rhizosphere, flavonoids can form stable complexes with Fe and Al of the insoluble Fe- and Al-phosphates thereby increasing the P solubility for plant uptake (Cesco et al. 2010; Dakora and Phillips 2002; Tomasi et al. 2008). Dissolution of barely available ferric-phosphate due to flavonoids released by roots of alfalfa plants has been shown by Masaoka et al. (1993). For this reason, high polyphenol concentrations might contribute to the maintenance of P availability in highly weathered acidic soils with high levels of Fe and Al minerals (Northup et al. 1998). In addition, the release of catechin and/or quercitin increased the P availability in calcareous rhizosphere soil under *C. maculosa* Lam. characterized by the presence of Ca-phosphate (Bais et al. 2002; 2003; Thorpe et al. 2006; Watt and Evans 1999). These flavonoid-type compounds also exhibited affinity for Fe and Al (Kidd et al. 2001) suggesting the relevance of root exudates not exclusively for calcareous soils.

The influence on S cycle

Sulfur (S) can occur in soil as organic (about 90–95% of the total) and inorganic forms, which can be chemically transformed by both biological and inorganic processes (Stevenson 1994). The main S processes include: mineralization of organic to inorganic S pools, immobilization, and various oxidation and reduction reactions. Sulfur in soil is mainly present as sulfurated aminoacids, proteins and peptides, sulfonates, aril-sulfates, alkil-sulfates, and glucosinolates. Although, to date, clear evidences of the flavonoid influence on the S-organic cycle in the soil are still lacking, it could be reasonable to assume, as already observed for the N and P, that flavonoids could affect the mineralization of S-containing organic molecules in soil, thus influencing thus S availability to plants. For example, sulfate, the most abundant soil inorganic S, may compete with phosphate for the same sorption sites in soil (Barnhisel and Bertsch 1989; Hsu 1989; Sparks 1995; Sposito 1996), and it may be reasonable to hypothesize that the same effects of flavonoids observed for phosphate might occur also for sulfate. However, contradictory evidences are reported concerning the mechanism of sulfate adsorption on soil surfaces because both inner-sphere (Elzinga et al. 2001; Liu et al. 1999; Peak et al. 1999; Violante et al. 2002) and outer sphere (Curtin and Syers 1990; Zhang and Sparks 1990) complexes have been suggested to occur. In addition to the adsorption, a precipitation of Al-hydroxy-sulfate minerals can also occur, particularly in acid sulfate soils and in temperate acid forest soils subjected to high atmospheric sulfate deposition (Prietzel

and Hirch 1998). Similar to what was observed by Tomasi et al. (2008) for P mobilization from a sparingly soluble P source (vivianite), it is reasonable to assume that flavonoids released by roots into the rhizosphere might favor sulfate availability via the complexation of the cation bound to the sulfate. The high Al affinity for phenolics has been already demonstrated by Tolrà et al. (2005); in this regard, it is interesting to note that flavonoids, for their high capability in mobilizing Fe and Al in organic soils, could promote the so-called podzolization process (Kennedy and Powell 1985).

Under reducing conditions, e.g., in waterlogged soils, organic S, or sulfate can be reduced to sulfide by sulfate-reducing bacteria (e.g., *Desulfotomaculum* (Stubner 2002), *Desulfosporosinus* (Stackebrandt et al. 1997), *Thermodesulfobacterium* (Liu et al. 2009)). In turn, depending on the redox conditions, sulfide can be oxidized to elemental S or sulfate by sulfur-oxidizing bacteria (e.g., *Thiothrix*, *Thiocystis* (Caldwell et al. 1975), *Thiovulum* (Jorgensen and Revsbech 1983)). The flavonoid impact on soil microorganisms could play an important role on oxidation and reduction of S in soil.

The influence on micronutrient cycles

Cationic micronutrients such as copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), etc., are essential micronutrients for plants which can occur in soil solution both in the free ionic and complexed forms. Their adsorption on soil–solid phases depends on cation exchange capacity, clay and organic-matter contents, and pH values of soil. Copper is also present in occluded oxides and in some minerals (Hartley et al. 2007). Iron in its oxidized form (Fe^{III}) can be precipitated as hydroxides, oxyhydroxides, and oxides, while the reduced form (Fe^{II}) is predominantly included in the crystal lattice of a range of primary and secondary ferromagnesian silicates (Cornell and Schwertmann 2003). For the low solubility of Fe oxide/hydroxide pools, the concentration of free Fe in the soil solution is extremely low (Lindsay 1979; Marschner 1995).

Soil organic matter can form soluble or insoluble complexes with micronutrients, depending on the molecular size of the organic ligands (Stevenson 1994); the concentration of these organic complexes depends on the contents of organic matter in soil and on the mineralization/immobilization processes. In this context, flavonoids, for their effects on soil bioactivities, can play an important role. Copper and Fe can be also complexed directly by flavonoids (El Hajji et al. 2006; Tomasi et al. 2008); however, the contribution of this phenomenon to Cu and Fe availability in the rhizosphere and to plant acquisition has not been comprehensively studied.

Manganese is taken up by plants in its reduced form (Mn^{II}), and the release of Mn-reducing compounds into the rhizosphere (Rengel et al. 1996; Timonin 1946) can increase Mn availability and Mn plant uptake through a chemical-reduction-based mechanism, as proposed by Marschner (1988). However, evidences of the involvement of flavonoids in these reductive reactions are still lacking.

Impact on soil enzymes

Enzyme activities in soil are used as indicators of soil health and are involved in important functions such as organic matter decomposition, release of inorganic nutrients for plant growth, N_2 fixation, detoxification of xenobiotics, nitrification, and denitrification (Dick 1997; Dick et al. 2000; Nannipieri 1994). Plants can positively affect enzymatic activity in soil directly and indirectly. Roots can release extracellular enzymes into soil, or stimulate microbial growth and thus the synthesis of microbial enzymes through the release of root exudates, mucilages, and root remains (Dick 1994; Ladd 1985; Nannipieri 1994; Pinton et al. 2001). Renella et al. (2006a) reported that different root exudates were mineralized to different extents and had different stimulatory effects on microbial growth and on hydrolase activities, mostly localized in the rhizosphere soil. As a consequence of the plant effect, enzymatic activities of the rhizosphere are often higher than those of the bulk soil, but it is difficult to discriminate between plant and microbial sources of enzymes in soil (Nannipieri et al. 2008; Renella et al. 2006a, 2007a).

Flavonoids exhibit a wide range of biological activities mainly their antioxidant properties and ability to modulate several enzymes or cell receptors (Hodek et al. 2002; Pietta 2000). Flavonoids can inhibit tyrosine kinase, topoisomerase, and α-glucosidase activities, and affect the cellular turnover of phosphorylated compounds of vertebrates (Wang et al. 2004; Weber et al. 1997). However, little is known about their effects on the enzyme activities when they enter the rhizosphere soil as a result of root exudation and senescence; this knowledge is essential to better understand the flavonoids role in the rhizosphere soil. Recently, Shawa and Hooker (2008) examined the adsorption, biodegradation, and toxic impact of the flavonoids naringenin and formononetin (Catford et al. 2006; Tsao et al. 2006), on soil dehydrogenase activity. Naringenin and formononetin were characterized by different lag phases (4 and 24 h, respectively) prior to the beginning of their rapid biodegradation, suggesting the requirement of different catabolic enzymes. Despite both flavonoids have antimicrobial properties, they did not inhibit soil dehydrogenase activities, probably due to the relatively low concentrations in the soil solution ranging from 0.005 to 50 μg ml^{-1} (Shaw and Hooker 2008). Naringenin at concentrations of 0.1 mM had no effect on *Bacillus subtilis* (Ulanowska et al. 2006). However, deydrogenases activity that quantifies the total oxidative activities

of the soil microbial communities should respond to the impact of toxicants on membrane-bound electron transport systems. Recourt et al. (1989) suggested that the protonated form of naringenin can accumulate in bacterial cytoplasmic membranes, with the possible direct inhibition of electron transfer activity, as it has been recorded for soybean mitochondrial membranes (Takahashi et al. 1998). Tomasi et al. (2008) reported that purified flavonoids isolated from white lupin cluster roots, with the exception of those extracted from senescent cluster roots, stimulated the soil urease activity, decreased soil microbial respiration, citrate mineralization capacity, and soil phosphatase activities but had no effect on soil protease and β-glucosidase activities. Thus, flavonoids released from the roots of P-deficient white lupins are involved in P acquisition both directly by mobilizing insoluble Fe-bound P and indirectly by reducing the microbial citrate mineralization and the activity of enzymes involved in organic P mineralization. Such selective inhibition of microbial phosphatase activities may help the plant to compete for P with rhizosphere microorganisms. Phenolic compounds can also prevent microbial degradation of extracellular phosphatases and organic acids released by roots as the response to the nutritional deficiencies (Aoki et al. 2000; Neumann and Römheld 2001). Among phenolic compounds, tannins can form stable cross-links with proteins and other compounds, and thus tannins can inactivate extracellular enzymes (Benoit and Scalbert 1968b). However, enzymes can retain their activity even when they are precipitated (Juntheikki and Julkunnen-Titto 2000; Scalbert 1991). Indeed, Fierer et al. (2001) observed very limited or no inhibition of activities of enzymes after their interaction with tannins. Further experiments are needed to examine the fate and impacts of flavonoids on soil enzyme activities. Because of the high complexity of the rhizosphere soil, the mineralization of different flavonoid exudates and their effects on enzyme activities may be studied in simple systems simulating the flavonoid gradient from rhizoplane to bulk soil (Badalucco and Kuikman 2001; Baudoin et al. 2003). Different soil types and different flavonoids should be tested by monitoring different enzyme activities.

Impact on soil bacteria

As already mentioned, flavonoids play a multifunctional role in plant–microbe interactions with their best-known function as signals in the N-fixing legume–rhizobia symbiosis. Effects of flavonoids on bacteria include induction of nodulation with gene transcription in rhizobial bacteria, promotion of chemotaxis in rhizobia, antimicrobial plant defense, and increase in growth rate of several bacterial species (Aoki et al. 2000; Blum and Shafer 1988; Dakora and Phillips 1996). Flavonoids such as flavanones, isoflavones, flavonols, and chalcones show *nod*-gene-inducing activity in different legume–rhizobia interactions (Aoki et al. 2000), and flavonoids are also involved in regulation of nodulation in actinorrhizal (*Frankia*) associations (Benoit and Berry 1997; Hocher et al. 2006; Hughes et al. 1999). Flavonoids function as specific chemoattractants for rhizobial bacteria (Caetano-Anolles et al. 1988). Once in the rhizosphere, many bacteria may multiply rapidly in response to growth stimulation by flavonoids, such as quercetin or other flavonoid molecules released by plants (Hartwig and Phillips 1991) and in turn promote further flavonoid exudation into the rhizosphere (Dakora et al. 1993a and b; Recourt et al. 1991). In addition, flavonoids can also attract pathogenic microbes (Morris and Ward 1992) and promote the growth of plants and of rhizobacteria antagonistic to pathogens (Cook et al. 1995; Siqueira et al. 1991). However, flavonoids can also present microbial toxicity (Veluri et al. 2004).

Nitrifying bacteria can be inhibited either in culture and soil by plant secondary metabolites including tannins (Baldwin et al. 1983; Thibault et al. 1982), low-molecular-weight phenolics (Lodhi and Killingbeck 1980), and terpenes (White 1986). Negative effects of polyphenols on net nitrification in soils (Erickson et al. 2000; Paavolainen et al. 1998) were partly explained by a direct inhibiting effect of the chemical compounds on mineralization and nitrification activity, but also by increased N immobilization (Northup et al. 1995; Schimel et al. 1996). However, other studies found no specific effects on activity of nitrifiers (Bradley et al. 2000; Fierer et al. 2001; Schimel et al. 1996). Bradley et al. (2000) suggested that tannins may be used as growth substrate by microbes and that their apparent inhibitory action on nitrification may be due to the increased NO_3^-–N consumption. The above observations dictate the unavoidability of using ^{15}N tracer techniques when correctly studying N processes in soil.

Although the effect of root exudated flavonoids on bacterial communities have been poorly studied, it is clear that these effects are reciprocal and dynamic, and depend on plant age and the target microbial species. The flux of organic compounds, such as flavonoids, from roots to the rhizosphere increases the concentration of available organic C, and this stimulates the activity of soil heterotrophic bacteria, which are largely prevailing over soil autotrophic microorganisms (Toal et al. 2000).

As far as we know, there are no studies on the effects of type and concentration of flavonoids on composition and activities of microbial communities of soil. Future studies should simulate the rhizosphere effect by adding specific flavonoids occurring in root exudates, for example, by using the approach by Landi et al. (2006), who showed that both oxalic and glucose changed the DGGE profiles of soil bacterial communities in the 0–2-mm soil layer of the model root system. However, extrapolation of these results to in

situ conditions is not straightforward, as these laboratory studies represent model systems under optimal conditions that rarely occur in real soils. Data on the amount and identity of flavonoids released from several crop plant species could form a new basis for molecular genetic and ecological studies of the rhizosphere; furthermore, the use of bacterial reporter gene-fusions as molecular sensors to track the release of nutrients and signal molecules in the rhizosphere could be an important tool for future work in soil microbial ecology (Farrar et al. 2003).

Impact on soil fungi

Fungi are important for soil functioning, since they carry out several functions such as helping plants to acquire mineral nutrients (mycorrhizae), inhibiting plant growth (phytopathogenic fungi), participating to nutrient cycling, and degrading organic matter. Inoculation of a plant with either a phytopathogenic fungus or a putative mycorrhizal partner induces changes in the pattern of secreted flavonoids (Carlsen et al. 2008), suggesting that flavonoids are also involved as signal molecules for the plant–fungal interactions. As an example of these interactions, we shall discuss the effects of plant-secreted flavonoids on mycorrhizal, phytopathogenic, and saprophytic fungal partners.

Effect of flavonoids on mycorrhizal fungi

Clarifying the chemical signals which are exchanged between plants and their fungal partners for successful recognition and establishment of symbiosis has been a long-standing aim in mycorrhizal research. Flavonoids were putative candidates for such plant–microbe dialogue, in view of the role of these compounds in the initiation of N-fixing symbiosis. Indeed, since the early 1990s, many studies have addressed this issue (see Table 1 for an overview of the obtained findings). Contrasting effects depending on the chemical structure of the flavonoids and on the target organism were reported. The major flavone exuded by *M. sativa* L. seeds, hyperoside, stimulated spore germination in *Glomus etunicatum* and *Glomus macrocarpum*, while other flavones, such as 4,7-dihydroxyflavone and 4,7-dihydroxyflavanone were only active in *G. etunicatum*, whereas the isoflavonoid formonetin inhibited spore germination in both species (Tsai and Phillips 1991). Formonetin and the other isoflavonoids biochanin A stimulated hyphal growth and mycorrhization of *Trifolium repens* L. by *Glomus* sp (Nair et al. 1991; Siqueira et al. 1991). Xie et al. (1995) tested a range of flavonoids produced by *Glycine max* L. Merr. on *Glomus mossae* and observed significant promotion of mycorrhizal colonization by daidzein, apigenin, and coumestrol. Interestingly, growth of mycorrhizal fungi was stimulated by higher CO_2 concentrations, and there was a synergistic effect by adding quercetin (10 μM) and increasing pCO_2 from 0.6% to 2% with higher growth of *Gigaspora margarita* (sevenfold promotion) than either the single treatment (Becard et al. 1992). Myricetin acted in a similar way (Becard et al. 1992), as well as kampferol (Chabot et al. 1992), but another flavonol, galangin, inhibited hyphal growth (Chabot et al. 1992). The isoflavones genistein and biochanin A, and the flavanone herperetin inhibited the growth of *G. margarita* at high pCO_2 levels (Chabot et al. 1992). The response of two *Glomus* (*G. mosseae* and *G. intraradices*) and *Gigaspora* (*G. margarita* and *G. rosea*) species to flavonoids exuded by tomato plants (*Lycopersicum esculentum* L.) was the same whether these flavonoids came from mycorrhized or non-mycorrhized roots (Scervino et al. 2006). While inhibitory effects of acacetin, rahmnetin, and 5,6,7,8,9-hydroxychalcone on fungal penetration seemed a general phenomenon affecting both *Glomus* and *Gigaspora* species, stimulation of host penetration caused by exposure to quercetin, 5,6,7,8-hydroxy-4-methoxyflavone, and 3,5,6,7,4-hydroxyflavone was more specific because only effective for two *Gigaspora* species (Scervino et al. 2005). Apigenin but not its glycosylated conjugate, 5,7,4′-hydroxy flavone glycoside, stimulated hyphal length, hyphal branching, and root colonization by *G. mosseae* and *G. intraradices,* and *G. margarita* and *G. rosea* (Scervino et al. 2006). Interestingly, Catford et al. (2006) used a split-root system to study the effect of external addition of flavonoids to already colonized (so-called "auto-regulated") roots of *M. sativa* L. They showed that ononin (formonetin 7′-*O*-glucoside), but not the aglycone formonetin, stimulated root colonization in auto-regulated roots (Catford et al. 2006).

While the bibliography of the effects of flavonoids on arbuscular mycorrhizae is extensive, few studies have investigated the response of ectomycorrhizal fungi to root-secreted flavonoids. Rutin, the major glycosylated flavonol exuded by the roots of *Eucalyptus globulus* spp. *Bicostata*, stimulated the growth of two *Pisolithus* species collected from *Eucalyptus* trees, while other *Pisolithus* species, collected under different tree species, did not respond to rutin, which also promoted hyphal growth of the pine symbiont *Suillus bovinus* (Lagrange et al. 2001). Remarkably, picomolar concentrations of rutin were sufficient to trigger the effects. Interestingly, the authors also tested a range of saprophytic fungi and observed no effect of rutin, indicating that the growth stimulation was only effective for putative symbionts. Among various flavonoids, hesperidin, rutin, quercetin, naringenin, and genistein stimulated germination of *S. bovinus* whereas biochanin A, luteolin, and quercetin had no effect (Kikuchi et al. 2007).

Provided that flavonoids should act as signals in the establishment of mycorrhizal association, one would expect

that the respective molecules would be exuded specifically when such association is required, e.g., under P-deficient conditions. This is what Akiyama et al. (2002) observed while studying the root exudates of P-starved melon plants (*Cucumis melo* L.). They identified isovitexin 2″-*O*-glucoside as the major compound only exuded under P-deficient conditions. They assessed the effect of the purified compound on mycorrhization of melon roots grown either at low or high P conditions. No effect was observed at low P conditions, where control roots (without flavonoids addition) were highly colonized by *Glomus caledonium*, but a slight stimulation of mycorrhization was obtained for high P grown plants upon addition of isovitexin 2″-*O*-glucoside, suggesting a possible involvement of this compound in recruiting the fungal partner. Unlike their mycorrhized homologues, non-mycorrhized plants most likely use chemical signals to repel potential mycorrhizal fungi and to avoid invasion. This question has been addressed recently by studying the effect of flavonoids exuded by a non-host plant (*Lupinus albus* L.) on the mycorrhizal fungus *G. margarita*. Akiyama et al. (2010) identified three pyranoisoflavones (see Table 1) which inhibited the germ tube growth of *G. margarita*. Two of them also reduced hyphal branching, indicating that these isoflavonoids might be involved in the repression of mycorrhization in white lupin roots (Akiyama et al. 2010). This study, as well as earlier work showing negative effects of flavonoids on mycorrhizal fungi (see Table 1), raise the possibility that flavonoids might have contrasting functions (stimulating or inhibiting) depending on the flavonoid molecule, the developmental stage, the nutrient status, the fungal colonization of the producing, and the species and developmental stage of the putative fungal partner. Flavonoids might also interact with other signals, e.g., strigolactones, which have been shown to be key regulators of mycorrhizal symbiosis (Akiyama et al. 2005; Steinkellner et al. 2007). The flavonoid-mediated regulation of mycorrhizal association thus appears to be highly complex and will require more detailed investigations in the future.

Effect of flavonoids on phytopathogenic fungi

The effect of flavonoids on putative plant enemies are less well documented than is the effect on mycorrhizal fungi. However, a few studies have shown stimulating or inhibiting effects on phytopathogenic fungi (see Table 2). Pisatin is, to our knowledge, the first flavonoid for which antifungal activity was demonstrated (Perrin and Bottomley 1961). Later, other pterocarpans (e.g., trifolirhizin, maackiain, and medicarpin) were also reported to inhibit growth of a wide array of phytopathogenic fungi (for details, please refer to Table 2) (Rao 1990 and references therein). In addition to pterocarpans, the isoflavone betavulgarin was shown to inhibit growth of two sugar beet pathogens (Rao 1990 and references therein). Likewise, the flavones hyperoside and galangin inhibited hyphal growth of various phytopathogenic fungi (Afolayan and Meyer 1997; Li et al. 2005). A reduction in abundance in cultivable fungi in both rhizosphere and non-rhizosphere soils was observed after tricin exudation from roots of allelopathic rice seedlings (Kong et al. 2008). Apart from growth inhibition, spore germination appears to be a developmental process which is readily stimulated or inhibited by a wide range of different flavonoids (see below), although most of evidence for this particular process might originate from its easy determination rather than from a truly preferential target for root-borne flavonoids. Flavonoids acting as inhibitors of spore germination include naringenin and kaempferol on the rice pathogen *Pyricularia oryzae* (Padmavati et al. 1997) and, more recently, rutin on *Verticillium dahliae* (El Hadrami et al. 2011). In contrast, pterocarpans, with the exception of trifolirhizin, stimulated germination of *Fusarium solani* (Ruan et al. 1995). *F. solani* also germinated better upon exposure to the flavones 7-hydroxyflavone and 4,7dihydroxyflavone. The flavanones hesperetin, eriodictyol, and naringenin, as well as the isoflavonoids biochanin A and genistein, displayed similar stimulating effects (Ruan et al. 1995). Interestingly, besides stimulation of germination, genistein was also reported to induce sporulation in *F. solani* (Weisskopf et al. 2006b), while it caused, similarly to daidzein, chemotropism in zoospores of *Phytophthora sojae* (Morris et al. 1998). As these two isoflavonoids did not cause any inhibitory effect on *P. sojae* (e.g., inhibition of germination or hyphal growth), it seems that this attraction of *P. sojae* is a deleterious side-effect of flavonoids secreted by soybean roots having the primary goal of recruiting beneficial symbionts like N-fixing bacteria or mycorrhizal fungi. They might serve as chemical clues for less beneficial or even pathogenic organisms to locate their host, as was reported for parasitic plants attracted by strigolactones (Bouwmeester et al. 2007).

Effect of flavonoids on saprophytic fungi

Very little attention has been paid to the effect of flavonoids on saprophytic fungi. Yet, some of the fungi tested as "phytopathogens" could also be considered saprophytes, e.g. *Aspergillus* spp., *Penicillium* spp., *Fusarium* spp., *Trichoderma* spp., and *Cladosporium* spp., which all can live on wood or decaying plant material. For example, 4′,6,7-trihydroxy-3′,5′-dimethoxyflavone inhibited the growth of *Trichoderma viride* (Zheng et al. 1996). This compound was purified from shoots of *Artemisia giraldii* (Zheng et al. 1996), but it is chemically similar to the root-exuded compound tricin (Kong et al. 2008). *Aspergillus flavus* was inhibited by 3,5,7-trihydroxyflavone, as was *Cladosporium herbarum*, albeit at higher concentrations (0.05 mg ml^{-1} instead of 0.01 mg ml^{-1}) (Afolayan and Meyer 1997). White rot fungi, which are responsible for lignin degradation, have

Table 1 Effect of root-borne flavonoids on mycorrhizal fungi

Trivial name	Chemical name	Target organism(s)	Effect	Reference
Flavones				
Acacetin	5,7-Dihydroxy-4′-methoxyflavone	*Gigaspora* sp., *Glomus* sp.	Inhibition of host penetration	(Scervino et al. 2005)
Rahmnetin	3,5,3′,4′-Tetrahydroxy-7-methoxyflavone	*Gigaspora* sp., *Glomus* sp.	Inhibition of host penetration	(Scervino et al. 2005)
	5,6,7,8-Tetrahydroxy- 4-methoxyflavone	*Gigaspora* sp.	Stimulation of host penetration	(Scervino et al. 2005)
	3,5,6,7,- Tetrahydroxyflavone	*Gigaspora* sp.	Stimulation of host penetration	(Scervino et al. 2005)
Apigenin	5,7,4′-Trihydroxyflavone	*Gigaspora* sp., *Glomus* sp.	General stimulation (hyphal length, branching, entry points and mycorrhization)	(Scervino et al. 2006)
Apigenin	5,7,4′-Trihydroxyflavone	*G. mossae*	Stimulation of mycorrhizal colonization	(Xie et al. 1995)
Luteolin	5,7,3′,4′-Tetrahydroxyflavone	*Gigaspora* sp., *Glomus* sp.	Stimulation of mycorrhizal colonization (of *L. esculentum*)	(Scervino et al. 2007)
	4′,7, Dihydroxyflavone	*G. etunicatum*	Stimulation of spore germination	(Tsai and Phillips 1991)
Quercetin	3,5,7,3′,4′-Pentahydroxyflavonol	*Gigaspora* sp.	Stimulation of host penetration	(Scervino et al. 2005)
Quercetin	3,5,7,3′,4′-Pentahydroxyflavonol	*G. margarita*	Stimulation of hyphal growth (under elevated CO_2)	(Chabot et al. 1992)
Quercetin	3,5,7,3′,4′-Pentahydroxyflavonol	*G. margarita*	Stimulation of hyphal growth (under elevated CO_2)	(Becard et al. 1992)
Hyperoside	Quercetin-3-*O*-galactoside	*G. etunicatum G. macrocarpum*	Simulation of spore germination	(Tsai and Phillips 1991)
Rutin	Quercetin-3-rutinoside	*Pisolithus* sp.	Stimulation of hyphal growth	(Lagrange et al. 2001)
		G. margarita	Stimulation of mycorrhizal colonization (of *L. esculentum*)	(Scervino et al. 2007)
		S. bovinus	Stimulation of spore germination	(Kikuchi et al. 2007)
Myricetin	3,5,7-Trihydroxyflavonol	*G. margarita*	Stimulation of hyphal growth (under elevated CO_2)	(Becard et al. 1992)
Kaempferol	3,5,7,4′-Tetrahydroxyflavonol	*G. margarita*	Stimulation of hyphal growth (under elevated CO_2)	(Chabot et al. 1992)
Galangin	3,5,7-Trihydroxyflavone	*G. margarita*	Inhibition of hyphal growth (under elevated CO_2)	(Chabot et al. 1992)
Flavanones				
Naringenin	5,7,4′-Trihydroxyflavanone	*S. bovinus*	Stimulation of spore germination	(Kikuchi et al. 2007)
	4′,7 Dihydroxyflavanone	*G. etunicatum*	Stimulation of spore germination	(Tsai and Phillips 1991)
Hesperetin	3′,5,7-Trihydroxy-4′-methoxyflavanone	*G. margarita*	Inhibition of hyphal growth (under elevated CO_2)	(Chabot et al. 1992)
Hesperidin	Glucoside of 3′,5,7-trihydroxy-4′-methoxyflavanone	*S. bovinus*	Stimulation of spore germination	(Kikuchi et al. 2007)
Isoflavones				
Daidzein	4′,7-Dihydroxy isoflavone	*G. mossae*	Stimulation of mycorrhizal colonization	(Xie et al. 1995)
Genistein		*S. bovinus*	Stimulation of spore germination	(Kikuchi et al. 2007)
		G. margarita	Inhibition of hyphal growth (under elevated CO_2)	(Chabot et al. 1992)
Licoisolfavone B		*G. margarita*	Inhibition of germ tube growth and of hyphal branching	(Akiyama et al. 2010)
		G. margarita		(Akiyama et al. 2010)

Table 1 (continued)

Trivial name	Chemical name	Target organism(s)	Effect	Reference
Sophoraisoflavone A			Inhibition of germ tube growth and of hyphal branching	
Alpinumisoflavone		*G. margarita*	Inhibition of germ tube growth	(Akiyama et al. 2010)
Ononin	Formonetin 7′-*O*-glucoside	*G. mossae*	Stimulation of mycorrhizal colonization	(Catford et al. 2006)
	Isovitexin 2″-*O*-β-glucoside	*G. caledonium*	Stimulation of mycorrhizal colonization	(Akiyama et al. 2002)
Formonetin	7-Hydroxy-4′-methoxyisoflavone	*G. etunicatum G. macrocarpum*	Inhibition of spore germination	(Tsai and Phillips 1991)
		Glomus sp.	Stimulation of hyphal growth and of mycorrhizal colonization	(Nair et al. 1991) (Siqueira et al. 1991)
Biochanin A	5,7-Dihydroxy-4-metoxyisoflavone	*G. margarita*	Inhibition of hyphal growth (under elevated CO_2)	(Chabot et al. 1992)
		Glomus sp.	Stimulation of hyphal growth and of mycorrhizal colonization	(Nair et al. 1991) (Siqueira et al. 1991)
Chalcones				
	5,6,7,8,9-Pentahydroxychalcone	*Gigaspora* sp., *Glomus* sp.	Inhibition of host penetration	(Scervino et al. 2005)
Coumestrans				
Coumestrol	3,9-Dihydroxy coumestan	*G. mossae*	Stimulation of mycorrhizal colonization	(Xie et al. 1995)

not yet been investigated for their response to root-borne flavonoids, despite their major role in organic-matter cycling. It thus appears necessary in the future to broaden our view on the putative target organisms for root-exuded flavonoids and to investigate how they might affect the abundance, diversity, and activity of saprophytic fungi fulfilling highly important functions such as cellulose and lignin degradation. In addition, the impact of these exudates on the soil organic matter dynamics may in turn affect the nutrient cycling and availability for plants.

Impact on soil macrofauna

Root–insect interactions might be classified as positive or negative associations, therefore, secondary metabolites as flavonoids released by plants can either attract or repel soil insects. However, most of the studies carried out so far focused on plant–insect interactions within stems and leaves (Simmonds 2003). Rhizosphere interactions are less explored both due to the complexity of the system and the lack of suitable experimental systems.

Among root exudates, flavonoids are known to be highly effective against nematodes in several plant species as potato, soybean, and lima bean (Rao 1990). For instance, the phytoalexin medicarpin inhibited the motility of *Pratylenchus penetrans* in alfalfa (*M. sativa* L.) plants (Balbridge et al. 1998) whereas the accumulation of isoflavonoids in roots of alfalfa has been considered as a response strategy to the infection at the shoot level, and its extent was correlated with resistance (Edwards et al. 1995). Flavonoids might also increase as a result of nematode infection as shown by Cook et al. (1995). These authors demonstrated that the infection of white clover roots with *Ditylenchus dipsaci* elicits the localized accumulation of antibiotic isoflavonoids and their conjugates.

Flavonoids are also candidate modulators of local auxin manipulation in nematode infection mechanisms as they are produced in feeding sites of root-knot nematodes induced in a leguminous plant. Flavonoids are also produced in developing syncytia induced by *Heterodera schachtii* and in galls induced by *Xiphinema diversicaudatum* in a non-leguminous plant, *Arabidopsis thaliana* (Jones et al. 2007). Studies of mutant lines (Jones et al. 2007) showed that flavonoids are definitely produced as part of the defense response to nematode infection but are unlikely to be an integral component of the mechanisms used by nematodes to induce feeding sites. Recently, Du et al. (2011) isolated and identified two flavonones-*C*-glycosides, schaftoside and isoschaftoside, from the extract of *Arisaema erubescens* (Wall.) with strong nematicidal activity against the root-knot nematode *Meloidogyne incognita*.

In addition to nematodes, Russel et al. (1978) demonstrated that roots of *Lotus pedunculatus* where resistant to larvae of

Table 2 Effect of root-borne flavonoids on phytopathogenic fungi

Trivial name	Chemical name	Target organism(s)	Effect	Reference
Flavones				
Apigenin	5,7,4′-Trihydroxy flavones	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
Apigetrin	Apigenin-7-glucoside	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
Luteolin	5,7,3′,4′-Tetrahydroxy flavone	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
	4′,7, Dihydroxyflavone	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
	7-Hydrox flavone	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
Hyperoside	Quercetin-3-*O*-galactoside	*P. guepinii Drechslera* sp. *F. avenaceum*	Inhibition of growth	(Li et al. 2005)
Rutin	Quercetin-3-rutinoside	*V. dahliae*	Inhibition of sporulation	(El Hadrami et al. 2011)
Kaempferol	3,5,7,4′-Tetrahydroxyflavonol	*P. oryzae*	Inhibition of spore germination	(Padmavati et al. 1997)
Galangin	3,5,7-Trihydroxyflavo ne	*A. tamari P. digitatum P. italicum*	Inhibition of growth	(Afolayan and Meyer 1997)
Tricin	5,7,4′-Trihydroxy-3′,5′-dimethoxyflavone	Fungi general (abundance of cultivable fungi)	Reduction in abundance	(Kong et al. 2008)
Flavanones				
Naringenin	5,7,4′-Trihydroxy flavanone	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
		P. oryzae	Inhibition of spore germination	(Padmavati et al. 1997)
Eriodictyol	5,7,3,4-Tetrahydroxy flavanone	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
hesperetin	3′,5,7-Trihydroxy-4′-methoxy flavanone	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
Isoflavones				
Daidzein	4′,7-Dihydroxy isoflavone	*P. sojae*	Chemotropism	(Morris et al. 1998)
Betavulgarin	7-(2-Hydroxyphenyl)-9-methoxy-[1,3]dioxolo[4,5-g]chromen-8-one	*C. beticola M. fructicola*	Inhibition of growth	(Rao 1990 and references therein)
Genistein	5,7,4′-Trihydroxy isoflavone	*P. sojae*	Chemotropism	(Morris et al. 1998)
		F. solani	Stimulation of sporulation	(Weisskopf et al. 2006b)
		F. solani	Stimulation of spore germination	(Ruan et al. 1995)
Biochanin A	5,7-Dihydroxy-4-metoxyisoflavone	*F. solani*	Stimulation of spore germination	(Ruan et al. 1995)
Pterocarpans				
Pisatin	6a-Hydrox-3-methoxy-8,8-methylenedioxypterocarpan	*A. euteiches A. pinodella F. solani M. pinodes R. solani A. niger H. carbonum R. stolonifer F. oxysporum f. sp. Lycopersici*	Inhibition of growth	(Rao 1990 and references therein)
		F. solani	Stimulation of spore germination	(Ruan et al. 1995)
Medicarpin	3-Hydroxy-9-methoxypterocarpan	*A. euteiches A. pinodella F. solani M. pinodes R. solani A. niger H. carbonum R. stolonifer F. oxysporum f. sp. Lycopersici*	Inhibition of growth	(Rao 1990 and references therein)
		Fusarium solani	Stimulation of spore germination	(Ruan et al. 1995)
Maackiain		*F. solani H. carbonum*	Inhibition of growth	

Table 2 (continued)

Trivial name	Chemical name	Target organism(s)	Effect	Reference
	3-Hydroxy-8,9-methylenedioxy pterocarpan			(Rao 1990 and references therein)
		F. solani	Stimulation of spore germination	(Ruan et al. 1995)
Trifolirhizin	Beta-D-glucopyranoside, 6a,12a-dihydro-6H [1,3] dioxolo[5,6]benzofuro [3,2-c][1]benzopyran-3-yl	*H. carbonum*	Inhibition of growth	(Rao 1990 and references therein)

black beetle attack thanks to the presence of the isoflavonoid vesitol in their roots. On the other hand, *Lotus corniculatus,* which did not show any vesitol content in the roots, was susceptible to the insect attack. Other soil organisms such as arthropods, enchytraeids, and earthworms may also be inhibited by flavonoids and flavonoid-like substances as tannins. These organisms are particularly important during the first stages of decomposition when litter is broken down into smaller fragments with greater surface area. Condensed tannins have been shown to decrease nematode mobility and survival in soil (Mian and Rodríguez-Kábana 1982; Mohamed et al. 2000). Tannin concentrations appear to affect litter palatability, thereby decreasing consumption by insects and earthworms (Slapokas and Granhall 1991). Benoit and Starkey (1968a) reported that condensed tannins markedly reduced also hemicellulose and cellulose decomposition.

Impact on roots of other plants

Apart from other groups of secondary metabolites, such as terpenoids, phenolic acids, and alkaloids, flavonoids and related compounds have also been implicated in allelopathic interactions. The term allelopathy was coined by Molisch (1937) to describe negative or positive interactions between compounds released from plants with other organisms. Meanwhile, it is mainly used in a more narrow sense for negative biochemical interactions between plants (Rice 1974). Allelopathic chemicals may be released by living plant roots, from decaying plant residues or produced from precursor compounds by biotic and abiotic activities. For many flavonoid compounds, biological activities have been reported, comprising (1) antagonistic effects against pathogens (Rao 1990; Iwashina 2003), (2) a frequently concentration-dependent stimulation or inhibition of plant growth and nutrient uptake (Stenlid 1961, 1968), (3) signal functions in plant–microbial communication (Shaw et al. 2006) but also interactions with plant hormones (Rao 1990; Taylor and Grotewold 2005). As phytohormones and their precursors, flavonoids, also stimulate specific enzyme activities in the rhizosphere (Renella et al. 2011), they may also indirectly influence the microbial and plant nutrition and possess all prerequisites for allelopathic interactions.

Direct effects

In accordance with the wide range of biological activities, an allelopathic potential has been postulated for numerous flavonoids as summarized in Table 3. According to Markham (1982), about 2% of the C fixed by photosynthesis may be converted into flavonoids and related compounds. Particularly in leguminous plants, huge amounts of flavonoids are released from intact roots into the rhizosphere comprising up to 20% of the total root content (Barz 1969; D'Arcy-Lameta 1986). The major flavonoids in the root exudates of *Glycine max* L. and *Phaseolus vulgaris* L. are *nod*-gene inducers involved in signal exchange during the establishment of the rhizobium symbiosis (genistein, daidzein, isoliquiritigenin) and the allelopathic and antimicrobial compound coumestrol (Bolanos-Vasquez and Werner 1997; Dakora and Phillips 1996; Rao 1990). Accordingly, the *nod*-gene inducers are mainly released in the apical root zones thus labelling the infection sites for *Rhizobia*, while the protective compound coumestrol is released over the whole root system (Haase et al. 2007a; Kape et al. 1992; Neumann 2006; Fig. 4).

Indirect effects

Allelopathic interactions are not always caused by direct toxicity of allelochemicals themselves. Various examples suggest that allelopathic effects are also induced by biotic or abiotic structural modifications induced by flavonoids in the rhizosphere. The released phlorizin (Hofmann et al. 2009) may also change the rhizosphere microbial community structure with promotion of certain pathogens. Indeed, chemical or microbial modifications of allelochemicals can show allelopathic effects in soils (Ohno 2001). Replant disease, also termed as "autotoxicity" or "soil sickness" in red clover, has been related to phenolics arising from

Table 3 Root-borne flavonoids as allelochemicals (Rao 1990; Iwashina 2003)

Chemical name	Source plant	Reference
2′,6′-dihydroxy-4′-Methoxychalcone 2′,6′-Dihydroxy-4′-methoxydihydrochalcone	*Pityrogramma ssp*	Star (1980)
Izalpinin		
Heliannones A,B,C Kukulkanin B	*Helianthus annuus*	Maciás et al. (1997)
Tambulin		
Taxifolin 3-*O*-arabinoside Hesperitin 4-*O*-rutinoside	*Pluchea lanceolata*	Inderjit and Dakshini (1992a, b)
Formononetin 7-*O*-glucoside		
Kaempferol Quercetin	*Erica australis*	Carballeira (1980)
Myricetin		
Quercetin Quercetin 3-*O*-arabinofuranoside Quercetin 3-*O*-galactoside	Cactaceae *(Astrophytum Notocactus, Neochilenia, Parodia)*	Parvez et al. (1982)
Quercetin 3-*O*-glucoside		
Quercetin 3-*O*-rhmnoside		
Quercetin 3-methylether 4′-*O*-glucoside		
Quercetin 3-methylether 7-*O*-glucoside		
Biochanin A	*Trifolium pratense*	Tamura et al. (1967; 1969)
Biochanin A 7-*O*-glucoside Biochanin A 7-*O*-glucoside-5-malonate		Chang et al. (1969)
Biochanin A-5-malonate		
Daidzein		
Daidzein 7-*O*-glucoside		
Formononentin		
Genistein		
Maackiain		
2,4-Dihydroxy-6,4′-methoxychalcone Bifloridin	*Pancratium biflorum*	Ghosal et al. (1986)
7-Hydroxy 4′-methoxyflavan		
4′,7-Dihydroxy, 3′,4′,7- trihydroxyflavone 4′7-Dihydroxy-3′-methoxy-flavone	*Lens culinaris*	D'Arcy-Lameta (1986)
Coumestrol Daidzein	*Glycine max*	D'Arcy-Lameta (1986)
Phloretin Phlorizin	*Malus domestica*	Borner(1959; 1960)
Luteolin Apigenin 7-*O*-glucoside	*Polygonum orientale*	Datta and Chatterjee (1980)
5,7,4′-Trihydroxy-3′,5′-dimethoxyflavone	*Oryza sativa*	Kong et al. (2006)

microbial degradation of isoflavonoids released as root exudates and from decaying residues of the red clover plants (Chang et al. 1969; Tamura et al. 1967, 1969). Similarly, replant disease of apple trees has been attributed to the release of phlorizin, a toxic flavonoid compound, present in high concentrations in the bark of apple roots, and by products of microbial phlorizin degradation (phloretin, phloroglucinol, parahydroxy cinnammic acid, and parahydroxy benzoic acid (Borner 1959, 1960)).

As above-mentioned, flavonoids act both as positive and negative signals mediating host recognition and infection during establishment of the legume–*Rhizobium* symbiosis, being active in the rhizospohere already at very low concentrations in the sub-micomolar range (Rao 1990). Therefore, it is reasonable to assume that this process also acts as a target for allelopathic interactions. Accordingly, inhibitory effects on nodulation and symbiontic N_2 fixation have been reported for leachates and root exudates of various plants

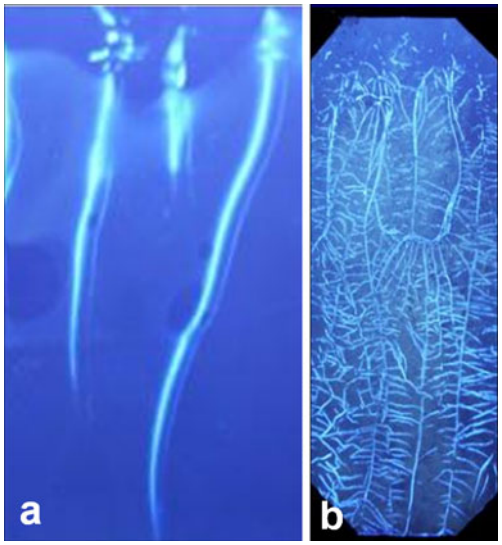

Fig. 4 Spatial distribution of coumestrol (*blue* auto-fluorescence UV 360 nm) along seedling roots of *V. unguiculata* (**a**) and along the root system of soil-gown *P. vulgaris* in rhizobox culture (**b**) (modified from Cesco et al. 2010). Exudates collected with filter paper (**a**) or nylon membranes (**b**) placed onto the root surface (modified after Neumann 2006)

including *Aristida, Ambrosia, Bromus, Digitaria,* and *Euphytica* species (Murthy and Nagodra 1977; Rice 1972). Tricin and tricetin are flavonoids potentially involved in the strong inhibition of growth of quackgrass, a serious weed in various leguminous crops (Fottrell et al. 1964). Even pterocarpan isoflavonoids acting as phytoalexins in various legumes can exert inhibitory effects on other legume species (Rao 1990), while certain *nod*-gene-inducing flavonoids are involved also in resistance induction against phytoalexins (Kape et al. 1992).

Apart from other phenolics, various root flavonoids, such as myricetin, quercetin-galactoside, and 3,4′-7-trihydroxy flavone show an inhibitory potential on nitrification, and this may provide a competitive advantage for N acquisition in various species of climax vegetation by reducing nitrate leaching (Putnam and Weston 1986; Rice and Pancholy 1974; Subbarao et al. 2006).

Positive interactions

In terms of the wider definition of allelopathy given by Molisch (1937), root flavonoids may also exert positive effects in plant–plant interactions. Pathogen suppression, inhibition of nitrification, and biological N_2 fixation involving flavonoids from plant roots may provide an advantage for the flavonoid producers themselves. The well-documented beneficial effects of rotation cropping or intercropping of leguminous and non-leguminous plants (Alvey et al. 2001; Hauggaard-Nielsen and Jensen 2005; Zhang and Li 2003) can at least partially be attributed to flavonoid compounds released from roots of leguminous crops. As already mentioned, in *L. albus* L, a cluster rooted plant leguminous crop species with an enormous capacity for chemical mobilisation of sparingly soluble phosphate (P) forms in soils, root exudation of flavonoids is not only involved in the establishment of symbiotic N_2 fixation but also in Fe and P mobilization (Tomasi et al. 2008) and the protection of P-mobilizing root exudates from microbial degradation (Weisskopf et al. 2006b). The resulting mechanism of P mobilization is sufficiently efficient to improve P acquisition also for intercropped plant species or in crop rotations (Hauggaard-Nielsen and Jensen 2005; Hens and Hocking 2004).

Due to structural similarities, the presence of flavonoids may also accelerate the biodegradation of xenobiotics in the rhizosphere through co-metabolism and stimulation of catabolic pathways in the respective microorganisms (Shaw et al. 2006).

Climate change effect on root flavonoids and its ecological implications

The increase in atmospheric CO_2 concentration and the associated global warming, as well as the increased N availability due to atmospherical deposition, are the main features of climate change. The effects of such changes on the synthesis of plant secondary metabolites, particularly flavonoids, and their release by roots into the soil may be important to better understand the changes in the soil–plant–microbe system induced by climate change. Very few scientific works have been conducted so far on this topic. Increase of photosynthesis rates has been generally observed under an elevated CO_2 concentration (Ceulemans and Mousseau 1994), but this does not always result in an increased plant growth, particularly in natural ecosystems that are frequently N-limited (Norby et al. 1986). Under higher CO_2 concentration and nutrient limitation conditions, a greater synthesis and accumulation of carbon-rich secondary metabolites in plant tissues has been observed (Bazzaz 1990; Reichardt et al. 1991). Among CBSM, polyphenols produced by the shikimic acid pathway such as soluble phenolics and flavonoids are quantitavely the most important (Boudet et al. 2003). Such evidences suggest that rising level of atmospheric CO_2 under nutrient-deficient conditions can stimulate the secondary metabolism and specifically the accumulation of flavonoids in plant organs, included the root system (Bazzaz 1990). Moreover, several studies show that the allocation of structural and non-structural carbohydrates to root system is enhanced under elevated CO_2 (Lewis et al. 1994; Norby et al. 1999). The increase in total belowground carbon allocation is often associated with an increase in root exudation, including flavonoids (Cheng and Johnson 1998; van Ginkel et al. 2000; Allard et al. 2006). For instance,

Ghasemzadeh et al. (2010) found a significant increase in phenolic compounds and flavonoids in *Zingiber officinale* Roscoe plants in response to CO_2 enrichment from 400 to 800 μmol, and these increases were greater in rhizomes compared with leaves. Specifically, kaempferol and fisetin showed the highest response to CO_2 enrichment.

Concerning the possible ecological effect of this extra C-input on soil–plant relationships, it has been suggested that the increase of flavonoid root exudation under elevated CO_2 may stimulate microbial growth and activity in the rhizosphere, which in turn could increase the competition between plant and microbes for nutrient uptake and immobilization (Haase et al. 2007a). This hypothesis fits with the reduced N-nutritional status of plants growing under elevated CO_2 concentration as found by several authors (Diaz et al. 1993; Haase et al. 2007b) due also to the usually low C/N ratio of the microbial biomass.

In this N-limited environment, N-fixing plants could play a crucial role in the future ecosystems by counterbalancing the CO_2-induced limitation of N availability in the rhizosphere. In this context, flavonoids were assumed to have a key role (Marilley et al. 1999; Cabrerizo et al. 2001). Indeed, increased root exudation of chemo-attractants, such as phenolic acids and specific flavonoids with the capacity to activate *nod* genes (*nod* gene inducing flavonoids) involved in establishing the *Rhizobium* symbiosis, have been found in plants growing under elevated CO_2 concentrations and nutritional limitations (Cabrerizo et al. 2001). As a consequence, flavonoids could be crucial in stimulating symbiotic N_2-fixation under elevated CO_2 environment. Haase et al. (2007a) found a release of *nod*-gene-inducing flavonoids (genistein, daidzein, and coumestrol) under elevated CO_2 in *Phaseolus vulgaris* L. plants. However, the reduction of soil N availability following the increase of root exudation is a common but not a general response to elevated CO_2. For example, recently, Philips et al. (2011) found that mature trees exposed to CO_2 enrichment increase the release of soluble C from roots to soil and that such increases are coupled to the accelerated turnover of N pools in the rhizosphere with positive effect on N availability and tree growth. So, further investigation is needed to understand how the quality rather than the quantity of root exudates can interfere with microbial community composition and activity. Few data are available on the effect of temperature on root exudation and flavonoids release into the soil. Uselman et al. (2000) analyzing the combined effect of two levels of CO_2 concentration (35 and 70 Pa), two of temperature (26°C and 30°C) and two of N fertilizer (0 and 10 mM N concentration) found that a temperature rise of 4°C significantly increased root exudation rate, but no data are available on the temperature effect on the chemical composition of root exudates. This latter is an important research gap to be filled in order to better understand the soil-plant relationship in a changing climate and to comprehend the adaptive capacity of terrestrial ecosystems to global climate change.

Concluding remarks and perspectives

In this review, the often neglected role of plant-derived flavonoids in plant nutrition and soil microorganisms and functions were highlighted as well as the related knowledge gaps.

In particular, considering the types, amounts, and persistence of flavonoids released by roots into the rhizosphere, soil complexity together with the different experimental conditions (sampling season, extraction method, and analytical detection) adopted in these studies have often led to contradictory results. Therefore, further research is needed to elucidate the actual residence time and active concentration of flavonoids in the rhizosphere soil, which are crucial to understand their behavior in soil and their role in influencing nutrient availability, plant nutrient uptake, allelopathy, and activity of soil organisms (bacteria, fungi, and microfauna).

With respect to the soil enzyme activities, they are strongly dependent on the concentration and availability of root exudates (Renella et al. 2007a). Both synthesis and persistence of enzymes have been quantified in studies based on the stimulation of microbial growth by adding easily degradable organic compounds to soil (Renella et al. 2006b, 2007b), but the effects of flavonoids on soil enzyme activities have been poorly studied (Tomasi et al. 2008). However, enzyme assays measure potential rather than real enzyme activity due to the optimal conditions of the enzyme assays, and moreover, they do not discriminate between intracellular and extracellular stabilized enzymes. Enzyme activity of soil should be combined with measurements of genes codifying the enzymes and with measurement of expression of these genes to evaluate the origin of the measured enzyme activities. Furthermore, the characterization of proteins protected against microbial degradation by their interactions with organic component such as tannins can give insights on the stabilization of organic N, including enzymes, in soil.

Considering soil bacteria, while the effect of flavonoids on rhizobia is well known (Mulligan and Long 1985; Spaink et al. 1989; Broughton et al. 2000; Cooper 2004b), only few studies have investigated the response of non-target bacteria to flavonoids secreted by roots. However, mechanisms by which phenolic compounds control microbial dynamics are unclear. For example, Shafer and Blum (1991) found that

phenolic acids, which suppressed cucumber seedling growth, were readily metabolized by soil microorganisms, sometimes without detectable changes in microbial community structures. Schimel et al. (1996) separated secondary metabolites from *Populus balsamifera* L. into two fractions, low molecular weight phenolics and tannins, and found that the former stimulated soil respiration whereas the latter inhibited it. The specific mechanism for this inhibition is unclear. Proteins complexed to tannins (Swain 1979) are less available as a substrate, but tannins may also complex exoenzymes, inhibiting polymer breakdown; they may also have toxic effects on specific groups of soil microbes (Baldwin et al. 1983; Field and Lettinga 1992). Benoit and Starkey (1968a), using tannins extracted from wattle, suggested that the principal effect of tannins on microbial development is not toxicity, whereas Schimel et al. (1996), using tannins extracted from balsam poplar, concluded that tannins act as microbial inhibitors. Thus, a few studies have shown stimulating or inhibiting effects on non-target microorganisms, and further research is necessary to investigate how flavonoid compounds might affect abundance, activity, and diversity of bacteria. In future studies, quantitative and qualitative analysis of flavonoids would be helpful to better understand the effect of the roots exudates on composition of bacterial communities. Since flavonoids are present in the rhizosphere, probably, the ability to exploit the flavonoids resource will have selective value in plant–microbe interaction (Shaw et al. 2006). Future experiment aiming to examine the fate and impact of flavonoids in the rhizosphere soil should attempt to mimic diversity and release of rhizodepositions.

With respect to the effect of flavonoids on soil fungi, while the available knowledge summarized above is still very scarce and the range of target organisms tested narrow, the data accumulated so far suggest that many root-borne flavonoids show activity, either stimulating or inhibiting, on the fungi tested (see Tables 1 and 2). Since the parameters assessed, the concentrations used, and the experimental setup designed highly varies between experiments, comparisons of results obtained in independent studies can only be interpreted with caution. However, based on the available data, it seems that some molecules affected mycorrhizal and phytopathogenic fungi in the same way (apigenin and luteolin, which stimulated both types of fungi) while others were promoting mycorrhizae but inhibiting phytopathogens (e.g., rutin or kaempferol). Moreover, naringenin was reported to inhibit spore germination in *P. oryzae* but to stimulate it in *F. solani*, suggesting a specific effect. However, studies assessing the impact of flavonoids on both types of interacting partners using the same experimental design and concentration range are needed for proper assessment of the specificity of flavonoid activity. In most studies reviewed here, flavonoids were applied in micromolar concentrations, with the exception of two studies, where nanomolar (Xie et al. 1995) or picomolar (Lagrange et al. 2001) concentrations were used. In future studies, care should be taken to apply flavonoids in concentrations which are relevant for the rhizosphere environment. Even if micromolar concentrations might occur in roots with high levels of exudation, like in white lupin cluster roots (Weisskopf et al. 2006a), in the rhizosphere of most other plants, nanomolar or picomolar concentrations might be more frequent. Furthermore, the in vitro response of fungi to exogenously applied flavonoids does not necessarily imply that the fungi would react in the same way if application would occur in the natural habitat (rhizosphere). To our knowledge, only one study until now analyzed the effect of flavonoids on mycorrhization of soil-grown plants (Siqueira et al. 1991). From the data available at present, no clear link between chemical structure and activity can be established, even if pterocarpans might be more likely than other flavonoids to inhibit phytopathogens and isoflavonoids to inhibit mycorrhizae. In contrast, flavones seem more prone to promote mycorrhizae than phytopathogens. Yet, to investigate what structural requirements are needed for the activity, studies comparing closely related flavonoids on the same target fungus should be carried out. A better understanding of the mode of action of flavonoids on fungal growth parameters might provide hints at which structural features are required for activity. To our knowledge, only a single study assessed this question until now (Bagga and Straney 2000) and reported that naringenin stimulated spore germination of *Fusarium solani* through inhibition of a cAMP phosphodiesterase. Elucidating the mode of action and the mechanisms underlying the observed effects is likely to represent the biggest challenge for future research in flavonoid-mediated plant–fungi interactions.

Considering the impact on roots of other plants, although allelopathic activity of flavonoids is well documented in the literature (Rao 1990; Iwashina 2003), the ecological significance of the reported observations is frequently not clear. Alellopathic effects are strongly dependent on the concentration and particularly on the bioavailability of allelochemicals in the rhizosphere. Flavonoids and other phenolics are not easily mobile in soils and are prone to adsorption by hydrophobic interactions with soil organic matter or by complexation with metal cations (Ohno 2001; Tomasi et al. 2008). In the rhizosphere, they may undergo biotic and abiotic structural modifications (Ohno 2001), and synergistic or antagonistic interactions with other rhizosphere products are poorly understood. Therefore, determining the rhizosphere concentrations of biologically active allelochemicals available to plant roots under field conditions is not an easy task, but it is a prerequisite for the evaluation of the allelopathic potential under natural growth conditions. Even in more recent studies, soil extraction of allelochemicals with organic solvents, such as methanol, is reported (Kong et al. 2006) instead of determining the potentially

plant available aqueous fractions. The comparatively higher extraction power of organic solvents for solubilization of lipophilic molecules most likely leads to an overestimation of plant-available allelochemicals in the respective soil samples and may result in misinterpretations of their allelopathic potential. A striking example in this context was the suggestion that secretion of the flavonoid compound (–)-catechin contributes to the invasive potential of *C. maculosa* in Northrica (Bais et al. 2002, 2003; Fitter 2003). Detailed physiological and gene expression studies revealed that (–)-catechin inhibits seed germination by disrupting mitochondrial respiration (Bais et al. 2003; Weir et al. 2004) eliciting the generation of reactive oxygen species in susceptible plants leading to cell death (Bais et al. 2003). However, many of the model experiments for evaluation of the allelopathic potential of (–)-catechin were conducted in sand culture, a substrate with low adsorption potential and completely different properties as compared with most field soils. More recent investigations suggest that, under real rhizosphere soil conditions, (–)-catechin may exhibit a much lower persistence as previously assumed, and the ecological role of this compound for the invasion potential of *C. maculosa* has been probably overestimated (Blair et al. 2005). Accordingly, many of the previous studies on flavonoid allelopathy need a thorough revision considering the conditions in the rhizosphere to separate allelopathic effects from other factors, such as resource competition.

Summarizing, future researches should increase the range of target organisms and concentration range of flavonoids in the rhizosphere. Comparisons should be also done among studies using the same experimental design and similar concentration ranges. Generally, the link between chemical structure and activity of the flavonoids needs to be assessed. The relative studies should be based on comparing closely related flavonoids on the same target organism.

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