Ferulic Acid: An Allelochemical Troublemaker

Wanderley D. dos Santos • Maria de Lourdes L. Ferrarese • Osvaldo Ferrarese-Filho*

Laboratory of Plant Biochemistry, Department of Biochemistry, University of Maringá, Av. Colombo, 5790, 87020-900, Maringá, PR, Brazil

Corresponding author: * oferrarese@uem.br

ABSTRACT

Ferulic acid, a cinnamic acid derivative, is a well-known allelochemical that is widely distributed in plants. Stress on plant roots by ferulic acid affects several physiological and biochemical aspects, such as water utilization, foliar expansion, root elongation, photosynthesis, cell respiration, membrane integrity and nutrient uptake, among others. Moreover, ferulic acid may be esterified with cell wall polysaccharides, incorporated into the lignin structure or form bridges that connect lignin with wall polysaccharides, rigidifying the cell walls and restricting cell growth. This review describes general aspects of allelopathy and focuses on the role of ferulic acid as an allelochemical and its supposed mode of action in plants.

CONTENTS

INTRODUCTION

Allelopathy: A complex science

For years, it has been known that plants release organic compounds into the environment from their aerial or sub-aerial parts, as exudates, volatiles, and/or decomposition residues. These compounds may accumulate in the soil environment and affect the growth and development of neighboring plants, an interaction called allelopathy (Weir *et al*. 2004). A main characteristic of allelopathy is the plant-plant interaction. Of the approximately 400,000 secondary metabolites assumed to exist in the plant kingdom, only about 3% of them have been studied to date, and many secondary metabolites have been reported to show allelopathic properties. Secondary metabolites might be separated into three chemically distinct groups: terpenes, nitrogen-containing secondary products and phenolic compounds (Taiz and Zeiger 1998). The latter group is very heterogeneous, with a diverse set of chemicals playing a variety of roles in the plant. While many are defense compounds against herbivores and pathogens, others have roles in mechanical support, in the attraction of pollinators and fruit dispersers, in the absorption of harmful ultraviolet radiation, or in allelopathy (Croteau *et al*. 2000).

Although there is growing evidence of the phenomenon of allelopathy, its existence is still debated by scientists since the mechanisms from production to release and the fate of allelochemicals are largely unknown. Responses to allelochemicals are also difficult to assess. This is further complicated by the wide range of chemicals of diverse molecular structures involved. Benzoic acid derivatives (e.g. *p*-hydroxybenzoic, vanillic and salicylic acids), cinnamic acid derivatives (e.g. *p*-coumaric and ferulic acids), non-protein amino acids (e.g. L-3,4-dyhydroxyphenilalanine) and flavonoids (e.g. quercetin and naringenin) have been referred to as allelochemicals.

Membrane perturbations are often reported to be the primary sites of action of many allelochemicals that trigger further modifications in the physiological processes of plant

Invited Review

Membrane Perturbations
(binding - structure- transport - energetics)

PRIMARY ACTION

ALTERED PROCESS

Specific Enzymes
Hormones
Organelle Interactions
Nucleic Acids
Protein Synthesis
Lignin Synthesis
Pigment Synthesis
Carbon Pools

Cell division and expansion

Inhibition of growth and development

Photosynthesis
Stomatal function
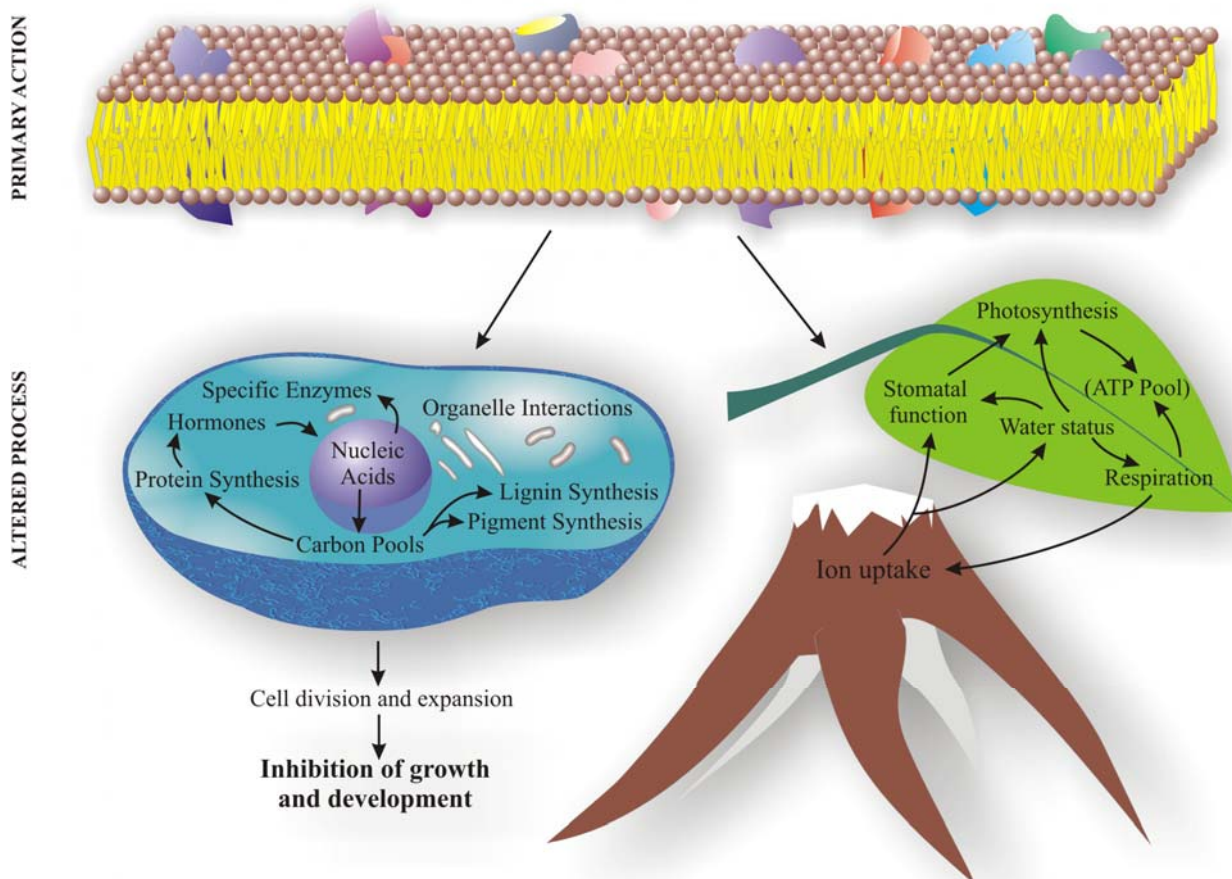(ATP Pool)
Water status
Respiration
Ion uptake

Fig. 1 Action model for allelochemicals in plants.

cells. However, clear insight into the primary allelochemical action on plant physiology has not been obtained. Several modes of action for allelochemicals are involved in the inhibition and modification of plant growth and development (**Fig. 1**). There are several factors that may influence the effects of an allelochemical. Temperature, photoperiod, mineral composition of the soil and interactions with other allelopathic compounds may affect the chemical stability, availability and toxicity of an allelochemical (Inderjit 1996). It is thus rather difficult to examine how each factor influences the response of plants. Another issue is that experiments with allelochemicals have been carried out under the restricted conditions of a laboratory, which controls temperature, light, nutrient solution and pH, among others. This is a relevant problem since laboratory conditions cannot be directly compared to natural conditions (Seigler 1996). However, many researchers are finding success in their comparative studies, especially when the concentrations of allelochemicals are similar in both systems (Sène *et al*. 2000).

Ferulic acid: Yesterday and today

Phenolic compounds contain aromatic substances formed via the shikimic acid pathway or the malonic acid pathway, including benzoic and cinnamic acid derivatives. These two pathways supply 60% and 40%, respectively, of carbon for the biosynthesis of phenolic compounds (Gross 1981). Linked to the shikimic acid pathway, the phenylpropanoid pathway starts with deamination of phenylalanine, by phenylalanine ammonia-lyase (PAL) or tyrosine ammonia-lyase (TAL) to form cinnamic acid, its first metabolite. Cinnamate is converted to monolignols by the subsequent actions of different enzymes (**Fig. 2**).

Ferulic acid (FA) is a cinnamic acid derivative that was initially isolated as a yellow precipitate by alcoholic extraction from the commercial resin of *Ferula foetida* (Umbelliferae, Apiaceae) by Hlasiwetz and Barth (1866). They then determined its chemical composition as $C_{10}H_{10}O_4$ and named it *Ferulasäure* or ferulic acid [3,(4-hydroxy-3-methoxyphenyl)-2-propenoic acid]. Over the next 60 years, no additional information was reported on this compound. Then between 1925 and 1988, it was chemically synthesized (Dutt 1925), its *cis* and *trans* isomers were separated (Comte *et al*. 1957), and stereochemistry was ascertained by NMR spectroscopy (Kelley *et al*. 1976) and unequivocally confirmed by X-ray crystallographic analysis (Nethaji *et al*. 1988). FA is a strong dibasic acid in which the first proton dissociation generates the carboxylate anion, while the second produces a phenolate anion. The anion has a high degree of resonance stabilization, which increases its acidity in comparison with similar phenolic acids (Graf 1992).

Several reports have evaluated its occurrence, soil levels, metabolism in plants and microorganisms, industrial applications, its physiological role during lignification, and its role as an allelochemical. In soils, FA has been detected at level up to 10 mM (Macias 1995). Widely present in the plant kingdom, it has also been studied for its properties as an anti-oxidant, food conservant (Graf 1992; Walters *et al*. 1997), co-adjuvant, anti-inflammatory, analgesic (de Campos *et al*. 1998) and anti-carcinogenic (Dobhal *et al*. 1999). Moreover, FA may be found as feruloyl-CoA in the phenylpropanoid pathway and as a component of cross-linked polymers in the cell wall (Smart and O'Brien 1979; Sánchez *et al*. 1996). As a metabolite of monolignols synthesis, FA is ester-linked to primary cell wall oligosaccharides,

Fig. 2 Simplified phenylpropanoid pathway. PAL, phenylalanine ammonia-lyase, C4H, cinnamate-4-hydroxylase, 4CL, 4-coumarate:CoA ligase, HCT, hydroxycinnamoyl CoA: quinate/shikimate hydroxycinnamoyl transferase, C3H, coumarate-3-hydroxylase, CCoAOMT, caffeoyl coenzyme A 3-*O*-methyltransferase, CCR, cinnamoyl CoA reductase, F5H, ferulate 5-hydroxylase, COMT, caffeic acid *O*-methyltransferase, CAD, cinnamyl alcohol dehydrogenase, ALDH, aldehyde dehydrogenase (Chen *et al*. 2006).

typically to arabino residue from glucuronoarabinoxylans. Smith and Harris (2000) reported that FA may be ester-linked in monocotyledons (Arecales, Commelinales, Poales, Zingiberales, etc). In dicots, FA may be present in Caryophyllales (Hartley and Harris 1981), Solanales (Keller *et al*. 1996), Brassicaceae (Chen *et al*. 1998), and Apiales (Parr *et al*. 1997). In soils, FA has been considered to be a strong allelochemical with several effects on plants, such as reduction in water utilization, inhibition of foliar expansion and root elongation, reduction in the rates of photosynthesis and inhibition of nutrient uptake (Siqueira *et al*. 1991; Einhellig 1995). Einhellig (2004) suggested that simple phenolic acids such as ferulic acid, coumarins and tannins appear to have similar modes of action that affect the growth of plants and microbes through multiple physiological effects that confer on them a general toxicity. More recently, Reigosa

and Pazos-Malvido (2007) reported the potential phytotoxic effects of different allelochemicals on germination and root growth of *Arabidopsis thaliana*. The authors observed that eleven of the 21 molecules showed significant inhibitory effects on germination, and 17 inhibited root growth. Although different physiological effects are known, its primary mode of action has not been conclusively established.

Allelochemical-soil-microorganism interactions: A big hindrance

With the elucidation of certain mechanisms by which allelochemicals cause their effects, researchers have been forced to realize that it is rare for a single allelochemical to exist alone under field conditions in concentrations large enough to have significant effects (Einhellig 1995). As described

earlier, an interfering factor in allelopathy is the interaction between the allelochemical and another chemical compound in the soil. Mixtures of non-inhibitory concentrations of individual phenolic acids may inhibit plant growth in an additive (equal to the sum of the effects of each allelochemical tested separately), synergistic (greater than the sum of the effects of each allelochemical) or antagonistic (lower than the sum of the effects of each allelochemical) manner (Rasmussen and Einhellig 1977). Blum *et al.* (1985) demonstrated that, in nutrient solutions, the leaf expansion and dry weight were reduced by single and multiple treatments of FA, vannilic acid (VA) and *p*-coumaric acid (*p*-CA). The effects of the mixture of allelochemicals were additive (for 0.5 mM FA plus 0.5 mM *p*-CA mixture) and antagonistic (for 0.5 mM FA plus 0.5 mM VA mixture). Using soil systems, Blum *et al.* (1985) and Gerig and Blum (1991) reported that the effects of FA plus VA, FA plus *p*-hydroxybenzoic (*p*-HBA) and *p*-CA plus *p*-HBA acid mixtures on leaf area expansion revealed additive effects. Similar additive (FA plus VA) effects on lettuce root growth were observed by Sampietro *et al.* (2006). Conducting split-root experiments, Lehman *et al.* (1994) verified that the simultaneous effects of FA and *p*-CA on leaf expansion were additive. The inhibition of leaf expansion was directly related to the concentrations of the acid(s) and the proportion of roots treated with the acid(s). Soybean roots cultivated in nutrient solution containing FA or VA (0.5 mM; 1.0 mM and equimolar mixtures) for 48 h were affected (Suzuki *et al.* 2003). Acting by themselves, both compounds (at 0.5 or 1.0 mM) decreased root length, and fresh and dry weights, and increased soluble and cell wall-bound peroxidase activities. At 1.0 mM, FA increased (but VA decreased) the phenylalanine ammonia-lyase (PAL) activity. Acting simultaneously, the effects of the allelochemical interaction were lower than the sum of the effects of each compound tested separately, an example of antagonism.

Another complex issue involves soil interactions. Reversible sorption of phenolic acids by soils provides short-term protection to FA and other phenolic acids from microbial degradation, affecting the intensity and the duration of this intensity (Blum 1998). Introduction of microorganisms into the soil indicates rapid utilization of allelochemicals. Differential soil fixation, microbial production of benzoic acids (VA, *p*-HBA) from cinnamic acids (FA and *p*-CA, respectively) and further differential utilization of cinnamic and benzoic acids by microorganisms reveal that these conditions may influence the magnitude and duration of the phytoxicity of the individual allelochemical. Furthermore, the rhizosphere and bulk-soil bacteria may affect the access of phenolic acid toward the root. Phenolic acid-utilizing bacteria are induced/selected by less than 0.1 μmol g^{-1} of phenolic acid. For a 0.6 μmol g^{-1} soil, equimolar phenolic acid mixture composed of *p*-CA, FA, *p*-HBA and VA, modeling indicated that a 500% increase of phenolic acid in the rhizosphere, utilizing bacteria, would decrease the inhibition of cucumber leaf expansion by about 5%. In some cases, there is an inverse relationship between the size of the microbial rhizosphere population and the intensity of the allelochemicals' effects (Blum *et al.* 2000).

Uptake of FA: More complexity

One of the aims of investigating allelopathic interactions has been to develop means of predicting plant effects after their uptake. In this context, the uptake of FA (as radiotracer U-ring-^{14}C ferulic acid) from solutions (0.1 to 1.0 mM, pH 4.0 to 7.0) was monitored in intact and excised cucumber roots by Shann and Blum (1987). Results revealed that FA uptake was directly proportional to its concentration and inversely to the pH of the nutrient solution. The effects were more evident in relation to the concentration of FA than its net uptake (Lehman and Blum 1999). After uptake, the intensity of the effects depended on the constant presence of the allelochemical surrounding the seedling roots. If removed from the nutrient solution, effects may be reverted.

Moreover, the proportion of the root system in direct contact with FA directly affects the allelopathic responses, such as root growth, water utilization and nutrient uptake (Klein and Blum 1990). In fact, Lehman and Blum (1999) demonstrated that the inhibition of net phosphorous uptake was related to the direct contact of the root system with FA rather than to its uptake.

A significant interaction has been verified between environmental temperatures and FA treatments. At 0.4 mM, FA reduced the dry weight of soybean seedlings grown at 34°C, while its effects were lower at 23°C. It may be plausible that temperature stress enhances allelochemical inhibition, indicating that interactions with the environment should be taken into account in understanding allelopathy (Einhellig and Eckrich 1984). Similarly, exudation of some benzoic and cinnamic acid derivatives by cucumber roots also increased with the temperature and/or photoperiod (Pramanik *et al.* 2000). FA caused more damage in root growth, water utilization, and leaf transpiration than other cinnamic and benzoic acids derivatives (Rasmussen and Einhellig 1977; Blum and Dalton 1985; Gerig and Blum 1991). In general, the main effects were associated with an increase in number of secondary roots and a reduction of the root/stem ratio (Blum and Rebbeck 1989; Vaughan and Ord 1990).

EFFECTS OF FA ON METABOLISM: SEEKING ANSWERS

There are several proposed modes of action for allelochemicals. As pointed out by Einhellig (1995), "*the phytotoxicity of many allelochemicals may be from a generalized cellular disruption rather than a specific mechanism*". Due to the diversity of compounds, a common allelochemical does not exist, nor is there a single mode of action for all allelochemicals. Therefore, the mode of action remains an open question. Some FA effects on plant metabolism will be related below.

Effects on carbon partition, carbohydrates and lipids

It has been verified that FA reduces the conversion of glucose to soluble amino acids, proteins and organic acids (Danks *et al.* 1975), and facilitates the incorporation of phenylalanine in proteins (van Sumere *et al.* 1971). A plausible explanation is that carbohydrate partitioning in plants drives toward growth and synthesis of secondary metabolites, during differentiation or under stress (Matsuki 1996). Under FA stress, glucose may be released into the cytosol and, further, used in the shikimic and phenylpropanoid pathways, reducing the carbon flux in the primary metabolism. In addition, FA decreases CO_2 reduction by photosynthesis (Yu *et al.* 2003), which may be related to changes in chlorophyll content (Einhellig and Rasmussen 1979; Blum and Rebbeck 1989), in glucose metabolism (Ferrarese *et al.* 2000). This might be associated with the conspicuous reduction in the starch stores of cap cells shown by ultrastructural assays (dos Santos *et al.* 2007).

Utilization of energy necessary for cells to grow and multiply in response to FA has been affected in plants. FA reduced lipid mobilization followed by the accumulation of unsaturated fatty acids in canola (*Brassica napus*) seeds during germination (Baleroni *et al.* 2000). It also increased the contents of saturated and unsaturated fatty acids of the polar and non-polar lipid fractions and xylose, fructose and sucrose in soybean root (Ferrarese *et al.* 2001), as seen in **Table 1**. Consequently, cellular structure changes appear to be, at least partially, associated with alterations in lipid and carbohydrate metabolism (Ho 1988; Ohlrogge and Browse 1995; Surjus and Durand 1996; Harwood 1997). Another fact is that malondialdehyde content, a product of lipid peroxidation, was strongly enhanced (152%) in cucumber roots by 0.5 mM FA. Moreover, the membrane injury, which indicates the integrity of the membrane, increased by 10% under FA action. It is well known that unsaturated fatty

Table 1 Changes in some physiological and biochemical indicators in plants submitted to the FA treatment.

Function		Indicator	Change	
		CO_2 fixation	(−)	
Energy carbohydrate		Glucose	(−)	
		Fructose	(+)	
		Sucrose	(+)	
Structural carbohydrate		Rhamnose	(−)	
		Xylose	(+)	
Lipid metabolism			Polar	Apolar
	Fatty acids	Palmitic acid	(+)	(+)
		Stearic acid	(+)	(+)
		Behenic acid	(+)	(+)
		Oleic acid	(=)	(+)
		Linoleic acid	(+)	(+)
		Linolenic acid	(+)	(−)
	Lipid peroxidation	Malondialdehyde	(+)	(+)
Enzyme activities		PAL	(+)	
		CAD/SAD	(−)	
		POD	(+)	
		ICL	(−)	
		ATPases	(−)	
		β-GT	(+)	
		β-GL	(+)	

Symbols: (−), decreased; (+), increased; (=): unchanged. CO_2, carbon dioxide; PAL, phenylalanine ammonia-lyase; CAD/SAD, coniferyl/sinapyl alcohol dehydrogenase; POD, peroxidase; ICL, isocitrate-lyase; β-GT, β-glucosyltransferase; β-GL, β-glycosidase.

acids are susceptible to free radicals. FA may then cause lipid peroxidation and membrane disruption leading to ion leakage, affecting nutrient uptake (Politycka 1996). In fact, the uptake of nutrients (Mg^{2+}, Ca^{2+}, K^{2+}, PO_4^{2-}, Fe^{3+}, Mn^{2+}, NO_3^- and NH_4^+) has been reduced by FA treatments in several plant species (Glass 1973, 1974; Danks *et al*. 1975; McClure *et al*. 1978; Kobza and Einhellig 1987; Lyu and Blum 1990; Bergmark *et al*. 1992; Booker *et al*. 1992).

Effects on enzymes

FA, as other allelochemicals, may be β-glucosylated by phenol β-glucosyltransferase and affect the activities of several enzymes, including amylase, catalase and IAA oxidase (Einhellig 1995; Devi and Prasad 1996; Politycka 1996, 1998). Special mention is made here regarding the effects of FA on phenylalanine ammonia-lyase (PAL) and peroxidases, enzymes of the lignin pathway, which are involved in the synthesis of phenolic compounds in plants.

Phenylalanine ammonia-lyase (PAL)

As noted in **Fig. 2**, PAL is the first rate-limiting enzyme of the phenylpropanoid pathway, leading to the synthesis of the phenolic acids and, later, to monolignols. Similar to POD, increased activity of PAL may be a response of plants to various biotic and abiotic stresses. Few studies have been carried out on the effects of exogenous FA on PAL, and results are contradictory. For example, Sato *et al*. (1982) pointed out that FA was ineffective on the PAL of sweet potato (*Ipomea batatas*) and pea (*Pisum sativus*). FA was unable to affect PAL activity in cucumber (*Cucumis sativus*) roots (Shann and Blum 1987). In contrast, increased PAL activities were associated with a decrease in cucumber (*Cucumis sativus*) roots after 24 and 48 h of FA treatment (Politycka 1998). In agreement with this author, dos Santos *et al*. (2004) demonstrated that PAL activities increase in soybean roots after 24 to 72 h of FA treatment. In addition, Politycka (1999) reported that an increase in the PAL activity induced by the action of FA and associated with reduced root growth of cucumber depended on ethylene synthesis. Application of an ethylene synthesis inhibitor (aminooxyacetic acid, AOA) cancelled out the effect of FA on PAL activity (Politycka and Mielcarz 2007). According to these authors, ethylene participates in the retardation of cucumber root growth by FA.

Peroxidases

Some researchers have reported alterations in POD activity under FA action. For example, in cucumber root treated with FA (0.5 or 1.0 mM), the soluble and bound form of POD increased significantly (Shann and Blum 1987; Politycka 1996; Politycka *et al*. 2004). Application of 1.0 mM FA also caused a significant increase in both soluble and bound POD in maize roots and correlated with a pronounced decrease in root growth (Devi and Prasad 1996). At 1.0 mM, FA also increased POD activity in soybean roots (dos Santos *et al*. 2004). Increase of soluble POD activity was accompanied by a decrease in root growth. Based on these results, the researchers above attributed FA effects to the production of free radicals. It is well known that soluble POD catalyzes the oxidation of diverse phenolic substrates and is often regarded as an antioxidant enzyme that protects cells from the destructive influence of oxygen radicals. However, if the cells ability to scavenger oxygen radicals is exceeded, phenolic acid oxidation by soluble POD leads to the production of quinones, which increase depolarization of the cell membrane and changes in lipid composition (Politycka 1996, 1998; Ferrarese *et al*. 2001; Doblinski *et al*. 2003). Moreover, cell wall-bound POD is associated with cell wall stiffening and growth-restriction (Passardi *et al*. 2005). POD is able to convert phenolic compounds, such as ferulic, *p*-coumaric and caffeic acids, into free radicals, which spontaneously polymerize. This essential role for POD in the stiffening of cell walls through the formation of biphenyl bridges between wall polymers and, thus, the reduction of the cell wall extensibility have been proposed by some researchers (Fry *et al*. 1992; Sánchez *et al*. 1996; dos Santos *et al*. 2004).

Effects on mitochondrial respiration

Several allelochemicals, such as sorgoleone, juglone, quercetin, umbelliferon, gramine and cineole, have been found to perturb respiratory metabolism. In general, the production of ATP in mitochondria was inhibited by a variety of flavonoids (Einhellig 1995). Sert *et al*. (1998) demonstrated the effects of FA on L-malate oxidation in mitochondria isolated from soybean seedlings. FA inhibited basal and coupled respiration during L-malate oxidation, depleting the amounts of pyruvate or oxaloacetate produced. The authors suggest that the site of FA is situated at some step that precedes the respiratory chain, although this action occurred at

a high allelochemical concentration.

CELL WALL, FA AND LIGNIFICATION: PERFECT LINKS

Integrated with the cytoplasm, the cell wall performs a role of exoskeleton, conferring to the cell its form, mechanical resistance, pathogen protection, adherence to vicinal cells, and limiting the influx of water and macromolecules. Polysaccharides as cellulose, hemicelluloses and pectins constitute its basic structure. Lignin is an important component of secondarily thickened plant cell walls. The biosynthesis of lignins proceeds through a long sequence of reactions that involve the cytosolic shikimate pathway. It supplies phenylalanine and tyrosine. Subsequently, the general phenylpropanoid pathway converts phenylalanine (or, in lesser extent, tyrosine) into *p*-hydroxycinnamoyl-CoA esters. The lignin-specific pathway starts with *p*-hydroxycinnamoyl-CoA esters and converts them into free cinnamic acids and monolignols (**Fig. 2**, Boerjan *et al*. 2003). FA and other cinnamic acids may covalently cross-link cell wall polymers (Fry 1986; Ramakrishna *et al*. 1989), hardening the cell wall. This process is important in stopping elongation (Fry 1986; Iiyama *et al*. 1990) and blocking access of pathogens (Assabgui *et al*. 1993) into the cytoplasm. Apoplastic peroxidases (ionic and covalently bound to the cell wall) are thought to catalyze the oxidation of both hydroxycinnamate cross-linkage and monolignol polymerization, which may be regulated by the supply of H_2O_2 and ascorbic acid (Córdoba-Pedregosa *et al*. 1996; Mehlhorn *et al*. 1996; Sánchez *et al*. 1996; Vianello *et al*. 1997).

As reported earlier (Ferrarese *et al*. 2001), a decrease in rhamnose and an increase in xylose contents were verified in soybean roots treated with FA. Rhamnose is a component of pectin and is related to the number of pectin gel ramifications and to reinforcement of the cell wall. It is thus possible that exogenous FA, esterified to polysaccharides, decreases free rhamnose content by reducing pectin hydrolysis. On the other hand, the increased content of xylose suggests an activation of cell wall hydrolases and esterases, which release oligosaccharides (Grant Reid 1997). In brief, FA might directly affect the structure of the cell wall. During treatment, root cells may accumulate FA in the apoplast (Akin *et al*. 1992) and peroxidases may catalyze the link of FA in the polysaccharides, lignin (Chakraborty *et al*. 1993; Politycka 1996; Wallace and Fry 1999) and other FA. Dehydrodiferulic acid may form diester, ester-ether or diester-ether cross-linkages between cell wall polymers, which may reinforce the cell wall against cellulases, pectinases (Akin *et al*. 1993; Wojtaszek 1997), laccase (Sterjiads *et al*. 1993) produced by pathogens, and involved in the cessation of cell elongation. In addition to free FA, FA-oligosaccharides also show biological activity as inhibitors of cell growth (Ishi 1997) and are involved in signal transduction between plants and microorganism (Peters and Verma 1990).

Exogenously applied FA incorporates into the lignin residues (Shann and Blum 1987), inducing lignification and related enzymes associated with the reduced root growth of treated plants (Devi and Prasad 1996; Politycka 1999; dos Santos *et al*. 2004). Shann and Blum (1987) verified an increase in lignin contents associated with a decrease in root growth. In maize (*Zea mays*) roots, FA increased the activity of cell wall-bound POD correlated to a significant increase in lignin content and a reduction in root growth (Devi and Prasad 1996). Politycka (1999) also verified that cucumber (*Cucumis sativus*) seedlings treated with FA stimulated lignin production, coupled to a decrease in root growth.

IS THE CELL WALL AN ACTION SITE OF FA?

Recent data obtained by dos Santos (2007) revealed that FA affects soybean root growth due to the incorporation of FA into the phenylpropanoid pathway. Using phenylpropanoid enzyme inhibitors, the authors concluded that 4CL catalyzes

the conversion of exogenously applied FA into feruloyl-CoA (**Fig. 2**). The feruloyl-CoA formed is then converted into coniferal- and sinapaldehydes, which must circumvent the inhibited CAD reaction by polymerizing toward lignin in the aldehyde state. Based on this fact, and linking the information available in the literature for FA, these authors suggested a mode of action for FA (**Fig. 3**) considering an elegant model for plant response throughout biotic stress proposed by Wojtaszek (1997).

In the model, the contact of exogenous FA with the root cell inactivates sulfhydryl groups of carrier proteins, causing an ionic disturbance and affecting nutrient uptake by the cell membrane (Baziramakenga *et al*. 1995). In the Wojtaszek's model, the pathogen infection generates a cascade of signaling events – including Ca^{2+} influx and proton efflux – that actives the NADPH-oxidase complex (generating $\cdot O_2^-$) and pH-sensible cell wall POD (producing H_2O_2), which produces an oxidative burst. To date, there are no data on signaling events caused by FA stress. However, the general disturbance caused by FA must be enough to increase the Ca^{2+} influx since its concentration is kept lower inside the cytoplasm by the action of ATPases. Short-time experiments revealed that the absence of Ca^{2+} in nutrient solution reduces FA effects on soybean roots (unpublished data). In addition, Converso and Fernandez (1996) found evidence that Ca^{2+} modulates POD isozymes.

The reduced linoleic acid content after FA treatment (Ferrarese *et al*. 2001) may also be related to signaling events. Linoleic acid is a precursor to oxylipins, such as traumatin, jasmonic acid, etc. (van der Selt *et al*. 2000), which are involved in the plant defense signaling mechanisms (Trawatha *et al*. 1995). The oxylipins pathway starts with the oxidation of linolenic acid by lipoxigenases, which are activated under stress/defense circumstances such as an increase of H_2O_2 (Fornaroli *et al*. 1999). On the other hand, jasmonic acid may inhibit plant growth and may be associated with the inhibition of root growth caused by FA (Creelman *et al*. 1992). Jasmonic acid is also related to the expression of specific POD isozymes during stress (Allison and Schultz 2004).

The control of pH in H_2O_2 production has been demonstrated. In beans, H_2O_2 is generated from $\cdot O_2^-$ by a pH-sensible cell wall POD that requires a reductant group (Wojtaszek 1997). FA oxidation by POD might produce H_2O_2 and the resulting phenoxy radical may undergo dimerization. These dimers are, eventually, esterified to hemicelluloses, linking the cell wall polymers, stiffening the cell wall and decreasing the root growth (Zimmerlin *et al*. 1994; Bolwell *et al*. 1995; Vianello *et al*. 1997; Blee *et al*. 2001; Bolwell *et al*. 2002; Stobiecki 2002). Furthermore, an increase in H_2O_2 contents enhances activities of cell wall POD and lignification (Whetten *et al*. 1998; dos Santos *et al*. 2004; Politycka *et al*. 2004). As cited earlier, FA cross-linkages are the initial steps of lignification (Boerjan *et al*. 2003).

Experiments using inhibitors of this pathway revealed that FA might be channeled into the phenylpropanoid pathway and, later on, may increase the lignin production (dos Santos 2007). In addition, FA-induced lipid peroxidation (Polyticka 1996; Doblinski *et al*. 2003) has been related to an oxidative burst (Baziramakenga *et al*. 1995; Devi and Prasad 1996). When the oxygen radicals exceed the scavenger capacity of the cells, phenolic acid oxidation by PODs will lead to accumulation of quinones (Appel 1993; Politycka 1998). These compounds may act as proton carriers, intensifying depolarization of the root cell membrane. In summary, excessive cross-linkages, lignification and changes in the membrane permeability may cause reduced root growth (Lee *et al*. 1982; Devi and Prasad 1996).

FERULIC ACID TOMORROW: WHAT HAPPENS NEXT?

Available data related to the effects of FA on plants indicate plausible action sites during FA stress, especially the putative starting effects on sulfhydryl groups of carrier proteins

Fig. 3 Proposed mode of action for ferulic acid on lignification of soybean roots. PAL, phenylalanine ammonia-lyase; C4H, cinnamate 4-hydroxylase; 4CL, 4-coumarate:CoA ligase; HCT, hydroxycinnamoyl-CoA: quinate/shikimate hydroxycinnamoyltransferase; C3H, *p*-coumarate 3-hydroxylase; CCoAOMT, caffeoyl-CoA *O*-methyltransferase; CCR, cinnamoyl-CoA reductase; F5H, ferulate 5-hydroxylase; COMT, caffeic acid/5-hydroxy ferulic acid *O*-methyltransferase; CAD, cinnamyl alcohol dehydrogenase; peroxidase (POD); ferulic acid (FA); piperonylic acid (PIP); 3,4-(methylenedioxy) cinnamic acid (MDCA). (1), Chen *et al.* (2006); (2), dos Santos *et al.* (2004); (3), Shann and Blum (1987); (4), Baziramakenga *et al.* (1995); (5), Wojtaszek (1997); (6), Boerjan *et al.* (2003).

and the irreversible reduction of cell wall extensibility. Root responses to the FA action include activation of POD, cross-links between cell wall polymers and reduction in cell wall extensibility. Moreover, exogenous FA activates cell wall POD, increases apoplastic H_2O_2 content, and may be incorporated into the metabolic pathway that leads to lignin production.

In spite of related findings, further studies are required to elucidate some of the possibilities suggested. These include: (1) identification of reactive oxygen species (ROS), such H_2O_2 and $\cdot O_2^-$, possibly involved in these responses; (2) determination of activities of the enzymes involved in

H_2O_2 production, for example, NADH-oxidase and pH-dependent cell wall POD; (3) verification of the involvement of other phenylpropanoid pathway enzymes (e.g. treatment of cell wall POD with specific inhibitors); (4) comparison of plants with CAD-deficient responses with non-deficient plants treated with FA and (5) identification of the aldehydes in induced lignin. Further data must strengthen the role of FA and other compounds in plant allelopathy.

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