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PHENOLIC COMPOUNDS AND THEIR IMPORTANCE

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ABSTRACT: *Plants produce a great variety of secondary products of which the most important group is called phenolic compounds. Phenolic compounds, which are synthesized primarily from products of the shikimic acid pathway, have several important roles in plants. Tannins, lignin, flavonoids and some simple phenolic compounds serve as defenses against herbivores and pathogens. Lignin also mechanically strengthens cell walls and many flavonoid pigments are important attractants for pollinators and seed disperser. Some simple phenolic compounds affect the growth of neighbouring plants and thus have allelopathic activity.*

Keywords: *Phenolic compounds, plant physiology, biosynthesis.*

INTRODUCTION

Phenolic compounds are secondary products which posses an aromatic ring bearing a hidroxyl substituent and most are of plant origin. Plant phenolics are a chemically heterogenous group: Some are soluble only in organic solvents, some are water-soluble carboxylic acids and glycosides. Another group of phenolics are insoluble polymers (Taiz and Zeiger, 1991).

In keeping with their chemical diversity, phenolics play a variety of important roles in the plant. Majority of phenolic substances have important effects on defense against herbivores and pathogens. Others have some role in mechanical support, in attracting pollinators and in reducing the growth of nearby competing plants.

BIOSYNTHESIS PATHWAYS OF PLANT PHENOLICS

Plant phenolics are biosynthesized by two basic pathways: The shikimic acid pathway and the malonic acid pathway (Fig. 1). The shikimic acid pathway participates in the biosynthesis of most plant phenolics. The malonic acid pathway is of more significance in fungi and bacteria than in higher plants.

Figure 1. Plant phenolics are biosynthesized in several different ways.

The shikimic acid pathway begins from simple carbohydrates and proceeds to the aromatic amino acids. One of the pathway intermediates is shikimic acid, which has given its name to his whole sequence of reactions. In most plant species the key step in these synthesis is the conversion of phenylalanine to cinnamic acid by the elimination of an ammonia molecule (Fig. 2). This reaction is catalyzed by phenylalanine ammonia-lyase (PAL) enzyme. In a few plants, particularly grasses , the key reaction in phenolic formation is similar conversion of tyrosine to 4-hydroxycinnamic acid (Hrazdina, 1992).

Figure 2. The deamination of phenylalanine to trans-cinnamic acid is an important step in phenolic biosynthesis in most species of plants.

The activity of PAL, which is an important regulatory enzyme of secondary metabolism in plants, is under the control of various external and internal factors, such as hormones, nutrient levels, light (through its effect on phytochrome), fungal infection and wounding. Fungal invasion triggers the transcription of messenger RNA that codes for

PAL, thus increasing the synthesis of PAL in the plant and stimulating the synthesis of phenolic compounds (Kuhn et al., 1984).

PHENOLIC COMPOUNDS

1. Simple Phenolic Compounds

a) Simple phenolics take part in plant-herbivore, plant-fungus and plant-plant interactions: (1) Simple phenylpropanes such as trans-cinnamic acid, which have a basic aromatic ring of C6 and a chain of C3. (2) Phenylpropane lactones (cyclic esters) called coumarins also with an aromatic ring of C6 and a chain of C3. (3) Benzoic acid derivatives having a basic aromatic ring of C6 and a chain of C1, formed from phenylpropanes by eleavage of a two-carbon fragment from the side chain (Fig. 3).

Figure 3. Some simple phenolic compounds that can act as inhibitors of plant growth.

Many simple phenolic compounds have important roles in plants as defenses against insects, herbivores and fungi. Furanocoumarins, which contain an extra furon ring, have the phototoxicity (Fig. 3).

These compounds activated by UV light can insert themselves into the double helix of DNA and bind to the pyrimidine bases cytosine and thymine. Thus, they block transcription and lead to cell death. Phytotoxic furanocoumarins are especially abundant, in members of Umbelliferae family (celery, parsnips and parsley). In celery, the level of these compounds can increase about 100-fold if the plant is stressed or diseased (Ames, 1983).

b) Simple phenolics that escape into the environment may effect the growth of other plants: Plants release a variety of primary and secondary products into the environment from their leaves, roots and decaying litter. The effects of these compounds on neighbouring plants are called "allelopathy". The term of allelopathy generally applies to the harmful effects of plants on their neighbours (sometimes may be beneficial effects).

Compounds such as caffeic acid and ferulic acid (Fig. 3) occur in soil in appreciable amounts and inhibit the germination and growth of many plants (Rice, 1987).

2. Complex Phenolic Compounds

a) Lignin: Lignin, which is the most abundant organic substance in plants, is generally formed from three different phenylpropane alcohols, coniferyl, coumaryl and sinapyl alcohol synthesized from phenylalanine via various cinnamic acid derivatives (Fig. 4) (Gottlieb, 1992).

Figure 4. The three phenylpropane alcohols that join to form lignin.

Lignin is found in the cell walls of various types of supporting and conducting tissue, especially xylem elements (tracheids and vessel elements). It is deposited chiefly in the thickened secondary wall but can also occur in the primary wall and middle lamella. The mechanical rigidity of lignin strengthens stems and vascular tissues, permitting water and minerals to be conducted through the xylem. By bonding to cellulose and protein, lignin also reduces the digestibility of these substances. Besides, lignin has significant protective functions in plants by blocking the growth of pathogens (Harborne, 1980).

b) The flavonoids : Flavonoids, which are widespread in the plant kingdom, may serve spesific functions in flower pigmentation, UV-protection, plant defense against pathogens and legume nodulations (Chappel and Hahlbrock, 1984; Dixon, 1986).

The basic carbon skleton of a flavonoid composed of two aromatic C6 rings held to gether by a 3-carbon bridge. Flavonoids are classified into different groups based primarily on the degree of oxidation of the three-carbon bridge. These groups are the anthocyanins, the flavones, the flavonols and the isoflavonoids (Fig. 5). Several genes encoding enzymes and regulatory proteins involved in flavonoid biosynthesis have been cloned from a number of plant species (Tunen and Mol, 1990). Phenylalanine ammonia lyase (PAL) is one of the best-studied enzymes of the phenylpropanoid pathway (Barend and Ferreira, 1992).

Anthocyanin: The anthocyanins are vitally important in attracting pollinators and seed dispersal by coloring flowers and fruit. The anthocyanins which are the most widespread group of pigmented flavonoids, are responsible for most of the red, pink, purple and blue colors observed in plant parts.

Anthocyanins are glycosides that have sugars at position 3 (Fig. 5). Without their sugars, anthocyanins are called "anthocyanidins". Anthocyanin color is influenced by the number of hidroxyl and methoxyl groups in ring B of the anthocyanidin, the presence of chelating metals such as iron and aluminum, the presence of flavone or flavonol copigments and the pH of the cell vacuole in which these compounds are stored (Taiz and Zeiger, 1991).

Flavons and flavonols: These flavonoids found in flowers, generally absorb light at shorter wavelenghts than anthocyanins and so are not visible to the human eye (Fig. 5). However, insects such as bees, which see farther into the ultraviolet range of the spectrum than we do, could respond to flavones and flavonols (MCrea and Levy, 1983).

Flavones and flavonols are not restricted to flowers but are also present in the leaves of all green plants. It has been suggested that these two classes of flavonoids protect cells from excessive UV radiation, because they absorb light strongly in the UV region while letting the visible (photosynthetically active) wavelengths pass through uninterrupted (Caldwell et al., 1983). Besides, flavones and flavonols secreted into the soil by legume roots regulate gene expression in nodulating nitrogen-fixing bacteria (Rolfe and Gresshoft, 1988).

Figure 5. Carbon skeletons of major flavonoid types.

Isoflavonoids: The isoflavonoids are a group of flavonoids in which the position of one aromatic ring (ring B) is shifted (Fig. 5). Isoflavonoids found mostly in legumes have several different functions. Some have strong insecticidal activities, others cause infertility in mammals.

Isoflavonoids are antimicrobial compounds called "phytoalexins". Phytoalexin accumulation in high concentrations has great importance of the resistance mechanism against pathogenic microbes. Phytoalexins are generally undetectable in the plant. They are synthesized very rapidly, within hours following microbial attack. Their formation is restricted to a local region around the infection site and they are toxic to a broad spectrum of fungal and bacterial pathogens of plants. Some researchers have suggested that phytoalexins are general plant stress metabolites, because their synthesis may be induced by factors other than fungal or bacterial attack. Stresses such as wounding, freezing, high levels of UV light and the application of fungicides or salts of various heavy metals can trigger the production of phytoalexins (Ebel and Grisebach, 1988).

c) Tannins: Besides, lignin, another plant phenolic polymer with defensive properties is tannin. There are two categories of tannins, condensed and hydrolyzable.

Condansed tannins are compounds formed by the linkage of flavonoid units (Fig. 6). They are frequent constituents of woody plants. Condensed tannins can often be hydrolyzed to anthocyanidins by treatment with strong acids and so are called "proanthochocyanidins". Hydrolyzable tannins are heterogenous polymers containing phenolic acids, especially gallic acid and simple sugars (Fig. 6). They may be hydrolyzed more easily with dilute acid.

Tannins are general toxins that significantly reduce the growth and survivorship of many herbivores when added to their diets. In addition, tannins act as feeding repellents to a great diversity of animals. In humans, tannins cause a sharp, unpleasant, astringent sensation in the mouth due to their binding of salivary proteins (Oates et al., 1980).

The defensive proporties of tannins have been attributed to their ability to bind proteins. The tannins can activate the herbivore's digestive enzymes by binding proteins and so creating complex aggregates (Clausen et al., 1992).

Plant tannins also serve as defenses against microorganisms. For example, the nonliving heartwood of many trees contains high concentrations of tannins that help prevent fungal and bacterial decay (Schultz et al., 1992).

Figure 6. Structures of some tannins formed from phenolic acids or flavonoid units.

CONCLUSION

The study of plant phenolics has many practical applications. Many of these compounds that are physiologically active against herbivores or pathogens are now used as insecticides, fungicides or pharmaceuticals. By breeding increased levels of secondary products directly into plants, it may be possible to reduce the need for certain costly and potentially harmful pesticides. On the other hand, the possible toxicity effects of high levels of naturally occurring defense compounds to humans must also be considered.

In the literature, generally, the effects of plant phenolics on the mechanism against diseases and pathogens are mentioned. On the other hand, it was also determined that these substances play important roles in many physiological events in the plants such as growth vigour, differentiation of flowers and roots, determination of gene activity and characterisation of some developmental stages (Tanrısever, 1982 a; Özeker, 1994; Özeker, 1996; Akıllıoğlu, 1994). Due to the easy analytical methods in determinations and suitability for histochemical examinations, cytological investigation of phenolics can also be performed (Tanrısever, 1982 b).

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