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Phenolic Compounds and Uses in Fruit Growing

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Abstract

Phenolic compounds are a class of chemical compounds in organic chemistry which consist of a hydroxyl group directly bonded to an aromatic hydrocarbon group. Phenolic compounds find in cell wall structures and play a major role in the growth regulation of plant as an internal physiological regulators or chemical messengers. They are used in the fruit growing field. They are related with defending system against pathogens and stress. They increase the success of tissue culture; can be helpful to identification of fruit cultivars, to determination of graft compatibility and identification of vigor of trees. They are also important because of their contribution to the sensory quality of fruits during the technological processes. In this review, the simple classification was given for these compounds and uses in the agricultural field were described.

Key words: Phenolic compounds, fruit quality, fruit growing, cultivar identification, grafting, tree vigor

Fenolik Bileşikler ve Meyve Yetiştiriciliğinde Kullanımı

Özet

Aromatik hidrokarbon grubuna bağlı bir hidroksil grubu içeren fenolik bileşikler organik kimyanın bir sınıfıdır. Fenolik bileşikler hücre duvarı yapısında bulunmakta ve içsel bir fizyolojik düzenleyici veya kimyasal haberci olarak bitki büyümesinin organizasyonunda önemli rol oynamaktadır. Meyve yetiştiriciliği alanında kullanılmaktadır. Bu bileşikler patojenlere ve stres koşullarına karşı savunma sistemi ile doğrudan bağlantılıdır. Doku kültürü çalışmalarında başarıyı artırmaktadır; çeşitlerin tanımlanmasında, aşı uyuşmazlığının belirlenmesinde ve ağaçların büyüme kuvvetinin saptanmasında kullanılabilmektedir. Meyve kalitesine etkilerinden dolayı, fenolik bileşikler ürün işleme sırasında da önem taşımaktadır. Bu derleme makalede fenolik bileşikler basitçe sınıflandırılmış ve meyve yetiştiriciliği alanında kullanımlarına yer verilmiştir.

Anahtar Kelimeler: Fenolik bileşikler, meyve kalitesi, meyve yetiştiriciliği, çeşit tanılama, aşılama, bodurluk

Introduction

Polyphenols are among the most widespread class of metabolites in nature, and their distribution is almost ubiquitous. It is estimated that 100,000 to 200,000 secondary metabolites exist and some 20% of the carbon fixed by photosynthesis is channeled into the phenylpropanoid pathway, thus generating the majority of the natural-occurring phenolics, such as flavonoids and stilbenes (Ralston et al., 2005; Lacikova et al., 2009; Pereira et al., 2009). Phenol is the simple structure form of these compounds. Chemically, they are compounds with an aromatic ring link to one or more hydroxyl groups and hydroxyl group of phenol determines its acidity whereas the benzene ring characterizes its basicity. Phenol is moderately soluble in water (Nguyen et al., 2003). Polyphenolic compounds are widely distributed in the vegetable and fruits and are essential for the growth of plants and affect various physiological events. They find in cell wall structures, features of woods and barks, flower color and they actively inhibited or stimulate some physiological process, such as defending system against pathogens and stress, some of the quality properties of fruits quality (aroma, flavors, color, and astringency), structure, pollination, germination process of seed after harvesting and growth as well as development and reproduction. They are considered as bioactive non-nutritional compounds, due to their antioxidant functions (Yordi et al., 2012; Reis Gaida, 2013).

This article, after a simple classification and biosynthesis of plant phenolic compounds, some affects as internal physiological regulators or chemical messengers and uses in the fruit growing field were investigated.

Biosynthesis of phenolic compounds

Although a large variety of plant phenols exists, most of these compounds arise from a common origin: the amino acids phenylalanine or tyrosine. The plant phenolic compounds are primarily derived from the phenylpropanoids (Castellano et al., 2012). Precursors of phenylpropanoids are synthesized from two basic pathway: the shikimic acid pathway and the malonic pathway. The shikimic acid pathway produces most plant phenolics, whereas the malonic pathway, which is an important source of phenolics in fungi and bacteria, is less significant in higher plants (Seabra et al., 2009; Pereira et al., 2009; Saltveit, 2010). Phenolic compounds have three main characteristics. First one is the presence of at least one aromatic ring hydroxyl-substituted (Morton et al., 2000). Another characteristic of these substances is that they are presented commonly bound to other molecules, frequently to sugars and proteins. However, it is less common, phenolic compounds occur in free form in the plants (Reis Giada, 2013).

Simple classification of phenolic compounds

Phenolic compounds divided in two groups mainly as simple phenols and polyphenols. Main classes of phenolic compounds are flavonoids, tannins, chalcones, coumarins and phenolic acids. The most important flavonoids are flavonols, flavanols, flavones, isoflavones, anthocyanidins and flavanones (Scalbert and Williamson, 2000). They are among the most potent antioxidants from plants. Tannins can be classified into two major groups, hydrolysable and condensed tannins (Chung et al., 1998). The phloretin and phloridzin are characteristics of apples, while arbutin of pears and strawberries. Chalcones is the main pigments of yellow flowers (Karakaya, 2004). Coumarins are more common in nature in the form of glycosides and are mainly found in olive oil (Sanchez-Moreno, 2002).

Phenolic acids can be divided into two groups: benzoic acids and cinnamic acids. In the group of benzoic acids there are protocatechuic acids, vanillic acids, syringic acid, gentisic acid, salicylic acid, p-hydroxybenzoic acid and gallic acid (Sanchez-Moreno, 2002).

Uses of phenolics compounds in the fruit growing

Role of phenolics as pigments and aromatic compounds

Many phenolic compounds are responsible for coloring of the plant flowers, fruits and are important for their quality. Factors affecting fruit color are primarily genetically determined. In addition, environmental factors such as nutrients, temperature and light conditions can have an effect on flavonoid composition and on the final hue of the fruit. The other important role of flavonoids is to serve as visual signals for animals in attracting pollinators in flowers and help to pollination and of course fruit set (Lattanzio et al., 2006). Anthocyanins range from hues to pink through deep red to purple in plants (Ryugo, 1988). Chalcones and aurones are two classes of flavonoids that contribute to yellow flower colour in plants (Karakaya, 2004; Lattanzio et al., 2006). Among the polyphenols, flavonols are responsible for cream-yellowish hue, which are found principally in the outer parts of fruits (Tomas-Barberan et al., 2000). Quercetin is a flavonoid present in green-yellow apples, cherries and grapes (Yordi et al., 2012).

Many phenolic compounds are responsible for some of the sensorial properties of fruit and related with the quality. There are bitter polyphenols, such as certain citrus flavanones (naringin from grapefruit and neohesperidine from the bitter oranges) or oleuropein present in olives. Proanthocyanidins (condensed tannins) and hydrolysable tannins confer astringency to fruits, and some simple phenols are important for the aroma of certain fruits, such as eugenol in bananas. Hydroxycinnamic acid derivatives such as caffeic, ferulic and sinapic acids are present in a number of fruits. Tannins are not pigments but when plant tissues are injured, these chemicals are oxidized to brownish-black pigments. When a fruit is bruised, cells rupture and these substances come into contact with the enzymes polyphenoloxidase and peroxidases and this cause to browning reaction. Tannis obtain the astringent taste because they are reacting with the proteins on the surface of tongue. Persimmon is a good example to this property of tannins (Ryugo, 1988).

Role of phenolic compounds on the growth and development physiology of fruit trees

Plant phenolics are internal physiological regulators or chemical messengers within the intact plants. They found in the hydroxycinnamic acids, particularly *p*-coumaric acid and ferulic acid, are found in the insoluble or cell wall fraction. Phenolic compounds have been shown to have both stimulatory and inhibitory effects on plant development. They play a significant role in cell wall development act in lignin biosynthesis (Fry, 1983; Hatfield et al., 1999). Some phenolic compounds have a role as natural auxin transport regulators in plants. Mono-and dihydroxy flavonoids are implicated as inhibitors of IAA transport (Jacobs and Rubery, 1988). There was a relationship between the polyphenol metabolism and seasonal development of plant tissues (Treutter et al., 1987). They can influence plant growth by promoting leaf expansion (Hegedus and Phan, 1982), stimulating callus growth (Gould and Murashige, 1985), and increasing rooting of cuttings (Jones, 1979; Gould and Murashige, 1985).

Allelopathy refers to the chemical inhibition of one species by another and describes the chemical interaction between two plants. Phenolics as a signal for growing and can directly affect the composition and activity of decomposer communities. Different types of soluble phenolics, such as ferulic acid, gallic acid or flavonoids, have been found to either stimulate or inhibit spore germination and hyphal growth of saprophytic fungi (Weir et al., 2004; Lattanzio et al., 2006). Phenolic acids strongly influence cell membrane potentials and supports the hypothesis that their influence on ion uptake (Glass and Dunlop, 1974). Phenolic acid effects on bud dormancy too. Several phenolics, e.g. catechin, caffeic acid, cinnamic acid, coumarin, 0- and p-coumaric acid, ferulic acid, salicyclic acid, kaempferol, quercetin and naringenin, have been identified as occurring in buds of woody species (Szember and Wocior, 1976; Altree-Williams et al., 1975). A correlation between the seasonal growth activity and endogenous levels of specific phenolics has been found in buds of sour cherry (Szember and Wocior, 1976). However, exogenously applied naringenin did not delay bud burst in peach Dennis and Edgerton (1961). It appears, that naringenin's role in peach bud dormancy is not one of causation or regulation.

Characterization of fruit cultivars with phenolic compounds

Varieties are often morphologically very similar and chemical analysis of plants is helpful for the distinction of closely related cultivars. Secondary compounds can play an important role in distinguishing cultivars. Whereas the conventional pomologist normally uses the fruit to distinguish cultivars, these techniques are lack of clear and are only semi quantitative (Martelock et al., 1994). Therefore, the phenolic “fingerprints” can be helpful to prove identification of cherry cultivars in an early stage of tree development (Geibel et al., 1990; Mısırlı, 2000a). Phenolic compounds occur in almost all higher plants; they show a high structural diversity within different tissues and therefore best suited as taxonomical markers (Geibel et al., 1990). The mean level of phenolic compounds in the apple cortex was different greatly among the cultivars and quantitative analysis of the phenolic compounds in the fruit with correspondence analysis of polyphenol profile has been found useful in taxonomic studies of apple cultivars for classification and identification (McRae et al., 1990). In order to identify cultivars of cherry cultivars, phenolic extracts of the inner bark layer (phloem) used to characterize a few cherry cultivars (Treutter and Feucht, 1985). Again, for characterization of cherry cultivars and seedlings HPLC method was used and unknown cultivars identified as a results (Geibel at al., 1990). Phenolic compounds of 23 sweet cherry varieties, including some local selections of the same variety, were analyzed to check their identity or distinctness. The high discriminatory potential of phenolic compounds for variety identification has been shown and different origins of the same variety have been identified (Martelock et al., 1994). Mısırlı (2000a) investigated the leaf phenolic compounds of apricot cultivars with thin layer chromatography and found different spot characteristics among parents and suggested that it was important from the point of parent-hybrid relations. Tannin content and other phenolic was determined as different in the mature and immature leaves of apricot cultivars (Mısırlı et al., 1993 a). Phenolic compounds and isoenzyme patterns of 12 cultivars of PRUNUS DOMESTICA were extracted from the inner bark (phloem) of 1-year-old shoots. The genetic relationship among these cultivars was studied by biochemical markers and compared with the systematical classification, as described by Hegi and Röder, based on morphological characters. As a result, a revised systematic, according to isoenzyme and phenolic marker is described (Groh et al., 1994). Comparision of peach cultivars for flavonoid and other phenolic compounds by high performance liquid chromatography (HPLC) procedures indicated that the cultivars were of 3 phylogenic types (LianSen et al., 1994)

Relationship between graft incompatibility and uses to detection incompatible graft

Graft incompatibility is an important criterion that should be considered during the selection process of new cultivars and rootstocks. It is suggested that biochemical causes, rather than anatomical ones, are responsible for the alterations at the cambial continuity. Phenolic compounds have been implicated in process of division, development and differentiation into new tissues (Errea, 1998; Mısırlı, 2000b). The concentration of phenolic compounds, the flavanols (catechins and proanthocyanidins) increase as a result of grafting stress (Feucht et al., 1992). Phenols escape from the vacuole into the cytoplasmic matrix where they are oxidized by peroxidases and phenoloxidases. These irreversible unions can also lead to protein precipitation resulting in cellular necrosis. These precipitations might be the cause of the necrotic line observed in the xylem of certain incompatible combinations. The field testing of newest graft combinations is of long duration and expensive. Phenol analysis is an applicable early sign for the prediction of graft incompatibility especially when new cultivars were used for different new cultivar/rootstock combinations. Phloem of *Prunus* spp. contains considerable amounts of polyphenols which are easily determined (Treutter et al., 1987; Usenik et al., 2006) and they can translocate around the graft union area. The accumulated polyphenols above the union were flavans, proanthocyanidins, chlorogenix acids. An increase of polyphenols as a symptom of incompatibility was frequently accompanied by more or less localized browning of phloem and is a symptom of graft compatibility. In *Prunus avium*, qualitative and quantitative amount of flavonoids changed and increased in the senescing interspecific graftings as compared to healthy homospecific ones, especially in the growing season (Treutter et al., 1987). Karadeniz and Kazankaya (1997) found a negative relationship between the graft success and the phenolic contents of the scions. Phenolic compounds are suggested as markers of graft incompatibility determination in the graft callusing stage in *vitis spp*. On the other hand, as a contribution to the investigation of the graft incompatibility of *P. avium*/*P. cerasus* combinations, the wall bound phenols of the phloem were determined and were found very slight quantitative differences due to the genotype. It has been assumed that wall bound phenols might not be responsible for bad union formation during the initial stage (Treutter et al., 1990).

Role of phenolic compounds in the resistance mechanism of fruit trees against pathogens and disease

There are numerous pests and pathogens in the natural environment of plants. The plant cell wall is a defensive system against external threats, including pollutants, mechanical wounding, and intrusion by pathogenic microorganisms and insects pests (Lagrimini et al., 1993). Plants produce secondary metabolites, many of which have antifungal activity. Some of these compounds are constitutive, existing in healthy plants in their biologically active forms. Some phenolics are stored in plant cells as inactive bound forms and are activated in response to tissue damage or pathogen attack (Osbourn, 1996). Well-known examples include phenols and phenolic glycosides, unsaturated lactones, sulphur compounds, saponins, cyanogenic glycosides, and glucosinolates. Phenolic compounds which play a major role in the growth regulation of living plant are known to be related with resistance. Naturally, resistant plants or specific tissues may have inherently higher phenolic contents. Activation of phenolic radicals with oxygen species obtains barriers (Southerland, 1991) such as lignin cellulose, callose, and suberin (DeLeeuw, 1985). Pecan and persimmon, which show resistance to the fungus *Dematophora necatrix*, the causal agent of white root rot disease, contain phenolic compounds which inhibit its growth. Roots of resistant crops contain higher concentrations of phenolic compounds than those of susceptible fruit species apple, almond and peach. Catechol, methylcatechol, hydroquinone and 8-hydroxyquinoline significantly inhibited the growth of the fungus (Sztejnberg et al., 1983). On the other hand, tannin content may increase after the infection as observed in Citrus cultivars that phenolic content in the leaves of the tolerant cultivars increased while remained same in the susceptible ones. Similarly, peach trees phenolics increase when attached by fungus (Wisniewski et al., 1984). It seems that differences in tannin content of apricot varieties strengthen them against to disease (Mısırlı et al., 1993b). Two constitutive secondary metabolites of the bitter orange *Citrus aurantium*, the flavanone-naringin, and the polymethoxyflavone-tangeretin showed antifungal activity against *Penicillium digitatum* (Arcas et al., 2000). Tyrosol, catechin, and oleuropein showed a greatest accumulation in the cortex of stem tissue and showed antifungal activity in vitro studies of olive (*Olea europaea* L.) thus affecting plant resistance against *Phytophtora* sp. (Del Rio et al., 2003). Phloridzin oxidation products has been found defensive in apple leaves against the scab fungus *Venturia inaequalis* (Raa and Overeem, 1968). Coumarin compounds have been reported to have some important physiological properties such as pathogen inhibition (Kim et al., 1991; Ortuno et al., 1997).

Effects of phenolic compounds on seed germination

It has been suggested that the inhibition of seed germination in fruit was generally not due to a single compound but was due to the synergistic action of several compounds. Some of phenolic compounds found in both seed coats and embryos and affect seed germination and dormancy. Hydroxycinnamic acids, coumarins, tannins and ferulic acid have been some of the common seed germination inhibitors (Bewley and Black, 1994). It has been suggested that phenolics may be active as germination inhibitors by inhibiting the transport of amino acids and the formation of proteins in the seeds (Lattanzio et al., 2006). Another possible function of the phenolic acids in seed germination may be their role in the synthesis and degradation of indole-3-acetic acid (IAA) (Rabin and Klein, 1957). In the peach seeds, products of amygdalin degradation (mandelonitrile, benzaldehyde and cyanide) do not seem directly related to the breaking of peach seed dormancy (Aitken, 1967). According to Bewley and Black (1994), testa of the seed protects the embryo, and contains some phenolics. There are some external applications of phenolic compounds for seed germination too. Peach juice is injurious to peach seed germination (Scot et al., 1942) while the flavonoid, naringenin, which has been isolated from peach buds by Hendershott and Walker (1959), has inhibited effect on lettuce seeds germination.

Dwarfing mechanism and phenolic compounds interactions

The use of small trees in orchard systems reduces manual labor thus provides economically advantageous. The most important issue in breeding studies is the determination of tree vigor. Phenolic compounds are thought to be related to the growth vigor of trees, however, there were not a causal link between phenolics compound content and dwarfism (Usenik and Stampar, 2002; Usenik et al., 2005). In the dwarfing mechanism, relationship of auxin with the bark stem is not clear but authors think that phenols are related to this mechanism, so mono-phenols has an antagonist effects with IAA while has an co-factor effects on peroxidase. Interaction of IAA and phenolic compounds in the bark tissue has a reducing effect on size of the scion. The presence of thick bark in apples has been associated with the dwarfing response and interested with the phenolic compounds (Lockard and Schneider, 1981; Weibel, 2008). The total phenolic content and some mineral nutrition of *Mahaleb* genotypes were found to different according to vigor capacity and suggested that total phenolic content and mineral nutrition can be used as a criterion for prediction vigor (Moghadam et al., 2007).

Uses of phenolic compounds in tissue culture

In vitro propagation of fruit species are very common and commercially use. The success of plant tissue culture as a means of plant propagation is greatly influenced by the nature of the culture medium used. The effects of adding phenols to culture media are mainly an enhancement of callus growth, more effective adventitious shoot formation, the improved rooting of shoots, and a greater rate of shoot proliferation in certain shoot cultures (George et al., 2008). The addition of phloroglucinol into culture media containing growth substances was able to enhance growth and the rate of axillary shoot production from shoot cultures in *Malus* and *Prunus* (Jones, 1976; Jones, 1979). Vitrification is prevented by phloroglucinol in most of plants (George et al., 2008). Rooting may be stimulated by phloroglucinol when added to rooting media together with auxin. This effect has been especially noted in apple (Zimmerman, 1984), in *Prunus* (Hammerschlag et al., 1987; Hammatt, 1994), strawberry and *Rubus* genotypes (James, 1979), and *Prunus cerasifera* (Hammerschlag 1982). Chlorogenic acid has been stimulating callus growth of *Prunus avium* stem segments (Feucht and Johal, 1977).

Importance of phenolic compounds during the storage of fruits

Phenolic compounds affect the strength of fruits during storage (Lattanzio et al., 2006). Many simple low molecular phenolic compounds are polymerized by oxidation to yield brown tannin-like substances for defensing system. Thus, oxidized phenolics in resistant varieties of apple play an important role in the restricted lesion formation associated with the brown rot disease of fruits caused by *Sclerotinia fructigena* Aderh (Byrde et al., 1960) or with rotting of stored Golden Delicious apples caused by *Phlyctaena vagabunda* (Lattanzio et al., 2001). Green mould caused by *Penicillium digitatum* is a big problem for stored citrus fruit and cause huge losses. Usually synthetic fungicides are employed to control this disease but they have adverse effects on human and environmental health. Some phenolic compounds, quercetin, scopoletin and scoporone, tested *in vitro* and *in vivo* against *P. digitatum*. These compounds present in several agricultural crops and associated with response to stress. As a result, phenolics significantly reduced disease symptoms and represent an interesting alternative to synthetic fungicides (Sanzani et al., 2014).

Phenolic compounds and effects on fruit processing

Phenolics are also important because of their effects during the technological processes used for obtaining the juices and other transformation products (Raynal et al., 1986, Spanos et al., 1990). It was showed that some phenolic compounds could be useful in characterization and differentiation of fruit juice too (Simon et al., 1992; Abad-Garcia et al., 2012).

Conclusion

Phenolic compounds are widely distributed in plant and play significant roles in their life-cycle. Different uses and advantages have been described in fruit growing. They are a part of the plant nature and need to deep research on these compounds.

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