



Review

# The Impact of Production Technology on Plant Phenolics

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**Abstract:** Due to rising public pressure in recent decades, alternatives for large-scale and industrial farming are being sought. Environmental and sustainability issues and the rising awareness of the link between the overuse of pesticides/fertilizers and negative health effects have been key factors for creating the integrated production approach, which encompasses environmentally friendly technologies. Moreover, the demand for organically grown products is constantly growing. The organic production model is a step towards further restriction of synthetic chemical use in plant production. Limited use of pesticides may boost the plant's investment into its own defense systems, which may result in a higher content of secondary compounds. Synthesis of secondary metabolites is a common plant response to any form of stress (biotic or abiotic), and their function is to help the plant overcome unfavorable conditions. Many compounds, especially phenolics, are also considered beneficial for human health; therefore, numerous studies comparing different production systems have been conducted in the past 20 years. Generally, organically produced food may contain greater amounts of health beneficial compounds and diminished levels of pesticide residues and nitrates. However, the results are not always clear, as other factors may influence the composition of natural products (e.g., environmental and varietal factors, sampling, and the design of experiments). Therefore, controlled field trials, in which most of the factors can be either controlled or at least recorded, should be encouraged. The present paper synthesizes the function of phenolics as a response to different forms of stress, which can occur during plant growth, with a special emphasis on different production systems. Examples of diverse horticultural crops are presented.

**Keywords:** organic; biodynamic; integrated; conventional; phenolics

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## 1. Introduction

In 2013, the UN forecast a world population of 9.6 billion people by 2050, presenting a major challenge for agriculture. Food production needs to increase in order to feed and sustain approximately two billion more people than there are today. At the same time, global awareness is rising, and consumers demand safe, high-quality food, produced according to environmental and animal friendly standards that take into account social and economic aspects [1]. This is a difficult task for any production technology whether based on conventional, integrated, or organic approaches and principles. High yields of excellent quality and the minimization of negative impacts on the environment seldom go hand in hand. Conventional agriculture strongly relies on the use of synthetic pesticides and mineral fertilizers as well as other off-farm inputs to control plant growth. Meanwhile, organic farming emphasizes sustainable technologies, replacing the synthetic pesticides and fertilizers with those of natural origin such as plant extracts, organic manures, and natural minerals. It also uses crop rotation, advanced orchard designs, and resistant cultivars [2]. Integrated production is a compromise between both production systems. It still relies on the use of synthetic pesticides and fertilizers; however, the application is restricted and the self-defense of plants is encouraged.

Food produced according to conventional or integrated practices can contain residuals of chemicals used for plant protection. However, their levels should not exceed maximum permitted limits. In a review by Smith-Spangler et al. [3], it was reported that organic fruit, vegetables, and grains have about a 30% lower risk of containing pesticide residues compared with conventional produce. Fourfold higher pesticide residues in conventional crops have also been reported by others [4]. Organic production is generally more energy-efficient, as energy use is much more effective compared with conventional farming [5]. However, the impact is not as significant in fruit production.

Increased organic production of various horticultural crops (especially fruits and vegetables) has been recorded over the last 20 years. Moreover, these production technologies have gained a great deal of scientific attention. The driving force behind such rapid increase in importance is the growing consumer demand for organic horticultural produce [2]. Consumers often believe that organic food is healthier and more nutritious compared with the conventional one and, for that reason, they are willing to pay more for the former [6]. However, are the differences really that evident? In the past several years, numerous studies have been undertaken to answer this question. Some were able to prove increased levels of health-beneficial compounds in organically grown natural products. In contrast, others have not been able to detect any differences between the two production systems, or have even attained less favorable results for organic crops. Different reviews consisting of diverse analytical approaches have been prepared. Even so, the results have not always been consistent. For example, Dangour et al. [6] based their review on 55 studies and summarized that organic versus conventional food does not conclusively show any differences in nutrient content except for nitrogen, which was higher in conventional food, while phosphorus and titratable acidity were higher in organic food. Smith-Spangler et al. [3] also reported higher phosphorus content in organic produce. Additionally (and beneficially), organic food is also characterized by higher phenolic levels. An increased amount of phytochemicals (particularly phenolics) in organically grown produce has similarly been reported by others [2,4].

## 2. Plant Secondary Metabolites with Special Emphasis on Phenolics

Plants synthesize an enormous variety of organic compounds that serve the plant in chemically mediated interactions in their biotic and abiotic environment [7]. Those compounds are often characterized as secondary metabolites to be distinguished from primary ones, which are involved in basic cell metabolic processes of the plant. Secondary metabolites may have beside other functions also an important protective role against different forms of stress. They are synthesized as a normal part of plant metabolism, often produced in specialized cells or tissues, and tend to be more complex than primary compounds [8]. Plants produce secondary metabolites as a response to non-favorable environmental conditions or in particular developmental stages. Their biosynthesis is initiated from a particular primary metabolite or from intermediates of primary metabolism. Many accumulate in surprisingly high levels in some species. So far, many thousands of molecules have been identified underlining the diversity and complexity of plant secondary metabolism. These compounds can be characteristic for a certain plant family, genus, or even species and therefore may be used as taxonomic tools in classifying plants [9].

Although ignored until recently, their function in plants is now attracting attention as some appear to have a key role in mutualistic interactions of plants and other organisms such as animals (pollinators, seed dispersals), fungi (mycorrhiza), and bacteria (formation of nitrogen-fixing root nodules in legumes). They are important in the protection of the plant against various abiotic stress forms (e.g., excessive UV radiation, drought, wounding) as well as in chemical plant defense against herbivores and pathogens [7]. They may also play an important role in plant–plant interactions, in which they function as allelochemicals with either positive or negative effects on the neighboring plants.

Secondary metabolites also represent an economic interest as they can be used for dyes, fibers, glues, oils, waxes, flavoring agents, drugs, and perfumes, and they are viewed as potential sources of new natural drugs, antibiotics, insecticides, and herbicides [10]. The role of selected secondary

metabolites as protective dietary constituents has become an increasingly important area of human nutrition research in recent years. These compounds are not essential for short-term well-being, but there is increasing evidence that modest long-term intake can have favorable impacts on the development (via suppression) of many chronic diseases [11].

Based on their biosynthetic origins, plant secondary metabolites can be divided into three major groups: (a) phenolics; (b) terpenoids; and (c) nitrogen-containing compounds.

Plant phenolics are one of the most important groups of secondary metabolites found throughout the plant kingdom with more than 10,000 molecules reported. Phenolics are synthesized from aromatic amino acids, predominantly from phenylalanine, and therefore are characterized as having at least one aromatic ring with one or more hydroxyl groups attached [12]. Phenolics range from simple, low molecular-weight compounds with a single aromatic ring, such as phenolic acids, to large and complex molecules such as tannins. The most prominent group of phenolics is the flavonoids with two aromatic rings. Sugars, organic acids, and other compounds are often bound to the rings, and the compounds are water-soluble. However, some flavonoids form large water-insoluble polymers. They are mostly stored in vacuoles of the epidermal cell of plant organs or specialized cells fulfilling their function as secondary metabolites. Another important group of phenolics, chemically related to flavonoids, are stilbenes with resveratrol as the most compound in this group [13].

Similar to other secondary metabolites, phenolics have been linked to numerous ecological functions. They often act as a part of plant responses to biotic and abiotic stimuli. They are not only indicators of plant stress responses to various abiotic factors such as intensive light or mineral deficiencies, but are also one of the most important compounds in plant resistance and tolerance against pests and diseases. They represent a biochemical basis for successful reproduction of the plants, which synthesize them to attract pollinators or seed-dispersing animals. Phenolic-based polymers, such as lignin, suberin, or tannins, contribute substantially to the stability and robustness of plant tissues, towards mechanical or environmental damage, such as drought or wounding [12].

Phenolics can act as allelopathic compounds. A good example is juglone, a chemical released from the decomposing plant material of *Juglans nigra* (black walnut). Plants which synthesize and release allelochemicals mostly influence the performance of neighboring plants in a negative way, gaining advantage in nutrient, water, or light acquisition. Targeted positioning of allelopathic plants could be utilized in crop rotations with the aim of reducing pesticide use and enhancing crop yields. However, additional research on allelopathic compounds and their dynamics is needed to efficiently implement these measures [1].

### 3. Factors Influencing the Level of Phenolics

In principal, phenolic content differs between species of the same family, even between cultivars. In the study of Veberic et al. [14], 22 apple cultivars were analyzed and it was clearly demonstrated that phenolic content was far more genotype-dependent than influenced either by organic or integrated production. Moreover, diverse plant organs or even tissues can be characterized by different phenolic composition. Normally, phenolics are concentrated in the epidermal tissue where they fulfill their biological function.

Ripening is an important factor affecting the phenolic content of horticultural crops, especially fruit. In red-colored fruit, such as red apple cultivars, their anthocyanin content increases with maturity. At the same time, the level of other phenolic groups, especially those responsible for the astringent taste, decreases [15]. In some cases, phenolic content is higher in unripe produce, but these crops are seldom edible. Still, they can be considered as potential sources for phenolic extraction [11].

Any form of important deviation from the environment is considered stress for the plant and provokes responses in its phenolic metabolism. One of the major triggers upregulating phenolic content is the exposure of plant tissue to intensive light, especially UV-light. In nature, this is often accompanied by high temperatures and results in photo-oxidative damage to the photosystem complex. The recognition of the stress event at the cellular level triggers repair processes in the cells as well as

de novo synthesis of protective substances. Many of these protective compounds belong to different groups of phenolics. The effect of excessive sun irradiation on phenolic accumulation has been confirmed in a study by Zupan et al. [16], in which light-exposed apples contained increased levels of total and several individual phenolics compared with the shaded part of the same fruit or fruit growing in full shade. The highest levels of phenolics have been measured in the part of the fruit damaged by sunburn. Jakopic et al. [17] demonstrated that anthocyanin content in apple skin was strongly light-dependent and that the use of reflective cover increased their synthesis. On the other hand, the use of hail nets can reduce their phenolic content as shown for the French bean (*Phaseolus vulgaris*) [18]. Both practices, reflective cover and various colors of anti-hail nets, are widely applied in different fields of horticulture production. Greenhouse covering can additionally affect the content of phenolics in vegetables, especially if it modifies UV radiation.

Stress factors can be prevented or, on the other hand, caused by different cultivation techniques. In this aspect, fertilization is especially important. It is well-known that high nitrogen doses improve plant growth but to some extent reduce the amount of phenolics, often making the plants more susceptible to pests and diseases. On the other hand, nutrient deficiency can cause accumulation of certain phenolics. One of the reasons could be that growth is inhibited with a deficiency and the carbon is allocated to secondary metabolites [10]. This was especially shown for phosphorus [12] where deficiency often results in increased accumulation of anthocyanins. However, foliar fertilization with a phosphorus–calcium mix significantly improved red color formation in apples [19]. Salt stress due to a high concentration of certain ions can increase the phenolic content as shown in a number of plant species [10]. An optimized water supply in cultivation technology is needed to guarantee normal growth and yield as well as phenolic composition of crops, where a mild water stress could be beneficial in this aspect [12].

#### 4. Phenolics and Plant Disease

Plants are constantly in contact with other organisms including those that are pathogenic which try to get nutrients from plants. Plants have developed defense mechanisms to protect themselves, and pathogens have established countermeasures to overcome these mechanisms. Plants invest in physical (e.g., cell wall, cuticle, trichomes) and chemical barriers (different secondary compounds), which should protect them from invading organisms. These barriers can be either pre-formed (stored phytochemicals are called phytoanticipins) or induced with pathogen attack (de novo synthesized phytoalexins) [9].

Each species, or closely related species, can form characteristic molecules that act as defense compounds against specific or nonspecific pathogens. Most antimicrobial natural products have relatively broad spectrum activity. Specificity is often determined by whether or not a pathogen has the tools to enzymatically detoxify a particular host product.

The first line of the defense response to a pathogen attack is the recognition of the pathogen molecules. These elicitors (peptides, oligosaccharides, or glycoconjugates) originate from the pathogen or are plant-derived molecules released at wounding. The host recognition of pathogen elicitors initiates early cellular responses, such as alterations in plant cell walls, changes in ion fluxes, the accumulation of reactive oxygen species and reactive nitrogen species, and gene transcription [20]. The second line of defense responses leads to the induction of plant defense genes and biosynthesis of endogenous secondary metabolites, cell wall fortification, and, very often, hypersensitive responses and the activation of systemic acquired resistance [20,21].

As shown for apple scab fungus (*Venturia inaequalis*), susceptible and resistant cultivars contain similar amounts of pre-formed phenolic compounds [15]. After infection, susceptible apple cultivars start to accumulate phenolic compounds and the corresponding enzymes are upregulated, especially around the symptomatic spot. However, they are unable to prevent the spread of the fungus [22,23]. The authors conclude that phenolics are not the only resistance mechanism present in apple plants. Moreover, not just the quantity but also the speed of the plant response is crucial for its increased

resistance. When the induced responses are triggered rapidly during a plant–pathogen interaction, the plant is resistant to the disease. Contrarily, post-infection defense mechanisms are established at a slower rate in susceptible plants.

## 5. Phenolics and Type of Production

In the organic cultivation of fruit crops, no synthetic chemicals such as fertilizers, pesticides, and fruit thinning agents are used. Only natural compounds are allowed, and their use is closely monitored. In theory, differences between organic and conventional cultivation may lead to enhanced content levels of phenolics in organically produced fruits. This was clearly demonstrated in apple leaves and fruits of four cultivars in a two-year trial, as the research reported a somewhat higher content of individual and total phenolics in leaves and fruit of organically grown apples compared with apples from integrated cultivation [24]. The authors concluded that this difference lay in the fact that trees exposed to various stress factors synthesized more protective compounds (i.e., phenolics). The lack of pesticides in organic production allowed the incidence of injuries and pathogen infections due to higher disease pressure and potentially elevated the phenolic content in plant tissue. Similarly, fully ripe biodynamic and organic mangoes, compared with conventional grown ones, were characterized by a significantly higher amount of flavonoids [25]. Lima et al. [26] compared different plant parts from organic and conventional production. They confirmed the hypothesis of higher total phenolic and flavonoid content in organically produced plants, but not in all cases.

Many studies have demonstrated the impact of fertilization on the phenolic content. In organic farming, nutrients are often supplied through compost, manure, and plant-derived byproducts. Organic nitrogen is transformed into the inorganic form by soil microflora, so the level of nutrient availability to plants may be difficult to control. Toor et al. [27] reported that tomatoes fertilized with chicken manure or grass-clover had lower shoot biomass compared with those fertilized by mineral nutrient solution, despite the fact that NPK macronutrient input per plant was higher in the organic fertilization treatments. However, the organic fertilization treatments led to a 17.6% higher soluble phenolic content. Toor et al. [27] summarized that the carbon surplus, which was not utilized for growth due to the slow release of nutrients from the organic manure, was allocated to the production of secondary metabolites, in particular phenolics. Bavec et al. [28] similarly demonstrated that biodynamic red beet (*Beta vulgaris* L. ssp. *vulgaris*) accumulated higher levels of total phenolics than did red beets from a conventional farming system. The authors also list, among other factors, lower availability of nutrients in the biodynamic farming system.

Nitrogen use efficiency and availability to plants is better in conventional production as inorganic nitrogen is applied. Roussos and Gasparatos [29] observed higher nitrogen content in conventionally grown apple fruit compared to organic apples. Increased width and higher fresh weight of the conventional fruit have been recorded, but there were no differences in major metabolites compared with organic apples. Additionally, organic apples contained more calcium, which influences the storability of the fruit. However, a higher copper content has been measured in conventionally grown apples due to the use of fungicides. Similarly, Jakopic et al. [30] reported that organically produced apples had 14% less weight than integrated ones. Integrated apples had higher amounts of sugars and higher organic acid levels, but decreased amounts of phenolics. In a trial on French beans, a yield reduction was noted in organic production compared with the integrated and conventional systems [31], although higher nitrogen input in the form of cattle manure was characteristic of the organic production. The sum of phenolics in the pods was not significantly different among the production systems, with a tendency for a higher amount in the integrated system. Meanwhile, ascorbic acid content was the lowest in the conventional system, and sugar levels were the highest in the organic system.

Orchard soil management is an important issue because of the reduction of weed occurrence, reduction of soil erosion, and optimal water and nutrient management. In conventional fruit production, herbicides are used under the trees to avoid any competition for nutrients. Living mulch

(green cover plants) is particularly important due to its benefits for orchard biodiversity and soil quality, which is crucial in organic production. In addition to generally reported benefits of their utilization in the orchard, it has been established that different types of living mulch positively influence the content of phenolics in the fruit [32].

It would be interesting to determine whether the storage life of fruits can be influenced by different production types. Production technology had little effect on the storage of cashew nuts, as it did not influence the content of phenolic for up to 180 days of storage. The soluble solids were higher in conventional farming [33]. Various quality parameters have been monitored over six months of apple storage, and it was demonstrated that changes mainly occurred due to different storage conditions rather than possible effects of organic versus integrated production systems [34].

## 6. Conclusions

Despite the fact that the literature lacks unequivocal evidence of a higher content of primary and secondary metabolites in organically produced food, there are some indications that higher biotic and abiotic stresses can influence plant secondary metabolism, especially the synthesis and accumulation of phenolics. There are still many areas, such as the use of allelopathic plants, natural pesticides, and stimulation of plant immune system, that can improve the performance and yield of organically grown plants. Conventional production could include more organic approaches without the fear of yield reduction or loss of quality as has been done in integrated production systems.

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