

Role of Secondary Metabolites in Plants

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Abstract

Secondary metabolites are chemicals that are ubiquitously found in plants. These metabolites are produced in a particular stage of development of plants, or due to particular environmental conditions provided to the plants. Secondary metabolites do not have a role in the growth or development of plants; however, they are known to provide protection to the plants. Recent studies have revealed that dietary consumption of secondary metabolites provide protection against cancers, diabetes and cardiovascular diseases. Secondary metabolites also provide antioxidant anti-inflammatory and antimicrobial properties.

Keywords: *Alkaloids, Polyphenols, Phenols, Terpenes, Secondary metabolites.*

Introduction

Secondary metabolites are biomolecules which are classified as non-nutrient molecules and are present in all parts of plants. Secondary metabolites also referred to as secondary products, specialized metabolites or natural products play a critical physiological role in plant metabolism. Recent studies have revealed an important role of secondary metabolites in various functions like defense mechanisms of plants, attractants of pollinators, allelopathy and pharmacognosy (Pagre et al., 2015; Ramakrishna and Gokare, 2011). The main type of secondary metabolites are terpenes phenolics and nitrogen containing compounds (Teoh, 2015).

Terpenes

Terpenes are the most diverse group of compounds found naturally in plants. These are having the formula $(C_5H_8)_n$ isoprene units and therefore, also referred to as isoprenoids. Terpenes include rubber, steroids, hormones, essential oils and carotenoids (Singh and Sharma 2015). On the basis of the number of isoprene units, terpenes may be monoterpenes (2 isoprene units), diterpenes (4 isoprene units), triterpenes (6 isoprene units) etc. Terpenes with less than 5C are known as hemiterpenes. Terpenes may further be classified on the basis of aromatic rings. Terpenes with aromatic rings are also known as essential oils. They cause the characteristic odor from the plant part and may be present in secretory cavities or glandular hair. Carotenoids are tetraterpenes and function as accessory pigments. Accessory pigments help in saving plants against photooxidation (Havau, 2013). They are also responsible for providing color to flowers and fruit and thus help in the dispersal of seeds. Terpenes are lipophilic and hence help in the adhesion of various electron carriers like plastoquinones, ubiquinones (Boronat and Rodríguez-Concepción, 2015). Sterols are also formed from terpenes, as they are formed by acyclic terpene, squalene. Sterols help in the enhancement of stability of membranes, as they help in the regulation of membrane fluidity permeability and rigidity. Saponins are triterpene glycosides which have soap/detergent like properties. They cause soap like foaming when shaken in aqueous medium. Saponins have the ability to interact with cell membranes of erythrocytes causing cell shrinkage and haemolysis. Saponins have also been known to cause necrosis of cancer cells, thus of medicinal usage (Sawai and Saito, 2011). Rubber is a polyterpene in which the terpenes are arranged in a spiral manner providing the special elastic effect to rubber (Sarkar and Bhowmick, 2018).

Functions and application of terpenes

Terpenes aid in growth and development of plants, in form of plant hormones. Gibberellins, Brassinosteroids, cytokinin, abscisic acid are all examples of terpenes and aid in the growth and development of plants (Tarkowská and Strnad, 2018). Many terpenes interact with the membrane and provide stabilization to the

membrane structures. Sterols form components of cell membrane and provide stability to the membranes. Terpenes also provide defense to the plants against pathogens. Leaves of *Chrysanthemum cinerariaefolium* accumulate pyrethroids which have insecticidal properties (Chrutek, 2018). Azadirachtin is present in leaves of *Azadiracta indica* which acts as insect deterrent (Chaudhary et al., 2017). Due to the properties of terpenes, they have a use in various industries like food industry, agrochemicals, pharmaceuticals, aroma and fragrance industries. Various terpenes are used to enhance the flavor of food (eg. Menthol in leaves of *Mentha*). Vitamin A, D, E, and K are terpenes which have nutritional values. Terpenes thus act as nutraceutical which are part of food and provide medical or health benefits. The example of golden rice can be quoted which has increased amount of β carotene, to treat vitamin A deficiency in kids and women. Terpenes from *Taxus brevifolia*, taxol is known to cure ovarian cancers (Witherup et al., 1990). *Artemisia annua* is known to contain artemisinin, a terpene which is used as a cure for malaria (Elfawal et al., 2012). Many terpenes can thus function to cure many life threatening diseases.

Phenolics

Phenols/Phenolic compounds/Polyphenols refer to a group of secondary metabolites which have six carbon benzene rings with one or more hydroxyl functional group. Phenols have a higher boiling point, and are more acidic than other hydroxyl group as the hydroxyl group is situated on the stable benzene ring. Phenols are extensively distributed in plants and may act as protective substances like lignin, suberin and sporopollenin present in pollen (Wallace and Fry, 1994). Some phenols, however, may be specific to a particular family or genus and thus be used as a taxonomic trait. In general, poly phenols may be classified into phenolic acids, lignans, flavonoids and stilbenes. Phenolic acids can be further divided into derivatives of benzoic acid and derivatives of cinnamic acid. Benzoic acid derivatives consist of C₆-C₁ unit. They include salicylic acid, gallic acid. Benzoic acid derivatives have allelopathic properties. Derivatives of cinnamic acid include p-caumaric acid, caffeic acid and ferulic acid. These phenols have been reported to have antioxidant and anti-inflammatory properties (Alam et al., 2016). Derivatives of coumaric acid provide anti-microbial and anti-germination properties (Hüseyin, 2015). Dicoumarin a derivative of coumaric acid causes fatal hemorrhage in cattle and is found in moldy hay. Furanocoumarins another derivatives of coumarins acts as toxic when activated by UV-A. They are present in members of Apiaceae and Rutaceae. Lignins are branched polymer of phenolic alcohols. Lignins are deposited mainly in the secondary cell wall and they provide strength and rigidity to plants. Lignification of various cells like tracheary tissues help them in conducting water. Lignins also provide protection against herbivorous animals as it is indigestible to them. Lignans are diphenolic compounds formed by dimerization of cinnamic acid. Some lignans are also considered as phytoestrogens (Pandey and Rizvi, 2009). Lignans are known to have medicinal properties and preventive action against carcinogenesis, atherosclerosis and osteoporosis (Patisaul and Jefferson, 2010). Flavonoids are polyphenolic compounds with 15-carbon chains arranged in two aromatic rings. They function in UV protection, pathogen resistance and pigmentation. Flavonoids can be mainly four groups, anthocyanins, flavones, isoflavones, flavonols and tanins. Most of the flavonoids are water soluble and have a sugar moiety attached to them. Flavonoids absorb UV-B rays, and provide protection to the plant. Anthocyanins are colored flavonoids which provide red, yellow, purple, blue coloration to plant parts. Anthocyanins are stored in vacuoles of epidermal cells, and attract insects in order to cause dispersal of seeds (Khoo, 2017). Flavones and flavonols differ from the anthocyanins by having different molecules in the central ring. They are not visible to human eye, but are visible to insects, especially bees. It has been reported that flavones and flavonol form symmetrical patterns or stripes to indicate the position of pollen and nectar. Isoflavonols are found in leguminous plants, which are secreted as a response to the pathogens. They mainly provide insecticidal properties in plants (rotenone) and can be used as pesticides (Kaufman et al., 1997). Stilbenes are produced in plants in response to an infection by fungi and hence act as antifungal phytoalexins. Resveratrol is found woody organs of plants and is produced in leaves and fruits and provides resistance against fungal pathogen (Kim et al., 2008). Tannins are polyphenolic compounds present in the bark, fruit, and fruits of plants. Tannins have the ability to bind and denature

proteins. Tannins protect the plants from fungi and bacteria as they coagulate cell wall degrading enzymes and prevent their infection. Tannins also cause astringent taste of unripe fruits (Chung,1998).

Function and application of Polyphenols

Polyphenols have a cardio-protective role. It has been known that atherosclerotic lesions cause sudden cardiac death. Polyphenols act as antioxidant, anti-inflammatory and thus have a role in protecting against cardiovascular disease. Resveratrol prevents platelet aggregation and inhibits vasoconstriction. Polyphenols also provide anti-cancer effects. Polyphenols reduce the growth and number of tumors. Quercetin and resveratrol have been reported to show anticancer activity (Del Follo-Martinez et al., 2013). It has been revealed that polyphenols can regulate cell growth, apoptosis due to its antioxidant activity. Polyphenols also show anti-ageing effects. Anthocyanins present in various fruits show protection against UV, and have antioxidant activities. They also inhibit lipid peroxidation. Polyphenols also provide taste (bitterness), hence causing flavor in tea and coffee.

Nitrogen containing compounds

Various secondary metabolites have nitrogen in their structure. They include alkaloids, cyanogenic glycosides, glucosinolates and non-protein amino acids (Bennett RN and Wallsgrave, 1994). Alkaloids are usually alkaline in nature and are present in cytosol or vacuoles. They are present in many families of angiosperms like Magnoliaceae, Solanaceae, Rubiaceae, Apocynaceae, Ranunculaceae, Papaveraceae. Glycosides are secondary metabolites in which sugar forms a glycosidic bond with hydroxyl group of another molecule. Glycosides have detergent-like properties and have an important role in growth and development, plant defense mechanisms and signaling pathways. Glycosides may further be classified into saponins, glucinolates, cardenolides and cyanogenic glycosides (Bolarinwa et al., 2016). Saponins, triterpene glycosides, are usually present in the roots where they act as antimicrobial molecules. Release of saponins in the rhizosphere also provides protection to the plant against soil borne pathogens. Cardioactive glycosides include alkaloids which act on the contractile force of heart muscles. Two major types of cardioactive glycosides include cardenolides and bufadienolides. Glycosides from Digitalis have been known to increase contractile force of heart muscle thus increasing the blood flow. Cyanogenic glycosides are nitrogen containing secondary metabolites that give rise to hydrogen cyanide under certain conditions. Hydrogen cyanide can inactivate respiratory enzyme, cytochrome, which blocks nervous system. Cyanogenic glycosides are present in various families of angiosperms including Poaceae, Rosaceae, Linaceae and Fabaceae. In plants, cyanogenic glycosides provide protection to the plants by repelling herbivores and other insects. Glucosinolates/ thioglycosides/mustard oil glycosides are sulfur-containing secondary metabolites, with nitrogen. They result in pungent taste and flavor present in various cruciferous vegetables like radish, broccoli (Fujioka, 2003). They are also present in Capparaceae, Caricaceae, and Resedaceae families of angiosperms. They have antibacterial properties and also break down to release isothiocyanates which provides protection to the plant (Ikekawa et al., 1991). Non- protein amino acids are unusual amino acids that are not incorporated into proteins. These non-protein amino acids are similar to other amino acids. These non- protein amino acids may be toxic as they may stop the synthesis or uptake of normal amino acids. As an example canavanine is the non-protein amino acid of arginine. An incorporation of canavanine in place of canavanine in place of arginine may cause the formation of nonfunctional protein, as its tertiary structure or catalytic site may be disrupted. Non-protein amino acids do not pose a challenge to the plants as the plants are able to recognize the nonfunctional amino acids. The non-functional amino acids however pose a challenge to the herbivores or other insects feeding on plants with non-protein amino acids (Rodgers,2014).

Functions and applications of nitrogen containing secondary metabolites

Alkaloids have medicinal properties. The first alkaloid isolated from plants was morphine and has been used as a cough medicine, sedative and a pain reliever. Chloroquinone, an antimalarial drug is also an alkaloid related to quinine. Many drugs have been synthesized on the basis of natural alkaloids. Many alkaloids also protect the

plant against herbivory. Many alkaloids are bitter in taste and cause poisoning in grazing animals when taken in large quantity. Alkaloids also have ecological functions. Many insects acquire alkaloids from plants and convert them enzymatically into pheromones, which are used for attracting mates or for defense purposes. Saponins from *Quillaja sponaria* bark are added as emulsifiers in shampoos, toothpastes and detergent (Maier et al., 2015) Glycosides from *Digitalis* have been reported to reduce atherosclerosis (Wasserstram JA and Aistrup, 2005).

Secondary metabolites thus form an important component of biomolecules in plant life. Plants are sessile in nature, and therefore secondary metabolites help the plants to interact with the environment, in form of pathogen protection, against abiotic stress (UV, heat), attracting insects for seed and pollen dispersal and also protect them against herbivory. The important role of secondary metabolites cannot be underestimated for plants and therefore, the secondary metabolites are important for the success of plant life.

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