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Secondary Metabolites in plants and their significance

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Introduction

Secondary metabolites (SMs) are not necessary for a cell (organism) to live, but play a role in the interaction of the cell (organism) with its surroundings, ensuring the continued existence of the organism in its ecosystems. Formation of SMs is generally organ, tissue and cell specific and these are low molecular weight compounds. These compounds often differ between individuals from the same population of plants in respect of their amount and types. They protect plants against stresses, both biotic (bacteria, fungi, nematodes, insects or grazing by animals) and abiotic (higher temperature and moisture, shading, injury or presence of heavy metals). SMs are used as especially chemical such as drugs, flavours, fragrances, insecticides, and dyes by human because of a great economic value.

Types of Secondary Metabolites

In plants, SMs can be separated into three groups (Terpenoids, Polyketides and Phenypropanoids) based on their biosynthesis origin. Alkaloids are additional class of SMs, which are nitrogenous organic molecules biosynthesized mainly from amino-acids, e.g., tryptophan, tyrosine, phenylalanine, lysine and arginine using many unique enzymes. Many of the most important therapeutic agents are alkaloids. The sites of biosynthesis are compartmentalised at cellular or sub-cellular level. However SMs can be transported long distances and accumulate from their location of synthesis.

Plants secondary metabolites can be divided into four chemically distinct groups viz: Terpenes, Phenolics, N (Nitrogen) and S (sulphur) containing compounds.

I)Terpenes : Terpenes comprise the biggest group of secondary metabolites and are free by their common biosynthetic origin from acetyl-coA or glycolytic intermediates. An immense bulk of the diverse terpenes structures produced by plants as secondary metabolites that are supposed to be concerned in defense as toxins and feeding deterrents to a large number of plant feeding insects and mammals. Terpenes are divided into monoterpenes, sesquiterpenes, diterpene, Triterpenes and polyterpenes. The pyrethroid (monoterpenes esters) occur in the leaves and flowers of Chrysanthemum species show strong insecticidal responses to insects like beetle, wasps, moths, bees, etc and a popular ingredient in commercial insecticides because of low persistence in the environment and low mammalian toxicity. In Gymnoperms (conifers) á-pinene, â-pinene, limonene and myrecene are found. A number of sesquiterpenes have been till now reported for their role in plant defense such as costunolides are antiherbivore agents of family composite characterized by a five member lactone rings (a cyclic ester) and have strong feeding repellence to many herbivorous, insects and mammals. ABA is also a sesquiterpene plays primarily regulatory roles in the initation and maintenance

of seed and bud dormancy and plants response to water stress by modifying the membrane properties and act as a transcriptional activator. Abietic acid is a diterpene found in pines and leguminous tress. It is present in or along with resins in resin canals of the tree trunk. Another compound phorbol (Diterpene ester), found in plants of euphorbiaceae and work as skin irritants and internal toxins to mammals. The milkweeds produce several better tasting glucosides (sterols) that protect them against herbivors by most insects and even cattle. Several high molecular weight polyterpenes occur in plants. The principal tetraterpenes are carotenoids family of pigments.

(II) Phenolic compounds : Plants produce a large variety of secondary products that contain a phenol group, a hydroxyl functional group on an aromatic ring called Phenol, a chemically heterogeneous group also. They could be an important part of the plants defence system against pests and disease including root parasitic nematodes. Elevated ozone (mean 32.4ppb) increased the total phenolic content of leaves and had minor effects on the concentration of individual compounds. Coumarin are simple phenolic compounds widespread in vascular plants and appear to function in different capacities in various plant defense mechanisms against insect herbivores and fungi. They derived from the shikimic acid pathway, common in bacteria, fungi and plants but absent in animals Some coumarin derivatives have higher antifungal activity against a range of soil borne plant pathogenic fungi and exhibit more stability as compared to the original coumarin compounds alone. Furano is Also a type of coumarin with special interest of phytotoxicity, abundant in members of the family umbelliferae including celery parsnip and parsley. Psoraline, basic linear furacoumarin, known for its use in the treatment of fungal defence and found very rarely in SO2 treated plants. Ligin is a highly branched polymer of phenyl- propanoid groups, formed from three different alcohols viz., coniferyl, coumaryl and synapyl which oxidized to free radical (ROS) by a ubiquitous plant enzymeperoxidises, reacts simultaneously and randomly to form lignin. Its physical toughness deters feeding by herbivorous animals and its chemical durability makes it relatively indigestible to herbivorous and insects pathogens. Lignifications block the growth of pathogen and are a frequent response to infection or wounding. Flavanoids perform very different functions in plant system including pigmentation and defence. Two other major groups of flavanoids found in flowers are flavanones and flavanols function to protect cell from UV-B radiation because they accumulate in epidermal layers of leaves and stems and absorb light strongly in the UV-B region while letting visible (PAR) wavelengths throughout uninterrupted. In addition exposure of plants to increased UV-B light has been demonstrated to increase the synthesis of flavanones and flavanols suggesting that flavanoids may offer measures of protection by screening out harmful UV-B radiation. Isoflavanoids are derived from a flavanones intermediate, naringenin, ubiquitously present in plants and a play a critical role in plant developmental and defence response. They secreted by the legumes and play an important role in promoting the formation of nitrogen fixing nodules by symbiotic rhizobia. Moreover, it seems that synthesis of these flavanoids is an effective strategy against reactive oxygen species (ROS). The analysis of activity of antioxidant enzymes like SOD, CAT, POX, APX, GPX and GR suggested that peroxidises were the most active enzymes in red cabbage seedlings exposed to Cu++ stress.Tannins included in the second category of plant phenolic polymers with defensive properties. Tannins are general toxins that

significantly reduce the growth and survivorship of many herbivores, and also act as feeding repellents to a great diversity of animals.

(III) Sulphur containing secondary metabolites: They include GSH, GSL, Phytoalexins, Thionins, defensins and allinin which have been linked directly or indirectly with the defence of plants against microbial pathogens. GSH is the one of the major form of organic sulphur in the soluble fraction of plants and has an important role as a mobile tool of reduced sulphur in the regulation of plant growth and development and as a cellular antioxidants in stress responses, reported as a signal of plant sulphur sufficiency that down regulates sulphur assimilation and sulphur uptake by roots.

GSL is a group of low molecular mass N (nitrogen) and S (sulphur) containing plant glucosides that produced by higher plants in order to increase their resistance against the unfavourable effects of predators, competitors and parasites because their break down products are release as volatiles defensive substances exhibiting toxic or repelient effects for example, mustard oil glucosides in cruciferae and allyl cys sulfoxides in alllum. They are metabolised and absorbed as isothiocyanates that can affect the activity of enzymes involved both in the antioxidant defence system and in the detoxification from zenobiotics abd significantly affect GST activity and cell protection against DNA damage whereas toxicity of glucosinolatic products is well documented but their mode of action has not yet been elucidated and results from experiments with Brassica plants modified in GSL content generated doubts about their contribution to plant defences.

Phytoalexins are synthesized in response to bacterial or fungal infection or other forms of stress that help in limiting the spread of the invading pathogens by accumulating around the site of infection, appears to a common mechanism of resistance to pathogenic microbes in a wide range of plants.

(IV) Nitrogen containing secondary metabolites: They include alkaloids, cyanogenic glucosides, and non-proteins amino-acids. Most of them are biosynthesized from common aminoacids. Alkaloids found in approximately 20% of the species of vascular plants, most frequently in the herbaceous dicot and relatively a few in monocots and gymnosperms. Generally, most of them, including the pyrrolizidine alkaloids (PAs) are toxic to some degree and appear to serve primarily in defense against microbial infection and herivoral attack. Cyanogenic glucosides constitue a group of N-containing protective compounds other than alkaloids, release the poison HCN and usually occur in members of families viz., Graminae, Roosaceae and leguminosesae.

Transport, Storage and Turnover: SMs can be water soluble (hydrophilic) compounds or lipophilic (needs organic solvents), therefore needs different cellular mechanism for their transport, storage and turnover. Most substances are synthesized in the cytoplasm, the ER or in the organelles. Hydrophilic SMs are usually stored in the vacuole after their formation in cytoplasm, whereas lipophilic substances are sequestered in resin ducts, laticifers, glandular hairs, trichomes, thylakoid membranes or on the cuticle.

Major Secondary Metabolite Pathways : In plants particularly three pathways are the source of most secondary metabolites: **The shikimate pathway, the isoprenoid pathway and the polyketide pathway.** After the formation of the major basic skeletons, further modifications result in plant species specific compounds. The shikimate pathway is the major source of aromatic compounds.

Significance of SMs:

- Many secondary compounds have signalling functions influence the activities of other cells, control their metabolic activities and co-ordinates the development of the whole plant.
- Other substances such as flower colours serve to communicate with pollinators or protect the plants from feeding by animals or infections by producing specific phytoalexines after fungi infections that inhibit the spreading of the fungi mycelia within the plant.
- Plants use secondary metabolites (such as volatile essential oils and colored flavonoids or tetraterpenes) also to attract insects for pollination or other animals for seed dispersion, in this case secondary metabolites serve as signal compounds.
- Compounds belonging to the terpenoids, alkaloids and flavonoids are currently used as drugs or as dietary supplements to cure or prevent various diseases and in particular some of these compounds seem to be efficient in preventing and inhibiting various types of cancer.
- It has been estimated that huge percent of higher plant species are used medicinally and that 74% of pharmacologically active plant derived components were discovered after following up on ethno-medicinal use of the plants.
- Secondary metabolites are a metabolic intermediates or product, found as a differentiation product in restricted taxonomic groups, not essential to growth and life of the producing organism and biosynthetized from one or more general metabolites by wider variety of pathways than is available in general metabolism.
- Presence of volatile monoterpenes or essential oils in the plants provides an important defense strategy to the plants, particularly against herbivorous insect pests and pathogenic fungi. These volatile terpenoids also play a vital role in plant-plant interactions and serve as attractants for pollinators. They act as signalling molecules and depict evolutionary relationship with their functional roles. Soluble secondary compounds such as cyanogenic glycosides isoflavoids and alkaloids can also be toxic to animals.

Difference between Primary and secondary Metabolites

1). Primary metabolites are found in all plants and execute vital metabolic responsibilities, by participating in nutrition and reproduction

(2). Sometimes it is hard to discriminate primary and secondary metabolites. For example, both primary and secondary metabolites are found among the terpenoids and the same compound may have both primary and secondary roles. Secondary metabolites are broad range of compounds from different metabolite families that can be highly inducible in stress

conditions. Carotenoids and flavonoids are also involved in cell pigmentation in flower and seed, which attract pollinators and seed dispersers. Therefore, they are also involved in plant reproduction

(3). Plant primary products refer to the compounds of nucleic acids, proteins, carbohydrates, fats and lipids and are related to structure, physiology and genetics, which imply their crucial role in plant development. In contrast, secondary metabolites usually take place as minor compounds in low concentrations.

4). Primary metabolism refers to the processes producing the carboxylic acids of the Krebs cycle. Secondary metabolites, on the other hand, are non-essential to life but contribute to the species' fitness for survival.

Table1. Secondary Metabolites from Plant Cell, Tissue and Organs Cultures

Plant Name	Active Ingredient	Culture Type
Adhatoda vasica	Vasine	Shoot culture
Arachis hypogaea	Resveratol	Hairy root
Artemisia annua	Artemisinin	Callus
Azadirachta indica	Azadirachtin	Suspension