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ROLE OF FLAVONOIDS IN PLANTS

Dr. Basudha Sharma
Associate Professor & Head
Department of Botany
Multanimal Modi College, Modinagar, Uttar Pradesh

ABSTRACT

Flavonoids are secondary metabolites which have diverse metabolic functions in plants. The present paper focuses on flavonoid biosynthesis and their biological functions in plants. Flavonoid a role to play in protection against Ultraviolet rays, abiotic stress management, plant-microbe interaction and even plant- plant interaction. Flavonoids have also been reported to provide health benefits to human beings. Flavonoids are also known to effect development of plants. The various roles of flavonoids makes them an interesting and inquisitive molecule for research.

KEY WORDS: Flavonoids, ROS, Secondary metabolites, Auxins

Living organisms grow and reproduce, maintain their structure and respond to the ever changing environment, by the help of enzyme catalysed reactions. These reactions also termed as metabolism, result in the production of energy and metabolites. Primary metabolites are central to metabolism and are required for the proper growth of an organism. They include, carbohydrates, proteins, fats membrane lipids, nucleic acid, chlorophyll etc., unlike the primary metabolites, secondary metabolites are not critical to growth and development of plants. Secondary metabolites also known as the accessory compounds involved in- plant-plant interaction and plant-environment interaction, for example signalling between the symbiotic/parasitic organisms, attracting pollinating insects. Secondary metabolites can be classified into three different categories: Terpenes, Phenolic compounds and nitrogen containing compounds.

Terpenes are strong smelling, water insoluble, diverse group of organic molecules formed by the mevalonic acid pathway and methylerythritol pathway in plants. Terpenes are derivatives of 5-carbon isoprene (C_5H_8), which may be linked linearly or forming rings. Terpenes may further be classified into- Monoterpenes, Diterpenes or sesquiterpenes. Terpenes are known to play an important role in plant defence against herbevory (Gershezon and Crotean, 1993). In Chrysanthemum pyrethroids are found which are known to act as neurotoxin and are also an ingredient in insecticides (Turlings et al., 1995). Certain volatile mixture of monoterpenes and sesquiterpenes (limonene and methanol in lemon oil and peppermint) are present in the glandular trichomes of leaves and protect the leaves against insect infestation. Resins in gymnosperms (α-pinene, β-pinene and limonene are present in needles and trunks) are toxins and play a role in defence against numerous insects (Turling et al., 1995). Certain steroids like Phytoecdysones are present in ferns (*Polypodium vulgare*) have a critical role in disrupting moulting and other developmental processes in insects thereby, having lethal consequences for the insects (Heftmann 1975; Slama, 1979, 1980). Saponins (tirterpenes) also have lethal effects on insects by causing cell disprution. Rubber (polyterpenes) is present in the laticiferous ducts of members of Sapotaceae and has a role in wound healing. It also provides protection against herbivores.

Nitrogen-containing coumpounds are group of secondary metabolites containing nitrogen as a part of their structure, and they include alkaloids, cyanogenic glucosides and non-protein amino acids. Alkaloids are synthesized from amino acid mainly, lysine, tyrosine or tryptophan. These are water soluble and present in cytosol or vacuole. Alkaloids ere earlier thought be nitrogenous waste in plants, however, now believed to play a role in plant defence (Hartmann,1991). An ingestion of various alkaloid-rich plants is known to cause death in livestock. Certain alkaloids, are pharmacologically useful at lower doses, for eg. Morphine, codeine and scopolamine. Some others are known to act as stimulants and sedatives, like nicotine, caffeine and cocaine. Cyanogenic glycosides are substances which are non toxic in plants, present in vacuoles of epidermal cells, but produce cynogenic toxic compounds when the plants are damaged (Poulton, 1990). Cyanogenic glycosides are common in many legumes, grasses and members of rosaceae, and they provide protective functions by repelling insects and herbivores. Glucosinolates are present in members of family brassicaceae and resemble the cyanogenic glycosdies as they liberate mustard oil when damaged. Mustard oil is a mixture of isothiocyanates, thiocyanates and related nitriles. When tissue containing glucosinolates are destroyed, it results in activation of hydrolytic enzyme, Thioglucosidase/myrosinase which causes the cleavage of bonds present between glucose and sulphur atoms that result in production of mustard oil, which function as repellents and herbivore toxins. Certain plant families mainly legumes and grasses have free unusual amino acids, also called non-protein amino acids which are associated with resistance to insects herbivory. Non protein amino acids, such as canavanine, may have toxic effects mainly, misincorprtation into the proteins, obstruction of primary metabolism, mimicking or obstruction insects various neurological processes. Some non protein may also act as stores of nitrogen, metabolically inaccessible to the herbivore, or may even act as signalling molecules for plant defence response (Huang et al., 2011).

Phenolics are organic compounds which have functional hydroxyl group on the benzene ring. These are produced by plants and function including, nutrient uptake, protein synthesis, provide mechanical strength, attract pollinators, act as allelopaths and provide protection against herbivores and pathogen (Stalikas, 2007). Phenolics are synthesized mainly by the shikimic acid pathways, occurring in plant. Most of the phenols are produced from phenylalanine, through pheylalanine ammonia lyase (PAL). Activity of PAL can be regulated by environmental factors like low nutrients level, light, fungal infection (Logemann et al., 1995). Plant phenolics can be divided into different groups by

1. Number of hydroxyl groups: 1,2 and polyatomic phenols
2. Chemical composition: mono, di, oligo and polyphenols
3. Number of aromatic rings and carbon atoms in the side chains: Phenolics with one aromatic ring,2 aromatic rings, quninoes and polymers

Simple phenolics have a single aromatic ring, and include phenols, with attached one, two or three carbon atoms. Simple phenolic have defensive roles and are toxic only when photo-activted. Lignin is a complex branched polymer of simple phenolic compounds, and binds to the cellulose of the cell wall. Coniferyl alcohol, sinapyl alcohol and p-comaryl alcohol act as building blocks of lignin. Lignin provides mechanical strength to the vascular tissue and provides protection against herbivory. Phenolics with two aromatic rings include benzoquinones, xanthones (linked with one carbon atom C6-C1-C6), stylbenes (linked with two carbon atom C6-C2-C6) and flavonoids (linked with three carbon links C6-C3-C6) (Kabera et al., 2014). Polyphenols may further be divided into flavonoids and tannins. Tannins aggregate to form complex compounds causing hardness in tissue rendering them inedible for the herbivores. Tannins can be further divided in Condensed tannins/ pro-anthocyanidins (formed by polymerization of flavonoids units) and hydrolysable tannins/ gallotannins containing gallic acid and simple sugars. Tannins form the active plant constituents of plant based medicines.

Flavonoids are water soluble pigments present in the vacuoles of plant cells. Most of the flavonoids are bound with sugars and exist as glycosides. Chemically flavonoids consist of a diphenylpropan ring system (C6-C3-C6) with a benzo-γ -pyrone skeleton.

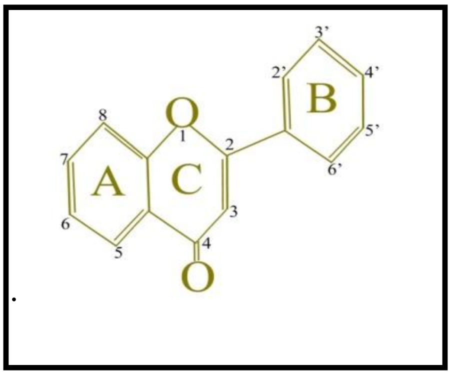

Fig.1: Structure of flavonoid

The double bond between C2 and C3 in the C ring in a flavonoid structure confers the antioxidative properties in flavonoids. OH group at C3 position of C ring, allow flavonoids to inhibit peroxidation of lipids. Carbonyl group at the C4 position allows it to scavenge hydroxyl radicals. The ability to scavenge hydroxyl radical increases with the number of hydroxyl groups present in the B ring, especially at the positions 3′ and 4′ (Rzepecka-Stojko et al., 2015). Seven groups of flavonoids are distinguished because of their chemical structure: flavones, flavonols, flavanones, flavanols, anthocyanidins and isoflavones.

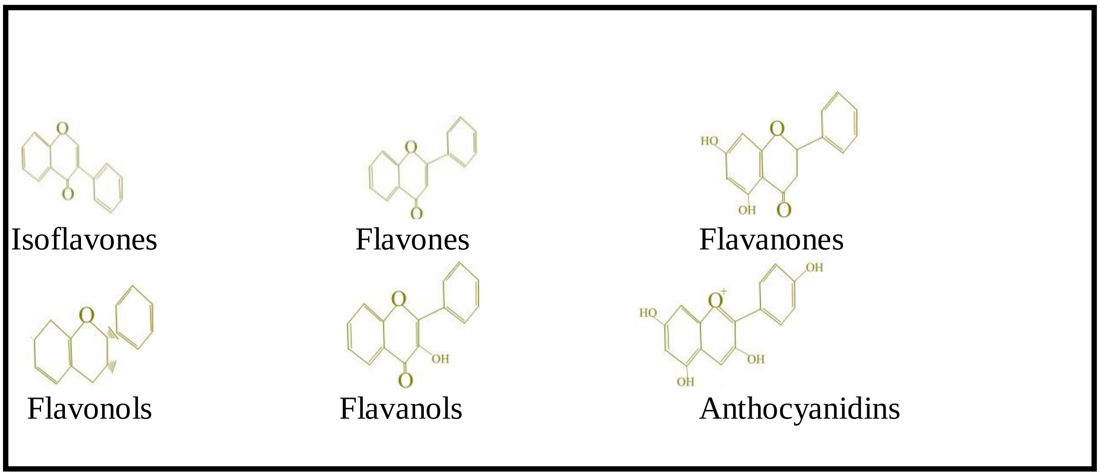

Fig. 2: Chemical structure of different groups of flavonoid

SYNTHESIS OF FLAVONOIDS

Flavonoids are diverse aromatic compounds present in all parts of a plant (Mierziak et al., 2014). They are synthesized by the shikimic acid pathway through phenylpropanoid phenyl propanoid andprovide a link to primary metabolism in the form of phenylalanine. Animal cells do not share this pathway and need to get aromatic amino acids (phenylalanine, tyrosine and tryptophan) through their food, essentially from plant.

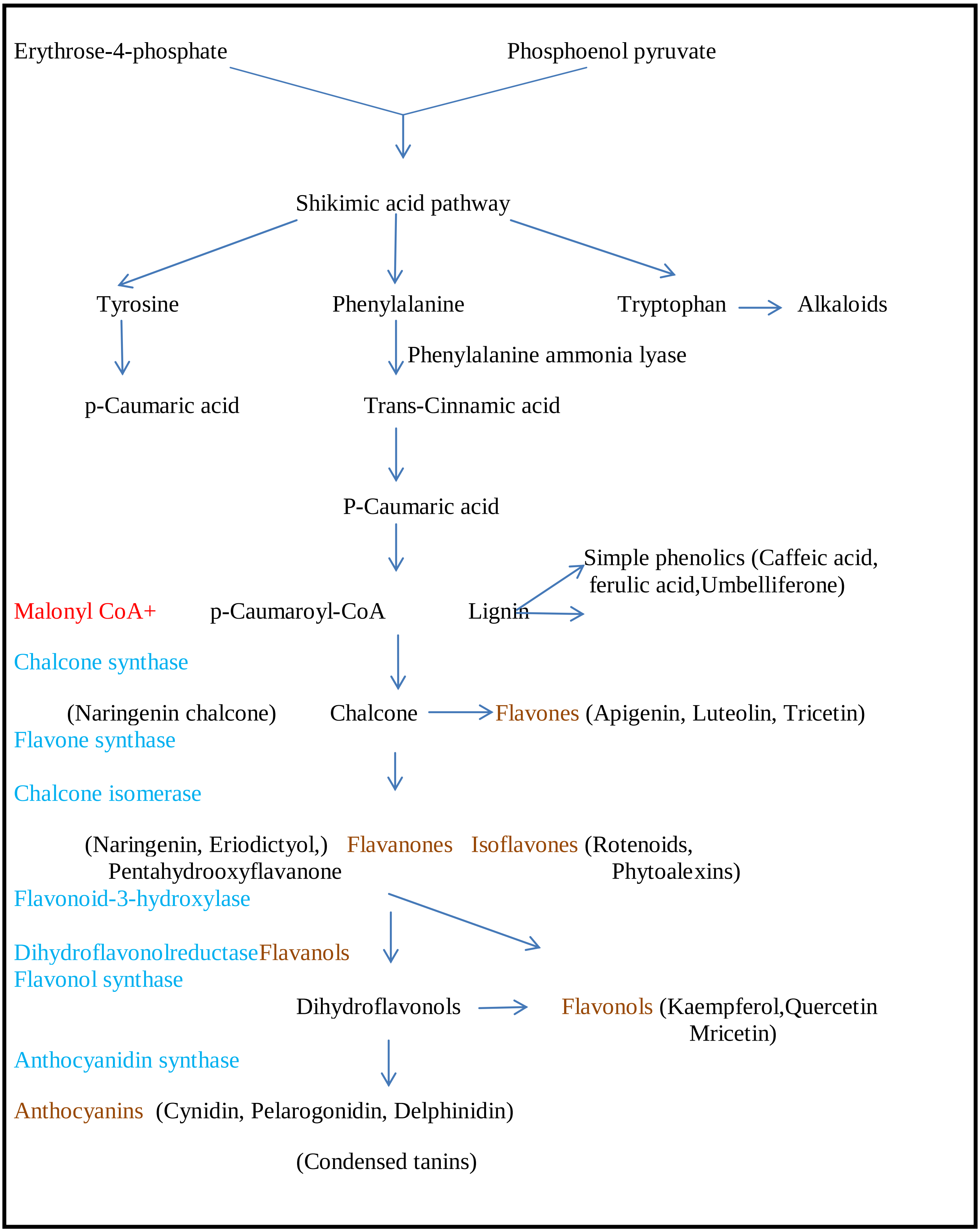

Fig. 3: Biochemical pathway depicting synthesis of flavonoids along with the enzymes involved in the process.

Flavonoids are derived from two pathways, the shikimic acid pathway and the malonic acid pathway. The 3-carbons of middle ring and Ring B are derived from shikimic acid pathway, whereas ring A and oxygen of middle ring are derived from acetate units (from acetyl-CoA) through malonic acid pathway. Anthocyanins are a group of flavonoids that are water soluble, vascular providing color to the plant organ, mainly the flowers, fruits and leaves. Anthocyanadin when attached to sugar moieties are known as anthocyanins. Substitution at 3`,4` and 5` positions lead to the characteristics colour of anthocyanins eg. Cynidin-purplish red, Pelarogonidin- orange red, Delphinidin- bluish purple. The color of anthocyanins may also vary according to the pH, interaction of different groups of anthocyanins, presence of anthocyanins and their interaction with other group of flavonoids and metal ions. In isoflavonids the aromatic B ring is attached to the 3rd carbon of C ring. Isoflavonoids (Phytoalexins,rotenoids) are known to have insecticidal properties. Flavones and Flvonols are important groups of flavonoids which absorb UV rays, and also act as nectar cues for attracting insects (Mouradov and Spangenberg, 2014).

BIOLOGICAL FUNCTIONS OF FLAVONOID

Flavonoids being present ubiquitously in plants are known to have diverse and crucial functions. Flavonoids have an important role in structural integrity of plant cells. Due to their structure, flavonoids are able to maintain redox state in a cell (Mierziak et al., 2014). Flavonoids are able to quench reactive oxygen species mainly, singlet oxygen, superoxides, alkyl radicals, hydroxyl radicals (Buettner, 1993). They are able to supress the activity of enzymes that generate reactive oxygen species, mainly cyclooxygenase, lipoxygenase, monooxygenase, xanthine oxidase. Flavonoids are known to react with cytotoxic substances and interact with enzymes through protein complexation. Flavonoids bind to the metals ions such as Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, Al^{3+} and Mg^{2+}due to the OH group in the 3-position of flavonoid skeleton. In roots of maize, catechin and quercetin, were found to reduce aluminium toxicity (Kidd et al., 2001). Flavonoids, however, do not bind with cations which act as signalling molecules like Ca^{2+}, Na+. It has been reported that flavonoids are present in the membranes where they stop lipid peroxidation by acting as chelates of Fe^{2+} and Fe^{3+}. Lipid peroxidation is dangerous process as it is a chain reaction which damages the membranes.

Since the plants are immobile, flavonoids have developed as one of the mechanisms, of the plants, to cope with unfavourable condition. It has been reported that flavonoid content is known to increase in stressful conditions, includingstrong light, ultraviolet (UV) radiation, low/high temperature, heavy metals, drought (Petrussa et al., 2013). Most fl avonoids exhibit absorption peak in two regions, one in the low-wavelength region, 210–290 nm (band II), and one in the longer-wavelength region, 320–380 nm (band I). Flavonoids reduce the penetration of UV lights to vulnerable tissues of plant by accumulating in epidermis, hypodermis of leaves and stems, apical meristem and pollen. Flavonoids, like flavones orientin and luteolin may also have a role in UV stress response (Van De Staaij et al., 2002). Stress factors induce the development of reactive oxygen species (ROS). Since ROS act as signalling agents, ROS are present in normal physiological conditions. The fine balance of ROS generation and degradation is maintained by antioxidants, and various ROS scavenging enzymes. An uninterrupted increase in ROS leads to damage of DNA, proteins and lipids leading to impaired functioning of cell membrane, chloroplast and mitochondria.

Flavonoids are also known to interact with microorganisms, leading to the development of nodules. Lack of flavonoid in *Medicago truncatula* and soybean resulted in absence of nodulation. Flavonoids have the ability to influence the expression of *nod* genes. Nod genes control the nodule formation in nitrogen fixing bacteria. The flavonoids released by plants bind to NodD which bind to promoter of nod genes leading to the formation of nod factors. These nod factors bind to the nod factor receptors present on the plant cell membranes initiating signalling events leading to root nodule formation (Billy et al., 2001). Flavonoids also control the process of auxin transport. Auxin are phytohormones having a role root development, mitiotic divisions and gene transcription. *In-vitro* studies have revealed that flavonoids compete for auxin transporters with NPA-(1-naphthylphthalamic acid) interacting proteins. Flavonoids can have an effect on the transport of auxins due to their interference with PIN, MDR/ABC proteins, and PID, WAK and PDK1 kinase. PIN and MDR are involved in intercellular auxin transport, whereas PID and WAK are membrane kinases having a role in auxin transport. Flavonoids such as quecetin, kampferol, apigenin are reported to have a role in polar transport of auxins (Kuhn et al., 2011). Flavonoids also protect plant against pathogens and herbivores. Flavonoids can modulate auxin activity and cause tightening of tissues, leading to promotion of callus, tylose formation for vascular closure to prevent pathogen infection.

Flavonoids provide color, fragrance and taste to various flowers, seeds and fruits, making them attractive for insects, birds and other animals which act as pollinators/dispersal agents. Among the flavonoids, anthocyanin results in the production of flower colors. Flavonoids are crucial for the correct development of plant (Petrussa et al., 2013). Various studies have indicated that flavonoids are required for male fertility in plants. Combination of various flavonoids (2-4% of dry weight) results in the production of yellow pollen with a range of visible and UV reflection spectra. Different mutants, deficient of producing flavonoids, lacking chalcone synthase in Petunia were observed to be male sterile as they were unable to produce functional pollen tube. In some cases, this effect was reversed by the addition of kaempferol at pollination (Mo et al., 1992) and quercetin in tobacco (Mahajan et al., 2011). In Arabiopsis mutants of chalcone synthesis, devoid of flavonols in flowers were fertile without having any effect on the pollen tube indicating that the flavonoids are not essential for pollen fertility universally (Shirley, 1996). In *Arabidopsis* polyketide synthases (LAP5 and LAP6) are required for pollen development and sporopollenin synthesis. *lap* mutants, were seen to be defective in pollen wall exine with deficiency in deposition of flavonoid containing tryphine (Kim et al., 2010). Some flavonoids have also been reported to have insecticidal, antiviral, antibacterial and antifungal properties (Mierziak, 2014;2014). Flavonoids have also revealed alleopathic properties against certain weeds (Kong et al., 2004). Recent studies indicate that flavonoids have beneficial effect on human health, by reducing the risk of diseases. Several studies have indicated that flavonoids reduce blood cholesterol level thereby protecting against cardiovascular diseases. Flavonoids have also indicated positive effect against Parkinson's disease (Kumar and Pandey, 2013). Quercetin exhibits anti-histamine, anti-cancer and anti-inflammatory activities due to its antioxidant activity

In conclusion, it can be stated that flavonoids are now emerging as molecules of immense importance. The diversity of plants has generated a variety of flavonoid, some of them yet to be discovered. Novel flavonoids and their role will contribute towards an improvement in floriculture, pharmaceutical and chemical industries. Recent studies on flavonoid metabolism have also shown their ecological and agronomic importance. Flavonoids, thus, are promising molecules which are providing benefits for human beings.

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REFERENCES

1. Billy DF, Grosjean C, May S, Bennett M, Cullimore JV (2001) Expression studies on AUX1-like genes in Medicago truncatula suggest that auxin is required at two steps in early nodule development. Mol. Plant-Microbe Interact. 14: 267–277.
2. Buettner G.R. (1993) The pecking order of free radicals and antioxidants: Lipid peroxidation, alpha-tocopherol, and ascorbate. Arch. Biochem. Biophys. 300: 535–543.
3. Gershenzon J and Croteau R (1993) Terpenoid biosynthesis: the basic pathway and formation of monoterpenes, sesquiterpenes and diterpenes. In: Moore TS Jr, ED.). Lipid Metabolism in Plants. Boca Raton, FL: CRC Press: 339–388

4. Hartmann T, 1991. Alkaloids. In herbivores; their interaction with secondary plant metabolites, Vol. I, The chemical participants, 2nd ed., G.A. Rosenthal and M.R. Berenbaum, eds Academic press, San Diego, pp: 33-85.
5. Heftmann E, 1975. Function of steroids in plants. Phytochemistry, 14: 891-901.
6. Huang T, Jander G, de Vos M (2011)Non-protein amino acids in plant defense against insect herbivores: representative cases and opportunities for further functional analysis. Phytochemistry. 72 :1531-7.
7. Kabera JN, Semana E, Mussa AR. And He Xin (2014) Plant Secondary Metabolites: Biosynthesis, Classification, Function and Pharmacological Properties. J of Pharmacy and Pharmacology 2: 377-392.
8. Kidd PS, Llugany M, Poschenrieder C abd Barcelo J (2001) The role of root exudates in aluminium resistance and silicon induced amelioration of aluminium toxicity in three varities of maize (Zea mays L.). J. Expt. Bot, 52, 1330-1352.
9. Kim SS, Grienenberger E, Lallemand B, Colpitts CC, Kim SY, Souza Cde A, Geoffroy P, Heintz D, Krahn D, Kaiser M, Kombrink EHeitz T, Suh DY, Legrand M and Douglas CJ (2010) LAP6/POLYKETIDE SYNTHASE A and LAP5/POLYKETIDE SYNTHASE B encode hydroxyalkyl alpha-prone synthases required for polen development and sporopollenin biosynthesis in Arabidopsis thaliana. Plant Cell 22, 4045-4066.
10. Kong, C.; Xu, X.; Zhou, B.; Hu, F.; Zhang, C.; Zhang, M. Two compounds from allelopathic rice accession and their inhibitory activity on weeds and fungal pathogens. Phytochemistry 2004, 65, 1123–1128.
11. Kuhn, B, Geisler M, Bigler L and Rinngli C (2011) Flavonols accumulate asymmetrically and affect auxin transport in Arabidopsis. Plant Physiol. 156, 585-595.
12. Kumar S and Pandey AK (2013) Chemistry and biological activities of flavonoids: An overview. Scientific World J. 2013, 162750.
13. Logemann E, Parniske M, Hahlbrock K (1995) Modes of expression and common structural features of the complete phenylalanine ammonia-lyase gene family in parsley. Proc Natl Acad Sci USA 92: 5905–5909
14. Mahajan M, Ahuja PS and Yadav SK (2011). Post transcriptional silencing of flavonol synthase mRNA in tobacco leads to fruits with arrested seed set. PLoS ONE 6:e28315. Doi: 10.1371/journal.pone0028315.
15. Mierziak J, Wojtasik W, Kostyn K, Czuj T, Szopa J and Kulma A (2014) Crossbreeding of transgenic flax plants overproducing flavonoids and glucosyltransferase results in progeny of improved antifungal and antioxidative properties. Mol. Breed doi:10.1007/s11032-014-0149-5
16. Mo Y, Nagel C, and Taylor LP (1992). Biochemical complementation of chalcone synthase mutants defines a role for flavonols infunctional pollen. Proc. Natl. Acad. Sci. USA 89: 7213-7217.
17. MouradovA and Spangenberg G (2014) Flavonoids: a metabolic network mediating plants adaptation to their real estate. Front Plant Sci 5: 620. Doi 10.3389/fpls.2014.00620
18. Petrussa E, Braidot E, Zancani M, Peresson C, Bertolini A, Patui S and Vianello A (2013) Plant Flavonoids—Biosynthesis, Transport and Involvement in Stress ResponsesInt. J. Mol. Sci. 14: 14950-14973.
19. Poulton JE, 1990. Cyanogenesis in plants. Plant Physiology, 94: 401-405.
20. Rzepecka-Stojko A, Stojko J, Kurek-Górecka A, Górecki M, Kabał a-Dzik A, Kubina R, Moź dzierz A and Buszma E (2015) Polyphenols from Bee Pollen: Structure, Absorption, Metabolism and Biological Activity .Molecules 20: 21732–21749.
21. Shirley BW (1996) Flavonoid biosynthesis: `new' functions for an 'old' pathway . Trends in plant Science 11, 377-382.
22. Slama K (1979). Insect hormone and antihormones in plants pages 683-700 in G.A. Rosenthal and D.H. Janzen (eds), herbivores: their interaction with secondary plant metabolites, Academic press, New York
23. Slama K (1980) Animal hormone and antihormones in plants. Biochemie Physiologie Pflanzen, 175: 177-193.
24. Stalikas CD (2007)Extraction, separation, and detection methods for phenolic acids and flavonoids. J Sep Sci.30 :3268-95.
25. Turlings, TCJ, Loughrin JH, McCall PJ, Röse USR, Lewis WJ, and Tumlinson JH (1995)How caterpillar-damaged plants protect themselves by attracting parasitic wasps. Proc. Nati. Acad. Sci. 92: 4169-4174.
26. Van de SJ,de bakker NV, Oosthoek A, Broekman R, Van BA, Stroetenga M, Aerts R and Rozema J (2002). Flavonoid concentrations in three grass species and a sedge grown in the field and under controlled environment conditions in response to enhanced UV-B radiation. J Photochem Photobio B: Biology, 66: 21-29.