The Role of Monoterpenoids and Sesqiterpenoids as defense Chemicals in Plants – a Review

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ABSTRACT

In natural systems, plants are surrounded by various kinds of biotic and abiotic environmental stress. Being immobile, some plants are easy targets for pathogens and are unable to avoid adverse environmental conditions which may reduce their ability to withstand infections. Thus plants have evolved multiple defense mechanisms by producing a wide variety of chemical compounds which are known as secondary metabolites. These metabolites can protect plants from attacks by insects, herbivores and pathogens, or make plants survive other biotic and abiotic stresses. These chemicals include terpenoids, alkaloids and phenolics. They are employed for specialized chemical interactions and protection in abiotic and biotic environments. This paper discussed terpenoids- monoterpenoids and sesquiterpenoids, a class of secondary metabolites, as defense chemicals which are the principal constituents of essential oils, stress factors affecting plant fitness and plant chemical defense mechanisms.

Keywords: defense chemicals; essential oil; monoterpenoids; plants; sesquiterpenoids.

INTRODUCTION

Nearly all ecosystems contain a wide variety of bacteria, viruses, fungi, nematodes, mites, insects, mammals and other herbivorous animals, which are greatly responsible for heavy reduction in crop growth and productivity [1].Plants protect themselves against a variety of herbivores and pathogenic microorganisms as well as various kinds of abiotic stresses by producing some chemical compounds known as secondary metabolites (terpenes, phenolics, nitrogen and sulphur containing compounds, etc.) which help them cope with these stresses and be adaptable to environments. These include initiating their own pollination and seed dispersal, local fluctuations in the supply of simple nutrients required to synthesize their own food, and coexistence of herbivores and pathogen in their immediate environment [2]. Generally, the roles played by these secondary metabolites are mainly for protection (as UV light absorbing and anti-proliferative agents), defense against pests and diseases, and as attractive agents [3]. Many plant species produce substances that protect them by killing or repelling the insects that feed on them. For example, the *Douglas fir* has a special sap that wards off beetles if it is attacked. Neem trees produce oil that alters the hormones of bugs so that they cannot fly, breed or eat [4].

Plants produce a large and diverse array of organic compounds (secondary metabolites) that appear to have no direct functions in growth and development i.e. they have no generally recognised roles in the process of photosynthesis, respiration, solute transport, translocation, nutrient assimilation and differentiation. They have a very restricted distribution. They are often found only in one plant species or a taxonomically related group of species [5]. Among the numerous compounds produced by plants, terpenoids (isoprenoids) represent the largest and most diverse class of chemicals. Specialized terpenoid metabolites in particular, have been recognized for an array of biological roles, and for the formation of a large number of terpenoid compounds with more specialized roles in the interaction of plants with their environment. It is this group of terpenoids that is characterized by its tremendous structural diversity as a consequence of divergent biosynthetic gene evolution [6].

As the largest class of natural products, terpenes have a variety of roles in mediating antagonistic and beneficial interactions among organisms. They defend many species of plants against predators, pathogens and competitors. Terpenes play a broad range of ecological roles in nature chiefly as intermediates in biosynthetic processes, as direct defenses against herbivores, or indirectly by attracting herbivore enemies (predators and parasitoids). Terpenes can also serve to attract pollinators and to stimulate cross-pollination, they take part in various symbiotic mechanisms, which include acting as attractants to specific insects species [7]. They act as communication cues between plants to alert the presence of enemies [8], or to protect plants from abiotic stresses such as the exposure to high temperatures or the oxidative damage due to accumulation of reactive oxygen. Therefore, terpenes mediate interactions that can have direct effects on plant fitness, and thus it is likely that their evolution may be molded by natural selection [9]. It is in the light of the aforementioned functions of terpenes that this paper is aimed at discussing the role of monoterpenoids and sesquiterpenoids which are the principal constituents of essential oils as defense chemicals in plants.

ESSENTIAL OILS

Essential oils are odorous complex mixtures of volatile secondary metabolites found in plants. Such oils are essential because they are thought to represent the very essence of odour and fragrance of such plants. The oils can be found in all plant organs (leaf, flower, root, stem, bark, seed, etc.). Essential oil production in plants is generally associated with the presence of specialized secretory structures (glandular trichomes, ducts, cavities, etc. These secretory structures are the primary sites of production of bioactive secondary products which are known to play crucial roles in attractive and defensive mechanism responses to environmental conditions [10, 11].

The oils have wide and varied application in many industries such as pharmaceutical, cosmetics and perfumes, food, agronomic, and sanitary [12-14]. They are also employed in the treatment of different ailments in folk medicine [15]. Nowadays, they are used in aromatherapy as they are believed to exhibit certain medicinal benefits for curing organ dysfunction or systemic disorder [16, 17]. The extensive applications of essential oils are largely attributed to a wide range of biological properties that are functionally important to the plant itself and also beneficial to humans [15]. Essential oil and its constituents belong to a class of natural products known as terpenes/terpenoids.

Formation of Terpenoids

All terpenoids are derived from the universal five-carbon building blocks, isopentenyl diphosphate (IPP) and its allylic isomer dimethylallyl diphosphate (DMAPP).The prenyl diphosphate intermediates built by condensation of these five-carbon units are used as precursors for the biosynthesis of terpenoids. Plants use two independent pathways to produce IPP and DMAPP: the primarily cytosolic mevalonic acid (MVA) pathway and the plastidial methylerythritol phosphate (MEP) pathway. It has been established that both pathways are heavily regulated at multiple levels [18, 19]. The simplest terpenoid is the hydrocarbon isoprene (C_5H_8) represented by figure 1. Terpenoids are classified according to the number of isoprene units used to construct them. For instance, monoterpenoids comprises of (two), sesquiterpenoids (three) isoprene units, etc.

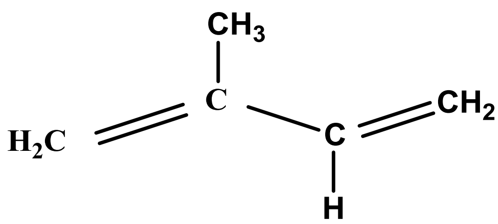
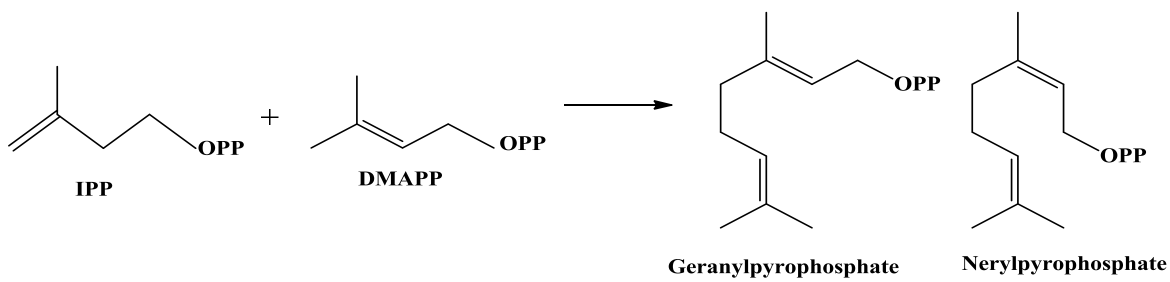


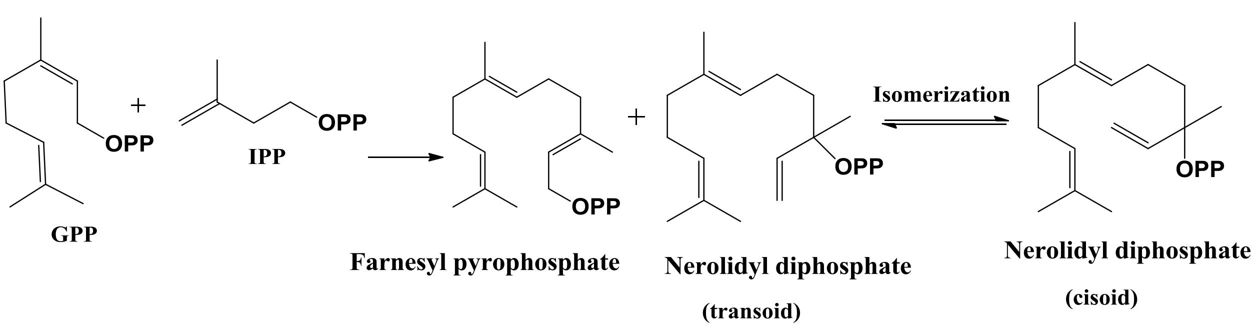
Figure 1 : Isoprene unit

Dimethylallyl diphosphate (DMAPP) and IPP are fused to form geranyl pyrophosphate and nerylpyrophosphate, which are the precursors in biosynthesis of monoterpenoids (C10), including highly volatile open chain and cyclic compounds (Reaction Scheme 1).



Reaction scheme 1: Formation of geranyl pyrophosphate and Neryl pyrophosphate [20]

Dimethylallyl diphosphate (DMAPP) and two units of IPP are fused to form farnesyl diphosphate and nerolidyl diphosphate which are the precursors for the synthesis of open chain and cyclic sesquiterpenes (C15), the largest group of isoprenoids (Reaction Scheme 2).



Reaction scheme 2: Formation of farnesyl pyrophosphate and Nerolidyl diphosphate [21]

Monoterpenoids as defense chemicals in plants

Monoterpenes have essential ecological role and could be induced by biotic and abiotic stresses, such as pathogen attack, wounding, ozone and high temperature. The substantial emissions of isoprene and monoterpenes from various plants have been associated with the protection against thermal stress [22]. It has been shown that monoterpenes can make the photosynthetic apparatus more resistant to high temperatures, thereby protecting plants against heat stress [23]. Terpenoids as constituents of floral scent are implicated in mutualistic interactions with plant pollinators. Various insects including bees, butterflies and beetles are known to be attracted by the aroma of plants. These insects aid pollination by acting as agents of dispersal of pollen grains. For instance, choice tests with bumblebees have indicated a role of monoterpenoids emitted by monkey flowers in pollinator attraction [24]. A vast majority of the different monoterpenes structures produced by plants as secondary metabolites function in defense as toxins and feeding deterrents to a large number of plant feeding insects and mammals.

For example, the pyrethroids (monoterpenes esters) produced in the leaves and flowers of *Chrysanthemum* species show strong insecticidal responses (neurotoxin) to insects like beetles, wasps, moths, bees, etc. It is a major ingredient in commercial insecticides because of its low persistence in the environment and low mammalian toxicity [25]. In conifers like pine and fir trees, monoterpenes accumulate in resin ducts found in the needles, twings and trunks mainly as α-pinene, β-pinene, limonene and myrcene, all of which are toxic to numerous insects including bark beetles, serious pest of conifer species etc [6].The mint plant, *Teucrium marum* (family Labiatae) contain methylcyclopentanoid monoterpenes. It is repellent to ants (*Monomorium pharaonis*) and induces preening reflexes in flies (*Phormia regina*) and cockroaches (*Periplaneta americana*) [26].

Furthermore, oils of plants like *Salvia leucopylla* and *Artemisia californica* play a role in allelopathy in which the plants release chemicals to prevent competing vegetation from growing within their area or zone. Plants release allelopathic terpenoids such as eucalyptol (1,8-cineole) and camphor into the surrounding area which effectively prevent other plant species from growing around them [27]. They use their essential oils to deter insects and other animals from approaching them [28]. In addition, plants release antimicrobial, antifungal and antibacterial agents against a wide range of pathogens that may threaten the survival of the plants [27, 29, 30].The structures of monoterpenoids acting as defense chemicals in plants are shown in figure 2.

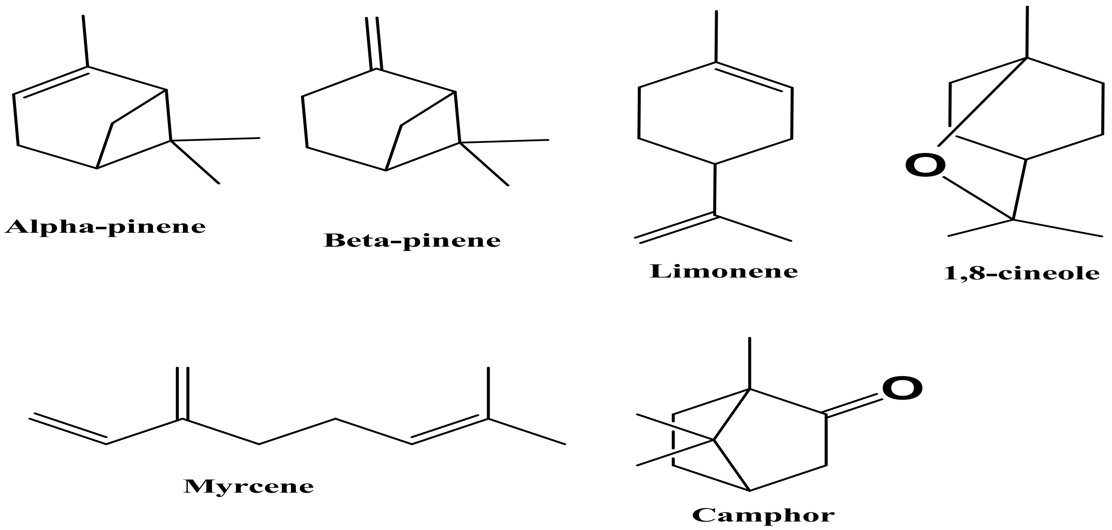


Figure 2: Monoterpenoid defense chemicals in plants

SESQUITERPENOIDS AS DEFENSE CHEMICALS IN PLANTS

The activity of sesquiterpenoids is numerous and many of them display often rather complex interactions. Often the interaction is more complex and produced compounds are further metabolized to the active compounds. Caryophyllene is oxidized by many organisms including fungi, plants and mammals to the epoxide, which act as a repellent against the leaf cutting ant, *Atta cephalotes* [31]. For sesquiterpenoids used as defense chemicals, a mixture may help to achieve simultaneous protection against numerous predators, parasites and competitors. Moreover, mixtures also reduce the risk of the development of resistances [32]. Some fungi produce volatile organic compounds for defence against enemies. The ascomycete *Muscodor albus* produces the sesquiterpenes β-selinene, α-guaiene, α-bisabolene, α-cedrene, caryophyllene, α-amorphene, β-chamigrene, β-bulnesene and valencene that collectively acted synergistically to kill a broad range of plant- and human-pathogenic fungi and bacteria [33].

Sesquiterpene lactones are a group of secondary metabolites found across the plant kingdom. They are one of the main constituents of latex in latex producing plants, and they are frequently potent antimicrobial agents as well as antifeedants to chewing insects and birds. They act as phytoalexins, antifeedants to deter herbivores, and conversely as attractants of pest predators, allelochemicals, hormones [34], and UV protection [35].They also have a range of other effects such as allelopathy, stimulation of germination in the parasitic plant *Orobanche*, and showing species and compound dependent modification of root growth in *Lactuca sativa* L., *Lepidium sativum* L., *Solanum lycopersicum* L., *Hordeum vulgare* L., *and Triticum aestivum* L. [36]. Sesquiterpene lactones also affect the insect's metabolism and central nervous system (CNS) and show varying degrees of toxicity. For example, 10-deoxylactucin and lactupicrin, the major lactones of chicory, *Cichorium intybus*, act to deter insect feeding and are bitter enough to protect the plant from mammalian browsing [37].

Conversely, some sesquiterpenes, such as α-farnesene, responsible for the characteristic smell of apples, attract animal feedants such as birds, and in doing so aid the spread of seeds, It is also believed that volatile sesquiterpenes are released as attractants to parasite predators, allowing for a form of defense against herbivores [38]. In some cases a single compound will have various functions, for instance, being toxic to insects while attracting predators, or warning other nearby plants of the insects, allowing them to prime their defenses in anticipation of an attack [39].

Sesquiterpene hydrocarbon β-farnesene has been reported to act as an alarm pheromone in aphids [40] whereas β-humulene, α- and γ- muurolene act as repellents against herbivores [41] and β-caryophyllene attracts nematodes which prey on insect larvae [42]. Ecological roles of volatile sesquiterpene alcohols produced by fungi are established from their interactions with insects where many of these alcohols can be identified. For example, cubenol, 1-epi-cubenol, and T-muurolol have been shown to be recognized by the insect pest *Hypsipyla grandella* [43]. Torreyol was also found in the male wings of the northern blue butterfly, *Lycaeides argyrognomon*, and may act as an insect pheromone [31]. Furthermore, T-cadinol stimulates the antennae of several insects including the American cockroach and α-cadinol is a repellent against termites [31].Structures of some sesquiterpenoids acting as defense chemicals are presented in figure 3. The functions of defense chemicals stated above depend largely on the stress factors affecting the plants.

Factors that can induce stress reaction in plants

Stress factors affecting plant fitness are derived from both natural and anthropogenic sources. Natural sources include factors such as adverse temperature fluctuations, high irradiation (photo-inhibition, photo-oxidation), osmotic imbalance (salinity, drought), flooding, mineral (macro- and micronutrient) deficiency, wounding, and pathogen attack. Stress factors from anthropogenic activities include use of pesticides in agricultural practices, environmental (air, soil and water) pollutants and increased UV radiation [44].Factors that can induce stress related reactions in plants is shown in figure 4.The mechanism of defense adopted by the plants is a function of the stress factors affecting the plants.

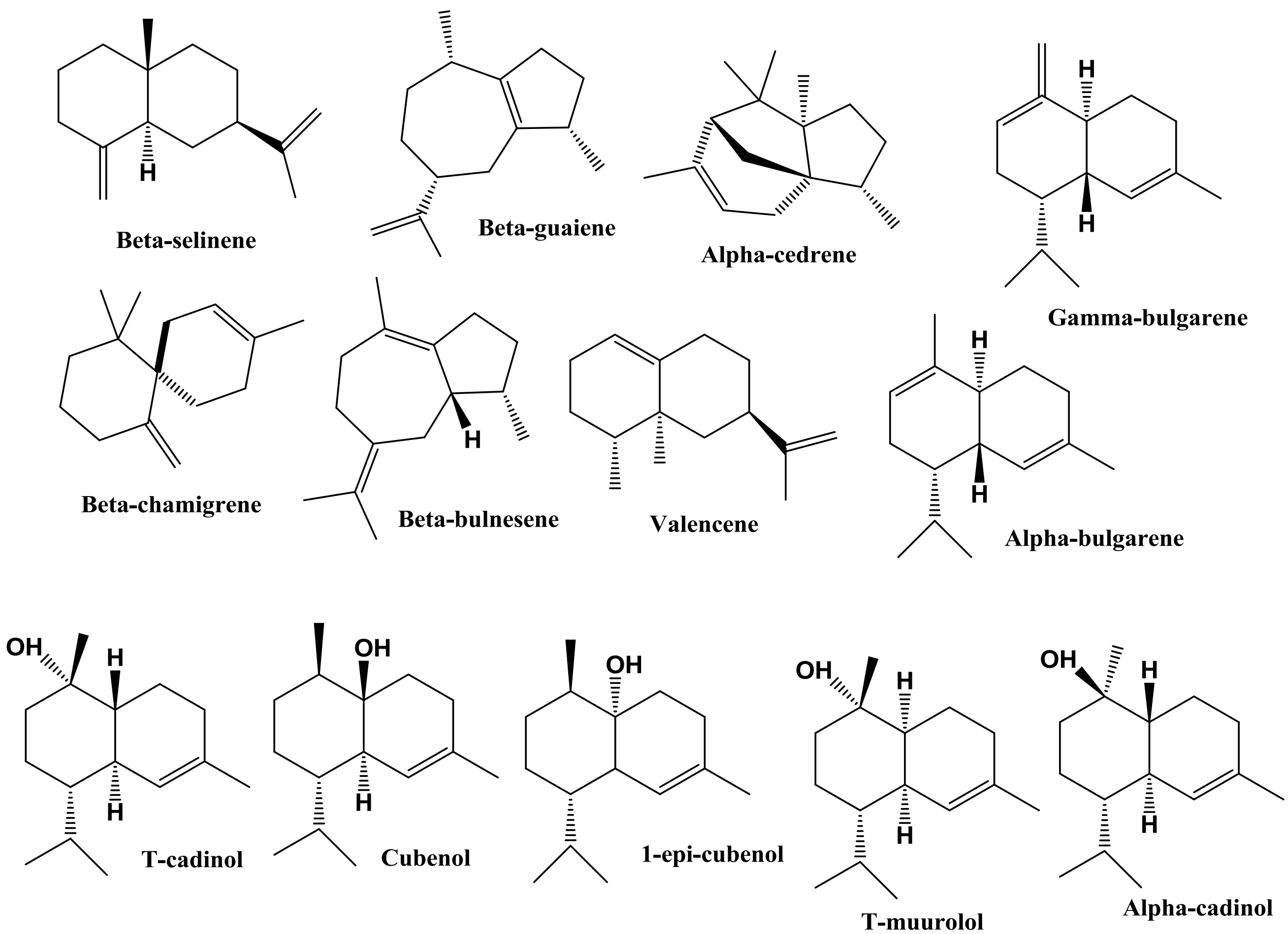


Figure 3: Sesquiterpenoid defense chemicals in plants [31].

PLANTS' CHEMICAL DEFENSE MECHANISMS

. A plant only has as much energy as it can collect from the sun and soil nutrients. It must balance its energy use amongst growth, reproduction, and defense. Every defense a plant employs lessens the amount of energy it can devote to growth and reproduction. Defensive chemicals have long been thought to be costly for plants because of the resources consumed in their biosynthesis, their toxicity to the plant itself or the ecological consequences of their accumulation [49, 50].

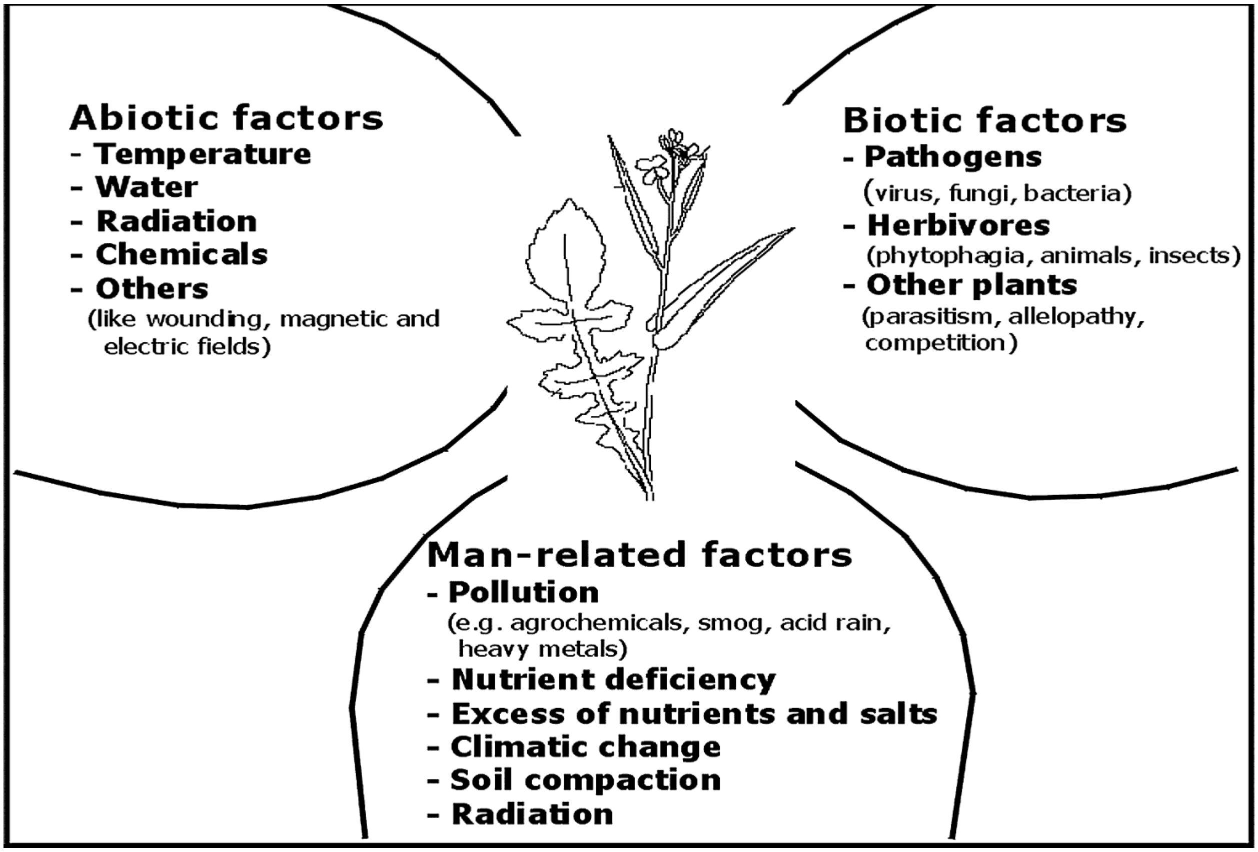


Figure 4. Factors that can induce stress related reactions in terrestrial plants [45-48]

Plant defenses can be classified as either constitutive (always present in the plant), or induced (produced in reaction to damage or stress caused by herbivores). A variety of molecular and biochemical approaches are used to determine the mechanism of constitutive and induced plant defenses responses against herbivores [51, 52] The biochemical defense mechanisms include the diverse chemicals which are synthesized by plants and stored in tissues. These organic chemicals include monoterpenoids, sesquiterpenoids, phenylpropanoids and compounds that act as precursor which on damage of the plant tissue release cyanide [53]. Many external mechanical defenses (such as the presence of trichomes, glands, thick cuticle, presence of wax, presence of spines on the leaves, etc) are constitutive, as they require large amounts of resources to produce and are difficult to mobilize [54]. Induced defenses include secondary metabolic products, as well as morphological and physiological changes.

Consequently, plants that are likely to suffer frequent and/or serious damage may invest mainly in constitutive defense, whereas plants that are attacked rarely may rely mainly on induced defenses. When applied to individual plant organs or developmental stages, the same considerations suggest that plant parts that are of high fitness value and/or are under a high risk of attack may be best protected by constitutive defenses, whereas others may be better defended by induced responses [55].

CONCLUSION

All organisms must cope with predators and competitors, and all organisms need defenses against these threats. Plants have evolved multiple defense mechanisms against microbial pathogens and various types of environmental stress. Chemical defenses often involve toxins of one sort or another or pungent aromas. Chemical defenses are enormously interesting and extremely sophisticated, but they are largely hidden from us until we are affected by them. This is part of the reason why eating unfamiliar plants is so dangerous. Chemical defenses represent a main trait of the plant innate immune system. Besides regulating the relationship between plants and their ecosystems, phytochemicals are involved both in resistance against pathogens and in tolerance towards abiotic stresses, such as atmospheric pollution. The better the plants are equipped with defensive chemicals, the more is the success of the plants to grow successfully and produce offspring. Thus, understanding the host pathogen defense mechanism may help in establishing novel approaches to enhance the plant resistance against this pathogen.

References

1. Sharma, M., Sharma, A., Kumar, A. & Basu, S.K. (2011). Enhancement of secondary metabolites in cultured plant cells through stress stimulus, *Am. J. Plant Physiol*., 6, 50–71.
2. Lee, Y. L. & Ding, P. (2016). Production of Essential Oil in Plants: Ontogeny, Secretory Structures and Seasonal Variations, *Pertanika Journal of Scholarly Research Reviews*, 2(1), 1-10.
3 Kennedy, D.O. & Wightman, E.L.(2011). Herbal extracts and phytochemicals: plant secondary metabolites and the enhancement of human brain function, *Advances in Nutrition,* 2, 32-50.
4 Subramaniam, S. & Kaushik, S. (2014). Cryptic but some potential Insecticidal Plants of India, *Journal of Medicinal Plants Studies*, 2(3),44-50.
5. M. I. Mazid, M.I., Khan, T.A. & Mohammad, F. (2011). Role of secondary metabolites in defense mechanisms of plants, *Biology and Medicine*, 3 (2), 232-249.

6. Tholl, D. (2015). Biosynthesis and Biological Functions of Terpenoids in Plants, *Adv Biochem Eng Biotechnol*, 148, 63–106. DOI 10.1007/10_2014_295.
7. Silvestre, A.D.J. & Gandini, A. (2008). *Terpenes:* Major Sources, Properties and Applications, In:Monomers, Polymers and Composites from Renewable Resources, Belgacem, M.N.& Gandini, A. (Eds.), *ELSEVIER*. p.17-38.
8. Frost, C.J.,Appel, H.M.,Carlson, J.E., De Moraes, C.M.,Mescher , M.C. & Schultz, J.C. (2007). Within-plant signalling via volatiles overcomes vascular constraints on systemic signalling and primes responses against herbivores, *Ecol. Lett*, 10, 490–498.
9. Zapata, F. & Fine , P.V.A.(2013). Diversification of the monoterpene synthase gene family (TPSb) in Protium, a highly diverse genus of tropical trees, *Molecular Phylogenetics and Evolution*, 68, 432–442.
10. Snoeren, T.A.L., Kappers, I.F., Broekgaarde, C., Mumm, R., Dicke, M. & Bouwmeester, H.J. (2010). Natural variation in herbivore-induced volatiles in Arabidopsis thaliana. *J. Exp. Bot*, 61,z 3041–3056.
11. Xiao, Y., Wang, Q., Erb, M., Turlings, T.C.J., Ge, L., Hu, L., Li, J., Han, X., Zhang, T., Lu, J., Zhang, G. & Lou, Y. (2012). Specific herbivore-induced volatiles defend plants and determine insect community composition in the field, *Ecol. Lett*, http:// dx.doi.org/10.1111/j.1461-0248.2012.01835.x.
12. Burt, S. (2004). Essential oils: their antimicrobial properties and potential application in foods-A review, *International Journal of Food Microbiology*, 94, 223-253.
13. Hammer, K.A., Carson, C.F., Dunstan, J.A., Hale, J., Lehmann, H., Robinson, C.J., Prescott, S.L. & Riley, T.V. (2008). Antimicrobial and anti-inflammatory activity of five *Taxandria fragrans* oils *in vitro*, *Microbiology and immunology*, 52, 522-530.
14. Hussain, A. I., Anwar, F., Sherazi, S.T.H. & Przybylski, R. (2008). Chemical composition. Antioxidant and antimicrobial activities of basil (*Ocimum basilicum*) essential oils depends on seasonal variations. *Food Chemistry*, 108, 986-995.
15. Bakkali R., Averbeck, S., Averbeck, D. & Idaomar, M.(2008). Biological effects of essential oils. – A review, *Food and Chemical Toxicology*, 46, 446–475.

16. Hajhashemi, V., Ghannadi, A. & Sharif, B.(2003). Anti-inflammatory and analgesic properties of the leaf extracts and essential oil of *Lavandula angustifolia* Mill, *Journal of Ethnopharmacology*, 89, 67–71.

17. Delamare, A. P. L., Pistorello, I. T. M., Artico Liane, S. L.A. & Echeverrigaray, S. (2007). Antibacterial activity of the essential oils of *Salvia officinalis L*. and *Salvia triloba L.* cultivated in South Brazil, *Food Chemistry*, 100, 603-608.

18. Hemmerlin, A., Harwood, J.L. & Bach, T.J. (2012)..A raison d'etre for two distinct pathways in the early steps of plant isoprenoid biosynthesis? *Prog Lip Res*, 51, 95–148.

19. Hemmerlin. A. (2013). Post-translational events and modifications regulating plant enzymes Involved in isoprenoid precursor biosynthesis, *Plant Sci*, 203,41–54.

20. Jörg, D., Tobias, G. K. & Jonathan, G. (2009). Monoterpene and sesquiterpene synthases and the origin of terpene skeletal diversity in plants, *Phytochemistry*, 70**,** 1621–1637.

21. Lahlou, M. (2004). Method to study the phytochemistry and bioactivity of essential oil, *Phytotherapy Research*, 18, 435-488.

22. Behnke , K., Ehlting, B.,Teuber, M., Bauerfeind , M., Louis, S., Hasch, R., Polle, A., Bohlmann, J. & Schnitzler, J.P . (2007). Transgenic, non-isoprene emitting poplars don't like it hot, *Plant J*, 51,485– 499.

23. Delfine, S.,Csiky, O., Seufert, G. & Loreto, F. (2000). Fumigation with exogenous monoterpenes of a non-isoprenoid-emittimg oak (*Quercus suber*): Monoterpeneacquisition, translocation, and effect on the photosynthetic properties at high temperatures, *New Phytol*, 146, 27-36.

24. Byers, K., Bradshaw, H.D. & Riffell, J.A .(2014). Three floral volatiles contribute to differential pollinator attraction in monkeyflowers (Mimulus), *J Exp Biol*, 217,614–623 245.

25. Turlings , T.C.J., Loughrin, J.H., Mccall , P.J., Roese, U.S.R., Lewis, W.J. & Tumlinson, J.H. (1995). How caterpillar-damaged plants protect themselves by attracting parasitic wasps. Proceeding of the National Academy of Sciences of the USA, 92, 4169-4174.

26. Lawrence, B. (2000). Essential Oils: From Agriculture to Chemistry. NAHA's world of aromatherapy III conference Proceedings. 8-26.

27. Eisner, T., Eisner, M., Aneshansley, D.J.,Wu & , W.Meinwald, J . (2000). Chemical defense of the mint plant, *Teucrium marum* (Labiatae), *Chemoecology* , 10(4),211-216 doi:10.1007/PL00001825

28. Shawe, K .(1996).The Biological Role of Essential Oils, *Aromatherapy Quarterly*, 50, 23-27.

29. Sell, C. (2010). The Chemistry of Essential Oils, In: Baser, C. & Buchbauer, G.(Eds). Handbook of Essential Oils: Science, Technology and Applications. CRC Press, Taylor and Francis Group, Chapter 5**,** 121-150.

30. Buchbauer, G. (2000). The detailed analysis of essential oil leads to the understanding of their properties, *Perfumer and flavourist*, 25, 64-67.

31. Kramer, R. & Abraham, W-R. (2011).Volatile Sesquiterpenes from fungi: What are they good for? Phytochemistry Reviews, 11(1), 15-37 doi10.1007/s11101-011-9216-2.

32. Anderson, B., Terblanche J.S. & Ellis, A.G .(2010). Predictable patterns of trait mismatches between interacting plants and insects, *BMC Evol Biol*, 10, 204.

33. Strobel, G.A., Dirkse, E., Sears, J. & Markworth, C .(2001).Volatile antimicrobials from *Muscodor albus*, a novel endophytic fungus, *Microbiology* , 147, 2943-2950.

34. Umehara, M.,Hanada, A., Yoshida, S., Akiyama, K., Arite, T.,Takeda-Kamiya, N., Magome, H., Kamiya, Y., Shirasu , K.& Yoneyama, K. (2008). Inhibition of shoot branching by new terpenoid plant hormones, *Nature*, 455, 195–200.

35. Loreto, F. & Schnitzler, J.P. (2010). Abiotic stresses and induced BVOCs, *Trends Plant Sci,* 15, 154–166.

36. Martin, C., Harriet, T., Frances, G. & Carol, W.(2013). Sesquiterpenoids Lactones: Benefits to Plants and People, *Int. J. Mol. Sci*, 14, 12780-12805.

37. Rees, S.B. & Harborne, J.B. (1985).The role of sesquiterpene lactones and phenolics in the chemical defence of the chicory plant, *Phytochemistry*,24, 2225–2231.

38. Holopainen, J.K. (2004). Multiple functions of inducible plant volatiles, *Trends Plant Sci*, 9, 529–533.

39. Poecke, R.M.P.V. & Dicke, M. (2003). Signal transduction downstream of salicylic and Jasmonic acid in Herbivory-induced parasitoid attraction by *Arabidopsis* is independent of JAR1 and NPR1, *Plant Cell Environ*, 26, 1541–1548.

40. Kunert, G., Otto, S., Rose, U.S.R., Gershenzon, J. & Weisser, W.W .(2005). Alarm pheromone mediates production of winged dispersal morphs in aphids, *Ecol Lett*, 8, 596-603.

41. Halls, S.C., Gang D.R. & Weber, D.J .(1994). Seasonal variation in volatile secondary compounds of *Chrysothamnus nauseosus* (Pallas) Britt.; Asteraceae ssp. *hololeucus* (Gray) Hall. & Clem. Influences herbivory, *J Chem Ecol*, 20, 2055-2063.

42. Rasmann, S., Kollner ,T.G., Degenhardt ,J., Hiltpold, I., Toepfer, S., Kuhlmann, U., Gershenzon, J. & Turlings ,T.C.J .(2005). Recruitment of entomopathogenic nematodes by insect-damaged maize roots, *Nature*, 434, 732-737.

43. Lago, J.H., Soares, M.G., Batista-Pereira, L.G., Silva, M.F., Correa, A.G., Fernandes, J.B., Vieira , P.C. & Roque, N.F .(2006). Volatile oil from *Guarea macrophylla* ssp. *tuberculata*: seasonal variation and electroantennographic detection by *Hypsipyla grandella*, *Phytochemistry*, 67,589-594.

44. Marcello, I. & Franco, F. (2009). Chemical Diversity and Defence Metabolism: How Plants Cope with Pathogens and Ozone Pollution, *Int. J. Mol. Sci*,10, 3371-3399.

45. Lichtenthaler, H.K.. (1996). Vegetation stress: An introduction to the stress concepts in plants, *Journal of plant Physiology*, 148, 4-14.

46. Reigosa , M.J.,Sanchez-Moreiras , A.M.& Gonalez ,L.(1999). Ecophysiological approach in allelopathy, *Critical Review of Plant Sciences*, 18, 577-608.

47. Reigosa , M.J., Pedrol , N., Sanchez-Moreiras, A.M. & Gonalez,L. (2002). Stress and allelopathy, In: Reigosa, M. & Pedrol, N.(Eds), allelopathy: from molecules to ecosystems, Enfield, New Hampshire: Science Publishers, p 231-256.

48. Bloem , E., Haneklaus, S. & Schnug,E. (2005). Significance of sulphur compounds in the protection of plants against pests and diseases, *Journal of Plant Nutrition*, 28, 763-784.

49. Gershenzon, J. (1994). Metabolic costs of terpenoid accumulation in higher plants, *J Chem Ecol*, 20, 1281-1328.

50. Purrington, C.B. (2000). Costs of resistance, *Curr Opin Plant Biol*, 3,305-308.

51. Wu, J. & Baldwin, I.T. (2009) . "Herbivory-induced signalling in plants: Perception and action". *Plant Cell Environ*, 32, 1161–1174.

52. Sangha, J.S., Yolanda, C.H., Kaur, J., Khan, W., Abduljaleel, Z., Alanazi, M.S., Mills, A., Adalla, C.B., Bennett, J., Prithiviraj, B.,Jahn, G.C. & Leung, H. (2013), "Proteome Analysis of Rice *(Oryza sativa* L.*)* Mutants Reveals Differentially Induced Proteins during Brown Planthopper *(Nilaparvata lugens)* Infestation", *Int. J. Mol. Sci*, 14, 3921–3945.

53. Schardl , C.L. & Chen, F. (2010). Plant defences against herbivore attack. In: Encyclopedia of Life Sciences (ELS). John Wiley & Sons, Ltd: Chichester.

54. Traw, B.M. & Todd, E.D. (2002). "Differential induction of trichomes by three herbivores of black mustard", *Oecologia,* 131 (4), 526–532.

55. Wittstock, U. & Gershenzon, J. (2002). Constitutive plant toxins and their role in defense against herbivores and pathogens, *Current Opinion in Plant Biology*, 5, 1-8.