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VOLATILE ORGANIC COMPOUNDS

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1. ABSTRACT

Diverse amount of volatile organic compounds is synthesized by plants, proven to be of utmost importance to the plants in various stages of their perpetuation cycle. Their functions are attraction of insects for pollination, dispersal of seeds, helping plants to withstand competition from neighboring plants, contributing towards maintaining plant biodiversity, helping in growth of agriculturally important plants and aiding plants in combating both abiotic stress and biotic stress. Calcium ions and ROS (reactive oxygen species) plays a crucial role as signaling molecules in plants in pathways dealing with induction of synthesis of VOCs in response to various biotic and abiotic stresses and the mechanisms elucidating the survival of plants in such conditions. Apart from this, the concern arising from the expected effects of global climatic changes on rate of synthesis and emission of VOCs in plants has also been expressed. The later part of the paper highlights the beginning of a novel field of metabolic engineering which deals with engineering of biochemical pathways of biosynthesis of VOCs in a manner so as to maximize the yield of beneficial VOCs and at the same time minimizing the yield of harmful VOCs to obtain desired results. The achievements that have been attained, the unintended effects that creep in and the challenges that need to be overcome to make advancements in the field of metabolic engineering have also been included.

2. INTRODUCTION

VOC or volatile organic compounds are lipophilic liquids or chemical compounds that exhibit low molecular weight and high vapour pressure at ordinary room temperature which allows them to evaporate or sublime from solid or liquid form of the compound into the surrounding environment (Pichersky et al., 2006).

VOCs are omnipresent and countless in number. They include both anthropogenic VOCs which are manmade and natural VOCs. Anthropogenic VOCs have to be strictly monitored by law and kept under effective surveillance since immense hike in their levels can pose an imminent threat to the environment. Harmful VOCs are not profoundly pernicious but they have long lasting effects on health such as short term exposure (acute) and long term exposure (chronic) to high level VOCs. Short term exposure leads to increased risk of infection and irritation in eye, nose, throat, headaches, difficulty for asthma patients. Whereas long term exposure increases the risk of some deadly diseases i.e. cancer, also damages kidney, liver and central nervous system.

Plants also congregate multitudinous no. of products that are natural and believed to help plants in communication with surrounding environment and perform a lot of functions including attracting beneficial insects for pollination (Knudsen et al., 2006) thus being of immense use in the perpetuation cycle of the plants, defending plants from the attack of herbivorous animals either by killing them and deterring them directly or in an indirect manner by attracting carnivorous animals which feed on herbivores (Shiojiri et al., 2006;Croft et al., 1993), signalling within the same plant to protect the undamaged plant parts following a herbivore attack and among different plants when one of the plants is damaged by the herbivore attack by venting out a blend of VOCs which warn the neighbouring plants of the emanating danger which leads to activation of defence mechanisms in neighbouring plants, promote plant competition (Franklin, K.A. 2008), protect the plant from prevailing abiotic stresses and contribute a great deal to promote biodiversity within various angiosperms by preventing inbreeding (Waelti et al., 2008). Above mentioned compounds are called secondary metabolites so, that it can get differentiated from primary metabolites which plays a role in the growth and development along with reproduction of an organism whereas secondary metabolites do not play direct role in the above processes but rather perform ecological functions and contribute to the sustenance of an organism in its ecological niche, thus contributing to reproductive fitness of an organism (Theis and Lerdan, 2003). More than 1700 VOCs have been discovered in angiospermic plants till date (Dicke and Loreto, 2010). Momentous significance of Volatile compounds was highlighted when the fact was revealed that almost 36% of the carbon assimilated by plants is released during photosynthesis as VOCs (Kesselmeier et al., 2002). Healthy unwounded plants dissolute accumulated VOCs, which depends on the physical and chemical properties along with the concentration of these VOCs (Niinemets et al., 2004). Opposed to it there are certain plants which do not synthesize and emit VOCs into the environment until and unless triggered by an external stimulus or stress. Such VOCs are induced VOCs which are dissipated from both stressed sites as well as systematically from undamaged plant leaves (Pare and Tumlinson, 1997). Since induced VOCs are induced only under stress conditions unlike constitutive VOCs, they do not cause a great deal of burden on the carbon content of the plant and are very economical (Dicke, 2000). A large number of induced VOCs are known to exist in the environment including alkenes, alkanes, carboxylic acids, nitrogen containing compounds and alcohols, but the dominating ones are isoprene, terpenes, and C6 green leaf volatiles (GLVs) (Holopainen and Gershenzon, 2010).

3. BIOSYNTHESIS OF VOCs

VOCs are produced from a number of biochemical pathways in plants. The common types of VOCs present in plants and the pathways contributing to their biosynthesis are as follows:

a. Isoprenoids: C5 unit which is chemically 3-methyl 1, 2-butadiene, is termed as isoprene. All isoprenoids are produced from dimethyl allyl diphosphate (DMAPP) and its isomer Isopentenyl diphosphate (IPP) which is synthesized by deoxyxylulose–5-phosphate (DXP or MEP) pathway in chloroplast or by mevalonate (MVA) pathway in cytoplasm. (Kesselmeier and Staudt, 1999). It is believed that C10 precursors of monoterpenes are synthesized within plastids by MEP pathway whereas precursors of sequiterpenes (C15) are synthesized in cytoplasmic MVA pathway.

Certain VOCs such as β-ionene are not generated directly from IPP, rather cleavage of tetraterpenes like carotene is the major backing force behind their production and this cleavage is brought about by carotenoid cleavage dioxygenases (CCDs). Homoterpenes such as 4, 8-dimethylnona-1, 3, 7-triene (DMNT) and 4, 8, 12-trimethyltrideca -1, 3, 7, 11 – tetraene (TMTT) are the terpenoids that are formed in response to herbivore feeding (Holopainen, 2004; Arimura et al., 2005, 2009). The biosynthesis of TMTT and DMNT is brought into action by oxidative degradation by CYP450 enzymes of the diterpene geranyl linalool and the sesquiterpene (E) – nerolidol as precursors respectively (Holopainen, 2004; Arimura et al., 2005, 2009). Quite a large number of terpenoids are synthesized by terpene synthases (TPS) using geranyl diphosphate (GPP) and farnesyl diphosphate (FPP) as precursors (Owen et al., 1997, 2001; Lin et al., 2007; Arimura et al., 2008 a, b, 2009; Wu and Baldwin, 2009).

b. Oxylipins: Oxylipins are derived from polyunsaturated fatty acids which are discharged from chloroplast membranes by lipase activity. They form the precursors for biosynthesis of a large number of oxygenated compounds including jasmonates as well as green leafy volatiles (GLVs). GLVs are synthesized from C18 polyunsaturated fatty acids like linoleic acid and linolenic acids via LOX (Lipoxygenase) pathway (Dudareva, 2005). C18 acids are initially cleaved to C12 and C6 compounds by hydroperoxide lyases (Engelberth et al., 2004). The first C6 compound so formed is 3-Z-hexanal which is later converted to other GLVs such as 2-hexanal, 3 hexanol, and 3-hexenyl acetate (Shiojiri et al., 2006).

c. Volatile Aromatic Compounds: Another class of VOCs is formed by class of compounds that consists of an aromatic ring involving shikimate pathway. VOCs that contain nitrogen or sulfur are synthesized by cleavage reactions of modified amino acids or their precursors as is seen is case of indole which is formed in maize by cleavage of Indole-3-glycerol phosphate which is an intermediate in tryptophan biosynthesis (Koeduka et al., 2006). Indole is released in plants in response to herbivore attack.

Certain aromatic VOCs are derived from phenylalanine. Eugenol is one such alcohol which is derived by decarboxylation and oxidative removal of amino group of phenylalanine (Pichersky et al., 2006). Salicylic acid can be formed via two pathways – either by delivering benzoate from cinnamate or using isochorismate. Methyl salicylate is synthesized from salicylic acid in a reaction involving transfer of a methyl group from S-adenosine-methionine (SAM) to the carbonyl group of salicylic acid in the presence of enzyme methytransferase (Vassao et al., 2006).

4. REGULATION OF VOC EMISSION

There are several factors controlling the rate of emission of VOCs in plants. Some of them are:

a) Control at transcriptional and translational level- Genes involved in biosynthesis of VOCs are upregulated subsequent to a herbivore attack on the plant via jasmonic acid, salicylic acid and ethylene signalling pathways (Hermsmeier et al., 2001; Kant et al., 2004 ; Ralph et al., 2006).

Emission of VOCs also seems to analogize with the activity of enzymes controlling their synthesis both under normal and stress conditions (Kuzma and Fall, 1993; Loreto et al., 2001a; Fischbach et al., 2002). Thus, we gather that emission of VOCs is regulated not just at transcriptional level but also at post transcriptional, translational and post translational level.

b) Substrate availability- It is a major factor controlling the biosynthesis and emission rates of VOCs. Though certain enzymes that are involved in biosynthesis of VOCs are very promiscuous and exhibit broad substrate specificity and thus synthesize different types of VOCs accordingly (Negre et al., 2003; Boatright et al., 2004; Pott et al., 2004). The significance of substrate availability for the biosynthesis of VOCs is clearly seen in transgenic tobacco in which genetic modification leading to switching of cytosolic or plastidic isoprenoid precursors led to increased biosynthesis of VOCs (Wu et al., 2006).

c) Circadian regulation - Emission of VOCs from flowers, leaves and other floral parts are seen to show diurnal or nocturnal patterns (Dudareva et al., 2005; Wilkinson et al., 2006; Loivamaki et al., 2007). The underlying cause behind this circadian regulation of emission of VOCs might be somehow related to substrate availability and transcriptional control (Yakir et al., 2007).

d) Physiological factors - Leaf temperature, stomatal conductance, leaf morphology, soil moisture availability, carbon dioxide concentration and ozone concentration also affects the rate of emission of VOCs.

e) Light availability - Certain plants like *Pinus, Eucalyptus* and those in Rutaceae family are equipped with storage compartments for VOCs like resin ducts, cavities, oil glands and glandular trichomes while others like oaks completely lack them. The emission rate in the latter is coupled to the incident light intensity (Staudt and Bertin, 1998) while in the former ones, the emission rate is controlled by leaf temperature which has a marked effect on volatilization of VOCs (Tingey et al., 1980). Certain VOCs like isoprene, being highly volatile are not stored at all.

5. FUNCTIONS OF VOCs IN PLANTS

VOCs form the lifeline of plants. Plants inhabit a hostile environment where they are constantly exposed to all sorts of biotic and abiotic stresses and competition from neighbouring plants for sharing the limited pool of nutrients, water and other resources in order to sustain their existence. VOCs play a remarkable role in enabling plants tackle all these stressful situations efficiently.

5.1 ROLE OF VOCs IN PLANT REPRODUCTION

Since plants are sessile and cannot move from one place to another for pollination and can neither avoid it because it is an indispensable part of their perpetuation cycle, so plants are in constant search for external agents that can aid them in fulfilling this purpose. Insects play a pivotal role in the life cycle of plants being major pollination agents and this is where the role of plant secreted VOCs come into play. Out of the five basic senses that every organism possesses, olfaction and visualization play an important role in pollination. As is said in one of the theories of epigenetics that external features or ornaments are key players in promoting the sexual selection, the same concept applies here as well, flowers are "biological markets" for pollinating insects from which only the ones which have compatible colors and scent which is appealing to the insects are chosen for pollination (Chitka and Raine, 2006). The presence of aromatic and chromatic cues enables the insects to differentiate between different flowers and thus insects inculcate the habit of repeatedly visiting the flower which is of their interest on the basis of retrieval of memories (Kunze and Gumbert, 2001).

Different floral parts like sepals, petals, pollen and nectar emit diverse blends of VOCs (Dudareva et al., 2000; van Schie et al., 2006). Floral VOCs are species specific. For example, plant species pollinated by moths emit high amount of benzenoids and to a lesser extent terpenoids and nitrogen containing compounds (Dobson, 2006) while bat pollinated flowers predominantly release sulfur containing VOCs (von Helverson et al., 2000). Pollinators are very shrewd and capable of distinguishing between complex multicomponent VOC profiles with unique ratios and intensities of compounds (Wright et al., 2005) and preferentially reach for the plant of specific volatile profile thus ensuring flower constancy and increasing pollen transfer to specific plants thereby avoiding stigma congestion with unspecific pollen. This phenomenon has been seen in honeybees which repeatedly visit the same flower even when other flowers in the surrounding environment offer better rewards. This is beneficial for the flower since pollen deposition on conspecific stigma is ensured but the honeybee seems to be disadvantaged in the whole process since it loses on the surrounding flowers that are offering better rewards (Gruter and Ratnieks, 2011). VOCs emitted from pollen are chemically different from the VOCs secreted by other plant parts majorly containing benzyl tiglate, isopinocamphone, dimethyl glutarate, dimethyl adipate and many other VOCs (Dobson et al., 1996; Flamini et al., 2002). Moreover, the diversity of compounds is often lower in pollen VOCs (Knudsen and Tollsten, 1991; Dobson et al., 1996). Odor emitted from pollen is advantageous to the plant since it attracts pollen plundering insects which leads to increased rates of pollen dissemination (Dobson and Bergstrom, 2000). But along with it come two disadvantages – need of use of specialized mechanisms to evade the effect of non-pollinating insects that uselessly capitalize on the plant without doing any good to it and a substantial amount of energy needs to be expended in improving the pollen odour to attract large number of insects for pollination (Hargreaves et al., 2009).

VOCs emitted from pollinated flowers play the unique and noble role of directing pollinator insects to yet unpollinated flowers (Schiestel and Ayasse, 2001).

A quite strange phenomenon of down regulation of the emission of VOCs has been seen in *Silene latifolia* flower wherein apart from acting as pollination signals, VOCs also act as flower antagonists by attracting the pollinator *Hadena bicruris* whose larvae feeds on the developing seeds of the plant ultimately killing it. To evade such disastrous cessation to the plant, the amount of VOCs has to be downregulated subsequent to pollination (Wolfe, 2002; Dotterl et al., 2006).

Nectar also acts as one of the components that a plant employs for attracting the insects. Apart from the primary metabolites like sugar and amino acids, nectar also contains certain secondary metabolites such as alkaloids, phenolics and nonprotein amino acids (Baker, 1977) which have deterrent effect on so called nectar thieves and sometimes also have undesired negative effects on pollinators' visits (Stephenson, 1981; Kessler and Baldwin, 2007).

Apart from being of immense importance in attracting insects for pollination, VOCs also play a crucial role in seed dispersal. VOCs secreted from fruits and seeds/spores attract various animals that aid in seed dispersal in the ecosystem. For example, blends of VOCs emitted from seeds of epiphyte *Peperomia macrostachyam* attract ant-garden ants in the Amazon rainforests and exploit their seed collecting behaviour (Youngsteadt et al., 2008). Similarly, VOCs secreted from mature fruits attract bats which help in fruit dispersal (Hodgkison et al., 2007).

5.2 ROLE OF VOCs IN NEIGHBOR DETECTION AND PROMOTING PLANT COMPETITION

Herbert Spencer rightly quoted the phrase "survival of the fittest". If you do not compete with others, you will fall off the wheel of life and be outcompeted. This applies to plant systems as well. There is an ongoing conflict between a plant with its neighbouring plants for water, nutrients, light and other resources. Depending on which resource plants are competing for, they will accordingly portion out more amount of carbon to roots (if competition is for water and nutrients) or shoot (if competition is for light). While competing for light, carbon is used for shade avoidance responses which involve movement of leaves towards light and enhanced internode elongation so that all the leaves can occupy positions in the well-lit area for effective photosynthesis to occur (Franklin, K.A., 2008).

In areas of dense vegetation where plants grow in clustered fashion, the urge for competition is even heightened because limited space harbours a large number of plants and they have to fall back on limited nutrients, water and light for survival. Role of VOCs becomes even more important in such areas. A large number of signals can be used by plants for detection of neighbouring plants growing in their vicinity.Reduced amount of R/FR and of blue light - Plants use red and blue light for photosynthesis while far red (FR) light is reflected back. Reduced levels of R/FR and reduced blue light fluence rates are detected by phytochrome, cryptochrome and phototropin family of photoreceptors respectively, this is followed by intense competition for light and instigation of shade avoidance response (Franklin, K.A., 2008). Ethylene – Being a volatile hormone, amount of ethylene serves as a neighbour detection signal in a canopy (Pierik, R. et al., 2004). Lowered wind exposure – Diminished wind flow rates also act as neighbour detection signal in dense vegetation (Anten, N.P.R. et al., 2005). Underground communication – Reduced availability of nutrients, groundwater and root exudates also act as neighbour detection signals (de Kroon, H. 2007). Neighbour detection is followed by cut throat competition within the neighbouring plants in order to sustain their own being and outcompete the neighbour. Resource limitation has a marked effect on the emission rates of VOCs. VOCs secreted from one plant can have the following effect on its neighbouring plants:

a) The growth and development of the neighbouring plants will be retarded. This phenomenon in which a plant secretes certain allelochemicals in its surrounding environment which arrest the growth and development of neighbouring plants is called allelopathy.

b) Certain neighbouring plants also exhibit the property of exploiting the HIPVs (Herbivore induced plant volatiles) emission from the allelopathic plant to their advantage by using VOCs as a signal for the presence of nearby competitors and accordingly inculcating responses that enhance the competitive powers of the snooping neighbour (Wouter Kegge and Ronald Pierik, 2009).

VOCs acting as allelochemicals can be secreted from any part of the plant, be it underground or above ground. Allelochemicals are tissue specific and this fact was highlighted when it was seen that root emitted monoterpenoid VOCs such as camphor, camphene, 1, 8 cineole and β-pinene from *Salvia leucophylla* root inhibited root germination and growth in *Brassica campestris* but at the same time the effect was localized only to the root region and no traces of any such effect were visible in the shoot apical region (Nishida, N. et al., 2005). Interestingly, it is seen that root germination of competitors is affected not just by the root emitted VOCs but by shoot emitted VOCs as well. This fact was highlighted when it was noticed that VOCs emitted from *Antirrhinum majus* flowers inhibit root growth in neighbouring *Arabidopsis* plants under laboratory conditions which was later investigated to have occurred due to methyl benzoate present in the blend of VOCs secreted from the plant which has adverse effect on the expression of genes regulating growth hormones such as auxin and cytokinin (Horiuchi, J. et al., 2007).

A strange observation noticed during study of *Artemisia tridenta* showed that when its leaves were cut, it inhibited the germination of neighbouring plants. But if somehow an arrangement was made to prevent the air contact and allow just the soil transmittance, no such inhibition was seen. This observation led to the inference that on clipping the leaves, *Artemisia tridenta* emitted VOCs that inhibited the growth of neighbouring plants as a means of avoiding competition (Karban, R., 2007). But if you look the whole scenario from another perspective, one more mind boggling idea pops up into your mind that rather than being an allelopathic effect at all, inhibition of root germination could just have been an adaptive measure up-taken by neighbouring plants upon detection of herbivore mediated clipping of the leaves of *Artemisia tridenta* to evade the ensuing threat of being damaged by herbivore in the early seedling stage. This clearly proves that apart from acting as allelochemicals in some of the plant species, VOCs also act as neighbour detection signals in certain species. A very common plant illustrating this behaviour is *Cuscuta pentagona*, a parasite which spots its host by monitoring the blend of different VOCs secreted by its host plant. This host detection system is so advanced and sensitive that *Cuscuta pentagona* can efficiently discriminate between different neighbouring species based on their volatile profiles (Runyon, J.B. et al., 2006).

5.3 ROLE OF VOCs IN CONTRIBUTING TOWARDS PLANT BIODIVERSITY

The exact mechanism which led to speciation in angiosperms is not known till date but VOCs are thought to play an important role in maintaining prezygotic isolation mechanisms within plants and contributing to maintenance of reproductive isolation. This is done by controlling pollinator behaviour which in turn is determined by pollinator's attraction to specific signals in a flower like flower colour, size and the blend of VOCs secreted by a particular flower. A pollinator very shrewdly manages to differentiate between closely related plant species by monitoring their volatile profiles. Volatile profile of each and every plant, even the ones belonging to closely related species differs from each other owing to different intensity, ratios of constituents and the presence of unique compounds in the blend of VOCs secreted from them. This phenomenon is clearly highlighted in case of sexually deceptive orchids belonging to the genera *Oophrys* and *Chiloglottis* in which flowers emit VOCs whose odour resembles the scent of female pollinator's sex pheromone thus masquerading laying the male pollinator into its trap (Schiestl, 2005). It has been seen that each orchid belonging to the above mentioned genera vents out a different species specific volatile profile providing a unique cue for a single pollinator species (Ayasse et al., 2011). Volatile profiles emitted by two very closely related species and differing just by a single VOC are good enough for a pollinator to distinguish between the two species and this behaviour has been seen in *Silene dioica* and *Silene latifolia* whose volatile profiles differing just by phenylacetaldehyde where volatile blends have the same constitution but in different relative amounts are good enough to cause reproductive isolation between the two species (Waelti et al., 2008).

When this phenomenon of reproductive isolation in sexually deceptive orchids belonging to genus *Oophrys* was traced back to find the cause underlying it, it was concluded that this occurred due to species specific alkene emission profiles that are defined by differences in enzyme activity and gene expression of a few stearoyl-acyl carrier protein desaturases (Schluter et al., 2011; Xu et al., 2012).

5.4 IMPACT OF VOCs ON AGRICULTURE

Pollinators play a very critical and unparalleled role in the life cycle of plants, especially in those plants which exhibit the trait of self-incompatibility. It has been observed that plants like *Citrus glandis* in which flowers are self-incompatible release more amount of VOCs because they are completely at the mercy of pollinators for effectuating their perpetuation cycle as compared to orange, grapefruit and lemon which have flowers with both male and female organs (Jabalpurwala et al., 2009).

A number of studies have been conducted which highlight the extreme dependence of pollinator attraction on the volatile profiles secreted by a plant. A very good example linking this phenomenon with the development of GM crops is seen in Bt gene (cry3Bb) expressing eggplant. The main aim of inserting Bt gene in egg plant was to confer an insect pest resistance to it. Apart from lending the intended property of insect pest resistance, Bt gene also fortuitously bestowed the property of causing emission of five major VOCs (methyl salicylate, Z-jasmone, a-pinene, a-methyl styrene and d-2-carene) all of which kindled positive responses in bee antenna and even drew a greater population of bumblebees as compared to the wild type varities despite possessing significantly smaller flowers and plant size.

To date there have been only two examples that corroborate the link between floral VOC emission and crop pollination failure. One of them is seen in Alfalfa which is completely at the mercy of honeybees for bringing about pollination and frequency of honeybees visiting its flower is very low because of the special composition of its volatile profile whose major constituent is ocimene which faces a negligent behaviour from honeybees and at the same time, the component which acts as a strong chemoattractant for honeybees that is linalool, is present in very minute quantities in its volatile profile. The delinquency exhibited by honeybees is the major determinant of low seed production in alfalfa (Henning and Teuber, 1992). Apart from this, alfalfa also emits certain deterrents that manacle honeybees from visiting its flower.

5.5 ROLE OF VOCs IN PLANT DEFENSE

A plant continuously thrives in a perilous environment under the threat of being attacked by herbivores and pathogens. It is the blends of VOCs secreted from flowers, roots and leaves of plants that come handy in such situations as they exhibit antimicrobial properties and work like magic wands in protecting the plants from the action of invading pathogens (Croft et al., 1993; Shiojiri et al., 2006).

5.5.1 BIOSYNTHESIS AND REGULATION OF TERPENOIDS IN RESPONSE TO HERBIVORY

This figure illustrates the mechanism underlying biosynthesis of terpenoids in response to herbivore attack in two different types of herbivores– chewing arthropods and sucking arthropods.

The very first event that occurs in a herbivore damaged plant is increased influx of Ca^{+2} into the cytoplasm from extracellular environment in response to the elicitors injected into the plant from insect oral secretions.

This increased influx of calcium ions leads to jasmonic acid mediated biosynthesis of terpenoids in chewing arthropods and both jasmonic acid and salicylic acid mediated biosynthesis of terpenoids in sucking arthropods. Ethylene also plays a significant role in terpenoid biosynthesis in response to attack by chewing arthropods in two ways:

- By effecting increased calcium ion influx into the cytoplasm.
- By regulating the downstream jasmonic acid mediated biosynthesis of terpenoids (Arimura et al., 2008a).

The terpenoids so produced attract predators that feed on herbivores thus killing them.

5.5.2 ROLE OF Ca^{+2} IN SIGNALING PATHWAY LEADING TO PRODUCTION OF TERPENOIDS

Calcium ions act as a second messenger in the biosynthesis of terpenoids synthesized in response to herbivory and also have a casting effect on the composition of terpenoids synthesized.

Maintenance of intracellular calcium levels is very important for the survival of the cell. The cytosolic concentration of calcium ions is kept low (0.0001 mM) as compared to the extracellular medium and subcellular compartments like mitochondria, endoplasmic reticulum and the vacuole

(0.1 mM). This concentration is maintained by Ca^{+2} homeostasis system which consists of large calcium ion stores which can release calcium ions, calcium ion channels/pumps which control both Ca^{+2} influx and efflux in cells and subcellular compartments and Ca^{+2} binding proteins like calmodulin that bind to Ca^{+2} and congregate them (Pandey et al., 2000). Ca^{+2} ATPases located in subcellular compartments play a momentous role in maintaining this gradient by relentlessly pumping Ca^{+2} out of the cytosol (Allen et al., 1995).

5.5.3 ROLE OF ROS IN SIGNALING PATHWAY LEADING TO FORMATION OF VOCs

Apart from Ca^{+2}, reactive oxygen species (ROS) also act as signaling and defense molecule in response to herbivory. Just like skin, which forms the first line of defense against invading pathogens in humans, production of ROS is the first barrier that a plant uses to combat an invading pathogen or insect. Under normal conditions, the level of ROS is kept low by the activity of antioxidant systems which include secondary metabolites and scavenging enzymes (Foyer and Noctor, 2005a, b; Pandhair and Sekhon, 2006). However, a biotic or abiotic stress leads to increased ROS production or decreased antioxidant potential (Apel and Hirt, 2004; Asada, 2006; Davies et al., 2006; Foyer and Noctor, 2003; Hancock et al., 2002).

Quite a large number of enzymes like NADPH oxidase, superoxide dismutase, peroxidase, polyamine oxidase and diamine oxidase are present in apoplast which function in production of ROS which directly kills the insect and can aid in strengthening the cell wall due to polymerization. This mechanism of herbivore killing is termed as apoplastic oxidative burst (Bhattacharjee, 2005; Bolwell et al., 2002).

Oral secretions from salivary glands of herbivores produces H_2O_2 which diffuses inside the plant cell through specific hydroperoxiporins which leads to an increase in cytosolic H_2O_2 concentration which is neutralized by scavenging enzymes like catalase, ascorbate oxidase and glutathione peroxidase which apart from it normally neutralize the ROS and H_2O_2 formed in subcellular compartments like peroxisome in which nitric oxide and H_2O_2 are formed on the cytosolic side of the membrane (Corpas et al., 2001; del Rio et al., 2006), mitochondria in which ROS is mainly formed in ETC (Navrot et al., 2007) and chloroplast in which ROS is mainly formed in reaction centres of PS1 and PSII of thylakoids (Asada, 2006).

Apart from operating at the above ground level, defense system also operates at below ground level as seen in maize roots, which on being attacked by the insects secretes sesquiterpene, β-caryophyllene, which in turn attracts another class of predators, nematodes, which feed on the insect larvae thus killing it (Rasmann et al., 2005).

5.5.4 BIOSYNTHESIS AND RREGULATION OF GREEN LEAF VOLATILES IN RESPONSE TO HERBIVORY

Another class of VOCs that are synthesized in response to herbivory include green leafy volatiles (GLVs) which are formed in plants in immediate response to a biotic or abiotic stress within a minute utilizing the LOX pathway (Matsui et al., 2006). Unlike terpenoids which are involved only in indirect defense, GLVs are involved in both direct and indirect defense responses following herbivory (Shiojiri et al. 2006a, Chehab et al. 2008). The very first product formed in the signalling cascade in response to the elicitors secreted by insects into the plants is (Z)-3-hexanal which can either kill the invading herbivore thus acting as a means of direct defense and can also diffuse from the wounded area to the nearby tissues and on oxidation with the help of alcohol dehydrogenases forms (Z)-3-hexen-1-ol which further gets oxidized using acyltransferase to form Z-3-hexen-1-yl-acetate. The GLVs so formed can be used for indirect defense involving attraction of predators for feeding on the herbivore and used as cues by the snooping neighbouring plant to inculcate defense responses within it in response to the ensuing herbivore attack.

It is seen that the first appearance of GLVs in response to herbivore damage takes only few seconds while herbivore induced production of terpenoids takes many hours since the latter involves activation of the genes controlling terpenoid synthases (TPS) which takes quite a long time. Moreover, the production of GLVs is brought about by pre-existing enzymes rather than induced enzymes which further hastens the process involving their formation. Apart from herbivore damage, GLVs have also been seen to be formed in plants even in cases of oxidative damage to plants and in exposure to high temperature and high light intensity (Beauchamp et al., 2005, Loretto et al., 2006).

Besides protecting the plant which has been attacked by a herbivore, VOCs like methyl jasmonate (Farmer & Ryan, 1990), methyl salicylate (Shulaev et al., 1997), some green leaf volatiles (Engelberth et al., 2004; Farag et al., 2005) and some terpenes (Arimura et al., 2002) also act as defence signals between neighbouring plants belonging to same or different species which on being sensed by the neighbouring plant lead to triggering of herbivore defence mechanism (Arimura et al., 2000; Engelberth

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et al., 2004; Kessler et al., 2006; Frost et al., 2007; Ton et al., 2007).

Though this mechanism is very efficient in triggering herbivore defense system in neighbouring plants but authentication of this mechanism cannot be guaranteed in every case as is seen in *Manduca sexta* infested *Nicotiana attenuata* in which VOCs released on being stimulated by herbivory failed to elicit herbivore defense system in the neighbouring *Nicotiana attenuate* (Paschold et al.,2006) while VOCs emitted from sagebrush *(Artemesia tridentate tridentata)* successfully initiated a defense system in *Nicotiana attenuata* against the attack by *Manduca sexta* (Kessler et al., 2006). The cause of this variability is still to be investigated.

The behaviour of sending warning signals to the neighbour seems very peculiar since there is no way that a damaged plant would be advantaged by any means by sending warning signals to its neighbouring plants telling them to watch out for the ensuing herbivore attack when on one side it is engrossed in a constant battle with its neighbouring plants competing for the limited amount of nutrients and water that they share. Plants seem to have evolved this signalling system involving VOCs for communication within an individual plant to protect the undamaged plant parts from herbivore attack but coincidentally this acts as a boon for the neighbouring plants also as they sense the VOCs secreted by the damaged plant though the concentration of VOCs goes on fading as distance increases (Karban et al., 2006).

5.5.5 ROLE OF VOCs IN ABIOTIC STRESS

Plants have developed an efficient system of dealing with the environmental fluctuations which defends them against all the odds that tend to hamper plant growth and development. This defense system is mediated by VOCs.

The very first event that occurs within a plant following a stress perception is the oxidative burst involving production of a large amount of ROS which causes oxidative damage and triggers the signalling cascades which serve to give rise to a number of mechanisms that further pave way for stress tolerance. The plant responds to ROS accumulation in two ways:

- The interplay of reactive oxygen species and reactive nitrogen species allows the instigation of programmed cell death, disturbance in the ion fluxes including Ca^{+2} and direct killing of pathogens. Salicylic acid and abscisic acid act as mediators in these responses in feedback with ROS and RNS.
- Another signalling cascade involves the production of ethylene and jasmonic acid which are required for resistance to necrotrophic pathogens.

6. GROWING AGITATION: EFFECT OF GLOBAL ENVIRONMENTAL CHANGE IN EMISSION OF VOCs

Anthropogenic activities are not a cause of concern just for the human beings but are also posing a menace to the plants. The emission rates of the very compounds responsible for the sustenance of plants by aiding in plant reproduction, defense and communication are fluctuating rapidly due to increased global warming, elevated carbon dioxide concentrations, precipitation patterns and tropospheric ozone. Global climatic change is not just a problem for the humans, but is also posing to be a great menace to the survival of plants. It can have even more far reaching and catastrophic side effects than ever thought of by anyone.

The above mentioned factors can modulate effective means of plant communication using VOCs by perturbing at two levels. Firstly, by modulating the rate of emission of VOCs. This may happen in case of tropospheric ozone, increased carbon dioxide, increased temperature (Llusia and Penuelas, 2000; Loreto and Schnitzler, 2010) due to global warming and drought which are perceived as stress condition by the plants and thus cause increased emission of induced VOCs in plants. Moreover, increased carbon dioxide and temperature may lead to increased rates of synthesis of VOCs and their volatility and diffusivity is also expected to increase owing to increased temperature (Monson et al., 1992). However, if these stress conditions persist for long, it might lead to decreased production of VOCs because of the reduced metabolic flux into the pathways regulating synthesis of VOCs. Drought may lead to closure of stomata as an adaptation to reduce the transpiration due to evaporation thus reducing the rate of emission of VOCs (Gerard Farré-Armengola, Iolanda Filella, Joan Llusia, Josep Penuelasa, 2012). Secondly, the above written compounds can modify the activity of VOCs once VOCs are released from plants. Ozone can affect at both the steps, in the first step ozone mediated damage to the plant causes emission of stress induced VOCs thus altering the overall volatile profile of plants while in the second step ozone reacts with the already released VOCs from the plants thereby reducing their lifetime (McFrederick et al., 2008; Blande et al., 2010) and modifying them thus altering the manner of the perception of VOCs by pollinators and giving rise to an altogether new cascade which will ultimately affect the reproductive fitness of the plant (Heiden et al.,1999; Vuorinen et al., 2004a).

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7. FUTURE PROSPECTS: METABOLIC ENGINEERING OF PLANT VOLATILES

Metabolic engineering aims at achieving two targets:
a) Manipulating the volatilome of those plants in which pollination is limited owing to low amounts of specific component which might act as an attractant for pollinators and thereafter increasing its proportion in the volatile profile of the plant.
b) Manipulating the volatilome of those plants in which production rates have declined due to lack of a key component/components which play key role in the defense system of plants by attracting predators which feed on plant eating insects following herbivory.
Thus, this newly introduced technique seems like a light at the end of the tunnel in enhancing the production of those economically important crops where agriculturists had completely abandoned hopes. Many tactics have been used including the introduction of new gene(s) and manipulation of existing pathways by down/upregulation of certain steps or by occluding the rival pathways.

7.1 ADVANCES IN METABOLIC ENGINEERING

7.1.1 POLLINATION

a) The first consequence of metabolic engineering of floral VOCs on pollinator attraction was scrutized in transgenic tobacco *Nicotiana attenuata* which showed that decreased amount of benzyl acetone attracted scarce number of hawkweeds and humming birds for pollination (Kessler et al., 2008).
b) Latent scent bouquet overexpressing Arabidopsis PAP1 transcription factor in rose flowers was easily perceived by honeybees thus demonstrating its role in pollinator attraction (Zvi et al., 2012).

7.1.2 DEFENSE

a) Introduction of gene coding for patchulol along with some other sesquiterpenes in transgenic tobacco, overexpressing *Pogostemon cablin* patchculol synthase (Wu et al., 2006) dissuaded the hornworms thus improving plant defense.
b) Overexpression of Linalool synthase gene (FaNES1) targeted to chloroplast leading to higher concentration of linalool in Arabidopsis successfully pushed back the aphid *Myzus persicae* thus contributing a great deal to its defense (Aharoni et al., 2003).
c) Overexpression of FaNES1 gene in mitochondria leading to increased production of (3S)-(E)-nerolidol and (E)-DMNT in Arabidopsis contributed to plant defense by attracting predatory mites (Kappers et al., 2005).
d) Overexpression of (E)-β-caryophyllene synthases in rice and maize plant leading to increased production of (E)-β-caryophyllene which contributed a great deal to both above and below ground plant defense by attracting parasitoid wasps and entomopathogenic nematodes that feed on root pests (Degenhardt et al., 2009a).

7.1.3 FRUIT FLAVOUR AND AROMA

Fruit flavour and aroma is a major determinant in attracting animals for dispersal of seeds thus aiding in increased production rates. Successful attempts have been made in tomato to improve its aroma by expressing geraniol synthase (GES) under the polygalacturonase promoter thus leading to production of transgenic fruits with improved flavor and stronger aroma (Davidovich-Rikanati R, Sitrit Y, Tadmor Y, Iijima Y, Bilenko N, Bar E, Carmona B, Fallik E, Dudai N, Simon JE et al., 2007).

In spite of the large number of achievements that metabolic engineering has achieved, some unintended side effects that come up along with the desired effect have been a cause of concern for the phytologists.

7.2 UNINTENDED SIDE EFFECTS OF METABOLIC ENGINEERING OF PLANT VOLATILES

a) Negative effect on plant growth and development:
- Due to decreased carbon availability for essential metabolites.
- Toxicity of newly expressed compounds (Aharoni et al., 2003, 2006; Orolava et al., 2009).
- Very low or no yields of the desired compound owing to insufficient amount of precursors for its biosynthesis (Guterman et al., 2006).
- Formation of unintended compounds as a result of diabolical metabolical activities of the host plant (Lewinsohn & Gijzen, 2009).

b) Certain ecological complications might also creep in along with the desired effect as seen in case of Cucurbita pepo var. texana, in which emission rates of 1, 4 dimethoybenzene was experimentally increased to aid in pollination by attracting squash bee population, but apart from fulfilling its desired effect it also acted as a powerful stimulus for florivorous beetles which damaged the plant (Theis and Adler, 2012).
A deeper understanding of plant and insect metabolomics and transcriptomics can help us in understanding of the mechanisms controlling plant-insect interactions and thus help in disencumbering unintended effects of metabolic engineering of plant

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volatiles by achieving desired effects like increased pollination rates while minimizing pest attraction and herbivory. Insects can prove to be a boon rather than bane for plants provided that effective regulation of emission timing of VOCs is achieved not just being concerned about the emission quantity.

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