Bioactive Volatile Metabolites of *Trichoderma*: An overview

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5.1 Introduction

The agricultural crop loss occurred worldwide due to various biotic factors which can lead up to 40% economic loss (Oerke and Dehne 2004). To combat loss which occurs due to plant diseases and feeding growing human population without causing loss to ecosystem, alternative measures demand for sustainable approaches including the use of biocontrol agents/plant probiotic agents (Godfray et al. 2010; Mishra et al. 2015; Rasmann et al. 2017; Sharma et al. 2017a, b, c, d). The filamentous and saprophytic life cycle of *Trichoderma* have attracted considerable attention worldwide and can help in achieving sustainable agriculture growth. So far *T. harzianum*, *T. virens*, *T. viride*, *and T. saturnisporum* (Sharma and Shanmugam 2012, Sharma et al. 2017d; Sharma et al. 2018a) have been studied for their biocontrol attributes and commercial development of bioformulations against wide range of soilborne and airborne phytopathogens (Kubicek and Harman 1998; Harman et al. 2004; Lorito et al. 2010). Presently, *Trichoderma*-based bioformulations constitute over 60% of the registered biopesticides and are also effective for bio-management of insects (Jassim et al. 1990; Ganassi et al. 2007; Shakeri and Foster 2007; Verma et al. 2007; Bisen et al. 2015; Singh et al. 2016).

The molecular attributes of *Trichoderma* spp. related to its success as biocontrol agents include mycoparasitism (Weindling 1932; Howell and Stipanovic 1983; Verma et al. 2007; Bailey et al. 2009; Szabo et al. 2012; Sharma et al. 2018b), antibiosis (Howell 1998; Vos et al. 2015), competition for space and nutrients (Chet

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1987), promotion of plant growth, stimulation of lateral root development, degradation or detoxification of toxic compounds (Sharma et al. 2013), enhanced nutrient solubility and subsequent acquisitions of minerals through siderophores, organic acids and volatile compounds secretion (Altomare et al. 1999; Gravel et al. 2007; Bae et al. 2009; Contreras-Cornejo et al. 2009; Martinez-Medina et al. 2011; Vos et al. 2015), and induction of systemic resistance (Yedidia et al. 2001; Hoitink et al. 2006; Mathys et al. 2012). The recruitment of molecular arsenals by biocontrol agents is quite complex in nature and multistage regulated (Sharma et al. 2017a). For example, mycoparasitism by *Trichoderma* strain is largely executed through the extracellular secretion of lytic enzymes targeting cell wall degradation of host fungi (Sharma and Shanmugam 2012; Sharma et al. 2016; Sharma et al. 2017c). The role of different transcripts against various fungal plant pathogens has been investigated at transcripts and protein level (Sharma et al. 2013; Sharma et al. 2016; Sharma et al. 2017b) using deactivated autoclaved mycelium as simulated antagonism conditions. These conditions revealed the role of chitinases, glucanases, proteases, and other cell wall degrading enzymes as well as its transporters system in host-specific manner (Sharma et al. 2016; Sharma et al. 2017c). In a broader sense, the biocontrol mechanisms of *Trichoderma* share remarkable similarity to probiotics (Sharma et al. 2017b).

The production of secondary metabolites of volatile and nonvolatile nature is another hallmark of *Trichoderma* and considered to play significant and effective role in plant pathogen suppression and plant growth promotion (Bisen et al. 2016; Singh et al. 2017). The production of bioactive secondary metabolites of both volatile and nonvolatile nature by *T. album* and *T. harzianum* is known to inhibit the mycelial growth on *Botrytis fabae* (Barakat et al. 2014). Similarly, the antagonistic activity of *T. gamsii* YIM PH3001 against *P. notoginseng* is correlated to the production of VOCs such as dimethyl disulfide, dibenzofuran, methanethiol, and ketones. The *T. gamsii* YIM PH3001 also improved the seedling emergence and protected plants from soilborne disease in field conditions (Chen et al. 2016). The deactivated mycelium of *Fusarium oxysporum* is reported to upregulate the production of five and eight different VOCs of *T. harzianum* T-E5 (Zhang et al. 2014). The VOCs of *T. virens* Gv29.8, *T. atroviride* LU132, *T. asperellum* LU1370, and *T. atroviride* IMI206040 are well demonstrated for their ability to promote plant growth (Nieto-jacobo et al. 2017).

Similar to plants and bacteria, fungi are known to produce plethora of VOCs such as alcohols, ketones, esters, small alkenes, monoterpenes, sesquiterpenes, and their derivatives (Korpi et al. 2009). The nature, proportions, and concentrations of these VOCs are known to vary with species/strain and age of culture, substrate concentration, and interactions surrounding the environment (Sunesson et al. 1995; Wheatley et al. 1997; Wilkins et al. 2000). Starting from the discovery of first antifungal substance from *T. virens* in 1936 by Weindling and Emerson, a number of volatile and nonvolatile bioactive secondary metabolites from *Trichoderma* spp. such as anthraquinones (Luo et al. 2009), pyrones (Evidente et al. 2003), terpenes (Li et al. 2011;

Yamamoto et al. 2012), butenolides (Fukuda et al. 2012), alkaloids (Garo et al. 2003), isoharziandione (Mannina et al. 1997a, b; Warin et al. 2009), and 6-pentyl-α-pyrone have been characterized (Evidente et al. 2006). These bioactive metabolites such as isoharziandione are found to inhibit *Colletotrichum capsici* (Warin et al. 2009) and *S. rolfsii* (Mannina et al. 1997a, b), whereas 6-pentyl-α-pyrone were reported to inhibit *Pythium ulttimun* (Vinale et al. 2008) and *Armillaria mellea* (Tarus et al. 2003). 6-pentyl-α-pyrone has also been reported for its plant growth promotion ability (Dennis and Webster 1971a, b; Howell 2003). This book chapter highlights the biosynthesis and role of volatile bioactive secondary metabolites produced by *Trichoderma* spp.

5.2 Volatile Metabolites of *Trichoderma* spp.

The soil microbes are potential source of VOCs and play immense role in various interactions between biotic and abiotic factors of ecosystem (Bitas et al. 2013). At present, around 500 bacterial and fungal species have been explored for the production of different VOCs including alcohols, ketones, mono- and sesquiterpenes, esters, thioalcohols, lactones, and thioesters (http://bioinformatics.charite.de/mvoc/) (Splivallo et al. 2011; Kramer and Abraham 2012; Lemfack et al. 2013; Effmert et al. 2012; Lemfack et al. 2014). The beneficial *Trichoderma* strains in plant rhizosphere are known to produce a plethora of VOCs including alcohols, ketones, esters, small alkenes, monoterpenes, sesquiterpenes, and other derivatives which positively affect plant growth and reduce disease incidence (Ryu et al. 2003; Vespermann et al. 2007; Zhang et al. 2008; Korpi et al. 2009; Hung et al. 2012). The VOCs of fungi have been explored intensively for their role in signaling, agricultural and aroma in fermented foods (Chiron and Michelot 2005; Kues and Navarro-Gonzales 2009; Bennett et al. 2012), and antimicrobial activity (Strobel et al. 2001 2006). The VOCs of *Trichoderma* are gas-phase and carbon-based molecules of both low and high molecular weight origin. According to the Antibase database, over 370 different compounds of *Trichoderma* origin have been identified with importance in medicinal, agronomic, and ecological perspectives (Howell et al. 1993; Sivasithamparam and Ghisalberti 1998; Laatsch 2007; Reino et al. 2008). These VOCs of *Trichoderma* help in distributing long-lasting effects which inhibit other plant pathogens (Dennis and Webster 1970; Wheatley et al. 1997; Humphris et al. 2001; Bruce et al. 2004) and promote growth of plants (Hung et al. 2012). In recent studies, efforts have been made in understanding additional role of volatiles in multiple interactions under field conditions (Kai et al. 2009; Vespermann et al. 2007; Minerdi et al. 2009; Wenke et al. 2010; Blom et al. 2011; Junker and Tholl 2013; Naznin et al. 2013; D'Alessandro et al. 2014; Piechulla and Degenhardt 2014; Kottb et al. 2015; Chung et al. 2016). For example, the soil application of 2-butanone and 3-pentanol in cucumber seedlings led to reduced infestation of *M. persicae* aphids and increase in predatory coccinellids (Song and Ryu 2013).

5.3 Structure and Biosynthesis of Fungal Secondary Metabolites

The continuous studies on biocontrol attributes of *Trichoderma* spp. have led to the identification of several bioactive compounds (Moffatt et al. 1969; Collins and Halim 1972; Fujiwara et al. 1982; Almassi et al. 1991; Keswani et al. 2016). The different compounds produced by *Trichoderma* spp. include 6-pentyl-α-pyrone, antibiotics gliotoxin, viridin, gliovirin, glisoprenin, heptelidic acid, koninginins, anthraquinones, trichodermamides, peptaibols, polyketides, terpenoids, polypeptides, trichothecenes, trichodermaides, azaphilones, harzialactones, and metabolites derived from alpha-amino acids (Howell 1998; Vey et al. 2001; Reino et al. 2008; Keswani et al. 2014; Keswani 2015). These bioactive metabolites of biocontrol strains of *Trichoderma* are broadly grouped into volatile and nonvolatile compounds. The VOCs with their role as interspecies communication are also known as infochemicals or semi-ochemicals (Herrmann 2010). The volatile organic compounds (VOCs) are carbon-based molecules that readily enter the gas phase by vaporizing at 0.01 kPa (Pagans et al. 2006), hydrophobic in nature with low boiling point and polarity (Insam and Seewald 2010), and easily evaporate and diffuse to long distance in soil, air, and through porous materials (Wheatley 2002; Zogorski et al. 2006; Hung et al. 2012). They are chemically diverse in their structural compositions including main skeleton composed of hydrocarbons such as alkane, alkene, alcohol, amines, thiols, and terpenes (Korpi et al. 2009; Lemfack et al. 2013). The VOCs secreted by biocontrol strain of *Trichoderma* include hundreds of compounds such as 6-pentyl-α-pyrone, α-farnesene, calamenene, cadinene, β-cubeben, β-chamigrene, 1,2,3,4,5-pentamethyl-1,3-cyclopentadiene, α-muurolene, 2,2-dimethoxy-1,2-diphenyl-ethanone, limonene, β-bisabolene, benzoic acid, β-sesquiphellandrene,4-nitroso-,ethyl ester, farnesol, propanoic acid, and β-himachalene. Structurally, these diverse classes of VOCs belong to different hydrocarbons such as aldehydes, esters, ketones, aromatics, amines, thiols, and terpenes (Bruce et al. 2000; Vinale et al. 2008; Splivallo et al. 2011; Kramer and Abraham 2012; Lemfack et al. 2013) (Fig. 5.1a–c).

The biosynthesis of VOCs in fungi is underexplored area of research compared to plants. The VOCs are produced as side products from both the primary metabolism including synthesis of DNA, amino acids, and fatty acids, whereas secondary metabolism includes intermediates of the primary metabolism (Berry 1988; Korpi et al. 2009) and biotransformed products produced in central metabolism like terpenes (Kesselmeier and Staudt 1999; Dudareva et al. 2013; Lee et al. 2016). A brief description of the VOC s produced by *Trichoderma* is given below:

5.3.1 6-Pentyl-alpha-pyrone (6PP)

6PP, a compound with coconut-like odor, is one of the first volatile compounds characterized from *Trichoderma*. Initially explored in food industry (Collins and Halim 1972; Parker et al. 1999), it is now also studied for its role in plant growth

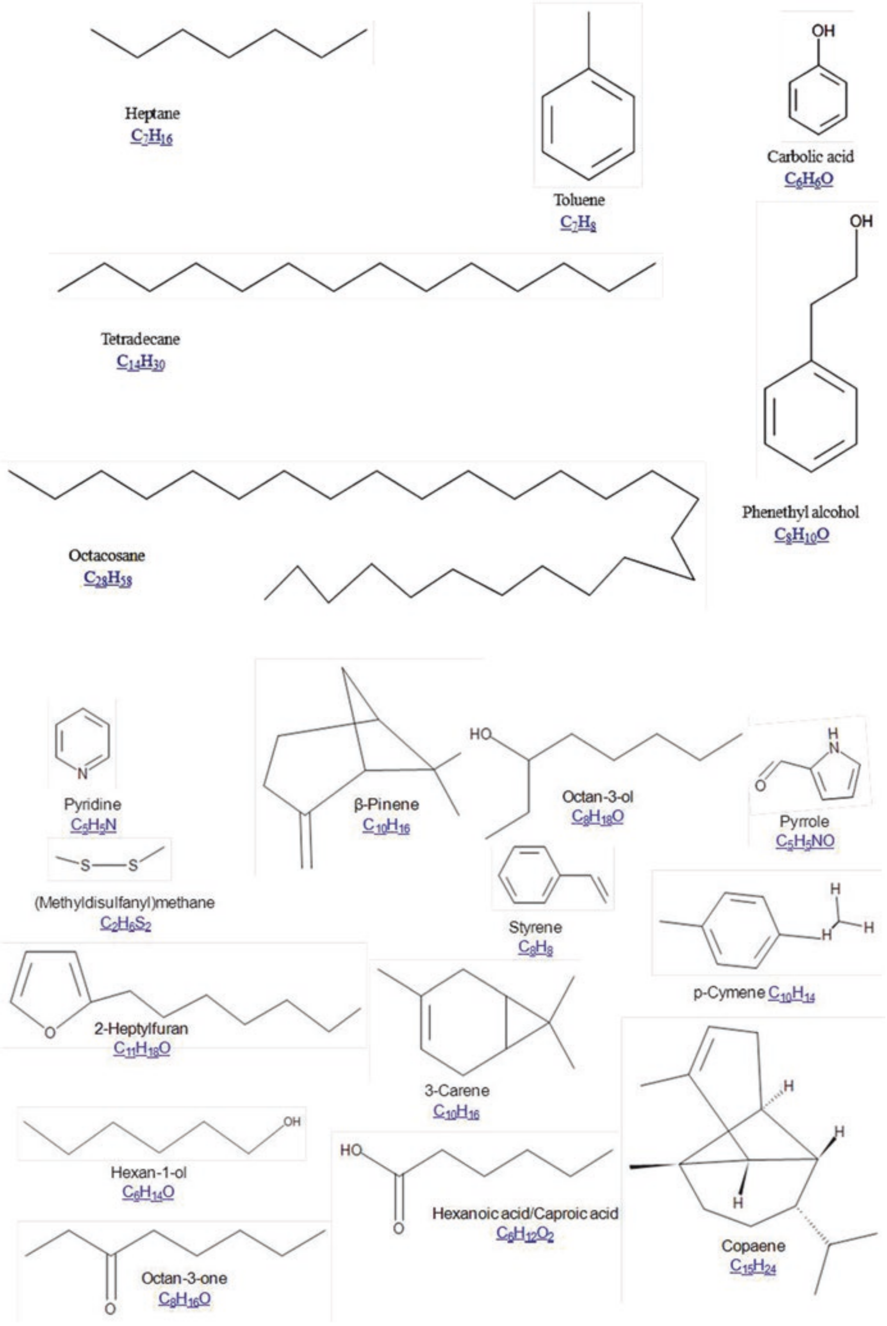

Fig. 5.1 (**a**–**c**) Structure of volatile compounds produced by *Trichoderma* spp.

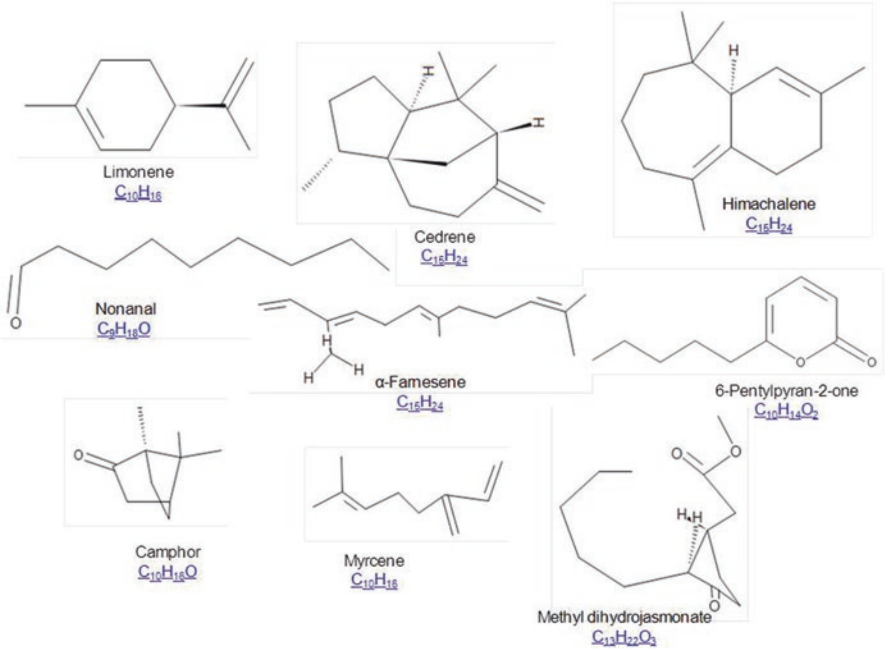

Fig. 5.1 (continued)

promotion and plant disease suppression. Addition of 6PP (0.166–1 mg/l) to plant growth media or directly applying its solution to plant leaves is known to induce growth promotion and decrease disease symptoms (Vinale et al. 2008; Lee et al. 2016). Even though all the species of *Trichoderma* do not synthesize 6PP (Atanasova et al. 2013), still most of them are known to induce plant growth promotion (Kottb et al. 2015) which indicates that 6PP alone is not involved in its role (Nieto-jacobo et al. 2017). It is detected in *T. atroviride* IMI206040 (Reithner et al. 2005; Stoppacher et al. 2010), *T. citrinoviride*, *T. hamatum* (Jelen et al. 2014), *T. viride* (Collins and Halim 1972), *T. asperellum* (Wickel et al. 2013; Kottb et al. 2015), *T. harzianum* (Claydon et al. 1987), and *T. koningii* (Simon et al. 1988). The production of 6PP by *T. atroviride* is shown to enhance lateral root formation in *A. thaliana* (Garnica-Vergara et al. 2015; Nieto-jacobo et al. 2017).

The production of 6PP can be detected by TLC and HPLC analysis based on ethyl acetate extraction. For its detection, 12–14-day-old cell-free filtrate of *Trichoderma* previously grown in potato dextrose broth is harvested with three volume of ethyl acetate. The solvent is then dried and evaporated using Rotavapor at 35 °C. The dried crude residue is solubilized in 1 ml of ethyl acetate and analyzed by HPLC after filtration. For TLC analysis, 6PP was obtained by purification of crude extract by TLC eluted with dichloromethane/methanol in a 97:3 (v/v) ratio.

6PP is known to be synthesized from linoleic acid using reduction, β-oxidation, and isomerization process (Fig. 5.2). They can be built up by the catalytic activities

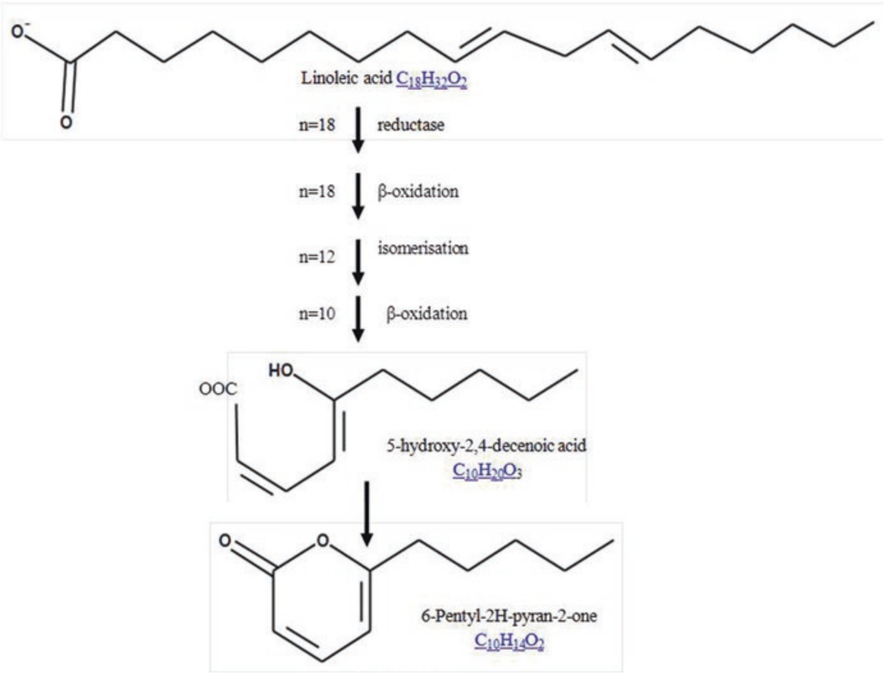

Fig. 5.2 Hypothetical biosynthetic pathway of 6PP in *Trichoderma* spp.

of different polyketide synthase (PKS) systems and final ring formation yielding the pyrone moiety accomplished in different ways. Different mechanisms have been proposed for the biosynthesis of 6PP, and it is assumed that the route toward pyrone biosynthesis has been developed several times in evolution.

5.3.2 Hydrocarbons

The hydrocarbons such as alkanes, alcohols, aldehydes, and acids can be enzymatically synthesized from fatty acids via head-to-head condensation in prokaryotes (Sukovich et al. 2010) or by elongation-decarboxylation in majority of eukaryotes (Brown and Shanks 2012), and conversion of aldehyde to alcohol occurs with the loss of hydroxyl group. In *T. koningii* and *P. janthinellum*, the biocatalysis of decanoic and undecanoic fatty acids is known to occur under specific growth conditions and stored in cell membranes and lipid bodies (Chahal et al. 2014). A mixed fungal cell culture is reported to produce seven classes of lipids into intracellular and extracellular pools (Monreal et al. 2014; Monreal et al. 2016). The investigations led to the identification of variable long-chain primary alcohols with general formula R-OH, wherein R can be unbranched, unsubstituted, linear aliphatic group. The long-chain alcohols are reported to be phagodeterrent and avoid aphids from settling on treated leaves at low concentration 0.15 mM. Eight carbon volatiles

1-octen-3-ol, 3-octanone, 3-octanol, and 1-octen-3-one typical to mushroom (Fisher et al. 1978) are reported for attracting insects and ants and exhibiting fungicidal and fungistatic activity (Pinches 2007; Wilkes et al. 2003; Schirmer et al. 2010; Bernard et al. 2012).

5.3.3 Terpenes

Terpenoids are built up of five-carbon isoprene units and represent hemi- (C5), mono- (C10), sesqui- (C15), di- (C20), sester- (C25), tri- (C30), and tetraterpenes (C40) classes. Terpenes constitute one of the largest groups of secondary metabolites with over 40,000 structures in cosmopolitan distribution (Bohlmann and Keeling 2008). In actual, the basic building unit to all terpenes is isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP). In fungi and animals, IPP and DMAPP are synthesized via mevalonic acid (MVA) pathway (Fig. 5.3), whereas in algae and bacteria, it is synthesized by MEP pathway. In plants and some bacteria, both the pathways are used (Rohmer 1999; Walter et al. 2000; Grawert et al. 2011). The MVA pathway starts with the combination of three units of acetyl-coenzyme A to form a six-carbon MVA which is transformed to the five-carbon IPP through series of events such as phosphorylation, decarboxylation, and dehydration.

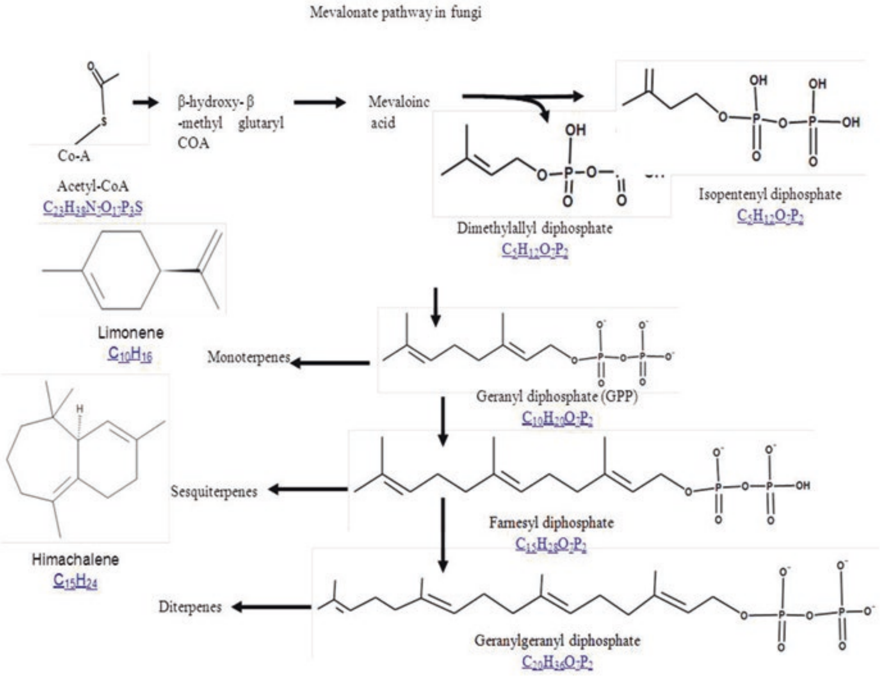

Fig. 5.3 Terpene biosynthetic pathway in fungi

The isomerization of IPP can lead to the formation of DMAPP. All terpenes are linear or cyclic and saturated or unsaturated and can be modified in various ways. Different structures and properties of terpenoids are the results of modifications accomplished via enzymatic reactions such as changes to the oxidation state of a molecule by oxidation and reduction reactions, alkylation, decarboxylation, glycosylation, rearrangement, and cyclization reactions. Many of them are formed as a result of rearrangement reaction and cyclization reaction which are often carbocation driven (Hansson 2013). They are generated mostly from geranyl pyrophosphate, sesquiterpenes, and geranylgeranyl pyrophosphate through the action of terpene cyclase. Fungi are capable of producing a number of terpenes such as carotenoids, gibberellins, and trichothecenes. A large number of terpene cyclases have been characterized from fungi (Keller et al. 2005). A cosmid clone containing a cyclase gene was sequenced, and several full-length genes were identified as members of a putative secondary metabolism-related gene cluster. These genes included cytochrome P450 and terpene cyclase. The role of gene cluster was established using mutant generation harboring this cluster in *T. virens* and nonproducing strains *T. atroviride* and *T. reesei* followed by profiling of volatile compounds in generated mutants (Crutcher et al. 2013).

Terpenes of sesquiterpenes were identified from *T. virens* Gv29.8 along with β-elemene and ε-amorphene which were significantly overrepresented in the mixture, whereas VOCs reported from *T. asperellum* LU1370 were 1,3-octadiene,limonene, β-eudesmol, and valerianol (Nieto-jacobo et al. 2017). Terpenoids have many biological properties and are widely used as flavors, fragrances, pharmaceuticals, and food additives (Forster-Fromme and Jendrossek 2010; Dewick 2009).

5.4 Analysis of Volatile Compounds

The VOCs produced by *Trichoderma* spp. are either intermediate or end products of various metabolic pathways and belong to diverse classes such as alkanes, alkenes, alcohols, esters, terpenes, ketones, and lactones or C8 compounds (Schnurer et al. 1999; Korpi et al. 2009). The studies on these volatile compounds have suffered compared to other secondary metabolites due to lack of proper methods, techniques, and their dynamic production. The identification of VOCs is usually done by gas chromatographic (GC) or flame ionization detection (FID) (Elke et al. 1999) and mass spectrometry (MS)-based methods (Fig. 5.4). For analysis, microbial cultures are usually grown on standard PDA or NA medium or broth at 25 °C and 12 h light/12 h darkness for 4 days. For fungi, actively mycelial culture in liquid or solid media (Nemcovic et al. 2008) is grown in amber glass headspace vial containing a blue PTFE/silicone septum and then sealed. The vials are incubated at 25 °C for 24 h (Stoppacher et al. 2010). The background of PDA plates without the fungus can also be extracted and analyzed for the volatiles. The compounds representing VOCs can be detected by flame ionization detection (Elke et al. 1999) and mass spectrometry (Hynes et al. 2007). Structure characterization and confirmation of

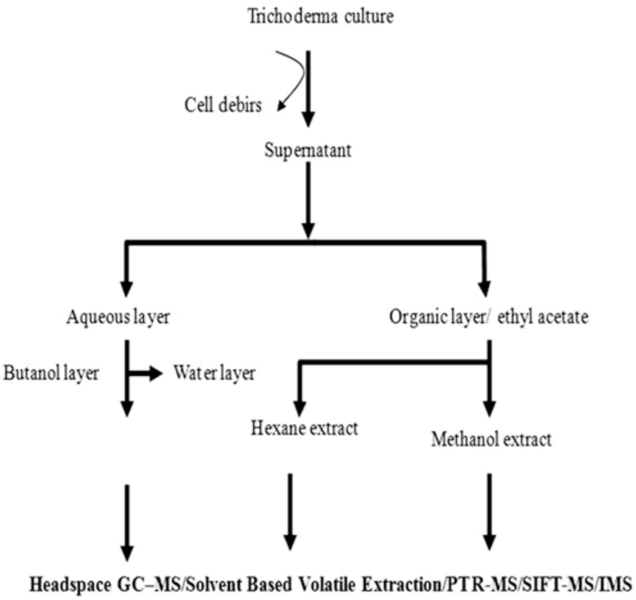

Fig. 5.4 Schematic extraction of volatile compounds from *Trichoderma* spp.

identity are achieved by matching their mass spectra and linear retention indices using GC-MS solution v. 2.72 software with NIST 11 and Wiley 10 mass spectrum libraries (Oprean et al. 2001; Jelen 2003) or by using the software MassFinder4 with a specialized terpenoids library.

5.4.1 Headspace Gas Chromatography-Mass Spectrometry (HSGC-MS)

Due to high sensitivity and powerful separation, GC-MS is the main method for detecting fungal VOCs (Matysik et al. 2009). Another method of adsorbing and desorbing VOCs in culture headspace is solid-phase micro-extraction (SPME), where desorption occurs in the GC injector itself. SPME has become increasingly popular in recent years because it reduces preparation time by combining extraction, concentration, and introduction into one step while increasing sensitivity over other extraction methods. In alternate methods, solid-phase micro-extraction (SPME) volatiles from the headspace or from solution can be pre-concentrated prior to routine analysis onto a glass fiber. Additionally, Headspace-SPME-GC-MS can be automated for direct profiling of living fungal cultures (Stoppacher et al. 2010). Compounds are then identified using a library or database of mass spectra or by comparison of retention times and spectra with those of known standards.

For headspace volatile analysis, active culture of *Trichoderma* is grown glass flask (Stoppacher et al. 2010). Samples can be collected and concentrated using headspace techniques such as closed-loop stripping analysis (static analysis) (Meruva et al. 2004) and dynamic headspace techniques (purge and trap) (Deetae et al. 2007; Qualley and Dudareva 2009). In static analysis, VOCs in samples are equilibrated with air in airtight container, and then a known volume of air is collected from that sample in a gastight syringe, for gas chromatography. In dynamic (purge and trap) headspace technique, purified air in known amount is passed over the sample, and then volatiles are concentrated onto an adsorbent trapping material such as graphite or an organic polymer. Alternatively, the air flow is recycled through the adsorbent trap known as closed-loop stripping. Volatiles can be removed over the adsorbent trap by elution with organic solvents (commonly with diethyl ether) and then heated with a stream of inert gas and transferred directly to the gas chromatograph (GC) and an autosampler for solid-phase micro-extraction (SPME). The desorption transfers all VOCs from the adsorbent trap onto the GC column thus provides better sensitivity and ability to analyze higher volatile compounds which will be difficult with organic solvent injection. For compound analysis, the compounds adsorbed onto the fiber after certain fixed time are desorped and inserted into the heated injection port of GC. SPME sampling usually occurs as an integrated process in real time although SPME fibers and desorption traps may be stored at low temperature (Rowan 2011).

5.4.2 Chromatography-Free Methods (PTR-MS/SIFT-MS/IMS)

The GC-MS-based techniques are time-consuming and need sample preparation, and chromatographic separation of metabolites requires a sufficiently low and stable temperature (30–40 °C) before introduction of the next sample. In proton-transfer-reaction mass spectrometry (PTR-MS), headspace air surrounding the sample is collected directly into the instrument where volatiles are ionized by protonated (charged) water molecules generated in a hollow cathode source. The protonated volatile compounds are then passed through a region by a quadrupole mass spectrometer. The other related technology such as ion flow tube mass spectrometry (SIFT-MS) generates ionized volatiles by interaction with a range of ions such as H_3O^+, NO^+, and O_2^+ with better opportunities for more selective ionization (Francis et al. 2007) for the resolution of compounds with same molecular mass (Lindinger and Jordan 1998). The PTR-MS/SIFT-MS has emerged as an alternative technology and offers real-time monitoring of volatiles, minimum sample preparation with maximum high sample throughput.

In addition, HPLC/LC-MS methods have been used for profiling of specific volatile classes like aldehyde lipid oxidation products and amines. The advent of liquid chromatography coupled to mass spectrometry (LC-MS) offers new possibilities in the analysis of volatile biosynthesis and the direct analysis of nonvolatile precursors that are frequently present in biological systems such as glycoside, glucuronide, sulfate, or phosphate derivatives (Beranek and Kubatova 2008). The availability of LC-MS can be helpful in routine metabolomic analysis of the volatile precursors, volatile biosynthesis, and their regulation in biological systems. Coupling SPME sampling with LC-MS may also allow direct in vivo sampling and measurement of these compounds in different organisms.

5.4.3 Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)

SIFT-MS is a rapid, broad-spectrum detection technique for traces of VOCs in moderately complex gas mixtures. SIFT-MS can quantify VOCs in real time from low part-per-billion (ppb) levels without pre-concentration (Senthilmohan et al. 2001). This technique has been used to study the VOCs produced by *Aspergillus*, *Candida*, *Mucor*, *Fusarium*, and *Cryptococcus* sp. (Scotter et al. 2005).

5.4.4 Proton Transfer Reaction Mass Spectrometry (PTR-MS)

PTR-MS ionizes VOCs through their reaction with H_3O^+, forming mostly molecules which can be detected by a standard quadrupole/multiplier mass analyzer (Lindinger and Jordan 1998). PTR-MS can be used to quantify fungal VOCs since it has fine detection capability and scale time response (Ezra et al. 2004). Additionally, analysis can be run in real time without sample preparation, derivatization, or concentration with the advantage of having sensitivity comparable to GC-MS. This technique is used to quantify the VOCs of *Muscodor albus* (Ezra et al. 2004).

5.4.5 The Electronic Nose or E-Nose

E-nose is a promising development for detecting fungal VOCs. Using arrays of electronic chemical sensors with appropriate pattern recognition systems, it can recognize simple or complex odors (Gardner and Bartlett 1992; Wilson and Baietto 2009). A typical E-nose relied on multisensor array, information collecting unit, pattern recognition software, and reference library. This technique can provide a qualitative overview of volatile compounds (Wilson and Baietto 2009, 2011).

5.4.6 Solvent-Based Volatile Extraction Method

The organic solvent-based extraction is generally better and gives a complete profile of metabolites including low molecular weight alcohols, hydroxyl acids, thiols, and flavor compounds such as acetoin (Zeppa et al. 1990; Keszler et al. 2000). But nonvolatile compounds such as leaf waxes, triterpenes, triglycerides, and complex lipids can impede analysis. The solvent systems used for the optimized extraction of metabolites include pentane-ether mixtures and dichloromethane. The contaminating compounds such as lipids, pigments, and other hydrocarbons can be removed by simultaneous distillation-extraction (SDE) (Chaintreau 2001), vacuum micro distillation, or solvent-assisted flavor evaporation (SAFE) (Engel et al. 1999) or by adsorption chromatography. The use of supercritical fluids (SCF) such as supercritical carbon dioxide, either pure or in the presence of modifiers, is an alternative to the organic solvent-based extraction. The polarity of these SCFs is comparable to pentane and has been used to extract volatiles from a wide range of plants (Pourmortazavi and Hajimirsadeghi 2007). While SCF extraction has the advantage of using totally volatile solvent, still these studies require specialized equipments (Pourmortazavi and Hajimirsadeghi 2007; Gressler et al. 2009).

5.5 Applications of *Trichoderma* Volatile Compounds

The VOCs produced by fungi have been intensively studied for their use as diagnostic agents as indicator for detecting contamination. The VOCs are implicated in "sick building syndrome" a controversial medical condition. The aromatic properties of these VOCs find applications in food fermentations and interkingdom signaling events (Chiron and Michelot 2005; Kues and Navarro-Gonzales 2009; Bennett et al. 2012). The VOCs of *Trichoderma* spp. are known to act as antibacterial and antifungal agents (Strobel et al. 2001, 2006). In agriculture, fungal VOCs have been used as part of biological control strategies to prevent the growth of plant pathogens and promoting plant growth. A number of VOCs have been reported from *Trichoderma* spp. which are beneficial to the plants (Wheatley et al. 1997; Van Loon et al. 1998; Stoppacher et al. 2010). In the food industry, the biological control through myco-fumigation is used to prevent postharvest fungal growth. The biotechnological potential of VOCs from *Trichoderma* is still underexplored. In recent studies, the role of these compounds in inducing systemic resistance through priming plants' immune response and nutrient acquisitions has been investigated (Van Wees et al. 2008). The soil application of 2-butanone and 3-pentanol in cucumber seedlings has been reported to reduce aphid *M. persicae* infestation and increase in predatory coccinellids (Song and Ryu 2013).

5.5.1 Antimicrobial Activity

The VOCs including nonanal, N-decanol, cyclohexanol, ethyl-1-hexanol, benzothiazole, and dimethyl trisulfide are identified for their inhibitory role (Fernando et al. 2005). Fungal endophytes are known to produce volatile mixtures having strong antibacterial effects (Strobel et al. 2001; Strobel 2006) which indicate the role of several VOCs in synergistic mode for antimicrobial activity. The VOCs of *Trichoderma* are known for their action against pathogenic fungi (Nemcovic et al. 2008; Vinale et al. 2008) and have potential for being used as biocontrol agent in agriculture. The GC-MS analysis of *T. viride* VOCs identified 51 metabolites among which isobutyl alcohol, isopentyl alcohol, and 3-methylbutanal are most prevalent and inhibit wood-decaying basidiomycetes and plant pathogens (Dennis and Webster 1970; Wheatley et al. 1997; Humphris et al. 2001; Bruce et al. 2004). The prominent headspace volatile identified as 6-pentyl-α-pyrone (6PP) from *T.*

asperellum showed significant reduction of disease symptoms in *Arabidopsis* when infected with *Alternaria brassicicola* and *Botrytis cinerea*. The volatile bioactive metabolites are also known to inhibit growth of fungal mycelium, spore germination, and pigmentation of plant pathogenic fungi. The VOCs of the endophyte *M. albus* can be used to control soilborne diseases caused by *Rhizoctonia solani* and *Phytophthora capsici* (Mercier and Manker 2005). Some VOCs are known to stimulate or enhance soilborne biocontrol agents (Wheatley 2002). The volatiles emitted by *T. atroviride* are known to increase the expression of a primary biocontrol gene of *Pseudomonas fluorescens* (Lutz et al. 2004).

5.5.2 Nutrient Acquisitions

In saline soil and other parts of the world, Fe^{2+} deficiency is a major limiting nutrient. The manipulation of iron homeostatic mechanisms by microbial VOCs is a feature conserved among different root-associated mutualists, ranging from bacteria to fungi (Wintermans et al. 2017). The numerous root-associated beneficial microbes such as *Trichoderma* play important role in nutrient uptake and are highly effective in promoting plant growth and resistance to both abiotic and biotic stresses (Zhao et al. 2014). Induction of Fe uptake-related genes by microbial volatiles has been previously demonstrated for VOCs of bacterial origin. VOCs released by the plant growth-promoting rhizobacterium *Bacillus subtilis* GB03 and the ISR-inducing rhizobacterium *Pseudomonas simiae* WCS417 are found to trigger the expression of Fe uptake-related genes in *Arabidopsis* roots, leading to elevated endogenous Fe levels in the plant (Zamioudis et al. 2015). The VOCs of *T. asperellum* and *T. harzianum* are known to trigger MYB72 expression and Fe^{2+} uptake in *Arabidopsis* roots. The volatile compounds of *Trichoderma* origin also enhanced resistance through priming of jasmonic acid-dependent defense against *Botrytis cinerea*. The VOCs of *Trichoderma* are reported for eliciting Fe deficiency responses and shoot immunity in tomato which suggest that the phenomenon worked across plant species. The VOCs of *Trichoderma* were able to trigger local readjustment of Fe homeostasis in roots through systemic elicitation of ISR by priming of jasmonic acid-dependent pathway (Zhao et al. 2014).

5.5.3 Induction of Conidiation

The VOCs produced fungal species that are known to exhibit a cross-species action both at intra- and interspecific level. The ability to influence their own development and other fungi is one of the interesting features of several fungi. The molecular mechanisms of the VOCs in fungal development are largely unknown, but the physiological significance and the stimulatory effect on conidiation may be associated to their role as inter-colony communication and warning signals under unfavorable conditions. The switching from vegetative growth to formation of conidia is marked by enhanced production of secondary metabolites (Calvo et al. 1999). The production of secondary metabolites of volatile nature such as 3-octanol, 1-octen-3-ol, and 3-octanone by *Trichoderma* during conidia formation clearly depicts the role of these metabolites in conidiation. The fungal isolates are capable of inducing conidia formation under dark conditions, and the amount is reported to vary with the concentration of each VOC. The signaling events are assumed to take place at cytoplasmic membrane level which leads to membrane potential and permeability (Chitarra et al. 2005). The compounds such as 1-octen-3-ol are found to be effective at 0.1 mM concentration, whereas at higher concentration of 500 mM, 3-octanone is found to induce highest levels of conidia formation (Nemčovič et al. 2008). The sporulating *T. viride* is reported to produce over 50 VOCs including isobutyl, isopentyl alcohols, and 3-methylbutanal.

5.5.4 Plant Growth Promotion

The role of volatile compounds can be realized from the fact that species of *Trichoderma* are able to stimulate *Arabidopsis thaliana* growth, enhanced lateral root formation, early-flowering and fruit development phenotypes in absence of any direct physical contact (Hung et al. 2013; Lee et al. 2016). Plants grown in the presence of fungal VOCs emitted by different *Trichoderma* spp. exhibited a range of effects. Exposure to the VOCs produced by these strains led to an increase in plant biomass (37.1 to 41.6%) and chlorophyll content (82.5 to 89.3%) in a strain and species-specific way. The VOCs of *T. pseudokoningii* (CBS 130756) showed highest *Arabidopsis* growth promotion. Similarly, tomatoes exposed to VOCs from *T. viride* BBA 70239 showed a significant increase in plant biomass (>9%) and significant development of lateral roots depending on the duration of the volatile exposure. VOCs produced by both *T. aggressivum* and *T. pseudokoningii* were able to enhance the *Arabidopsis* growth. The continuous exposure to VOCs of *Bacillus*, a plant growth-promoting rhizobacterium, is reported to trigger plant growth and development which signifies the importance of volatile exposure in plant growth development (Xie et al. 2009; Bailly and Weisskopf 2012; Lee et al. 2015). Similar effects are also reported in lettuce (Minerdi et al. 2009). The VOCs from bacteria and *F. oxysporum* in combination enhanced the growth promotion; however VOCs of fungal origin alone were not able to enhance plant growth (Hung et al. 2012).

Experiments conducted using grafts of fungal volatile compounds preexposed and nonexposed *Arabidopsis* seedlings established that these compounds in roots were able to transduce plant immunity through unknown ISR pathways to leaves systematically (Zhao et al. 2014). GC-MS analysis of VOCs from *Trichoderma* strains identified over 141 unique compounds including sesquiterpenes, diterpenes, and tetraterpenes which are not reported earlier. The nature of volatiles produced by actively growing fungi influences the outcome of interactions. Compounds such as 6-pentyl-2H-pyran-2-one were not common to all promising and bio-stimulatory strains and instead have higher number of complex terpenes which may be involved for variation in growth accelerated by different *Trichoderma* strains (Lee et al. 2016).

5.5.5 Biofuels

The terpenes representing VOC such as monoterpene derivative 1,8-cineole have potential to be explored as fuel additive similar to VOCs released by *Hypoxylon* sp. (Tomsheck et al. 2010). Fungal species are known to produce various biofuel substrates including alkane and alkene such as ethane, propane, ethylene, and propylene (Ladygina et al. 2006), while others can produce terpenes and isoprenoids which may be explored for fuels (Grigoriev et al. 2011). In summary, fungi are an excellent platform for exploiting biosynthetic routes to hydrocarbon biofuels or its precursors (Grigoriev et al. 2011).

5.6 Conclusion

Trichoderma spp. are already explored as bio-fungicides to agricultural soils to enhance crop productivity. The research on bioactive volatile compounds of *Trichoderma* is challenging, emerging, and frontier area of research. The emergence of latest techniques has already played vital role in the identification of several classes of volatile compounds. The VOCs have the ability to suppress plant diseases and promotion of plant growth and productivity through overlapping mode of action including induced systemic resistance, antibiosis, and enhanced nutrient efficiency. Presently, the coupling of modern omics technologies can help in the identification of volatile compounds and bioprospection of vast untapped potential of volatile compounds in agriculture and mining the promises for new products for agricultural exploitation and will begin a new era in fundamental biology.

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