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Volatile hydrocarbons from endophytic fungi and their efficacy in fuel production and disease control

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Abstract

Endophytic fungi are the microorganisms which asymptomatically colonize internal tissues of plant roots and shoots. Endophytes produce a broad spectrum of odorous compounds with different physicochemical and biological properties that make them useful in both industry and agriculture. Many endophytic fungi are known to produce a wide spectrum of volatile organic compounds with high densities, which include terpenes, flavonoids, alkaloids, quinines, cyclohexanes, and hydrocarbons. Many of these compounds showed anti-microbial, anti-oxidant, anti-neoplastic, anti-leishmanial and anti-proliferative activities, cytotoxicity, and fuel production. In this review, the role of volatile compounds produced by fungal endophytes in fuel production and their potential application in biological control is discussed.

Keywords: Endophytic fungi, Biocontrol, Biofuel, Mycodiesel, Volatile organic compounds

Background

Endophytic fungi are the microorganisms, which asymptomatically colonize the internal tissues of plant roots and shoots (Bacon and White 2000). Endophytes provide beneficial effects on host plants in deterring pathogens, herbivores, increased tolerance to stress drought, low soil fertility, and enhancement of plant biomass (Redman et al. 2002; Rodrigues et al. 2008 and Ghimire et al. 2011). Plants have many mechanisms to limit the growth of endophytes by producing a variety of toxic metabolites, but over a long period of co-evolution, the host-endophyte may develop genetic systems, allowing for transfer of information themselves, and endophytes have gradually formed a variety of tolerant mechanisms towards host metabolites by producing exoenzymes, mycotoxins, enormous secondary metabolites, and volatile compounds (Tan and Zou 2001; Schulz et al. 2002; Shankar Naik et al. 2006; Newman and Cragg 2015 and Muller et al. 2013). These secondary metabolites are related to terpenes, flavonoids, alkaloids, quinines, cyclohexanes, and hydrocarbons. Many of these shown anti-microbial, anti-oxidant, anti-neoplastic, anti-leishmanial and anti-proliferative activities, and cytotoxicity (Firakova et al. 2007; Korpi et al. 2009; Kharwar et al. 2011; Zhao et al. 2016 and Wu et al. 2016).

Volatile organic compounds (VOCs) are a large group of carbon-based chemicals with low molecular weights and high vapor pressure produced by living organisms as part of their metabolic process (Bennett and Inamdar 2015). Several biodiesel hydrocarbons are terpenes, a chemically diverse class of high-density compounds produced by plants, fungi, and bacteria. Due to their high energy densities, terpenes (e.g., pinene and bisabolene) are actively being investigated as potential 'drop-in' biofuels for replacing diesel and aviation fuel (Wu et al. 2016).

The composition of all biodiesel fuels is straight chained hydrocarbons like hexane, heptanes, octane, nonane, and decane along with many other compounds including branched alkanes, cyclic alkanes, a plethora of benzene derivatives, and poly aromatic hydrocarbons (Campos et al. 2010 and Song et al. 2000). Several reviews (Kramer and Abraham 2012 and Morath et al. 2012) have reported on endophytic fungal VOCs and their potential for biotechnological applications in biofuel production, antibiotics against human pathogen, biosensors, flavor, and fragrance additives in development of sustainable agriculture (Wheatley 2002 and Zhi-Lin et al. 2012).

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The importance of fungal volatile compounds in fuel production and their efficacy in biological control have been emphasized with comprehensive chemical analyses (Dennis and Webster 1971 and Stoppacher et al. 2010). Currently, different methods are being used to assess VOCs from fungi which include GC-MS (gas chromatography-mass spectroscopy) (Matysik et al. 2009 and Wani et al. 2010), solid-phase micro extraction (SPME) (Zhang and Li 2010), headspace-SPME GC-MS (Stoppacher et al. 2010), selected ion flow tube-mass spectrometry (SIFT-MS) (Senthilmohan et al., 2001), the proton transfer reaction-mass spectrometry (PTR-MS) (Ezra et al. 2004), and E-nose (Wilson and Baietto 2009 and Booth et al. 2011) etc.

Volatile compounds with biofuel potential

Fungal endophytes produce a broad spectrum of volatile compounds with different physicochemical and biological properties that make them useful in industry, agriculture, and pharmacy (Yuan et al. 2012) (Table 1). Volatile organic compounds with high energy densities have potential energy applications, which have been described as mycodiesel (Strobel 2014). Endophytic fungi of several Ascomycota lineages (especially members of *Xylariaceae*) are found to be capable of producing hydrocarbons (Strobel et al. 2001). The genus *Muscodor* (e.g., *M. albus*) has evoked general interest among mycologists due to its obligate endophytism, comprehensive spectrum of antimicrobial activity, and fuel production (Strobel et al. 2001). *Gliocladium roseum* (NRRL 50072) (now *Ascocoryne sarcoides*) (Griffin et al. 2010) is known to produce a series of volatile hydrocarbons and hydrocarbon derivatives (e.g., heptane, octane, benzene, and some branched hydrocarbons) on both oatmeal and cellulose-based agar medium (Strobel et al. 2008). An endophytic fungus *Hypoxylon* sp. (CI-4A) was isolated as its imperfect stage (*Nodulisporium* sp.) from *Persea indica* (an evergreen tree native to the Canary Islands). On cultivating this fungus on PDA plates, the volatiles produced by this fungus were primarily consisted of 1,8-cineole and 1-methyl-1,4-cyclohexadiene and compounds of high densities (Tomsheck et al. 2010). Ahamed and Ahring (2011) reported production of hydrocarbons from *Gliocladium* culture directly from cellulosic biomass. The GC–MS–SPME of head space gases from *Gliocladium* cultures demonstrated the production of C6–C19 hydrocarbons. Hydrocarbon production was 100-fold higher in co-cultures of *Gliocladium* and *Escherichia coli* than in pure cultures of *Gliocladium*. An unusual *Phomopsis* sp. was isolated as endophyte of *Odontoglossum* sp. (*Orchidaceae*) associated with a cloud forest in Northern Ecuador. This fungus produces a monoterpene known as sabinene isolated only from higher plants earlier. In addition, some of the other more abundant VHCs recorded by GC-MS in this organism were 1-butanol, 3-methyl; benzene-ethanol; 1-propanol, 2-methyl and 2-propanone (Singh et al. 2011). Gianoulis et al. (2012) characterized *A. sarcoides*, using transcriptomic and metabolic data, to establish a hypothetical base for biofuel production pathways. Hassan et al. (2012) selected endophytic *Hypoxylon* sp. (strain CI-4) and exposed to the epigenetic modulators suberoylanilide hydroxamic acid (SAHA, a histone deacetylase) and 5-azacytidine (AZA, a DNA methyl transferase inhibitor). The GC–MS analyses of the VHCs produced by the variants produced the terpenes including several primary and secondary alkanes, alkenes, organic acids, and derivatives of benzene.

An endophytic *Nodulisporium* sp. has been isolated from *Myroxylon balsamum* found in the upper Napo region of the Ecuadorian Amazon. This fungus produces 1,4-cyclohexadiene, 1-methyl-, 1–4 pentadiene and cyclohexene, 1-methyl-4-(1-methylethenyl)—along with some alcohols and terpenoids of interest as potential fuels under microaerophilic growth environments (Mends et al. 2012). The fungus was scaled up in an aerated large fermentation flask, and the VHCs trapped by Carbotrap technology and analyzed by headspace SPME and fiber-GC-MS. Under these conditions, *Nodulisporium* sp. produced a series of alkyl alcohols, a few terpenoids, and some hydrocarbons (Mends et al. 2012). *Nodulisporium* sp. (*Hypoxylon* sp.) was also isolated as an endophyte of *Thelypteris angustifolia* (broadleaf leaf maiden fern) in a rainforest region of Central America. This fungus uniquely produces a series of ketones. The most abundant identified compound was 1,8 cineole, 1-butanol, 2-methyl, and phenyl ethanol alcohol and most importantly cyclohexane, propyl, which is a common ingredient of diesel fuel when cultured on PDA. Furthermore, the volatiles of the isolate *Nodulisporium* sp. were selectively active against a number of plant pathogens including *Daldina* sp. and *Hypoxylon* spp. teleomorphs (seems to produce its own unique set of VOCs) (Hassan et al. 2013). Wu et al. (2016) characterized 26 terpene synthases (TPSs) derived from four endophytic (*Xylariaceous*) fungi known to produce mycodiesel hydrocarbons. Shaw et al. (2015) suggested the evolutionary relationship of fungal terpene synthases to those in plants and bacteria. Authors identified 1,8-cineole, a commercially important monoterpenes from endophytic *Hypoxylon* sp.

Biological control potential of volatile compounds

Volatile compounds are typically lipophilic liquids with high vapor pressures. These are lethal to a wide variety of plant and human pathogenic fungi and bacteria and are also effective against nematodes and certain insects (Strobel 2006 and Grimme et al. 2007) (Table 1). Emission of volatiles by bacteria and fungi has been known

Table 1 Volatile compounds from endophytic fungi and their activity

Endophytic fungi	Host plant	Volatile compounds	Potential activity	Target organism	References
Alternaria sp. *Epicoccum* sp. CID66 *Fusarium* sp. CID124	*Centaurea stoebe*	Unidentified sesquiterpenes	Insecticidal	*Larinus minutes* (Weevil)	Newcombe et al. (2009)
Annulohypoxylon sp.	*Neolitsea pulchella*	1,8-cineole	Biofuel		Wang et al. (2017)
Ascocoryne sarcoides	*Eucryphia cordifolia*	Hydrocarbons (short and medium chain alkenes, Ketones, alcohols) and sesquiterpenes	Biofuel, antifungal	*Pythium ultimum*	Griffin et al. (2010), Strobel et al. (2010)
Aspergillus nomius	*Eusideroxylon zwageri*	Saturated hydrocarbons, alkyl halides, alcohols and unsaturated hydrocarbons	Biofuel		Azeez et al. (2016)
Fimetariella rabenhorstii A20	*Aquilaria sinensis*	Frabenol (sesquiterpene alcohol)	Biofuel		Tao et al. (2011)
Geotrichum sp. *Botrytis* sp. *Penicillium* sp. *Cladosporium* sp. MIF01	*Musa* spp. *Mimosa pudica*	Butane 2-methyl; β-butyrolactone, 2-butenedinitrile Butane 2-methyl, 1-propanol 2-methyl	Antifungal	*Fusarium oxysporum* F. sp. *cubense* race 4	Ting et al. (2010)
Gliocladium roseum	Unknown	Hydrocarbons (benzene, heptane,1-octene, octane, m-xylene,3-methylnonane, dodecane, ridecane,hexadecane and nonadecane)	Biofuel		Ahamed and Ahring (2011)
Hypoxylon sp.	*Persea indica*	1,8-cineole, 1-methyl-1,4-cyclohexadiene; (+)-.alpha.-methylene-.alpha.-fenchocamphoron (monoterpene)	Antifungal	*Botrytis cineria, Phytophthora cinnamomi, Cercospora beticola, Sclerotium sclerotiorum*	Tomsheck et al. (2010)
Hypoxylon sp. E7406B		1,8-cineole synthase	Biofuel		Shaw et al. (2015)
Lasiodiplodia spp. Neofusicoccum sp., *Botryosphaeria* sp., *Pseudofusicoccum* sp.	Plants in Caatinga Biome, Brazil	Sesquiterpenes, ketones, alcohols	Antibacterial, antispasmodic		Oliveira et al. (2015)
Muscodor fengyangensis	*Pseudotaxus chienii*, *Actinidia chinensis*, *Abies beshanzuensis*	Naphthalene derivatives;a-phellandrene; β-phellandrene; 2-cyclohexen; propanoic acid, its2-methyl-, and methyl ester	Antimicrobial		Zhang et al. (2010)
M. roseus	*Grevillea pteridifolia*	2-butenoic acid, ethyl ester; 1,2,4-trimethylbenzene; 2,3-nonadiene	Antibiotic		Worapong et al. (2002)
M. tigerii	*Cinnamomum camphora*	4-Octadecylmorpholine, 1-Tetradecanamine, N,N-dimethyl and 1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester.	Antifungal, antibacterial		Saxena et al. (2015)
M. vitigenus	*Paullinia paullinioides*	Naphthalene	Insecticidal	Wheat stem sawfly (*Cephus cinctus*)	Daisy et al. (2002)
M. yucatanensis	*Bursera simaruba*	Octane; 2-methyl butyl acetate; 2-pentylfuran; caryophyllene; aromadendrene	Biofuel		González et al. (2009)
Meliniomyces variabilis *Phialocephala fortinii*	*Pinus sylvestris*	Ethanol; acet-aldehyde	Biofuel		Bäck et al. (2010)
Muscodor albus	*Cinnamomum zeylanicum*	1-Butanol, 3-methyl-, acetate;vitrene	Antibacterial,		Strobel et al. (2001)

Table 1 Volatile compounds from endophytic fungi and their activity *(Continued)*

Endophytic fungi	Host plant	Volatile compounds	Potential activity	Target organism	References
		(terpenoid);	antifungal		
M. albus	*Grevillea pterifolia* *Kennedia nigricans* *Terminalia prostrata*	Naphthalene, naphthalene,1, 1-oxybis	Antibacterial, antifungal		Ezra et al. (2004)
M. albus GBA	*Ginkgo biloba*	1-Butanol, 3-methyl-, acetate;vitrene (terpenoid);	Antibacterial, antifungal	*Sacharomyces cerevisiae, Candida albicans*	Banerjee et al. (2010)
M. albus MOW12	*Piper nigrum* L.	Acetic acid, ethyl ester, propanoic acid, 2-methyl-methyl ester and acetic acid, 2-methyl propylester	Antifungal	*Fusarium solani, Trichoderma* sp.	Banerjee et al. (2014)
M. crispans B23	*Ananas ananassoides*	Propanoic acid, 2-methyl-, methyl ester;propanoic acid, 2-methyl-	Biofuel		Mitchell et al. (2008)
M. sutura	*Prestonia trifidi*	Thujopsene, chamigrene, isocaryophyllene, butanoic acid, 2-methyl	Antifungal		Kudalkar et al. (2012)
Myrothecium inundatum	*Acalypha indica*	3-octanone; 3-octanol; 7-octen-4-ol	Antifungal	*Pythium ultimum, S. sclerotiorum*	Banerjee et al. (2010)
Neotyphodium sp.	*Lolium perrene* L.	Phenolics	Antifungal	*Fusarium poae*	Pańka et al. (2013)
Nigrograna mackinnonii E5202H		(3E, 5E, 7E)-nona-1,3,5,7-tetraene (NTE)			Shaw et al. (2015)
Nodulisporium sp	*Lagerstromia loudoni*	Alcohols, acids, esters, monoterpenes	Antifungal		Suwannarach et al. (2013)
Nodulisporium sp.CF16	*Cinnamomum loureirii*	β-elemene; β-selinene; α-selinene; 1-methyl-1,4-cyclohexadiene	Antifungal	*P. ultimum, Rhizoctonia solani, F. oxysporum,* *P. Capsici, S. sclerotiorum, Colletotrichum coccodes, Magnoporthe oryzae, A. panax, B. cineria*	Park et al. (2010)
Oidium sp.	*Terminalia catappa*	Butanoic acid, 3-methyl-, methyl ester; butanoic acid, 3-methyl-, ethyl ester	Antifungal	P. ultimum	Strobel et al. (2008)
Phoma sp.	*Larrea tridentata*	alpha.-humulene (sesquiterpene);alcohols; reduced naphthalenederivatives; trans-caryophyllene	Antifungal	*Verticillium, Ceratocystis, Cercospora, Sclerotinia, Trichoderma, Colletotrichum, Aspergillus* sp.	Strobel et al. (2011)
Phomopsis sp.	*Odontoglossum* sp.	Sabinene (monoterpene); 1-butanol,3-methyl; benzeneethanol; 1-propanol, 2-methyl; 2-propanone	Antifungal	*Pythium, Phytophthora, Sclerotinia, Rhizoctonia, Fusarium, Botrytis, Verticillium, Colletotrichum*	Singh et al. (2011)
Trichoderma gamsii	*Panax notoginseng*	Dimethyl disulphide, dibenzofuran, methanethiol, ketones	Antifungal	*Scytalidium lignicola*	Chen et al. (2016)
Xylaria sp.	*Haematoxylum brasiletto*	3-Methyl-1-butanol, thujopsene, unidentified amine, 2-methyl-1-butanol, 2-methyl-1-propanol	Antifungal	*Ophandi dermatum, P. capsici, A. solani, F. oxysporum*	Ortiz et al. (2016)

and reviewed by many authors for a long time (Kai et al. 2009). Volatile production is species-specific and serve as info chemicals for inter-and intra-organismic communication, cell-to-cell communication signals, a possible carbon release valve, or growth-promoting or growth-inhibiting agents (Kai et al. 2009). The inhibitory mode of action, when it involves one plant pathogen among interacting organisms, will be of interest in biological control. Strobel et al. (2001) reported that the volatiles produced by endophytic fungus *M. albus* inhibited the germination of the teliospores of *Tilletia horrida*, *T. indica*, and *T. tritici* (pathogenic fungi cause the plant diseases rice kernel smut, wheat kernel bunt and wheat common bunt, respectively). The VOC molecules produced from *M. albus* were 1-butanol, 3-methyl-acetate, esters, alcohols, acids, lipids, and ketones. The most effective class of inhibitory compounds tested against fungi was the esters, of which 1-butanol, 3-methyl-acetate was the most biologically active, reducing growth of *Cercospora beticola, Fusarium solani, Pythium ultimum, Rhizoctonia solani, Sclerotinia sclerotiorum, Tapesia yallundae,* and *Xylaria* sp. (Strobel et al. 2001). An endophytic isolate of *Gliocladium* sp. was obtained from the Patagonian Eucryphiacean tree (*Eucryphia cordifolia*), producing a mixture of volatile organic compounds (VOCs) lethal to plant pathogenic fungi such as *Pythium ultimum* and *Verticillium dahliae*. Some of the volatile bioactive compounds exuded by *Gliocladium* sp. (1-butanol, 3-methyl-, phenylethyl alcohol and acetic acid, 2-phenylethyl ester, and various propanoic acid esters) are also produced by *Muscodor albus,* a well-known volatile antimicrobial producer (Stinson et al. 2003).

Soil fungistasis is a natural process in which fungal propagules fail to survive under favorable temperature and moisture content (Morath et al. 2012). Several VOCs such as trimethyl amine, 3-methyl-2-pentanone, dimethyl di sulphide-methyl pyrazine, 2,5-dimethyl-pyrazine, *N*-dimethyl octyl-amine and nonadecane (Xu et al. 2004 and Garbeva et al. 2011) inhibited three fungal species *Paecilomyces lilacinus, Pochonia chlamydospora, and Clonostachys rosea* in the soil suggesting that direct competition is not needed for microbial interaction (Xu et al. 2004).

Fungal pathogen *Rhizoctonia solani*, which causes damping off of broccoli and *Phytophthora casici*, which causes root rot of bell pepper, could not be able to survive in the soil consisting of *M. albus* (Mercier and Manker 2005). In addition, fungal VOCs stimulate or enhance soilborne biocontrol agents (Wheatley 2002). The VOCs of *Trichoderma atroviridae* increase the expression of a primary biocontrol gene of *Pseudomonas flourescencs* (Lutz et al. 2004). The VHCs of endophytic fungi may also benefit the host plant by production of additional line of defense against pathogens of their host plants (Rubalcava et al. 2010). The fungi in genus *Muscodor* produces VHCs that inhibit and kill various plant pathogenic fungi and bacteria. The VHCs of *M. albus*, *M. yucatanensis*, and *M. fengyangensis* inhibited pathogenic species of bacteria fungi and oomycetes (Strobel et al. 2001; Atmosukarto et al. 2005 andZhang et al. 2010). The culture of *M. crispans* produces hydrocarbons that inhibited *Mycosphearella fijiensis* (causes black sigatoka disease in bananas) and *Xanthomonas axonopodis* pv.*citri* (a bacterial pathogen of citrus) (Mitchell et al. 2010). An endophytic *Phoma* sp. isolated from Creosote bush (*Larrea tridentata*) emits volatile compounds such as transcaryophyllene, a series of sesquiterpenoids, some alcohols, and naphthalene derivatives, which inhibited or killed isolates belonged to *Cercospora, Ceratocystis, Sclerotinia,* and *Verticillium* (Strobel et al. 2011). The extracts of endophytic fungi *Colletotrichum truncatum* isolated from oil seed crop *Jatropa curcas* produce volatile compounds effective against *Fusarium sclerotiorum* (Kumar and Kaushik 2013). Rubalcava et al. (2010) reported allelochemical effects of volatile hydrocarbons from tropical endophytic fungi *M. yucatanensis* isolated from *Bursera simaruba* growing in forests of Mexico. The VOCs were lethal to *Alternaria solani*, *Colletotrichum* sp., *Giugnardia mangifera*, *Phomopsis* sp., *Phytophthora capsici*, *Phytophthora parasitica*, and *Rhizoctonia* sp. New fungitoxic sesquiterpenoids, chokols A–G, have been isolated from *Epichloe typhina*, an endophytic fungus of *Phleum pratense*, and have been found to be toxic to the leaf spot disease pathogen *Cladosporium phlei* (Koshino et al. 1989). Other endophytic fungi isolated from plum (*Prunus domestica*) leaves showed antagonistic activity against *Monilinia fructicola* (Pimenta et al. 2012).

Post-harvest diseases often result in serious loss during storage of fruits and vegetables. The application of microbial antagonists is generally considered as a safe and eco-friendly alternative to control fruit spoilage (Jamalizadeh et al. 2011). Sulphur dioxide (SO_2) and ozone (O_3) are often used as fumigants for control of post-harvest decay (Gabler et al. 2010). SO_2 and O_3 have disadvantages over the large-scale commercial use, and fruits are more likely to be attacked by pathogens again after fumigation (Gabler et al. 2006). The volatiles produced by endophytic fungi can overcome these limitations and represent an attractive and promising biofumigation option for organic food production (Zhi-Lin et al. 2012). Microbial antagonists can effectively control fruit spoilage and minimizes the loss. Volatiles offer safe and effective strategy for controlling the post-harvest diseases. The volatiles possess long distance mechanism of antagonistic action leading to direct penetration at spatial scales (Fialho et al. 2011) without spraying or drenching as application methods (Park et al. 2010). The volatiles of *M. Albus* are useful for the control of post-harvest plant diseases which is popularly known as "mycofumigation" (Stinson et al. 2003). Some endophytic fungal volatiles effectively inhibit or kill the most common postharvest fruit pathogens (Gabler et al. 2006; Lee et al. 2009 and Park et al. 2010), including species of *Botrytis cinerea* (gray mold), *Penicillium expansum* (blue mold), *Sclerotinia sclerotiorum* (white mold), and *Monilinia fructicola* (brown rot) (Kanchiswamy et al. 2015). The volatiles produced by endophytic fungi have been used to replace methyl bromide (MeBr), a traditional soil fumigant that is now being banned in many parts of the world because its involvement in depletion of ozone layer. Both greenhouse and field trials showed that *Muscodor* spp. were effective in reducing soilborne disease severity in many crops and vegetables, including *Phytophthora* blight (*Phytophthora capsici*), common bunt of wheat (*Tilletia caries*), damping-off (*Rhizoctonia solani*), and root rot (*Pythium ultimum*) (Camp et al. 2008; Mercier and Jiménez 2009; Worapong and Strobel 2009; Goates and Mercier 2011). Additionally, the volatiles of *Oxyporus latemarginatus* EF069, an endophyte isolated from red pepper, inhibited the mycelial growth of several plant pathogens, which are known to damage post-harvest fruits (Lee et al. 2009). The volatiles of *O. latemarginatus* EF069 reduced post-harvest decay of apples caused by *B. cinerea* and *Rhizoctonia* root rot of moth orchid (Lee et al. 2009). Endophytic *Nodulisporium* sp. CMU-UPE34 isolated from *Lagerstromia loudoni* is able to produce 31 different volatiles especially eucalyptol. This fungus is able to inhibit or kill 12 different plant pathogens including control of green mold decay on *Citrus limon* caused by *Penicillium digitatum*, blue mold decay of *Citrus aurantifolia* and *Citrus reticulata* caused by *P. expansum* (Suwannarach et al. 2013).

Fungal volatiles could serve as signaling molecules ("info chemicals" or "semio-chemicals") as pheromones, allomones, kairomones, food sources, and attract insects (Rohlfs et al. 2005 and Mburu et al. 2011). Emission of VHCs produced by *Trametes gibbosa* (wood-rotting white rot fungus) serves as an attractant for fungus-eating beetles (Coleoptera) (Kline et al. 2007 and Thakeow et al. 2008). The *M. albus* VHCs demonstrated nematostatic and nematicidal properties. It has shown a great capacity to control of the root-knot nematode *Meloidogyne incognita* (Grimme and Zidack 2007). Riga et al. (2008) tested the VHCs produced by the fungus *M. albus* and found in vitro mortality of *Paratrichodorus allius*, *Pratylenchus penetrans*, and *Meloidogyne chitwoodi*. The VHCs produced by *M. albus* were capable of inhibiting the development of the pupal stage of *P. operculella* and cause mortality in several growth stages of the codling moth (Lepidoptera) (Lacey et al. 2009). Fumigation with VHCs produced by *M. albus* for 3 days caused mortality of codling moth adults and neonate larvae, and it was reported that VHCs, including nitrosoamides produced by *Muscodor* spp., were highly efficient at killing insects (Strobel (2011); Schalchli et al. 2016). *M. vitigenus* produces naphthalene, an effective insect repellent (Daisy et al. 2002). Liarzi et al. (2016) reported the biological activities of VOCs produced from *Daldinia* cf. *concentrica*, an endophytic fungi isolated from olive tree (*Olea europaea* L.) grown in Israel. The GC–MS analysis of volatiles produced from this fungus led to identification of 27 VOCs. The post-harvest experiments demonstrated that *D.* cf. *concentrica* prevented development of molds on organic dried fruits and also eliminated *Aspergillus niger* infection in pea nuts (Liarzi et al. 2016).

VOCs in controlling human pathogens

Endophytes have recently attracted a great attention due to their production of strong antimicrobial volatile compounds. *Muscodor* species are known to produce five classes of volatiles (acids, alcohols, esters, ketones, and lipids). *M. albus* emitted a number of volatiles such as tetrohydrofuran, aciphyllene, and an azulene derivative. The volatiles produced by *M. albus* effectively inhibited or killed a wide range of plant and human pathogenic bacteria (Atmosukarto et al. 2005) and fungi such as *Aspergillus fumigates* and *Candida albicans* (Strobel et al. 2001 and Schmidt et al. 2015). The VOCs of *M. crispans* isolated from wild pineapple known to antagonistic against several human pathogens including *Yersinia pestis*, *Mycobacterium tuberculosis*, and *Staphylococcus aureus.* (Mitchell et al. 2010). Another endophyte, *M. fengyangensis*, has the ability to kill pathogenic *E. coli* (Zhang et al. 2010 and Yuan et al. 2012). The majority of fungal VOCs from endophytic fungi are used as controlling fungal deterioration of crops, fruits, and vegetables under pre and post-harvest conditions. However, presently, these volatiles are not being actively applied to humans in controlling fungal infections (Deshmukh et al., 2018).

Conclusions

Endophytic fungi represent a relatively untapped pool of wide array of metabolites with potential applications. Volatiles represent a new frontier in bioprospect avenues. The study of these gas-phase compounds promises the discovery of new products for human exploitation in fuel production, biocontrol, plant growth, and biotechnology. Technological advances with respect to profiling and analyzing VOCs; genome sequencing and functional genomics tools; and way forward studying the molecular, physiological, and cellular changes in plant and microbial systems will open a new area of research on volatiles of immense applications.

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