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Review of the chemical ecology of homoterpenes in arthropod–plant interactions

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Abstract
The homoterpenes 4,8-dimethyl-1,3,7-nonatriene (DMNT) and 4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT) are volatile products of plant metabolism reported from diverse plant taxa and multiple plant tissues. As such, they have a range of potential ecological functions. Here, we review the key literature to assess evi-dence for roles in contrasting plant–arthropod interactions. TMTT, and DMNT especially, have been reported as sometimes dominant constituents of floral scents from angiosperm taxa ranging from primitive Magnoliales to more advanced, taxonomic orders of economic significance such as Fabales and Sapin-dales. Although all taxa producing TMTT and DMNT in floral scents are entomophi-lous ('insect pollinated'), experimental evidence for an assumed role of these homoterpenes in pollinator attraction is limited. Representing a trade-off, in some cases, homoterpenes in floral scents have been shown to act as kairomones, attracting herbivores. Additionally, both TMTT and DMNT are released by plant foliage in response to arthropod feeding, mechanical damage simulating feeding, or even egg deposition. Evidence for a functional role in herbivore-induced plant volatile (HIPV) blends comes from a wide range of angiosperm orders, including anemophilous ('wind pollinated') taxa, as well as from gymnosperms. We con-clude by considering how TMTT and DMNT function in community-level interac-tions and highlighting research priorities that will reveal how plants avoid trade-offs from contrasting ecological functions of DMNT and TMTT release and how homoterpene production might be exploited to develop improved crop varieties.

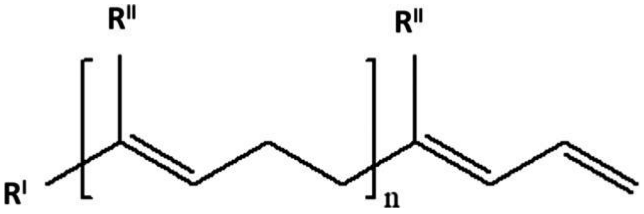
KEYWORDS
DMNT, HIPV, kairomone, pest management, plant defence, pollination, synomones, TMTT

INTRODUCTION

Plants produce a wide range of secondary compounds, many of which are volatile (Dicke 2009; Tholl et al. 2011). The functions of these include, and may have originally been solely for, rapid signalling between differing parts of the same plant in order to systematically activate defences against environmental factors such as herbivore attack (Frost et al. 2007). Plant volatiles have also played an important role in the co-evolution between angio-sperms and insects, leading to intricate pollination mech-anisms that depend—in part—on flower volatiles to optimise pollination by flower visitors. Selection pressure acting on other community members, such as herbivores and their natural enemies (parasitoids and predators), has led these actors to exhibit responses to plant volatiles (Turlings et al. 1990). Selection has led to a progression from natural enemies simply 'eavesdropping' on plant-generated volatiles to co-evolution such that plant–enemy communication can now result in finely tuned herbivore-induced plant volatile (HIPV) blends (D'alessandro et al. 2006; De Vos et al. 2005; Tholl et al. 2011) that attract appropriate enemies, informing them which species of herbivore is present on a given plant (De Boer et al. 2004). Each of the foregoing types of plant–arthropod interaction has been well studied in sim-ple bipartite or tripartite systems, but the last 15 years have seen a progressive broadening of attention to con-sider community-level, multi-partite interactions. This is important in the context of a group of plant volatiles such as homoterpenes because exaptations, the phenomenon of a feature taking on a new function, have been demonstrated to intricately link differing plant–herbivore interactions. A detailed phylogenetic study of the plant genus Dalechampia (Euphorbiaceae) (Armbruster 1997), for example, provided a timeline for varying chemical and morphological adaptations that were involved in plant defence and pollinator attraction. Triterpene resins originally evolved to defend flowers but later allowed the evolution of terpenoid resin-based systems to reward pollinators that use this material for nest construction. A second example from the Dalechampia system is the evo-lution of bracts that likely were involved in pollinator attraction but later developed an herbivore defence role via nocturnal closure around otherwise vulnerable flowers. Accordingly, plant features—whether chemical or otherwise—are not ‘fixed’ in terms of function. Rather, they are available to differing selection pressures to take on new or multiple functions including pollinator attraction or defence.

From a human perspective, it has never been more important, indeed urgent, to better understand the inter-play of the infochemical webs, of which plant volatiles are a key component, and the trophic webs they affect. Agri-cultural production will need to expand greatly in the next 50 years in order to support the burgeoning needs of humans (Godfray & Garnett 2014; Tilman et al. 2011). There is increasing recognition that relying on a business-as-usual approach and entrenching reliance on non-renewable and often hazardous inputs is unsustainable. Rather, an ecological intensification approach, in which ecosystem services such as those provided by robust communities of pollinators and natural enemies of pests, offers better scope to enhance agricultural productivity and resilience (Bommarco et al. 2013; Gurr et al. 2016; Loos et al. 2014). Aside from agricultural production, con-servation of biodiversity, including that in terrestrial habi-tats where angiosperms and insects are the dominant higher taxa for plants and animals, respectively, is a prior-ity (Losey & Vaughan 2006; Vanbergen & Insect Pollinators Initiative 2013). Atmospheric gas regulation, provision of clean water and valuable bioproducts such as pharma-ceuticals are among the ecosystem services provided by global biodiversity (Costanza et al. 1997) and that cur-rently are being eroded by habitat destruction and high extinction rates (Tollefson 2019). Related to this, recent evidence suggests that large declines in insect numbers and diversity are occurring (Seibold et al. 2019). This is alarming given that the members of this taxonomic class have been described as ‘the little things that run the world’ (Wilson 1987).

We approach this Gordian knot of challenges from the perspective of a particular pair of plant homoterpenes 4,8-dimethyl-1,3,7-nonatriene (DMNT) and 4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT, usually as the E isomers) (Figure 1). These are dominant compo-nents of the scent produced by insect-pollinated flowers (Kaiser 1994) and in some cases are responded to by pollinators, yet are also present within the volatiles emitted by plant foliage when attacked by herbivores, and attract their natural enemies (Tholl et al. 2011). Further, herbivores also respond directly to plant release of these homoterpenes in some systems (Bichao˜ et al. 2005). Con-sidering the potentially mixed messages sent by DMNT and TMTT emissions from plants serves as a particular lens through which the wider issue of arthropod–plant interactions and associated ecological interactions can be viewed.



F I G U R E 1 Chemical structures of homoterpenes central to arthropod–plant interactions: n = 1, 4,8-dimethyl-1,3,7-nonatriene (DMNT); n = 2, 4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT). R^0, R^{00} = methyl

POLLINATOR ATTRACTION

Pollination by animals, particularly insects, is required in approximately 90% of angiosperms (Ollerton et al. 2011), whereas 75% of the most important crop species benefit from animal pollination especially fruits, nuts and vegetables, which are important for healthy diets (Klein et al. 2007; Potts et al. 2016). Thus, pollination is a key insect–plant interaction for human needs and for terres-trial ecosystems more fundamentally. Pollinators select flowers using a variety of chemical and visual cues (odours, colour/pattern and flower shape) through learned or innate preferences (Dafni et al. 1997; Daly & Smith 2000; Chittka 2017; Giurfa et al. 1995; Goyret et al. 2008). Alternatively, flowers may filter out preferred pollinators through specialist adaptations of floral morphology and chemistry that limit access to nectar (Brosi 2016). One of the classic examples of co-adaptation of plants and pollinators is Angraecum sesquipedale (Orchidaceae), which has an extraordinarily long nectar spur. This flower was legendarily predicted by Charles Darwin in 1862 to be pollinated by a long-tongued flower visitor and which was eventually discovered 40 years later as a sphinx moth species Xanthopan morganii praedicta (Lepidoptera: Sphingidae) (Arditti et al. 2012). Some flower visitors have learned to rob nectar from inaccessi-ble nectaries by chewing through corollas so plant spe-cies may complement specialist morphology with selectively toxic plant chemicals, the basis for other forms of co-adaptation. The nectaries of Aconitum spp. (Ranunculaceae), for example, restrict access to long-tongued bumble bees (Thøstesen & Olesen 1996), whereas floral toxins protect nectar from robbers ensuring that the reward is conserved for the pollinator (Barlow et al. 2017). Plant chemicals also manipulate learning in bees to augment pollination. Nectar caffeine, for example, enhances memory in honeybees for floral traits associ-ated with food rewards increasing revisitation to food rewards and increased pollen transfer to caffeinated flowers (Couvillon et al. 2015; Thomson et al. 2015; Wright et al. 2013).

Volatile organic compounds from flowers also medi-ate pollinator behaviour. When combined with morpho-logical adaptations, these provide some of the most remarkable examples of behaviour manipulation to opti-mise pollination. Drakaea thynniphila (Orchidaceae), for example, produces a suite of methylpyrazines that closely resemble the sex pheromone of the female thynnid wasps (Agriomyia spp.) (Hymenoptera: Thynnidae) that attract sexually active males to the thynnid wasp-shaped flowers (Bohman et al. 2014). During the subsequent pseudo-copulation, a pollinium is deposited on the back of the wasp thorax, which is then transferred to a subse-quent flower as the male continues to search for a mate.

Blood feeding invertebrate taxa also visit flowers for nectar with some, such as ceratopogonid midges, providing critical pollination services (Billes 1941; Bogarín et al. 2018; Posnette 1944). In doing so, they must respond to different cues depending on their requirements. For example, Forcipomyia and Culicoides spp. (Ceratopogonidae) are attracted to 1-octen-3-ol, acetone and carbon dioxide when seeking an animal host for blood meal (Blackwell et al. 1996; Isberg et al. 2017; Liu et al. 2009) and with the (R)-1-octen-3-ol enantiomer defined for Culicoides (Harrup et al. 2012). Theobroma cacao (cocoa), which is pollinated by these biting midges, produces specific alkenes and dienes that are unusual and distinctive floral volatiles attractive to the midges when locating flowers where they harvest pollen and which they subsequently pollinate (Arnold et al. 2019).

The survey by Tholl et al. (2011) lists 29 angiosperm families in which one or both of TMTT and DMNT have been reported, mostly in broad works by Kaiser (1994) and Knudsen et al. (2006), though there are species-specific studies by Azuma et al. (1997) (Magnolia grandi-flora), Svensson et al. (2005) (Yucca filamentosa) and Schultz et al. (1999) (Cyclanthus bipartitus). Recent func-tional genomics work on the terpene gene family of apple (Malus domestica Borkh, cv Royal Gala), a plant reliant on cross-pollination by insects, found that)-DMNT (along with linalool) was predominant among floral terpenes (Nieuwenhuizen et al. 2013). Intriguingly, however, DMNT was also emitted by non-floral tissues, especially stipules and young leaves. Production by these vegetative tissues is likely associated with plant defence (explored in detail below) rather than attraction of pollinator attraction (Arimura et al. 2004; Ghirardo et al. 2012). The response of western flower thrips (WFT) (Frankliniella occidentalis (Pergande)) to DMNT and TMTT was evaluated in studies on floral volatiles of Verbena hybrids, but they were reported to be not attractive (Pow et al. 1998). Although this study was undertaken from the perspective of pest attraction to flowers, the role of thrips as pollinators could be more common with pollen herbivory considering this recent work and in the knowledge that thrips are one of the earliest recorded pollinators (Peñalver et al. 2012; Scott-Brown et al. 2019; Terry et al. 2007).

Despite the foregoing evidence of widespread occurrence of DMNT and TMTT in flower volatiles, and the well-established phenomenon of species-specific floral chemicals driving pollinator interactions (Stevenson et al. 2017), there is little experimental evidence that homoterpenes such as DMNT and TMTT function as synomones in influencing pollinator behaviour and enhancing pollina-tion. This may be because these homoterpenes occur so widely and do not present a unique or sufficiently distinc-tive trait for a pollinator to distinguish a preferred flower. Where they have been identified in pollination studies, their role in mediating pollinators was mostly not signifi-cant. For example, Yucca species that are pollinated by moths (including Tegeticula cassandra, a pollinating seed-eater, and Prodoxus decipiens, an herbivore) produce a range of branched alkenes along with several homoter-penes including DMNT (Svensson et al. 2006). However, only the unbranched alkenes (i.e., not homoterpenes) were reported to have any behaviour-modifying effects. One of these, (Z)-9-nonadecene, also elicited an electro-physiological response from Tegeticula antennae, so the moths seem likely to use these rather than homoterpenes to locate flowers (Tröger et al. 2019). More recent work (Tröger et al. 2019) has demonstrated a role for a set of novel tetranorsesquiterpenoids putatively derived from (E)-DMNT in attraction of the yucca moth to yucca flowers.

The most compelling example of a homoterpene mediating pollinator behaviour comes from work on Cyclopogon (Schultz et al. 1999). DMNT was by far the major component in the floral odour of Cyclopogon elatus (>99% DMNT), which is pollinated exclusively by halictid bee species including Augochlora nausicaa. This bee spe-cies located enclosed (i.e., not visible) flowers in an upwind direction providing evidence that the odour is used as the cue. The high relative amount of DMNT in the floral odour was unusual, and homoterpenes typically occur at lower relative concentrations typically alongside numerous other compounds that may influence how insects respond to them in other interactions. Why DMNT has potentially such an important role in pollinator orientation behaviour for halictid bees may be because DMNT is easy to learn by bees searching for nectar when it is so relatively abundant compared to other floral volatiles. Its attractiveness in other systems, particularly where it is a relatively minor component of a complex mixture, might depend on the contextual presence of other volatiles (e.g., Raguso 2004).

The role of monoterpenes and other alkenes in mediating pollinator behaviour is more widely studied than for homoterpenes. This may be because the conjugated diene structure of the specific homoterpenes, DMNT and TMTT, renders these compounds highly labile and readily lost by oxidation on storage in contact with air allowing detection and study to be overlooked. β-Ocimene, which is structurally related to homoterpenes, and linalool occur widely in angiosperm flower odours and are reported to mediate flower finding by pollinators, particularly at night (Farré-Armengol et al. 2017). Although some compounds may be attractive to pollinators, few studies of the behavioural responses to monoterpenes unequivocally demonstrate an enhancement of pollen transfer despite several reports where emissions correlate with visits to flowers. For example, in the specialist system of a hawkmoth Sphinx pinastri pollinating the orchid Platanthera chlorantha, (E) and (Z) isomers of β-ocimene have peak emissions coinciding with visitation by the moth so could be influencing moth orientation, although this was not demonstrated to influence pollen transfer (Steen et al. 2019). A recent more convincing example reports that (E)-β-ocimene and the terpene alcohol linalool that are produced by flowers of Paullinia cupana were attrac-tive to Megalopta bees, which were specialist pollinators of the plant and were already carrying P. cupana pollen when trapped (Krug et al. 2018).

Monoterpenes, structurally related to homoterpenes, have helped to establish a chemical basis of interaction for some non-bee pollinators including thrips. For example, β-myrcene and (E)-β-ocimene that were emitted by cones of the cycad Macrozamia lucida elicited an electrophysiological response in the pollinating thrips Cycadothrips chadwicki. The thrips were attracted to (E)-β-ocimene and low concentrations of β-myrcene but deterred at high concentrations of the latter and the variations in the emission of β-myrcene at different stages of cone development explained the diel thrips pollination behaviour (Terry et al. 2007). Interestingly, C. chadwicki did not respond to (Z)-β-ocimene, highlighting the importance of stereochemistry in establishing ecological functions for plant chemicals. The related monoterpene, linalool, was also reported to mediate flower visitation by Thrips major Uzel, which was also shown to be an effective pollinator of elder flowers (Sambucus nigra L.) (Scott-Brown et al. 2019), whereas Thrips obscuratus (Crawford) was attracted to Japanese honeysuckle flowers, Lonicera japonica (Thunberg) (Caprifoliaceae), which also emit high levels of linalool at night, although it is not known whether this thrips species contributes to pollen transfer between conspecific flowers (EL-Sayed et al. 2009; Miyake et al. 1998).

HERBIVORE ATTRACTION

Reflective of earlier discussion of exaptations that link differing plant features with contrasting insect–plant interactions, hypotheses on the evolutionary origin of flower odour suggest that damage-associated volatiles were used originally as kairomonal attractants by some florivores whose activities resulted in pollination (Knudsen et al. 2006; Pellmyr & Thien 1986). Indeed, floral volatiles can attract flower feeders as well as pollinators. For exam-ple, 1,2,4-trimethoxybenzene, a volatile produced by the flowers of Cucurbitaceae, is attractive to the striped cucumber beetle, Acalymma vittatum Fabricius (herbi-vore), and the squash bee, Peponapis pruinosa Say (a specialist pollinator of Cucurbitaceae) (Andrews et al. 2007). In such a system, a selective advantage would accrue if a plant was able to produce a chemical signal with more specific effects: attracting a pollinator, yet with a weaker trade-off of attracting an herbivore. Indeed, indole was found to be attractive only to the herbivore in this system whereas (E)-cinnamaldehyde was attractive to the pollinator (Andrews et al. 2007). Thus, compounds may have contrasting selection pressure (i.e., favouring and disfavouring production) caused by the different responses by mutualists and antagonists.

Relatively few studies are available that provide insight into the possibility that homoterpenes serve as kairomones by constituting chemical cues by which herbivores locate host plants. A clear opportunity for this to occur is in the case of flower-feeding insects because these are most likely to benefit from responding to flower volatiles intended for pollinator attraction. An example is the pollen-feeding pest of oilseed rape, bronzed blossom beetle (Meligethes aeneus). This was the subject of study of the flower volatiles released by the non-host brassica plant Iberis amara L., and DMNT was found to be one of seven volatiles that elicited an antennal response (Bartlet et al. 2004). Further, field attraction of this pest to DMNT was demonstrated in a study of traps baited with single compounds including this homoterpene, though the effect was confined to traps baited with a high rate of DMNT and was less attractive than some other com-pounds such as linalool and 1,8-cineole hexanoic acid (Smart & Blight 2000). In a contrasting system, the volatiles emitted by green grape berries contained DMNT as one of the major constituents and the blend was highly attractive to a potentially serious herbivore pest, European grapevine moth, Lobesia botrana (Denis & Schiffermüller) (Tasin et al. 2006). Attraction was also high to a synthetic blend containing DMNT with (E)-β-farnesene and (E)-β-caryophyllene. Importantly, a functional role of DMNT was confirmed by its omission from the synthetic blend leading to levels of attraction of female moths no greater than the blank control.

A broadly similar study detected DMNT in the headspace of hawthorn (Crataegus spp.) fruits (Nojima et al. 2003). In that work, electroantennographic detection (GC-EAD) was used to confirm that this homoterpene was one of six compounds eliciting a response by the fruit pest, apple maggot fly (Rhagoletis pomonella (Walsh)). Again, confirming a functional role of DMNT, its omission from four- or six-compound synthetic blends resulted in significantly decreased numbers of upwind flights by the insect. Finally, evidence of effects of flower volatiles comes from studies of the strawberry blossom weevil (Anthonomus rubi Herbst). Headspace volatiles from strawberry flowers contained DMNT, and the antenna of adult A. rubi was found to have an olfactory receptor neurone tuned to be particularly receptive to DMNT (Bichão et al. 2005). Moreover, strawberry plant production of DMNT, and the four other volatiles for which tuned receptor neurones were identified, was found to be induced by A. rubi feeding on the flowers. Accordingly, adults are adapted for detection of host plants upon which conspecifics are already feeding rather than being attracted to a pollinator-attracting semiochemical.

Having established that DMNT release by plants can have effects on herbivorous insects and that these herbivores can be exquisitely co-adapted for the detection of DMNT, we consider in the next section a further complica-tion in the community-level effects of homoterpenes: effects on natural enemies. This builds on the finding by (Bichão et al. 2005) of herbivore response to induced pro-duction of DMNT.

NATURAL ENEMY ATTRACTION

The production of HIPVs has been recognised as an important induced plant defence strategy against herbivores that operates by recruiting natural enemy 'bodyguards' to plants under attack. Homoterpenes are common components of HIPVs in many plant species (Tholl et al. 2011) including lima bean Phaseolus lunatus L. (Zhang et al. 2009), maize Zea mays L. (Signoretti et al. 2012) and Malabar spinach Basella alba L. (Aboshi et al. 2019) when under attack by herbivores.

The blends of HIPVs produced by plants can be remarkably consistent under circumstances of attack by contrasting herbivore taxa. For example, a study of lima bean compared volatiles produced by damage from the insect pest, Spodoptera littoralis (Boisduval), and the snail Cepaea hortensis Muller and found these to be similar, both including relatively large amounts of DMNT and TMTT. More widely, there is evidence in the form of gene expression profiles of Arabidopsis (Arabidopsis thaliana L.) that plant responses to herbivory can be general rather than specific (Reymond et al. 2004). In broad agreement, the parasitoid Cotesia rubecula Marshall did not discrimi-nate between volatiles of Arabidopsis fed upon by Pieris rapae L. (a host) or by Spodoptera exigua Hübner (a non-host), despite the clear fitness advantage that would have been gained from a capacity to discriminate (Van Poecke et al. 2003).

In contrast, HIPV blends in other systems can differ qualitatively and quantitatively according to identity of the attacking herbivore, providing cues that lead to attraction of appropriate natural enemy taxa (De Moraes et al. 1998). Simultaneous attack by more than one taxon of herbivore can also change the HIPV blend. In a study of lima bean, the HIPV blend produced when attacked by spider mite (Tetranychus urticae Koch) included both DMNT and TMTT among the dominant compounds (Zhang et al. 2009). Earlier work demonstrated that TMTT production in concert with other HIPVs from spider mite-infested lima bean leaves influenced the foraging behaviour of the predatory mite, Phytoseiulus persimilis (Athias-Henriot) (De Boer et al. 2004). When the plants in Zhang et al.'s study were simultaneously attacked by whitefly (Bemisia tabaci Gennadius), the HIPV blend was altered to the extent that attraction of P. persimilis was compromised. Treatment of mite-infested plants with exogenous salicylic acid (to mimic the effect of phloem feeding by the whitefly) resulted in reduced production of multiple compounds, including homoterpenes, with significant effects on (Z)-β-ocimene, (E)-β-ocimene and an unresolved $C_{10}H_{16}O$ compound.

Direct evidence for a role of homoterpenes in HIPV-based plant defence was obtained in work treating lima bean with the fosmidomycin (a terpenoid pathway inhibi-tor). This led to markedly reduced emission of homoter-penes and reduced attraction of predatory mites (Mumm et al. 2008). Similarly, in more recent work using trans-genic rice studies of defences against the lepidopteran pest, Chilo suppressalis Walker, homoterpenes were pre-sent in HIPVs and led to attraction of the parasitoid Cote-sia chilonis (Matsumura) (Li et al. 2018). Expression of the terpene synthase gene Pltps3 increased emission of DMNT (and (S)-linalool) in volatile blends compared with wild-type rice, whereas expression of Pltps4 increased emission of DMNT and TMTT (and (S)-linalool) in HIPV blends. Both transgenic rice lines produced HIPV blends that were more attractive to the parasitoids than were volatiles from wild-type rice. Further work (Li et al. 2018) has demonstrated that overexpression of the rice cytochrome P450 gene, OsCYP92C21 (responsible for the oxidation of terpene tertiary alcohols to the homoterpenes in rice), in a background of a genetically increased precur-sor pool produces enhanced homoterpene levels in rice, thereby raising the performance in the laboratory of bio-logical control parasitoids against a rice pest.

NON-NATURAL ENEMY-MEDIATED NEGATIVE EFFECTS ON HERBIVORES

The preceding sections considered the phenomenon of chemically mediated attraction of arthropods to plants, whether pollinators, herbivores and natural enemies. Repellency can also result from plant volatiles, and a func-tional role of DMNT in volatile defences was evident in a study of sweet potato (Ipomoea batatas L.) var. TN57 HIPVs whereby plant defence was directly operating on the herbivore rather than being mediated by natural enemies. Production of DMNT was increased when attacked by a mechanical caterpillar ('MecWorm') or by S. littoralis larvae. Remarkably, airborne DMNT led to systemically induced direct anti-herbivore defences in neighbouring sweet potato plants. This potent trigger of plant defences led to reduced S. littoralis larval weight gain after 7 or 10 days, an effect shown not to be attributable to toxicity of DMNT to larvae but to higher sporamin protease inhibitor (SPI) in the neighbouring undamaged plant (Meents et al. 2019). A further example of a direct effect of DMNT comes from studies of the responses of adult S. littoralis to the HIPVs of cotton plants (Hatano et al. 2015). DMNT was demonstrated to suppress the plant odour- and pheromone-induced behaviours, reducing attraction of induced plant sites by female moths and to pheromone-releasing females by male moths.

The direct effects of homoterpenes on herbivores have been exploited for practical pest management in the successful 'push–pull' system developed for protect-ing maize crops from stemborer pests such as Busseola fusca (Füller) and Chilo partellus Swinhoe (Khan et al. 2016). In this system, molasses grass (Melinis minutiflora P.Beauv.) is intercropped as a groundcover below the taller maize plants and constitutively produces DMNT in its volatile blend. This emission has the dual effect of repelling female stemborer moths and attracting parasitoids such as Cotesia sesamiae Cameron. The 'pushing' effect on moths is thought to occur because it is perceived by the pest as a signal of heavily infested maize plants that are already heavily utilised by conspecifics and likely to be harbouring high densities of parasitoids that have responded to these volatiles. Desmodium uncinatum Jacq., an alternative intercrop species, also produces large amounts of DMNT that repels stemborers though appears not to attract parasitoids to the extent of increasing field parasitism levels (Khan et al. 2000). More recent work has shown how this push–pull system can be adapted to pro-vide effective control of the highly invasive lepidopteran pest, fall armyworm Spodoptera frugiperda (J. E. Smith) (Midega et al. 2018) that is currently a new threat to pro-duction in Asia and Oceania.

Remarkably, recent work on volatile release of DMNT has shown a distinct additional mode of action by which herbivores may be adversely affected in a physiological manner rather than via affecting insect behaviour, and this suggests entirely new possibilities for pest management (Chen et al. 2021). Studies with transgenic A. thaliana revealed that resistance to larvae of the major lepidopteran pest, diamondback moth (Plutella xylostella L.), could be conferred by overexpression of the gene responsible for DMNT synthesis. To elucidate the mechanism for this effect, larvae were fed with a diet containing a blue dye (erioglaucine disodium salt) that cannot pass through the intact gut wall. Larvae exposed to DMNT turned blue in this 'Smurf test' indicating lesions in the gut, whereas control larvae that were not exposed to DMNT defecated the dye. Exogenous application of DMNT to larval diet altered the gut microbiota, and this was found to be linked to damage to the peritrophic matrix, a barrier protecting the midgut, resulting in larval mortality. Reflecting the adverse effects of DMNT on P. xylostella, other studies showed that larvae orientated away from the odour of this compound.

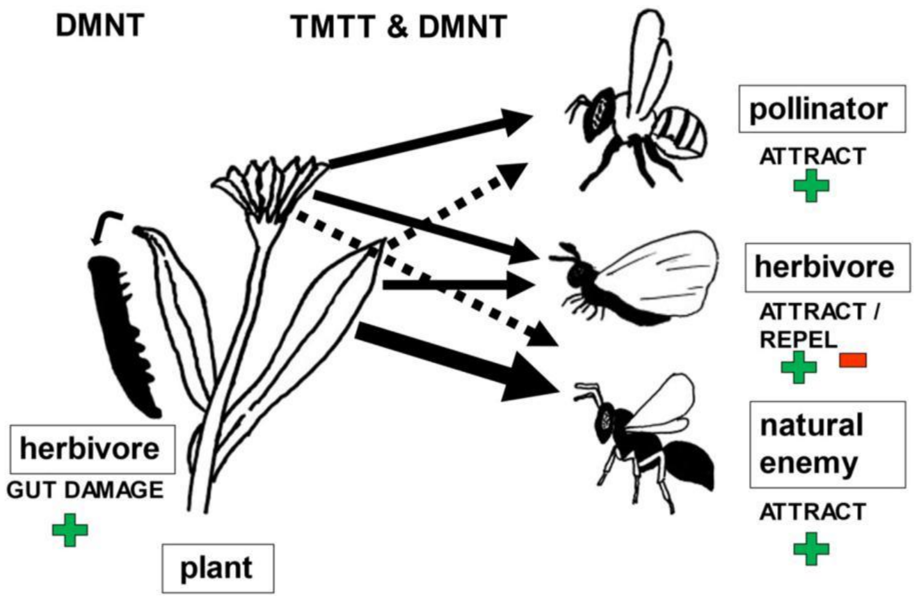
COMMUNITY-LEVEL INTERACTIONS

Given the evidence that herbivores induce DMNT and TMTT production by plant foliage as defence against those herbivores by attracting natural enemies, and these same compounds attract pollinators when produced by the flowers of the same plant (Azuma et al. 1997), this presents potential trade-offs. Thus, herbivory, pollination and the attraction of natural enemies of pests present a potentially complex interaction web (Figure 2). This web includes direct negative consequences for pollinators and a trade-off for the plant in balancing the effects of its volatile emissions on survival and growth (defences) and reproduction (pollination).

DMNT is produced in response to herbivory, so its role as a behaviour-modifying compound for flower visitors that pollinate may be more complex in flowers where it is not the primary constitutive component but where it is also important to attract natural enemies of herbivorous antagonists. Similarly, some but not all floral volatiles can attract both a flower feeder and a pollinator. For example, in the previously mentioned Cucurbitaceae flower system (Andrews et al. 2007), whilst 1,2,4-trimethoxybenzene is attractive to both a serious pest and a pollinator, indole is attractive only to the herbivore and (E)-cinnamaldehyde attractive to the pollinator. Thus, some compounds may have dual effects with conflicting selection pressures imposed by mutualists and antagonists, whereas other compounds avoid this by having specific effects on either pollinators or herbivores. Accordingly, in a case of herbi-vores inducing homoterpene production in HIPVs and these compounds also attracting pollinators, this presents a conflict where—for example—the pollinator may be at greater risk of predation from the plant's recruited body-guards. Thus, herbivory, pollination and the attraction of natural enemies of pests present an enigma with complex and potential negative consequences for pollinators and plants.

How might a plant manipulate homoterpene signals in response to environmental cues in order to reduce possible trade-offs and maximise fitness? The release of homoterpenes as HIPVs from the foliage of attacked plants prior to anthesis is straightforward because pollinator attraction is irrelevant at this early stage of plant development. Signalling can focus on attraction of natural enemies and suppression of herbivores. After anthesis, however, there is scope for mixed messages leading to trade-offs in plant fitness arising from homoterpenes produced to attract pollinators and those induced as part of an HIPV blend. Potentially, the stereochemistry of the homoterpene produced under differing selection pressures differs in order to avoid confusing signals, but there

FIGURE 2 Major ecological functions of DMNT and TMTT production by foliage and flowers in insect–plant interactions. Effect on plant fitness indicated by + and symbols for each interaction. Weight of arrows indicates the relative importance of each benefit to the plant in terms of reported cases. Dashed arrows indicate the potential non-beneficial effects of production by flowers on natural enemies and by foliage on pollinators.



is little published information available to support this speculation. Alternatively, the homoterpene signals may be identical, and it is down to the receiver (pollinator and natural enemy) to determine appropriate responses from the context of the wider blend of volatile cues. These decisions are potentially important because a natural enemy responding to homoterpenes in floral scents that are intended to attract pollinators would waste effort because this cue was not a signal of herbivore presence and the availability of a host or prey. This scenario seems likely because studies of the responses of natural enemies to HIPV blends suggest that attraction can operate by vir-tue of the ratios of volatile constituents in HIPV blends rather than a binary presence/absence of a single com-pound (Liu et al. 2017). Further, learning is likely to be important in mediating responses by insects. In the case of pollinators, honeybees especially are well known to employ learning to optimise foraging (Couvillon et al. 2015; Thomson et al. 2015; Wright et al. 2013), and interpretation of homoterpene detection may involve integration with visual cues. This is important because a pollinator attracted to a plant by homoterpenes within HIPV blends (rather than as floral synomones) will encounter a plant under herbivore attack and this may reduce the plant's capacity to produce nectar and pollen so rendering it less rewarding than an uninfested plant that was not releasing homoterpene-containing HIPVs. Indeed, studies have shown that pollinators can exhibit a preference for herbivore free plants over those signalling herbivore attack (Kessler & Halitschke 2009), though a series of experiments with white mustard (Sinapis alba L.) (Pareja et al. 2012) illustrate that idiosyncratic responses at multiple trophic levels make it difficult to make sweep-ing generalisations. In that work, herbivory by a specialist brassica phloem feeder (Lipaphis erysimi (Kaltenbach)) inhibited the emission of floral volatiles, especially the production of benzaldehyde and methyl salicylate in the 48–72 and 72–96 h periods after commencement of her-bivory, and the extent of suppression was positively cor-related with the numbers of those aphids per plant. In contrast, there was a weaker effect from feeding by the generalist herbivore Myzus persicae (Sulzer) and a slight elevation in floral volatile production caused by the chew-ing feeder P. xylostella, including the production of 6-methyl-5-heptene-2-one, which is biosynthetically related to homoterpenes. A further point of contrast is with volatile production from the foliage of the same plants. Composition discriminant analysis revealed that 6-methyl-5-heptene-2-one production was elevated by feeding of either aphid species compared with uninfested plants whereas TMTT was released only from M. persicae-infested foliage. These results indicate that feeding mechanism of the herbivore (chewing vs sucking) and the degree of specialisation (monophagy vs. polyphagy) can profoundly affect plant response. Con-sidering the trophic effects of these contrasting volatile patterns, reductions in floral volatile production did not translate to a reduced level of field visitation by pollinator insects, but the experimental conditions led to only low levels of visitations to plants (13.9–14.5 per day), and so real-world effects remain possible. Importantly, natural enemies (a predatory ladybird, Coccinella septempunctata L., and a parasitoid, Diaeretiella rapae (McIntosh)) responded in olfactometer assays in ways that did dem-onstrate recognition of the contrasting volatile profiles. For both natural enemies, most responses to infested versus uninfested or versus clean air choices reflected an adaptive advantage for the natural enemies' capacity to locate prey/hosts. However, the ladybird exhibited a sig-nificant preference for volatiles from uninfested flowers than for flowers infested by its prey, L. erysimi. Reasons for this seemingly maladaptive response are not clear but may reflect an artefact of the experimental conditions because attraction to the volatiles from whole infested plants was greater than that to whole uninfested plants, and these clearly reflect more biologically realistic cues. Notwithstanding this, the negative responses of ladybirds to floral volatiles in isolation from the whole plant volatile indicate that contrasting plant parts can produce functionally contrasting signals to insects. More generally, plants could potentially up- or down-regulate production of functional volatiles under circumstances where fitness would be maximised by the attraction of a given guild of insect. For example, in circumstances such as early plant growth and development, or of a species that flowers in an indeterminate (extended) manner, natural enemy attraction might take precedence. Foregoing pollinator attraction in the short term may allow herbivore infestation to be checked by recruiting natural enemies with HIPVs. At a later phenological stage, however, or in cases where the plant blooms for only a short period and is short-lived, emphasising pollinator attraction is likely to optimise fitness even at the cost of failure to check herbivore attack. Such hypotheses are attractive targets for rel-atively simple future studies.

A further possible mechanism for reducing mixed messaging is the diurnal separation of ecological func-tions as suggested by the fact that homoterpenes are characteristic constituents of the ‘white floral image’ of night-scented plants such as Orchidaceae and Liliaceae (Donath & Boland 1994). For example, Kaiser (1994) described TMTT as the main floral volatile of the highly fragrant, moth-pollinated African orchid Aerangis frie-siorum and of floral scent emitted from Selenicereus hama-tus (known as ‘queen of the night’). Though parasitoid activity is not strictly diurnal (Marchiori et al. 2007), they are generally assumed to be chiefly day active (Marchiori et al. 2007) and plants need light for de novo synthesis of HIPVs (Paré & Tumlinson 1997; Signoretti et al. 2012). Thus, at least some plants that produce homoterpenes as floral blends are pollinated nocturnally whereas HIPV-based effects on natural enemies occur chiefly during the day. The well-studied case of (E)-α-bergamotene emission in Nicotiana attenuata illustrates the significance of tem-poral kinetics in resolving the dilemma of attracting adult Manduca sexta as pollinators whilst defending foliage from damage by that insect’s herbivorous larvae (Zhou et al. 2017). Synthesis of (E)-α-bergamotene in that plant is mediated by a single monoterpene synthase-derived sesquiterpene synthase gene but with tissue-specific expression such that floral production is mainly nocturnal (corresponding with moth activity) whereas production in foliage is slight unless induced by herbivory and then peaks during daytime. Such diurnal separation of ecologi-cal functions by plants seems likely to be significant in minimising the maladaptive trade-offs by homoterpene production from flowers and foliage (Figure 2). Notably, though, herbivores, natural enemies and pollinators are not passive actors in these interaction webs. Each of these insect guilds will be subject to natural selection to sensory and behavioural traits to optimise advantage from available DMNT and TMTT cues. For example, studies of naive adult Campoletis flavicincta parasitoids to the volatiles produced by maize when treated with regurgitate of the fall armyworm revealed attraction only if the plants had been induced (i.e., treated with fall armyworm larval regurgitant) during scotophase, 5–6 h beforehand (Signoretti et al. 2012). The HIPV blend produced at that time had higher amounts of DMNT than did blends produced by plants induced during photophase, and those authors speculated that the parasitoid may have evolved to respond to volatiles produced nocturnally because this herbivore feeds most actively at night.

CONCLUSION AND FUTURE DIRECTIONS

The homoterpenes DMNT and TMTT are produced in relatively large amounts in the volatile blends of a wide vari-ety of plant taxa, especially entomophilous angiosperms. They are responsible in some studies of a functional role in the attraction of pollinators, pests and—especially—of natural enemies. Other studies have shown them to repel pests. Among these effects, the strongest and most taxo-nomically ubiquitous evidence is for homoterpenes to be functionally active in HIPV blends. Overall, however, there is relatively less experimental evidence for ecological functions of TMTT in comparison to DMNT.

The key opportunity for future research programs is to harness the biological functions of this group of com-pounds to suppress pests (via natural enemy effects or more directly) to support ecological intensification of agri-culture. Consistent with this broad aim, Li et al. (2018, 2021) demonstrate in studies of terpene synthase genes in transgenic rice lines, especially OsCYP92C21, that the transformation of crop varieties has the potential to enhance plant emission of defence volatiles, though this effect is dependent on pools of precursor compounds. Introgressed GM rice plants emitted elevated levels of homoterpenes, and this translated to greater attractive-ness to a parasitoid (C. chiloni). Such studies demonstrate the functional role of homoterpenes and associated scope for exploitation by increasing precursor pools and overexpression of relevant genes by genetic transforma-tion. Indications of the more general scope for genetically enhancing homoterpene production in both monocots and dicots come from the fact that homoterpene biosyn-thetic pathways have been elucidated for a range of eco-nomically important crop plants including rice, maize and cotton (in addition to Arabidopsis) (Richter et al. 2016; Tholl et al. 2011). Ultimately, this could confer varieties with ‘built-in’ protection that will lessen subsequent need for insecticide use to protect the crop. Broadly consistent with this, Khan et al. (2000) consider that plants such as M. minutiflora and Desmodium spp. that produce homo-terpenes constitutively could be used in development of crop protection strategies that extend the success of the use of these plants in 'push–pull' plant protection systems. Such approaches will, however, depend on biological control either directly or indirectly. Any 'built-in' protection system that exerted direct negative effects on herbivores, such as that suggested by the work of Chen et al. (2021), will benefit from being complemented by strong levels of biological control in order to protect the plant traits from adaptation by pest populations resulting in resistance. And in systems based on attraction of natural enemies, there is direct dependency on local natural enemy availability. Unless these biological control agents are made available via costly mass-rearing and release programs, there is a need for agroecological approaches to ensure the presence of donor habitat and ecological resources such as nectar and pollen by conservation biological control approaches (Gurr et al. 2017).

Ultimately, interest in engineering crop plants to increase production of homoterpenes in pursuit of more effective plant protection reinforces the need to better understand the complexities of homoterpene production in the context of DMNT and TMTT also being emitted in flower scents for the attraction of pollinators. Globally, populations of pollinators face mounting threats from factors that include insecticide use and habitat destruction. Accordingly, habitat manipulation measures taken to promote natural enemy availability to respond to HIPV cues will not only alleviate pressure on pollinators via reduced insecticide use (as in rice work by Gurr et al. 2016) but also provide food resources and shelter for pollinators (Arnold et al. 2021).

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CONFLICTS OF INTEREST

The authors declare no conflict of interests.

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