For *Austral Entomology*

Running header: Homoterpenes in arthropod-plant interactions

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

Gurr GM[1*], Liu J[1], Pickett JA[2], Stevenson PC[3,4]

[1]*Gulbali Institute, Charles Sturt University, PO Box 883, Orange, NSW 2800, Australia.*

[2]*School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK.*

[3]*Royal Botanic Gardens Kew, Kew Green, Richmond, London, TW9 3AE, UK*

[4]*Natural Resources Institute, University of Greenwich, Chatham, Kent, UK*

* *ggurr@csu.edu.au*

Abstract

The homoterpenes 4,8-dimethylnona-1,3,7-triene (DMNT) and 4,8,12-trimethyltrideca-1,3,7,11-tetraene (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 evidence 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 Sapindales. Whilst all taxa producing TMTT and DMNT in floral scents are entomophilous ('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 conclude by considering how TMTT and DMNT function in community-level interactions 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.

Key words: TMTT , DMNT, plant defence, pollination, HIPV, kairomone, synomones, pest management

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 angiosperms and insects, leading to intricate pollination mechanisms 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 coevolution such that plant-enemy communication can now result in finely tuned herbivore-induced plant volatile blends (De Vos et al., 2005, D'Alessandro et al., 2006, 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 simple bi- or tri-partite systems but the last 15 years have seen a progressive broadening of attention to consider 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 time-line 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 evolution of bracts, that likely were involved in pollinator attraction but later developed a 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 interplay of the infochemical webs, of which plant volatiles are a key component, and the trophic webs they affect. Agricultural production will need to expand greatly in the next 50 years in order to support the burgeoning needs of humans (Tilman et al., 2011, Godfray and Garnett, 2014). 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 (Gurr et al., 2016, Bommarco et al., 2013, Loos et al., 2014). Aside from agricultural production, conservation of biodiversity, including that in terrestrial habitats where angiosperms and insects are the dominant higher taxa for plants and animals, respectively, is a priority (Vanbergen and Initiative, 2013, Losey and Vaughan, 2006). Atmospheric gas regulation, provision of clean water and valuable bio-products such as pharmaceuticals are among the ecosystem services provided by global biodiversity (Costanza et al., 1997) and that currently are being eroded by habitat destruction and high extinction rates (Tollefson, 2019). Related to this, recent evidence suggests large declines in insect numbers and diversity are occurring (Seibold et al., 2019); 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. DMNT (4,8-dimethylnona-1,3,7-triene) and TMTT (4,8,12-

trimethyltrideca-1,3,7,11-tetraene, usually as the *E* isomers) (Figure 1). These are dominant components 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 (Bichão et al., 2005). Considering 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.

POLLINATOR ATTRACTION

Pollination by animals, particularly insects, is required in approximately 90% of angiosperms (Ollerton et al., 2011) while 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 terrestrial ecosystems more fundamentally. Pollinators select flowers using a variety of chemical and visual cues (odours, colour/pattern, flower shape) through learned or innate preferences (Chittka, 2017, Daly and Smith, 2000, Goyret et al., 2008, Giurfa et al., 1995, Dafni et al., 1997). 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 inaccessible nectaries by chewing through corollas so plant species 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 and Olesen, 1996) while floral toxins protect nectar from robbers ensuring 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 associated with food rewards increasing revisitation to food rewards and increased pollen transfer to caffeinated flowers (Wright et al., 2013, Couvillon et al., 2015, Thomson et al., 2015).

Volatile organic compounds from flowers also mediate pollinator behaviour. When combined with morphological adaptations, these provide some of the most remarkable examples of behaviour manipulation to optimise 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 pollinia is deposited on the back of the wasp thorax which is then transferred to a subsequent 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, Posnette, 1944, Bogarín et al., 2018). 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, Liu et al., 2009, Isberg et al., 2017) 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, produce 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 (1991) and (Knudsen et al., 2006) though there are species-specific studies by Azuma et al. (1997) (*Magnolia grandiflora*), Svensson et al. (2005) (*Yucca filamentosa*) and Schultz et al. (1999) (*Cyclanthus bipartus*). Recent functional 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 *(E)*-DMNT (along with linalool) was predominant among floral terpenes (Nieuwenhuizen et al., 2013). Intriguingly, however, *(E)*-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). While 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 (Terry et al., 2007, Scott-Brown et al., 2019, Peñalver et al., 2012).

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 pollination. This may be because these homoterpenes occur so widely and do not present a unique or sufficiently distinctive 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 significant. For example, *Yucca* species which are pollinated by moths (including *Tegeticula cassandra*, a pollinating seed-eater, and *Prodoxus decipiens,* a herbivore) produce a range of branched alkenes along with several homoterpenes 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 electrophysiological 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., 2021) has demonstrated a role for a set of novel tetranorsesquiterpenoids putatively derived from (*E*)-4,8-dimethyl-1,3,7-nonatriene 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 species 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 which 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). While 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 (*E*)-β-ocimene and the terpene alcohol linalool that are produced by flowers of *Paulinia cupana* were attractive 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 which 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) while *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 suggests that damage-associated volatiles were used originally as kairomonal attractants by some florivores whose activities resulted in pollination (Pellmyr and Thien, 1986, Knudsen et al., 2006). Indeed, floral volatiles can attract flower feeders as well as pollinators. For example, 1,2,4-trimethoxybenzene a volatile produced by the flowers of Cucurbitaceae is attractive to the striped cucumber beetle, *Acalymma vittatum* Fabricius, (herbivore) and the squash bee, *Peponapis pruinosa* Say, (a specialist pollinator of Cucurbitaceae). In such a system, a selective advantage would accrue if a plant were able to produce a chemical signal with more specific effects: attracting a pollinator, yet with a weaker trade-off of attracting a herbivore. Indeed, indole was found to be attractive only to the herbivore in this system whilst

(*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 it was less attractive than some other compounds such as linalool and 1,8-cineole hexanoic acid (Smart and 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). Head space 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 complication 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 production of DMNT.

NATURAL ENEMY ATTRACTION

The production of herbivore induced plant volatiles (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 discriminate 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 defense was obtained in work treating lima bean with the fosmidomycin (a terpenoid pathway inhibitor). This led to markedly reduced emission of homoterpenes and reduced attraction of predatory mites (Mumm et al., 2008). Similarly, in more recent work using transgenic rice studies of defences against the lepidopteran pest, *Chilo suppressalis* Walker, homoterpenes were present in HIPVs and led to attraction of the parasitoid *Cotesia 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, whilst 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., 2020) has demonstrated that over expression 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 precursor pool produces enhanced homoterpene levels in rice thereby raising the performance in the laboratory of biological 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 functional role of DMNT in volatile defences was evident in a study of sweetpotato (*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 sweetpotato 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 protecting 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 it 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 utililised 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 provide effective control of the highly invasive lepidopteran pest, fall army worm *Spodoptera frugiperda* (J E Smith) (Midega et al., 2018) that is currently a new threat to production 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 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 whilst 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, 1997a,b), 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 system where 1,2,4-trimethoxybenzene is produced by the flowers of Cucurbitaceae and is attractive to a serious pest and a pollinator whilst indole is attractive only to the herbivore and (*E*)-cinnamaldehyde attractive to the pollinator (Andrews et al., 2007). Thus, some compounds may have dual effects with conflicting selection pressures imposed by mutualists and antagonists whilst other compounds avoid this by having specific effects on either pollinators or on herbivores. Accordingly, in a case of herbivores 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 bodyguards. Thus, herbivory, pollination and the attraction of natural enemies of pests presents 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 a HIPV blend. Potentially, the stereochemistry of the homoterpene produced under differing selection pressures differs in order to avoid confusing signals but there 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 virtue of the ratios of volatile constituents in HIPV blends rather than a binary presence/absence of a single compound (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 (Wright et al., 2013, Couvillon et al., 2015, Thomson et al., 2015) 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 which 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 and Halitschke, 2009) though a series of experiments with white mustard (*Sinapis alba* L.) (Pereja et al. 2012) illustrate that idiosyncratic responses at multiple trophic levels make it difficult to make sweeping 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 the 72–96-hour periods after commencement of herbivory and the extent of suppression was positively correlated 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 chewing 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 whilst 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. Considering 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) so real-world effects remain possible. Importantly, natural enemies (a predatory ladybird , *Coccinella septempunctata* L., and a parasitoid, *Diaeritriella rapae* (McIntosh)) responded in olfactometer assays in ways that did demonstrate 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 significant 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 uninfested whole 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 relatively simple future studies.

A further possible mechanism for reducing mixed messaging is the diurnal separation of ecological functions 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 and Boland, 1994). For example, Kaiser (1991) described TMTT as the main floral volatile of the highly fragrant, moth-pollinated African orchid *Aerangis friesiorum* and of floral scent emitted from *Selenicereus hamatus* (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 (Signoretti et al., 2012, Paré and Tumlinson, 1997). Thus at least some plants that produce homoterpenes as floral blends are pollinated nocturnally whilst 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 temporal 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) whilst production in foliage is slight unless induced by herbivory and then peaks during daytime. Such diurnal separation of ecological 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 *C. 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 hr 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 variety 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 taxonomically 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 compounds to suppress pests (via natural enemy effects or more directly) to support ecological intensification of agriculture. 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 attractiveness 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 transformation. Indications of the more general scope for genetically enhancing homoterpene production in both monocots and dicots comes from the fact that homoterpene biosynthetic pathways have been elucidated for a range of economically 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 homoterpenes 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. 2021b).

ACKNOWLEDGEMENTS

We thank the Australian Entomological Society and the Graham Centre for Agricultural Innovation (an Alliance between Charles Sturt University and the NSW Department of Primary Industries and predecessor of the Gulbali Institute) for funding a visit to Australia by JAP and PCS during which this article was conceived and planned.

REFERENCES

ABOSHI, T., TODA, A., ASHITANI, T. & MURAYAMA, T. 2019. A herbivore-induced homoterpene volatile is emitted from Basella alba leaves. *Bioscience Biotechnology and Biochemistry,* 83**,** 1989-1991.

ANDREWS, E. S., THEIS, N. & ADLER, L. S. 2007. Pollinator and herbivore attraction to Cucurbita floral volatiles. *Journal of chemical ecology,* 33**,** 1682-1691.

ARDITTI, J., ELLIOTT, J., KITCHING, I. J. & WASSERTHAL, L. T. 2012. 'Good Heavens what insect can suck it'–Charles Darwin, Angraecum sesquipedale and Xanthopan morganii praedicta. *Botanical Journal of the Linnean Society,* 169**,** 403-432.

ARIMURA, G.-I., OZAWA, R., KUGIMIYA, S., TAKABAYASHI, J. & BOHLMANN, J. 2004. Herbivore-induced defense response in a model legume. Two-spotted spider mites induce emission of (*E*)-β-ocimene and transcript accumulation of (*E*)-β-ocimene synthase in Lotus japonicus. *Plant Physiology,* 135**,** 1976-1983.

ARNOLD, S. E., FORBES, S. J., HALL, D. R., FARMAN, D. I., BRIDGEMOHAN, P., SPINELLI, G. R., BRAY, D. P., PERRY, G. B., GREY, L. & BELMAIN, S. R. 2019. Floral odors and the interaction between pollinating Ceratopogonid midges and Cacao. *Journal of chemical ecology,* 45**,** 869-878.

BARLOW, S. E., WRIGHT, G. A., MA, C., BARBERIS, M., FARRELL, I. W., MARR, E. C., BRANKIN, A., PAVLIK, B. M. & STEVENSON, P. C. 2017. Distasteful nectar deters floral robbery. *Current Biology,* 27**,** 2552-2558. e3.

BARTLET, E., BLIGHT, M. M., PICKETT, J. A., SMART, L. E., TURNER, G. & WOODCOCK, C. M. 2004. Orientation and feeding responses of the pollen beetle, Meligethes aeneus, to candytuft, Iberis amara. *Journal of chemical ecology,* 30**,** 913-925.

BICHÃO, H., BORG-KARLSON, A.-K., ARAÚJO, J. & MUSTAPARTA, H. 2005. Five types of olfactory receptor neurons in the strawberry blossom weevil Anthonomus rubi: selective responses to inducible host-plant volatiles. *Chemical senses,* 30**,** 153-170.

BILLES, D. J. 1941. Pollination of Theobroma cacao L. in Trinidad, B.W.I. *Tropical Agriculture,* 18**,** 151-156.

BLACKWELL, A., DYER, C., WADHAMS, L. & MORDUE, W. 1996. The role of 1‐octen‐3‐ol as a host‐odour attractant for the biting midge, Culicoides impunctatus Goetghebuer, and interactions of 1‐octen‐3‐ol with a volatile pheromone produced by parous female midges. *Physiological Entomology,* 21**,** 15-19.

BOGARÍN, D., FERNÁNDEZ, M., BORKENT, A., HEEMSKERK, A., PUPULIN, F., RAMÍREZ, S., SMETS, E. & GRAVENDEEL, B. 2018. Pollination of Trichosalpinx (Orchidaceae: Pleurothallidinae) by biting midges (Diptera: Ceratopogonidae). *Botanical Journal of the Linnean Society,* 186**,** 510-543.

BOHMAN, B., PHILLIPS, R. D., MENZ, M. H., BERNTSSON, B. W., FLEMATTI, G. R., BARROW, R. A., DIXON, K. W. & PEAKALL, R. 2014. Discovery of pyrazines as pollinator sex pheromones and orchid semiochemicals: implications for the evolution of sexual deception. *New Phytologist,* 203**,** 939-952.

BOMMARCO, R., KLEIJN, D. & POTTS, S. G. 2013. Ecological intensification: harnessing ecosystem services for food security. *Trends in Ecology & Evolution,* 28**,** 230-238.

BROSI, B. J. 2016. Pollinator specialization: from the individual to the community. *New Phytologist,* 210**,** 1190-1194.

CHITTKA, L. 2017. Bee cognition. *Current Biology,* 27**,** R1049-R1053.

COSTANZA, R., D'ARGE, R., DE GROOT, R., FARBER, S., GRASSO, M., HANNON, B., LIMBURG, K., NAEEM, S., O'NEILL, R. V. & PARUELO, J. 1997. The value of the world's ecosystem services and natural capital. *nature,* 387**,** 253-260.

COUVILLON, M. J., AL TOUFAILIA, H., BUTTERFIELD, T. M., SCHRELL, F., RATNIEKS, F. L. & SCHÜRCH, R. 2015. Caffeinated forage tricks honeybees into increasing foraging and recruitment behaviors. *Current Biology,* 25**,** 2815-2818.

D'ALESSANDRO, M., HELD, M., TRIPONEZ, Y. & TURLINGS, T. C. 2006. The role of indole and other shikimic acid derived maize volatiles in the attraction of two parasitic wasps. *Journal of chemical ecology,* 32**,** 2733-2748.

DAFNI, A., LEHRER, M. & KEYAN, P. 1997. Spatial flower parameters and insect spatial vision. *Biological Reviews,* 72**,** 239-282.

DALY, K. C. & SMITH, B. H. 2000. Associative olfactory learning in the moth Manduca sexta. *Journal of Experimental Biology,* 203**,** 2025-2038.

DE BOER, J. G., POSTHUMUS, M. A. & DICKE, M. 2004. Identification of volatiles that are used in discrimination between plants infested with prey or nonprey herbivores by a predatory mite. *Journal of chemical ecology,* 30**,** 2215-2230.

DE MORAES, C. M., LEWIS, W., PARE, P., ALBORN, H. & TUMLINSON, J. 1998. Herbivore-infested plants selectively attract parasitoids. *Nature,* 393**,** 570-573.

DE VOS, M., VAN OOSTEN, V. R., VAN POECKE, R. M., VAN PELT, J. A., POZO, M. J., MUELLER, M. J., BUCHALA, A. J., MÉTRAUX, J.-P., VAN LOON, L. C. & DICKE, M. 2005. Signal signature and transcriptome changes of Arabidopsis during pathogen and insect attack. *Molecular plant-microbe interactions,* 18**,** 923-937.

DICKE, M. 2009. Behavioural and community ecology of plants that cry for help. *Plant, cell & environment,* 32**,** 654-665.

DONATH, J. & BOLAND, W. 1994. BIOSYNTHESIS OF ACYCLIC HOMOTERPENES IN HIGHER-PLANTS PARALLELS STEROID-HORMONE METABOLISM. *Journal of Plant Physiology,* 143**,** 473-478.

EL-SAYED, A., MITCHELL, V., MCLAREN, G., MANNING, L., BUNN, B. & SUCKLING, D. 2009. Attraction of New Zealand flower thrips, Thrips obscuratus, to cis-jasmone, a volatile identified from Japanese honeysuckle flowers. *Journal of chemical ecology,* 35**,** 656-663.

FARRÉ-ARMENGOL, G., FILELLA, I., LLUSIÀ, J. & PEÑUELAS, J. 2017. β-Ocimene, a key floral and foliar volatile involved in multiple interactions between plants and other organisms. *Molecules,* 22**,** 1148.

FROST, C. J., APPEL, H. M., CARLSON, J. E., DE MORAES, C. M., MESCHER, M. C. & SCHULTZ, J. C. 2007. Within‐plant signalling via volatiles overcomes vascular constraints on systemic signalling and primes responses against herbivores. *Ecology Letters,* 10**,** 490-498.

GHIRARDO, A., HELLER, W., FLADUNG, M., SCHNITZLER, J. P. & SCHROEDER, H. 2012. Function of defensive volatiles in pedunculate oak (Quercus robur) is tricked by the moth Tortrix viridana. *Plant, cell & environment,* 35**,** 2192-2207.

GIURFA, M., NUNEZ, J., CHITTKA, L. & MENZEL, R. 1995. Colour preferences of flower-naive honeybees. *Journal of Comparative Physiology A,* 177**,** 247-259.

GODFRAY, H. C. J. & GARNETT, T. 2014. Food security and sustainable intensification. *Philosophical transactions of the Royal Society B: biological sciences,* 369**,** 20120273.

GOYRET, J., PFAFF, M., RAGUSO, R. A. & KELBER, A. 2008. Why do Manduca sexta feed from white flowers? Innate and learnt colour preferences in a hawkmoth. *Naturwissenschaften,* 95**,** 569-576.

GURR, G. M., LU, Z. X., ZHENG, X. S., XU, H. X., ZHU, P. Y., CHEN, G. H., YAO, X. M., CHENG, J., ZHU, Z. R., CATINDIG, J. L., VILLAREAL, S., CHIEN, H. V., CUONG, L. Q., CHANNOO, C., CHENGWATTANA, N., LAN, L. P., HAI, L. H., CHAIWONG, J., NICOL, H. I., PEROVIC, D. J., WRATTEN, S. D. & HEONG, K. L. 2016. Multi-country evidence that crop diversification promotes ecological intensification of agriculture. *Nature Plants,* 2.

GURR, G. M., WRATTEN, S. D., LANDIS, D. A. & YOU, M. 2017. Habitat management to suppress pest populations: Progress and prospects. *Annual Review of Entomology,* 62**,** 91-109.

HATANO, E., SAVEER, A. M., BORRERO-ECHEVERRY, F., STRAUCH, M., ZAKIR, A., BENGTSSON, M., IGNELL, R., ANDERSON, P., BECHER, P. G., WITZGALL, P. & DEKKER, T. 2015. A herbivore-induced plant volatile interferes with host plant and mate location in moths through suppression of olfactory signalling pathways. *BMC Biology,* 13**,** 75.

ISBERG, E., BRAY, D. P., HILLBUR, Y. & IGNELL, R. 2017. Evaluation of host-derived volatiles for trapping Culicoides biting midges (Diptera: Ceratopogonidae). *Journal of chemical ecology,* 43**,** 662-669.

KAISER, R. 1994. Trapping, investigation and reconstitution of flower scents. *Perfumes.* Springer.

KESSLER, A. & HALITSCHKE, R. 2009. Testing the potential for conflicting selection on floral chemical traits by pollinators and herbivores: predictions and case study. *Functional Ecology,* 23**,** 901-912.

KHAN, Z., MIDEGA, C. A. O., HOOPER, A. & PICKETT, J. 2016. Push-Pull: Chemical Ecology-Based Integrated Pest Management Technology. *Journal of Chemical Ecology,* 42**,** 689-697.

KHAN, Z. R., PICKETT, J. A., BERG, J. V. D., WADHAMS, L. J. & WOODCOCK, C. M. 2000. Exploiting chemical ecology and species diversity: stem borer and striga control for maize and sorghum in Africa. *Pest Management Science: Formerly Pesticide Science,* 56**,** 957-962.

KLEIN, A.-M., VAISSIERE, B. E., CANE, J. H., STEFFAN-DEWENTER, I., CUNNINGHAM, S. A., KREMEN, C. & TSCHARNTKE, T. 2007. Importance of pollinators in changing landscapes for world crops. *Proceedings of the royal society B: biological sciences,* 274**,** 303-313.

KNUDSEN, J. T., ERIKSSON, R., GERSHENZON, J. & STÅHL, B. 2006. Diversity and distribution of floral scent. *The botanical review,* 72**,** 1.

KRUG, C., CORDEIRO, G. D., SCHÄFFLER, I., SILVA, C. I., OLIVEIRA, R., SCHLINDWEIN, C., DÖTTERL, S. & ALVES-DOS-SANTOS, I. 2018. Nocturnal bee pollinators are attracted to guarana flowers by their scents. *Frontiers in plant science,* 9**,** 1072.

LI, F., LI, W., LIN, Y.-J., PICKETT, J. A., BIRKETT, M. A., WU, K., WANG, G. & ZHOU, J.-J. 2018. Expression of lima bean terpene synthases in rice enhances recruitment of a beneficial enemy of a major rice pest. *Plant Cell and Environment,* 41**,** 111-120.

LIU, W.-Y., LEE, S.-J. & YANG, E.-C. 2009. Evaluation for attractiveness of four chemicals to the biting midge, Forcipomyia taiwana (Diptera: Ceratopogonidae). *Journal of the American Mosquito Control Association,* 25**,** 448-455.

LOOS, J., ABSON, D. J., CHAPPELL, M. J., HANSPACH, J., MIKULCAK, F., TICHIT, M. & FISCHER, J. 2014. Putting meaning back into “sustainable intensification”. *Frontiers in Ecology and the Environment,* 12**,** 356-361.

LOSEY, J. E. & VAUGHAN, M. 2006. The economic value of ecological services provided by insects. *Bioscience,* 56**,** 311-323.

MARCHIORI, C., LUSSARI, M., ROSA, D. & PENTEADO-DIAS, A. 2007. Parasitoid Hymenoptera collected during the diurnal and nocturnal periods in Itumbiara, Goiás. *Brazilian Journal of Biology,* 67**,** 581-582.

MEENTS, A. K., CHEN, S.-P., REICHELT, M., LU, H.-H., BARTRAM, S., YEH, K.-W. & MITHOFER, A. 2019. Volatile DMNT systemically induces jasmonate-independent direct anti-herbivore defense in leaves of sweet potato (Ipomoea batatas) plants. *Scientific reports,* 9**,** 17431-17431.

MIDEGA, C. A., PITTCHAR, J. O., PICKETT, J. A., HAILU, G. W. & KHAN, Z. R. 2018. A climate-adapted push-pull system effectively controls fall armyworm, Spodoptera frugiperda (JE Smith), in maize in East Africa. *Crop protection,* 105**,** 10-15.

MIYAKE, T., YAMAOKA, R. & YAHARA, T. 1998. Floral scents of hawkmoth-pollinated flowers in Japan. *Journal of Plant Research,* 111**,** 199-205.

MUMM, R., POSTHUMUS, M. A. & DICKE, M. 2008. Significance of terpenoids in induced indirect plant defence against herbivorous arthropods. *Plant, cell & environment,* 31**,** 575-585.

NIEUWENHUIZEN, N. J., GREEN, S. A., CHEN, X., BAILLEUL, E. J. D., MATICH, A. J., WANG, M. Y. & ATKINSON, R. G. 2013. Functional Genomics Reveals That a Compact Terpene Synthase Gene Family Can Account for Terpene Volatile Production in Apple. *Plant Physiology,* 161**,** 787-804.

NOJIMA, S., LINN, C., MORRIS, B., ZHANG, A. & ROELOFS, W. 2003. Identification of host fruit volatiles from hawthorn (Crataegus spp.) attractive to hawthorn-origin Rhagoletis pomonella flies. *Journal of chemical ecology,* 29**,** 321-336.

OLLERTON, J., WINFREE, R. & TARRANT, S. 2011. How many flowering plants are pollinated by animals? *Oikos,* 120**,** 321-326.

PARÉ, P. W. & TUMLINSON, J. H. 1997. De novo biosynthesis of volatiles induced by insect herbivory in cotton plants. *Plant physiology,* 114**,** 1161-1167.

PELLMYR, O. & THIEN, L. B. 1986. Insect reproduction and floral fragrances: keys to the evolution of the angiosperms? *Taxon,* 35**,** 76-85.

PEÑALVER, E., LABANDEIRA, C. C., BARRÓN, E., DELCLÒS, X., NEL, P., NEL, A., TAFFOREAU, P. & SORIANO, C. 2012. Thrips pollination of Mesozoic gymnosperms. *Proceedings of the National Academy of Sciences,* 109**,** 8623-8628.

POSNETTE, A. 1944. Pollination of cacao in Trinidad. *Trop. Agric., Trin*.

POTTS, S. G., IMPERATRIZ-FONSECA, V., NGO, H. T., AIZEN, M. A., BIESMEIJER, J. C., BREEZE, T. D., DICKS, L. V., GARIBALDI, L. A., HILL, R. & SETTELE, J. 2016. Safeguarding pollinators and their values to human well-being. *Nature,* 540**,** 220-229.

RAGUSO, R. A. 2004. Flowers as sensory billboards: progress towards an integrated understanding of floral advertisement. *Current opinion in plant biology,* 7**,** 434-440.

REYMOND, P., BODENHAUSEN, N., VAN POECKE, R. M., KRISHNAMURTHY, V., DICKE, M. & FARMER, E. E. 2004. A conserved transcript pattern in response to a specialist and a generalist herbivore. *The Plant Cell,* 16, 3132-3147.

SCHULTZ, K., KAISER, R. & KNUDSEN, J. T. 1999. Cyclanthone and derivatives, new natural products in the flower scent of Cyclanthus bipartitus Poit. *Flavour and Fragrance Journal,* 14, 185-190.

SCOTT-BROWN, A. S., ARNOLD, S. E., KITE, G. C., FARRELL, I. W., FARMAN, D. I., COLLINS, D. W. & STEVENSON, P. C. 2019. Mechanisms in mutualisms: a chemically mediated thrips pollination strategy in common elder. *Planta,* 250, 367-379.

SEIBOLD, S., GOSSNER, M. M., SIMONS, N. K., BLÜTHGEN, N., MÜLLER, J., AMBARLı, D., AMMER, C., BAUHUS, J., FISCHER, M. & HABEL, J. C. 2019. Arthropod decline in grasslands and forests is associated with landscape-level drivers. *Nature,* 574, 671-674.

SIGNORETTI, A. G. C., PENAFLOR, M. F. G. V., MOREIRA, L. S. D., NORONHA, N. C. & BENTO, J. M. S. 2012. Diurnal and nocturnal herbivore induction on maize elicit different innate response of the fall armyworm parasitoid, Campoletis flavicincta. *Journal of Pest Science,* 85, 101-107.

SMART, L. E. & BLIGHT, M. M. 2000. Response of the pollen beetle, Meligethes aeneus, to traps baited with volatiles from oilseed rape, Brassica napus. *Journal of chemical ecology,* 26, 1051-1064.

STEEN, R., NORLI, H. R. & THÖMING, G. 2019. Volatiles composition and timing of emissions in a moth-pollinated orchid in relation to hawkmoth (Lepidoptera: Sphingidae) activity. *Arthropod-Plant Interactions,* 13, 581-592.

STEVENSON, P. C., NICOLSON, S. W. & WRIGHT, G. A. 2017. Plant secondary metabolites in nectar: impacts on pollinators and ecological functions. *Functional Ecology,* 31, 65-75.

SVENSSON, G. P., PELLMYR, O. & RAGUSO, R. A. 2006. Strong conservation of floral scent composition in two allopatric yuccas. *Journal of chemical ecology,* 32, 2657-2665.

TASIN, M., BÄCKMAN, A.-C., BENGTSSON, M., IORIATTI, C. & WITZGALL, P. 2006. Essential host plant cues in the grapevine moth. *Naturwissenschaften,* 93, 141-144.

TERRY, I., WALTER, G. H., MOORE, C., ROEMER, R. & HULL, C. 2007. Odor-mediated push-pull pollination in cycads. *Science,* 318, 70-70.

THOLL, D., SOHRABI, R., HUH, J.-H. & LEE, S. 2011. The biochemistry of homoterpenes - Common constituents of floral and herbivore-induced plant volatile bouquets. *Phytochemistry,* 72, 1635-1646.

THOMSON, J. D., DRAGULEASA, M. A. & TAN, M. G. 2015. Flowers with caffeinated nectar receive more pollination. *Arthropod-Plant Interactions,* 9, 1-7.

THØSTESEN, A. M. & OLESEN, J. M. 1996. Pollen removal and deposition by specialist and generalist bumblebees in Aconitum septentrionale. *Oikos*, 77-84.

TILMAN, D., BALZER, C., HILL, J. & BEFORT, B. L. 2011. Global food demand and the sustainable intensification of agriculture. *Proceedings of the national academy of sciences,* 108, 20260-20264.

TOLLEFSON, J. 2019. One million species face extinction. *Nature,* 569, 171.

TRÖGER, A., SVENSSON, G. P., ALTHOFF, D. M., SEGRAVES, K. A., RAGUSO, R. A. & FRANCKE, W. 2019. The Pattern of Straight Chain Hydrocarbons Released by Yucca Flowers (Asparagaceae). *Journal of chemical ecology,* 45, 46-49.

TURLINGS, T. C., TUMLINSON, J. H. & LEWIS, W. J. 1990. Exploitation of herbivore-induced plant odors by host-seeking parasitic wasps. *Science,* 250, 1251-1253.

VAN POECKE, R. M., ROOSJEN, M., PUMARINO, L. & DICKE, M. 2003. Attraction of the specialist parasitoid Cotesia rubecula to Arabidopsis thaliana infested by host or non‐host herbivore species. *Entomologia Experimentalis et Applicata,* 107, 229-236.

VANBERGEN, A. J. & INITIATIVE, T. I. P. 2013. Threats to an ecosystem service: pressures on pollinators. *Frontiers in Ecology and the Environment,* 11, 251-259.

WILSON, E. O. 1987. Causes of ecological success: the case of the ants. *Journal of Animal Ecology,* 56, 1-9.

WRIGHT, G., BAKER, D., PALMER, M., STABLER, D., MUSTARD, J., POWER, E., BORLAND, A. & STEVENSON, P. 2013. Caffeine in floral nectar enhances a pollinator's memory of reward. *Science,* 339**,** 1202-1204.

ZHANG, P. J., ZHENG, S. J., VAN LOON, J. J., BOLAND, W., DAVID, A., MUMM, R. & DICKE, M. 2009. Whiteflies interfere with indirect plant defense against spider mites in Lima bean. *Proc Natl Acad Sci U S A,* 106**,** 21202-7.

LIST OF FIGURES

Figure 1. Chemical structures of homoterpenes central to arthropod-plant interactions: n = 1, (*E*)-4,8-dimethyl-1,3,7-nonatriene (DMNT); n = 2, (*E,E*) 4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT); R’, R”, R’” = methyl.

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 – symbol for each interaction. Weight of arrows indicates the relative importance of each interaction in terms of reported cases. Dashed arrows indicate the potential mal-adaptive interactions of production by flowers on natural enemies and by foliage on pollinators.

FIG 1

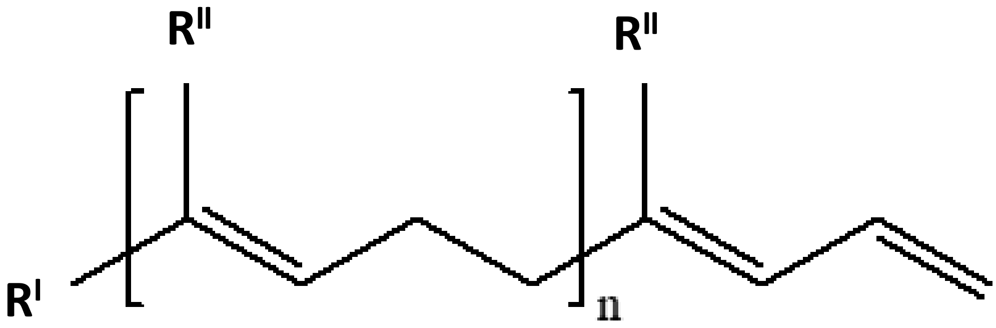
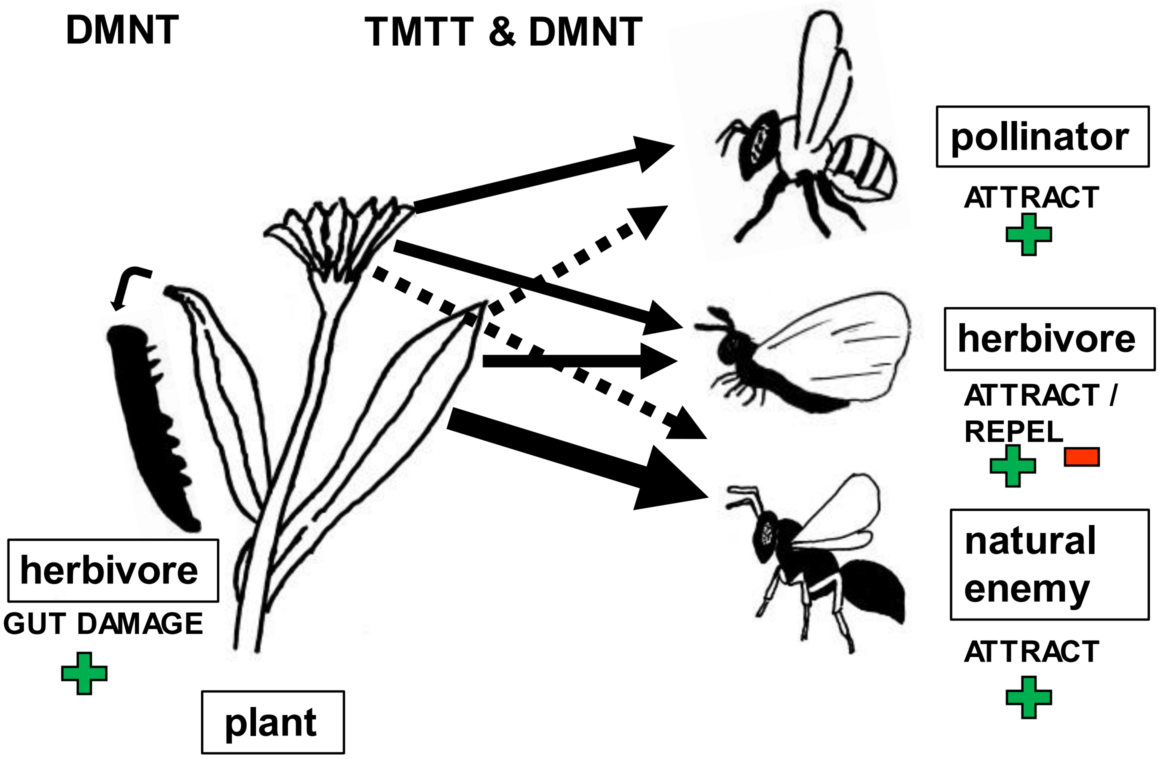


FIG 2.


DMNT
TMTT & DMNT
pollinator
ATTRACT
+
herbivore
ATTRACT / REPEL
+ −
natural enemy
ATTRACT
+
herbivore
GUT DAMAGE
+
plant