



For antagonists and mutualists: the paradox of insect toxic secondary metabolites in nectar and pollen

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Abstract The plant kingdom produces an extraordinary diversity of secondary metabolites and the majority of the literature supports a defensive ecological role for them, particularly against invertebrate herbivores (antagonists). Plants also produce secondary compounds in floral nectar and pollen and these are often similar to those produced for defense against invertebrates elsewhere in the plant. This is largely because the chemical armoury within a single plant species is typically restricted to a few biochemical pathways and limited chemical products but how their occurrence in floral rewards is regulated to mediate both defence and enhanced pollination is not well understood. Several phytochemicals are reviewed here comparing the defensive function alongside their benefit to flower visiting mutualists. These include caffeine, aconitine, nicotine, thymol, linalool, lupanine and grayanotoxins comparing the evidence for their defensive function with their impacts on pollinators, their behaviour and well-being. Drivers of adaptation and the evolution of floral traits are discussed in the context of recent studies. Ultimately more research is required that helps determine the

impacts of floral chemicals in free flying bees, and how compounds are metabolized, sequestered or excreted by flower feeding insects to understand how they may then affect the pollinators or their parasites. More work is also required on how plants regulate nectar and pollen chemistry to better understand how secondary metabolites and their defensive and pollinator supporting functions are controlled, evolve and adapt.

Keywords *Bombus* · Nectar chemicals · Bee pathogens · *Crithidia bombi* · Caffeine · Nicotine · Pollinator specialization

Introduction

Animals and plants show adaptive selection for physical traits that optimize the efficiency of pollen transfer. Typically, adaptations augment greater fidelity or attention from flower visitors to a plant species that optimises pollen transfer between conspecific flowers; typically referred to as specialization (Brosi 2016). One of the most frequently cited examples of pollinator specialization is a physical adaptation; the extraordinarily long nectar spur of the moon orchid, *Angraecum sesquipedale* (Orchidaceae). This flower was predicted by Charles Darwin in 1862 to be pollinated by a moth with an equally long

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proboscis and 40 years later turned out to be the case with the discovery of Darwin's Sphinx moth *Xanthopan morgani praedicta* (Lepidoptera: Sphingidae) (Arditti et al. 2012). Numerous other examples exist where flower morphology has adapted to restrict nectar access to specialist taxa for example, *Aconitum* spp. (Ranunculaceae) (Thøstesen et al. 1996) and so garner greater pollinator focus and increase pollen transfer.

Phytochemicals also optimise pollination service in many plant species. For example, naïve honeybees show innate attraction to blue colours (Giurfa et al. 1995) which, in flowers, are produced by anthocyanins such as delphinidins (Katsumoto et al. 2007) or more stable metal chelated floral pigments such as

commelinin from *Commelina communis* (Commelinaceae) (Kondo et al. 1992). In some cases, the capacity to produce blue has driven highly specialised interactions based on mimicry and pseudocopulation. The blue colour produced at the heart of the flower of *Ophrys speculum* (Orchidaceae) by cyanidin glycosides, predominantly the 3-*O*-(3''-*O*-malonylglucoside), is enhanced by surface structural features giving it a highly reflective quality that is much closer to the thorax of the mimicked insect (Vignolini et al. 2012).

Flower colours may even change with age or after pollination to dissuade further visitation although this may be dependent upon environmental context and is not common (Ruxton and Schaefer 2016). Pollinators are proposed to be the main selective agent driving the evolution of flower colour (Wang et al. 2013) and in concert with insect pheromone mimicry, illustrate further the extraordinary capacity of plants to mediate the services pollinators and present irresistible attraction for sexually active males. A notable example of floral odour mimicry is the production of a variety of pyrazines by hammer orchids such as *Drakaea thynniphila* (Orchidaceae) which very closely mimic the sex pheromone of the female Thynnid wasps (*Agriomyia* spp.) (Hymenoptera: Thynnidae) and prove irresistible to sexually active males (Bohman et al. 2014). So clearly floral chemistry is understood to play a significant role in optimising pollination service.

Floral phytochemistry has seen increased interest in recent years particularly around the chemistry of nectar and pollen and in part stimulated by Adler (2000) and the contemporary scientific popularity of pollination systems as standard bearers for healthy ecosystems. The most comprehensive phytochemical survey of nectar and pollen to date was published recently, analysing 31 cultivated and wild plant species from multiple sites and of different cultivars and established that pollen typically had the highest concentrations of secondary metabolites (Palmer-Young et al. 2019a, b). Since these plant compounds were typically reported to be associated with defence this finding was consistent with optimal defence theory and the importance of pollen as the male gamete but the occurrence in nectar presents an ecological paradox since this is the reward for flower visitors (Stevenson et al. 2017). And furthermore

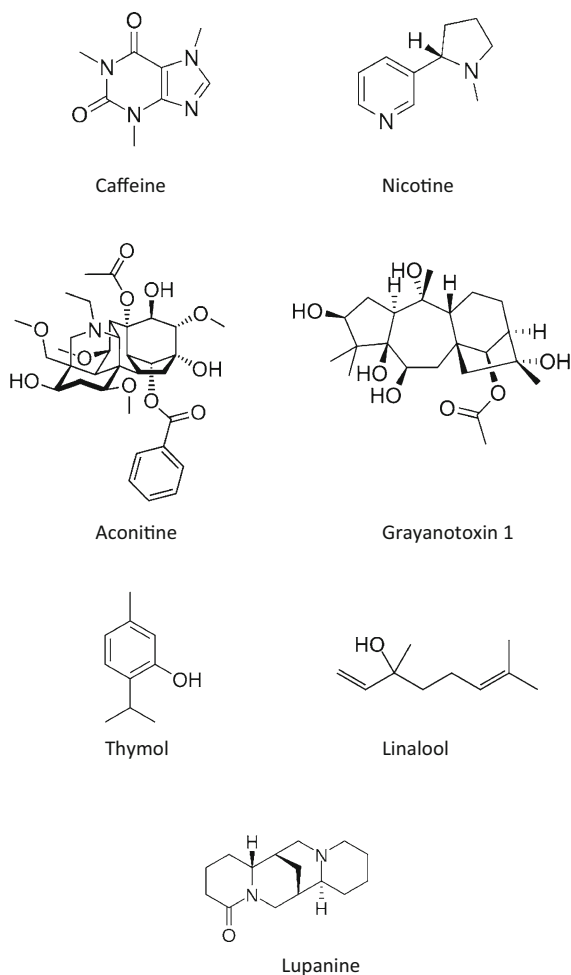


Fig. 1 Chemical structures of phytochemicals having a defensive role against insect antagonists but also various beneficial effects for pollinators

Table 1 Phytochemicals with dual ecological functions that protect against antagonists and optimise pollination services through attraction, behaviour mediation or improved pollinator health

Compounds	Defence function for plants against antagonists	Potential benefits to pollination or pollinators	References
Caffeine	Inhibition of phosphodiesterase and increase in intracellular cAMP in insects Bioactive versus <i>Spodotera littoralis</i> in transformed tobacco Toxic to honey bees	Enhances memory for cues associated with good food reward Increases pollen deposition of <i>Bombus</i> spp Improves recruitment behaviours and foraging focus Reduces parasite load in bees	Nathanson (1984), Kim et al. (2006), Detzel and Wink (1993), Wright et al. (2013), Thomson et al. (2015), Couvillon et al. (2015), Richardson et al. (2015a, b), Bernklau et al. (2019)
Grayanotoxin 1	Provides defence against <i>Thrips major</i> in <i>Rhododendron simsii</i> Related grayanotoxins bioactive against Lepidoptera Toxic against honey bees and <i>Andrena scotica</i>	Selective toxicity to flower visitors permits preferential nectar access to <i>Bombus</i> spp	Scott-Brown et al. (2016), Klocke et al. (1991), Tiedeken et al. (2016), Tiedeken et al. (2016)
Aconitine	Insect repellent activity to <i>Tribolium castaneum</i> Insect repellent to <i>Leptinotarsa decemlineata</i>	Protection against nectar robbery by <i>Bombus terrestris</i> with adaptation by the pollinating bee species <i>Bombus hortorum</i>	Ulubelen et al. (2001), González-Coloma et al. (2004), Barlow et al. (2017)
Nicotine	Reduced nectar robbery by ants Toxic to bees	Reduced <i>Crithidia bombi</i> parasite loads in <i>Bombus</i> spp	Kessler and Baldwin (2007), Köhler et al. (2012), Richardson et al. (2015a, b)
Thymol	Toxic to <i>Trichoplusia ni</i>	Reduces <i>Crithidia bombi</i> parasite loads in <i>Bombus impatiens</i> Bioactive against the parasite at ecologically relevant concentrations	Wilson and Isman (2006), Richardson et al. (2015a, b), Palmer-Young et al. (2016)
Linalool	Repellent to <i>Nilaparvata lugens</i> <i>Botanical insecticide</i>	Attracts <i>Thrips major</i> to <i>Sambucus nigra</i> flowers for pollination service Attracts natural enemies of herbivores	Xiao et al. (2012), Isman (2006), Scott-Brown et al. (2019), Yuan et al. (2008), Xiao et al. (2012)

many allelochemicals occurring in plants are toxic or deterrent to bees (Detzel and Wink 1993).

One of the earliest reviews of secondary metabolites in nectar had postulated a defensive function for these compounds and noted that many of the compound groups occurring in nectar were also deterrent or toxic. Why would a flower secrete a toxin into the nectar since this is the reward for flower visitors that transfer pollen from one flower to a conspecific so provide a service to the plant (Baker 1977)? Subsequent reviews (Adler 2000; Irwin et al. 2014; Stevenson et al. 2017) have synthesised the role of nectar toxins around their various bioactivities—many of

which have been convincingly argued to optimise pollen transfer between conspecific flowers. Palmer-Young et al. (2019a) reported that of over 100 compounds identified in pollen nectar and corolla tissue across the plant taxa, most were unique to a single species and that nectar and pollen chemistry always comprised of compounds that occurred in other plant tissues in the same species. Thus, if defence compounds occur in the foliage to protect against antagonists, they are likely to also occur in the nectar and pollen and be encountered by mutualists. While concentrations of secondary metabolites varied more in nectar than pollen the consistency with which they

occur in nectar is nevertheless unexpected particularly since they are often cited as defensive against other invertebrates. Six examples are reviewed here that illustrate how plant secondary metabolites that have a reported defence function may have a dual role that is in conflict with its protective purpose (Fig. 1; Table 1). Existing knowledge gaps are also highlighted relevant to each compound.

Caffeine enhances bee memory and learning

Caffeine is a purine alkaloid that has established toxicity to invertebrates and is considered a potential natural biopesticide (Hollingsworth 2002). Its toxicity in insects is manifest by paralysing and intoxicating insects through inhibition of phosphodiesterase activity and increasing the intracellular levels of cyclic AMP (Nathanson 1984). It also inhibits feeding in the tobacco armyworm (*Spodoptera litura*) (Lepidoptera: Noctuidae) demonstrated through taste assays using leaf discs from a genetically transformed *Nicotiana tabacum* that biosynthesised caffeine (Uefuji et al. 2005; Kim et al. 2006). Most familiarly caffeine occurs at very high concentrations in coffee beans to protect against insect damage although the coffee berry borer (*Hypothenemus hampei*) (Coleoptera: Curculionidae), the major insect pest of coffee beans, has overcome this mechanism of defence through a symbiosis with a *Pseudomonas* species of gut symbiont that detoxifies caffeine for the host (Ceja-Navarro et al. 2015).

The role of caffeine in plant defence against invertebrate herbivores is therefore apparent so its occurrence in nectar, the food reward for invertebrate pollinators, was unexpected (Kretschmar and Baumann 1999) especially in the knowledge that it is also toxic to honeybees (Detzel and Wink 1993). Subsequent evaluation of the biological effect of caffeine against bees in learning and taste assays revealed more surprises. Firstly, caffeine is reportedly a feeding deterrent to honey bees in a dose dependent manner and it was detected in the nectar of several commercially important *Citrus* spp (Rutaceae) and *Coffea* spp. (Rubiaceae) (Wright et al. 2013). However, this was at concentrations that were below the bee's taste detection threshold. Secondly, bees fed caffeine at ecologically relevant concentrations during a learning experiment were three times more likely to recall a trait associated with a food reward than bees fed a

control diet. This effect lasted for up to 72 h and was manifest through depolarisation of the membrane potential of Kenyon cells in the mushroom body of the bees brain where associative memory formation occurs indicating that this was a pharmacological effect acting on the brain directly (Menzel et al. 1980; Wright et al. 2013). Memory is an important attribute in generalist pollinators facilitating the rapid relocation of previously encountered and reliable sources of food (Menzel and Muller 1996). Wright et al. (2013) postulated that this enhancement of memory would provide an evolutionary advantage to the plant by manifesting enhanced fidelity to a caffeine containing reward in free flying bees and increased recruitment of nest mates. Shortly after Couvillon et al. (2015) demonstrated this prediction to be the case. How plants manage this dual role in defence and maximising attraction is quantitative as demonstrated by Thomson et al. (2015) who reported that artificial flowers containing caffeinated nectar at 10^{-5} M received more pollen than flowers containing no caffeine or flowers containing artificial nectar with caffeine at 10^{-4} M. The behavioural change that enhances pollination is that caffeine enables bees to recall a trait or cue associated with food and be more likely to locate it, but this has yet to be demonstrated experimentally.

Ultimately it is conceivable that commercial bees utilised to maximise pollination services in horticulture could be trained to provision more efficient pollination services through exposure to the floral odours of target crops flowers while feeding on caffeinated food supplements; effectively training the bees to pollinate a target crop.

Caffeine occurs widely in the plant kingdom in at least 6 families of flowering plants. In floral tissues this includes *Chamelia sinensis* (Theaceae) (P. Stevenson unpubl.), *Coffea* spp. (Wright et al. 2013), *Citrus* spp. (Kretschmar and Baumann 1999), and *Tilia* spp. (Malvaceae) (Naef et al. 2007; Mathona et al. 2014). The flowers of these species are characterised by being small white and generally indistinct but with a strong aroma so these species may employ odour as the primary tool for attraction. This may suit pollination services by flower visitors susceptible to the effects of caffeine with a similar mechanism across these families. Koch and Stevenson (2017) suggest that this mechanism of increasing floral focus through enhanced memory for the odour associated with the

food reward is so effective in *Tilia* spp. it may explain the phenomenon of dead bees under these trees—bees that overvalue the food source and continue to forage long after the tree has stopped producing nectar and ultimately run out of energy and drop to the ground and die since the nectar of *Tilia* spp. is reported to contain caffeine (Naef et al. 2007; Mathona et al. 2014).

More recently caffeine is reported to be a potential antimicrobial that could reduce disease load in honeybees caused by *Nosema bombi* (Dissociodiplasida: Nosematidae) (Bernklau et al. 2019) thereby offering an additional benefit to the pollinators that provide this most important service to plants. Although Richardson et al. (2015a, b) reported no effect against another parasite, *Crithidia bombi* (Trypanosomatida). The biological activity of nectar and pollen compounds against bee parasites is discussed in more detail below. The biological effects of related purine alkaloids including xanthine, theophylline and theobromine would be worthy of investigation.

Diterpenoid nectar toxins in *Rhododendron* filter specialist pollinators

Rhododendron (Ericaceae) is a large Genus of > 1000 species found across the Northern hemisphere and into the Malaysian Peninsula and islands (Chamberlain et al. 1996). In the British Isles *Rhododendrons* are popular ornamentals but one species, *R. ponticum* subsp. *baeticum*, introduced from the Iberian Peninsula, has become highly invasive along with hybrids between *R. ponticum* and congenics in parts of Britain (Milne and Abbott 2000). Invasive species may contribute to pollinator decline (Gonzalez-Varo et al. 2013) although considering the potential impacts only a few studies have investigated this (Stout and Morales 2009). Grayanoid diterpenes are the compounds responsible for the various biological activities attributable to mad honey and have been reviewed recently (Hanson 2016). Grayanoid diterpenes are tetracyclic diterpenoids with their biosynthetic origins in the isoprenyl pathway and the ecological function of these compounds is reportedly in defence. Rhodojaponin III, grayanotoxin III, and kalmanol were identified as the active components in flowers of the Chinese insecticidal plant, *R. molle*, with the most abundant compound rhodojaponin III, showing anti-feedancy, growth inhibition and insecticidal activity

against larvae of two Lepidoptera (Klocke et al. 1991). However, only one study by Scott-Brown et al. (2016) has reported grayanoid diterpenoids as a defense to an herbivore that targets *Rhododendron*. Grayanotoxin I (GTX I) was recorded in higher concentrations in young foliage of *R. simsii* and at a concentration that was biologically active as both a deterrent and as an entomotoxin against the glass house thrips *Heliothrips haemorrhoidalis* (Thysanoptera: Thripidae) (Scott-Brown et al. 2016). The occurrence of grayanotoxins in nectar of *Rhododendron* is unexpected but has largely been assumed owing to its occurrence in honey and was, only very recently, reported directly from the nectar (Tiedeken et al. 2014). In this study GTX I was identified as the principal diterpene but did not have a deterrent effect against *Bombus terrestris* (Hymenoptera: Apidae) the buff-tailed bumble bee which is known to be a pollinator of the plant. However, later studies investigating the impact of an invasive plant species with toxic nectar in the British Isles on native fauna established that GTX I was both deterrent to and highly toxic to native honey bees *Apis mellifera* subsp. *mellifera* (Hymenoptera: Apidae) and a solitary mining species of bee *Andrena scotica* (Hymenoptera: Andrenidae) but *Bombus terrestris* remained unharmed (Tiedeken et al. 2016). The authors postulated that adaptation by the plant and the pollinator may have arisen to harness specialised foraging on this otherwise entomotoxic nectar and so secure the nectar reward for *Bombus* species which are the primary pollinator of *R. ponticum* in the British Isles. When an introduced species provides nectar containing invertebrate toxins poorly adapted pollinators that did not co-evolve with it could be intolerant of the effects (Callaway and Ridenour 2004). Further, this effect could serve to filter the most efficient pollinators—in this case *Bombus* spp.—and may co-evolve rapidly in the introduced range of *R. ponticum* (Tiedeken et al. 2016). So GTX I provides *Rhododendron* with effective protection against antagonists and enhances pollination service by mutualists in the same plant. How this mechanism adapts in the introduced populations is discussed further below.

Grayanotoxins have been considered as candidates for botanical insecticides since they have activity against a range of pest insect species (Mei-Ying et al. 2015). Commercially produced *B. terrestris* are used increasingly by farmers to supplement pollination services—particularly in polytunnels and greenhouse

crops such as tomatoes and strawberries. Since *Bombus* spp. are tolerant of grayanotoxins and these compounds have a wide-ranging activity against invertebrate antagonists it is possible they could provide candidates for bee friendly botanical insecticides.

Diterpene alkaloids in *Aconitum* spp. and nectar robbery

Species in the Genus *Aconitum* produce potent mammalian toxins with reports of human poisonings associated with the norditerpenoid alkaloids that occur in all plant parts (Kolev et al. 1996). As with grayanotoxins and caffeine the ecological function to the plant of these compounds is likely to be for defense against herbivory since several compounds of this class from *Aconitum* and related species have deterrent properties against insects (Ulubelen et al. 2001; González-Coloma et al. 2004). Flowers of *Aconitum* spp. are notable for having highly adapted nectaries on two long nectar spurs protected by a sepaloid hood or galea restricting nectar access to only long-tongued species of Bumble bee (Thøstesen et al. 1996). Despite these efforts to limit access to a few species of more forage focussed pollinators and increase the likelihood of pollen transfer to conspecific flowers, *Aconitum* flowers suffer from nectar robbery. Nectar robbing occurs when a hole is chewed through the corolla to access nectar that is otherwise unavailable via the route intended by the plants (Inouye 1980). However, this doesn't appear to come with any fitness cost to *Aconitum* (Utelli and Roy 2000). This can be explained because fewer than 10% of flower visits are by robbing species and only a small fraction of these visits result in a successful robbing event due to the occurrence of insect repellent norditerpenoids in nectar of *Aconitum* flowers (Barlow et al. 2017). These compounds vary in concentrations from one flower to the next and at the highest concentrations are too toxic even for the pollinator but importantly the robbing species of *Bombus* (*B. terrestris* in UK) are poorly adapted to their effects compared to the pollinating species which can tolerate concentrations of the nectar toxins that are 10 times higher than the robbing species.

Bee species may not be particularly sensitive to toxins in food (Wright et al. 2010; de Brito Sanchez et al. 2015) but adaptation to toxins differs among

species since the short tongued species *B. terrestris* was more likely to be deterred by artificial food containing aconitine than a long-tongued specialist like *B. hortorum* and this may be related to short tongued species outcompeting long-tongued species for flowers with generalist pollinator syndrome.

So, again, the limited chemical armoury of *Aconitum* species serves both to protect the plant from antagonists such as folivores and nectar robbers while concurrently conserving the nectar in their morphologically adapted nectaries for long tongued species that can access the nectar through the intended route, tolerate the toxins and pollinate the plant. It would be interesting to determine how widespread tolerance to these diterpene alkaloid toxins is among long-tongued species including *B. gerstackerii* the *Aconitum* specialist and how consistently intolerant short-tongued and potentially robbing species are.

Nectar phytochemistry and pollinator health

Diseases are a major biotic challenge for bees and can contribute to pollinator declines particularly in combination with other stressors including habitat loss, invasive species and pesticide exposure (Vanbergen et al. 2013). Bees transmit and acquire diseases on flowers, but flower phenology including chemistry may influence transmission and disease spread (McCart et al. 2014; Koch et al. 2017). The role of plant species and variation in these traits is largely unexplored and may inform how disease transmission can be better managed (Adler et al. 2018). Flower chemistry can influence bee disease by killing bee pathogens and reducing transmission, and secondary metabolites in nectar and pollen could be active against gut parasites and reduce levels of infections in foraging adults or larvae (Koch et al. 2017). Indeed recent work has established that nectar phytochemicals are biologically active against *Crithidia bombi* gut parasites of *Bombus impatiens* in artificially inoculated animals (Richardson et al. 2015a, b). Several commercially available compounds known to occur in nectar and be relevant to foraging by *Bombus* spp. from earlier reports including the alkaloids, nicotine and anabasine, and the phenolic monoterpene thymol were tested in inoculated bees and shown to reduce levels of infection in test bees. This potential benefit to bees is in conflict with the knowledge that some of these compounds have established roles as defence

compounds but since honeybees response to nicotine is nuanced when it is encountered it may serve to effect more frequent visits between flowers by pollinators (Köhler et al. 2012) and reduce the amount of nectar required to maintain successful pollen transfer by native pollinators (Kessler and Baldwin 2007; Kessler et al. 2008).

Thymol is a phenolic based essential oil component of many plants; most notably *Thymus vulgaris* (Lamiaceae), and has biological activity against a number of insects with scope for commercialisation as a biopesticide (Isman 2006; Wilson and Isman 2006) and can confer resistance to invertebrate antagonists. Richardson et al. (2015a, b) reported minor activity of this compound against *Crithidia bombi* in *B. impatiens* but tested only at concentrations found in honey. Thymol occurs in nectar in higher levels than in honey and is more active at this ecologically relevant concentration against *C. bombi* (Palmer-Young et al. 2016). So, thymol may have potential benefit for bees in a landscape setting for the provision of nectar but also with the added value of reducing disease incidence. Thymol also occurs in a wide range of species including *T. vulgaris*, a popular and commercially cultivated plant. Furthermore, thymol is less harmful to bees than some of the other compounds tested by Richardson et al. (2015a, b) which can be directly toxic to them (Köhler et al. 2012) or cause malaise behaviours and sublethal effects (Hurst et al. 2014; Oliver et al. 2015). However, thymol did not limit acquisition of parasites and any effects of thymol against *C. bombi* in isolation may reflect indirect host-mediated, effects of chronic thymol ingestion (Rothchild et al. 2018) so other more consistently effective compounds are required before we can envision medicinal plants for bees in field margins and flower strips. Most studies on the biological activity of nectar compounds against bee pathogens however have not investigated the fate of the metabolites so have not fully explained the chemical processes that might be influencing the effects. Testing compounds in vitro for example may provide some activities but these may not necessarily reflect the chemistry of the insect gut where metabolism of compounds could influence activity—for example glycosylation or methylation having effects on the bioactivity. Phytochemical analysis of the contents of the hindgut where *C. bombi* proliferate would be informative for some target compounds and evaluation of the parasite itself

to understand the mechanisms of effects are required. More studies to investigate free flying bees would be welcome to determine if they can reduce their pathogen load or uptake when foraging on the flowers that produce bioactive compounds in nectar and would be informative for understanding their capacity to contribute to bee health or influence transmission.

Pollen chemistry and pollination

A priori, herbivore defense of pollen makes sense since this is the male gamete; vital plant tissue, so conforms to optimal defence theory as a priority for protection (McCall and Fordyce 2010; Cook et al. 2013). Little surprise then that the concentrations of secondary metabolites in pollen is typically one or two orders of magnitude greater than in nectar (Palmer-Young et al. 2019a, b). Again, the consistency of occurrence of secondary metabolites across tissue reveals that components occurring in pollen are invariably similar to those occurring elsewhere in the plant for defense. For example, the genus *Lupinus* includes several crop species such as *Lupinus mutabilis* (Leguminosae); a food crop cultivated in South America. *Lupinus* species produce several quinolizidine alkaloids including sparteine and lupanine which occur throughout the plant but notably in the seeds at very high concentrations (3% by weight) (Hatzold et al. 1983). Evidence suggests their primary function is to protect the plants from insect attack, because D-lupanine is toxic and repellent to insects including beneficial arthropods that feed on the herbivores (Emrich 1991; Kordan et al. 2012). More recently D-lupanine along with its 13-*O*-tigloyloxy, 13-*O*-angeloyloxy, 13-hydroxy and 4-*O*-hydroxy-13-*O*-angeloyloxy derivatives have been found in pollen at concentrations in excess of 2 mg g⁻¹ and although at these concentrations did not increase mortality in *Bombus terrestris*, a pollinating species for Lupins, they did cause experimental micro-colonies to produce fewer and smaller males which could have longer term colony and population impacts (Arnold et al. 2014). The function of toxins in pollen as a defence makes sense but to cause existential impacts on a key mutualist does not. In these experiments, insects were provisioned treated pollen with no choice and it is the choice that may provide a more effective experimental arena to understand how pollen defence chemistry functions. *Bombus* species were deterred from

collecting saponin-containing pollen from two *Dipsacus* spp. (Caprifoliaceae) and pollen containing the highest levels of a saponin were less groomed off, meaning the bees carried more pollen for pollination (Wang et al. 2019). Some evidence exists for repellent and attraction to function together to optimise temporal visitation patterns of pollinators to coincide with stigma receptiveness and pollen maturation (Scott-Brown et al. 2019). *Thrips major* Uzel (Thysanoptera: Thripidae) occurs abundantly on flowers of the common Elder (*Sambucus niger* L.) (Adoxaceae) (Raspudić et al. 2009). *Thrips major* is widely recognised as a flower damaging pest species (Moritz et al. 2004). However, when *T. major* was excluded from inflorescences of *S. niger* the flowers failed to produce fruit indicating a role in pollination through pollen feeding behaviour. Peak abundance of linalool, the major monoterpenoid in the headspace of the inflorescence, coincided with the highest numbers of adult thrips on flowers and is an attractive compound to *T. major*. Thrips declined in senescing flowers correlating with higher concentrations of the cyanogenic glycosides prunasin and sambunigrin in reproductive tissue which were deterrent to the thrips (Scott-Brown et al. 2019). Cyanogenic glycosides are well-established defence compounds for invertebrates (Zagrobelny et al. 2004). This work provides a fresh view of thrips as beneficial insects along with evidence of a mutualistic relationship between *T. major* and *S. nigra* highlighting the possibility that their value in food production maybe overlooked and their systematic control may have unintended negative consequences. So, while plant defence compounds in plants can function simply to protect it the mechanisms of protection may themselves mediate more effective pollination by flower visitors carrying more pollen to conspecific flowers in adapted species. Elsewhere linalool is a deterrent to colonisation of rice by the rice brown planthopper (*Nilaparvata lugens*) (Hemiptera: Delphacidae) indicating its function in some plant species in defense (Xiao et al. 2012). How pest species remain deterred by a single compound while mutualists remain attracted to the same compound remains unclear although Xiao et al. (2012) also report that linalool attracts natural enemies of the brown planthopper so it is possible that the deterrence in the brown planthopper could be through association with greater predation.

Conclusions

For decades scientific evidence has strongly supported the primary adaptive function of secondary metabolites in plants for defense against herbivory—especially against invertebrates. There are countless reports of the biological activity of plant extracts and compounds against insects (Isman and Grieneisen 2014) consolidating this view but surprisingly little on the effects of phytochemicals on pollinators. Understanding how traits associated with food reward and reward chemistry would help inform the ecology and evolution of plants and pollinators (Parachnowitsch and Manson 2015).

Here, examples have been review that review ecological functions that benefit the plant through maximizing pollen transfer by repelling less preferred pollinators, supporting healthier pollinators or enhancing their behaviour to deliver more efficient pollination. This compelling evidence for ecological functions based on these biological effects raises the question of what is driving adaptation in plants for secondary metabolites and how does adaptation to herbivory and pollination interact? Ramos and Schiestl (2019) argue that pollination and herbivory are both concurrent drivers of diversity and should be studied together. They showed that plants under selection by pollinators (bees) evolved increased floral attractiveness, but this was compromised by herbivores. Plants under selection from pollinators and herbivores evolved higher degrees of self-compatibility and autonomous selfing, as well as reduced herkogamy.

A similar question is considered across large spatial scales in Egan et al. (2016) who measured levels of the entomotoxic diterpenoids grayanotoxin I (GTX I) and GTX III in leaves and nectar of *Rhododendron ponticum* in its native and introduced ranges. As mentioned above, high concentrations of GTX I in young *Rhododendron* leaves provide defense against insects (Scott-Brown et al. 2016) so its primary role appears from this evidence to be defense. But GTX I is also toxic to some pollinating species when encountered in nectar including honeybees and a solitary mining bee species, (*Andrena scotica*) whereas another pollinator, *Bombus terrestris* remains unaffected (Tiedeken et al. 2014, 2016) suggesting adaptation by *Bombus* permitting exclusive access to nectar for the pollinator and specialist pollinator service for

the flowers. Occurrence of GTX I, the most active against bees, was significantly lower or absent from nectar in introduced plants whereas GTX III—inactive against the bees—was similar across locations. The occurrence of nectar GTX was not affected by environmental variation, and considering the specificity of change to GTX I, and its differential toxicity to some bee species, its occurrence in the plant may have been influenced during invasion by interaction with herbivores or via pollinator-mediated selection owing to local populations of pollinators in the introduced range being poorly adapted to nectar toxins which in the native range serve to filter out preferred pollinators (Egan et al. 2016). A comprehensive survey of the genus and correlation of the presence of toxic nectar and generalist pollinator syndromes or absence of toxins and specialists' flowers may provide stronger evidence that GTX I serves to filter specialists.

Crop domestication can also drive down plant defenses reducing inherent resistance to herbivory and disease so may similarly affect secondary metabolites in nectar and pollen with consequences for pollinators. In *Vaccinium corymbosum* (Ericaceae), domestication altered plant chemistry of nectar and pollen, and reduced pollen chemical diversity. These changes included the antimicrobial caffeic acid ester 4-*O*-caffeoylshikimic acid which could have implications for pollen protection because caffeic acid esters of cyclitols are established herbivore antagonists (Stevenson et al. 1993) but these compounds also protect *Bombus impatiens* against the gut pathogen *Crithidia bombi* at concentrations found in wild but not cultivated plants (Egan et al. 2018). This suggests that domestication changed floral traits with consequences for bee health and investigations of pollinator-dependent crops more generally are required to determine broader implications of domestication on floral chemistry associated with domestication (Egan et al. 2018). Further work to establish how chemical adaptation responds to pollinator needs and herbivore defense including spatially discrete studies of nectar secondary compounds to show how variation affects plant ecology is required along with a broader view of phytochemistry beyond antagonistic interactions, that integrates the consequences of chemically defended mutualist rewards. Ultimately many of the knowledge gaps would be filled with more work on free flying bees to understand in realistic ecological settings how

these effects manifest (e.g., Singaravelan et al. 2005; Manson et al. 2013; Couvillon et al. 2015).

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