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Effects of Plant Secondary Metabolites and Host Specificity on Growth, Development, and Oviposition of Lepidopteran Herbivores

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EFFECTS OF PLANT SECONDARY METABOLITES AND HOST SPECIFICITY ON GROWTH, DEVELOPMENT, AND OVIPOSITION OF LEPIDOPTERAN HERBIVORES

A Thesis

by

SUKHMAN SINGH

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EFFECTS OF PLANT SECONDARY METABOLITES AND HOST SPECIFICITY ON GROWTH, DEVELOPMENT, AND OVIPOSITION OF LEPIDOPTERAN HERBIVORES

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ABSTRACT

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Chapter 1: This chapter provides a review of recent and critical literature on the role of polyphenols in mediating plant-insect interactions. I particularly focused on plant defense induction and mode of action of polyphenols, defense fitness trade-offs, and storage of polyphenols for future defense responses.

Chapter 2: This chapter is about the effects of polyphenol rich purple corn pericarp extract on the growth and development of generalist caterpillar i.e., fall armyworm (*Spodoptera frugiperda*). This study shows that purple corn pericarp extract rich in polyphenols negatively effects the growth and development of *S. frugiperda*.

Chapter 3: This chapter is focused on the role of diet variation in oviposition success and progeny growth of tobacco hornworm (*Manduca sexta*). In this study I show that alteration in diet plays differential role in oviposition and progeny success of *M. sexta*. *M. sexta* fed on tomato had higher egg laying and hatching capacity than four *Solanum* species. This could be due to higher PPO amount and trichome density in four *Solanum* species than tomato plants.

In conclusion, our results indicates that plants have different suites of defenses that defend them against insect herbivores. Also, plant secondary metabolites play important role in plant defenses and protect them from insect pests.

DEDICATION

I dedicate my thesis to my grandfather, Mr. Harminder Singh, my father and my mother, Mrs. Gurjit Singh and Amandeep Kaur, my elder sister Ms. Jasnoor Kaur and my best friend Navdeep Kaur. I am thankful for your constant love, blessings and motivation to work hard.

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CHAPTER I

THE MULTIFUNCTIONAL ROLES OF POLYPHENOLS IN MEDIATING PLANT-HERBIVORE INTERACTIONS

This chapter has been previously published as ‘The Multifunctional Roles of Polyphenols in Mediating Plant-Herbivore Interactions’ in ‘International Journal of Molecular Sciences’ journal. Below is the link to the paper:

Singh, Sukhman; Kaur, Ishveen; Kariyat, Rupesh. 2021. "The Multifunctional Roles of Polyphenols in Plant-Herbivore Interactions" *Int. J. Mol. Sci.* 22, no. 3: 1442

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Abstract

There is no argument to the fact that insect herbivores cause significant loss to plant productivity in both natural and agricultural ecosystems. To counter this continuous onslaught, plants have evolved a suite of direct and indirect, constitutive and induced, chemical and physical defenses, and secondary metabolites are a key group that facilitates these defenses. Polyphenols- widely distributed in flowering plants, are the major group of such biologically active secondary metabolites. Recent advances in analytical chemistry and metabolomics have provided an opportunity to dig deep into extraction and quantification of plant-based natural products with insecticidal/insect deterrent activity, a potential sustainable pest management strategy. However, we currently lack an updated review of their multifunctional roles in insect-plant interactions, especially focusing on their insect deterrent or antifeedant properties. This review focuses on reviewing the role of polyphenols in plant-insect interactions and plant defenses including their structure, induction, regulation, and their anti-feeding and toxicity effects. Details on mechanisms underlying these interactions and localization of these compounds are discussed in the context of insect-plant interactions, current findings, and potential avenues for future research in this area.

Introduction

The millions of years of dynamic co-existence and relentless competition for survival has led plants to evolve complex strategies to survive against the onslaught of damaging insect herbivores (Karban, 2010; Erb and Reymond, 2019; Zunjarrao et al., 2020), primarily mediated through tolerance and resistance mechanisms (Howe and Jander, 2008; Mitchell et al., 2016).

While resistance traits assist plants to prevent the attack of insects, tolerance allows them to combat herbivory or offset fitness consequences- by increasing the photosynthetic activity at the damaged site, and utilization of stored resources for compensatory growth (Howe and Jander, 2008). Resistance mechanisms also include mechanical defenses to deter the insects from feeding- using morphological adaptations including, but not limited to waxy cuticle, trichomes, thorns, and spines (Kariyat et al., 2017a,b). Being the first line of defense, herbivores have to face these challenges pronto as they come in contact with plants, although these defenses can also act in tandem to successfully ward off herbivory (Howe and Jander, 2008). However, selection pressure for survival in this never ending co-evolutionary arms race has also led to the development of complex, biochemically based, and tightly regulated second line of defenses. These include the production of toxins that deter herbivores from feeding, reduce the palatability/digestibility of plant tissue, and compounds that can negatively affect herbivore growth and development (Tayal et al., 2020a; Singh et al., 2020). These defenses also include the release of constitutive and herbivore induced plant volatiles that attract predators and parasitoids, and in many cases, selectively repel herbivores (Moraes et al., 1998; War et al., 2011). Collectively, these compounds are defined as plant secondary metabolites.

Plant cells produce two types of compounds; primary metabolites and secondary metabolites (plant secondary metabolites; PSM) (War et al., 2012; Furstenberg et al., 2013). Primary metabolites include compounds vital for plant growth, development and fitness. These include carbohydrates, lipids, nucleic acids and proteins inevitable for cell structure, and physiological and biochemical functioning in plants; whereas PSM, although not directly involved in growth and metabolism, are essential for interactions with the environment. They are synthesized and can also be induced during biotic and abiotic stresses- protecting the plant from insects, mammalian herbivores, micro-organisms, UV radiation, high temperature, shading, mechanical injury, wounding, and heavy metal toxicity to name a few (Zaynab et al., 2018; Sharma et al., 2019; Naikoo et al., 2019; Chen et al., 2020). As an anti-herbivory defense, they improve host plant survival and fitness (Rani and Jyothsna, 2010; Chamarthi et al., 2010; War et al., 2012) by negatively affecting the survivability, vigor, host location and fitness of the herbivores (Jiani et al., 2019; Marciniak et al., 2019; Kariyat et al., 2019; Tayal et al., 2020a,b). Furthermore, the production of these compounds is tightly regulated and decreases once they regain normal state post induction, since they require huge investment of resources; making it expensive to continuously produce them, leading to growth-fitness trade-offs (Howe and Jander, 2008; Huot et al., 2014; Campos et al., 2016).

Classification

Plant secondary metabolites are generally divided into three broad classes: terpenoids, phenolics and alkaloids, with phenolics (polyphenols) being the largest, diverse, and most widely distributed class among them. Several thousands of polyphenolic compounds are found in plants, synthesized via shikimate acid derived phenylpropanoid and/or polyketide pathways (Cheynier et al., 2013). They have a basic structure consisting of benzene ring with a hydroxyl group attached, without any nitrogen-based functional group (Swain and Smith, 1962; Quideau et al., 2011; Lattanzio, 2013). L-phenylalanine is the primary compound in this pathway to be synthesized and form the basis for downstream synthesis of other polyphenols (Figure 1). Major groups of polyphenols include flavonoids (C6-C3-C6), phenolic acids (C6-C1), stilbenes (C6-C2-C6) and lignans (C6-C3). Polyphenol synthesis not only contributes to the flavor, color, odor, astringency, oxidative stability and bitterness (Pandey and Rizvi, 2009; Li et al., 2014) of different plant parts, but also play a critical role as plant chemical defenses (Pandey and Rizvi, 2009).

The idea of plant-insect interactions either positively or negatively affected by polyphenols was first proposed by Fraenkel in 1959 (Fraenkel, 1959). Following that, numerous studies investigated defensive as well as stimulatory roles of such metabolites on insect herbivores. For instance, grain aphid (*Sitobion avenae* F.) infestation in triticale wheat seedlings induce bioactive compounds such as phenolic acids that provide resistance against them (Chrzanowski and Leszczynski, 2008). Kariyat et al. (2019) showed that 3-Deoxyanthocynadin (flavonoids) present in wild type sorghum (*Sorghum bicolor* (L.) Moench Family: Graminaceae) caused significantly higher mortality and reduced population growth in corn leaf aphid (*Rhopalosiphum maidis* Fitch), when compared to null mutants devoid of them (Kariyat et al., 2019). More recently, we also showed that polyphenol rich pericarp extract of purple corn negatively affected growth, development and adult fitness traits in tobacco hornworm (*Manduca sexta* L.), a specialist herbivore on Solanaceae (Tayal et al., 2020a,b). Consistent with these observations, it has been well documented that different groups of polyphenols collectively protect most plant species against wide range of attackers. For example, chlorogenic acids in chrysanthemum (*Dendranthema grandiflora* (Ramat.) effectively defend against thrips (Leiss et al., 2009), pisatin (flavonoid) deters pea-aphid (*Acyrthosiphon pisum* Harris) in pea (Morkunas et al., 2015) Table 1 and ferulic acid in rice impart resistance against brown planthopper (*Nilaparvata lugens* Stål) (Yang et al., 2017) to name a few. Increase in phenolic acids and flavonoids, especially quercetin has also been observed in white cabbage (*Brassica oleraceae* L. *var. capitata f. alba*; Family:

Brassicaceae) upon infestation by cabbage butterflies (*Pieris brassicae* L.) and flea beetles (*Phyllotreta nemorum* L.) (Kovalikova et al., 2019). A detailed version similar examples and effects of polyphenols are described in Table 1. Taken together, it is clear that polyphenols (the primary group of PSM's) can not only protect plants against broad spectrum of insect herbivores but can also be specific and highly regulated based on particular host-herbivore system and genotype X environment interactions- clearly warranting further in-depth look at synthesis, distribution and role in plant-herbivore interactions, the focus of this review.

Biosynthesis of Polyphenols

In plants, polyphenols are synthesized through the phenylpropanoid pathway (Hu et al., 2017). The first compound in this pathway is L-phenylalanine, synthesized by shikimate pathway (Shadle et al., 2003). And the first step towards formation of phenolic acids is cinnamic acid synthesis by the action of phenylalanine ammonia-lyase (PAL) on L-phenylalanine (Jun et al., 2017). Further, cinnamic acid 4-hydroxylase catalyze cinnamic acid to form p-coumaric acid. Cinnamic acid also leads to the formation of the O-coumaric acid, which then give rise to salicylic acid → Genitisic acid → o-Pyrocatechuic acid. P-coumaric acid further leads to the formation of the caffeic acid and to the p-hydroxybenzoic acid as well, which is derivative of hydroxybenzoic acid (El-Basyouni et al., 1964). Ferulic acid is formed by methylation of caffeic acid. Further methylation of ferulic acid give rise to Sinapic acid (Figure 1). However, the formation of derivatives of benzoic acids is more complex. Either they are produced from the derivatives of the cinnamic acid or directly from the intermediary compounds formed in shikimate pathway (Neelam et al., 2019). Vanillic acid can be formed from the ferulic acid, syringic acid from sinapic acid, protocatechuic acid from caffeic acid or p-hydroxybenzoic acid.

Gallic acid, protocatechuic acid, vanillic acid and syringic acid can be also synthesized from hydroxybenzoic acid (Srinivasulu et al., 2018). These phenolic acids are commonly found in families Apiaceae, Asteraceae, Fabaceae, Moraceae, Rosaceae, Rubiaceae and Solanaceae and play significant roles as anti-herbivore defenses (Lattanzio, 2013) Table 2.

Biosynthesis of flavonoids are initiated with one p-coumaroyl-CoA and three malonyl-CoA molecules, where p-coumaroyl-CoA is synthesized from phenolic acids in the pathway. Further, involvement of different enzymes at different levels alter the structure of the compounds formed at different levels in pathway. The very first enzyme involved in the formation of basic flavonoid skeleton i.e., C-15 is chalcone synthase (CHS). The other various enzymes involved in pathway are chalcone isomerase (CHI), flavonoid 3-hydroxylase (F3H), flavanol synthase (FLS), dihydroflavonol reductase (DFR), anthocyanin synthase (ANS)/glucose transferase (UGTS) leading to the formation of naringenin, dihydroflavonols, flavanols, leucoanthocyanidins and anthocyanins respectively (Harborne, 1980; Winkel, 2001; Tohge et al., 2017) Figure 2. Flavonoids are commonly found in angiosperms, gymnosperms and pteridophytes (Harborne, 1980; Tohge et al., 2017).

Stilbenes are also synthesized by phenylpropanoid biosynthetic pathway. Stilbene synthase is the main enzyme required for stilbene biosynthesis and stilbene synthase gene (STS gene) is responsible for synthesis of these enzymes (Supurn et al., 2019). Generally, one P-coumaroyl-CoA and three malonyl-CoA molecules leads to the synthesis of stilbenes by action of STS enzyme (Austin and Noel, 2003) Figure 2. Stilbenes are most commonly found in Vitaceae (Lambert et al., 2013), Fabaceae, Pinaceae (Underwood and Pearce, 1991), Gnetaceae (Yao et al., 2003), Polygonaceae (Matsuda et al., 2004), Ericaceae (Luteyn et al., 1980), and in different plant parts including leaves, roots, fruits, bark, and stem (Table 2).

Finally, lignans are also synthesized through phenylpropanoid pathway. Coniferyl alcohol, sinapyl alcohol and 4-hydroxycinnamyl alcohol are the precursors for lignan synthesis. p-Coumaryl acid, ferulic acid and Sinapic acid synthesized in the phenolic acid pathway leads to the formation of the 4-hydroxycinnamyl alcohol, coniferyl alcohol and sinapyl alcohol respectively. Formation of p-Coumaryl acid 4-hydroxycinnamyl alcohol, ferulic acid coniferyl alcohol, Sinapic acid Sinapyl alcohol are catalyzed by the 4-hydroxycinnamate CoA and cinnamoyl CoA reductase. Coniferyl alcohol give rise to the lignans with 9(9′) oxygen such as furofuran (pinoresinol, lariciresinol, secoisolariciresinol), dibenzylbutane, dibenzylbutyrolactone, aryltetralin, arylnaphthalene. On the other side, p-coumaric acid leads to the formation of the lignans without 9(9′)-oxygen such as furan, dibenzocyclooctadiene, and dibenzylbutane without 9(9′)-oxygen (Umezawa et al., 2003) Figure 2. Lignans are widely distributed in Gramineae including cereals like wheat bran, rye bran, oats (*Avena sativa* L. Family: Poaceae), barley (*Hordeum vulgare* L. Family: Poaceae), millet triticale, and corn to name a few) (Zanella et al., 2017). Pumpkin (*Cucurbita pepo* L. Family: Cucurbitaceae), flax (*Linum usitatissimum* L. Family: Linaceae; richest source), sunflower (*Helianthus annus* L. Family: Asteraceae), poppy (*Papaver somniferum* L. Family: Papaveraceae), sesame (*Sesamum indicum* L. Family; Pedaliaceae) and oilseed crops are also observed to have high lignin content mostly concentrated in the seeds (Moazzami et al., 2007).

Plant Defense Induction Mediated by Polyphenols

Herbivores attack plants by scratching, mining, chewing, biting, sucking, galling, wounding, parasitizing or by phloem feeding and even evading leaf surface using their secretions (Voelckel et al., 2004; Howe and Jander, 2008; Stam et al., 2014). This attack in turn initiates a suite of defenses in form of physical (spines, trichomes and sclerophylly) and chemical defenses in plants (Freeman, 2008; Kaur et al., 2020a,b) through signaling molecules (Gandhi et al., 2020), phytohormone pathways (Grover et al., 2020), and the initiation and synthesis of physical defense structures and/or defense compounds in active such as alkaloids (Howe and Jander, 2008) or inactive form cyanogenic glycosides (Spiteller, 2008; Yeats, 2018) and benzoxazinoids (Ahmad et al., 2011; Wouters et al., 2016) forming a part of activated defense Figure 3 to name a few. For example., two major weeds in Solanaceae; *Solanum carolinense* L. and *Solanum elaeagnifolium* Cav. possess a diverse suite of constitutive defenses including non-glandular stellate trichomes that negatively affect herbivore feeding (Kariyat et al., 2017b), internode spines that deter herbivores (Kariyat et al., 2017a) and . More interestingly, these defense traits are also highly inducible post herbivory leading to a well-coordinated induced defense phenotype (Aljbory and Chen, 2017). Induced defenses are also thought to be primarily induced by elicitors produced by herbivores in their oral secretions. For example, the regurgitant of caterpillars or salivary secretions contain polyphenol oxidase, peroxidase and reductase which activate plant responses and signaling pathways ultimately leading to the production of polyphenolic compounds which are either toxic or repellent to herbivory (Walling, 2000; Tian et al., 2013) Figure 3. These include oral secretions isolated from lepidopteran species (e.g., glucose oxidase from saliva of *Helicoverpa zea* Bodie and β-glucosidase from *P. brassicae*), oviposition fluid contains elicitors in the form of long chain diols known as bruchins and the fatty-acid-amino-acid conjugates (FACs) found in the regurgitant of larvae of Sphingidae (Hawk moths), Noctuidae (cut worms) and Geometridae (inch worms) (Kessler and Baldwin, 2002).

After recognizing these compounds possibly through surface receptors (Steinbrenner et al., 2020), plants activate phytohormones such as jasmonic acid (JA), salicylic acid (SA) and ethylene which act as signaling molecules that spread throughout the plant apart from the wound site (local) to other plant parts (systemic) to induce various transcriptional factors and consequently, differential defense gene expression (Walling, 2000; Kessler and Baldwin, 2002) Figure 3. In their classic work, Farmer and Ryan (1992) showed that wound signaling speeds up JA production through octadecanoid pathway, which in turn activates the plant defense genes (Farmer and Ryan, 1992). These compounds in general, are part of the octadecanoid defense pathway, primarily mediated by JA and methyl jasmonate (Kariyat et al., 2012a; Louis et al., 2012) to produce herbivory induced secondary metabolites (Thaler et al., 1996; Reymond et al., 2004). In tomato, expression level of polyphenol oxidase (PPO), proteinase inhibitor (PIs), and lipoxygenase (LOX) gene expression levels have been found to increase at local and systemic levels, regulated via octadecanoid pathway in response to wounding (Macdonald and Cunha, 2007). More specifically, the phytohormones produced through the octadecanoid pathway increases the expression of Phenylalanine Ammonia Lyase (PAL; chief enzyme necessary for regulation and operation of phenylpropanoid shikimate pathway), which in turn diverts the amino acids from primary metabolism towards secondary metabolite production (Koomneef and Pieterse, 2008). However, induction of signaling pathways is herbivore specific (e.g., feeding guild) and usually crosstalk is observed between different signaling molecules in the presence of multiple herbivory attack. This crosstalk can be either antagonistic or synergistic to utilize minimum resources to sustain plant growth and development and to mount most effective defense strategy depending on the type of herbivores in action (Spoel et al., 2007).

Most of these interactions between the hormones have been well understood at the molecular level (Li et al., 2019; Erb and Reymond, 2019). For example, SA pathway induced by sucking pest and biotrophs through the regulatory protein NPR1 that also reduces the activity of JA. For instance, in tobacco (*Nicotiana tabacum* L.) SA induces defense response against *Tobacco mosaic virus* and JA against chewing herbivores (Preston et al., 1999) when plants are under multiple herbivores. JA is primarily induced by lipoxygenase (LOX) genes when plants are attacked by chewing herbivores (Reymond and Farmer, 1998). Furthermore, it has also been observed that plants respond much faster to herbivory attack in comparison to mechanical damage, owing to the fact that some of the polyphenols produced after prior herbivory are stored in tonoplasts, and fast tracked for a rapid defense response (Figure 3).

Mode of Action of Polyphenol Mediated Defenses

Polyphenols affect herbivore growth by antibiosis, antixenosis or antisymbiosis modes of action. Antibiosis, in this context refers to the production of antibiotic compounds by the host plant inhibiting the growth, survival, development, and reproduction, of insect herbivores (Eigenbrode and Trumble, 1993) Figure 3. As discussed earlier, insect herbivore regurgitant produced during feeding, can alter defense gene expression, leading to the production of key defense compounds including defense proteins and phytohormones. As a general mechanism, once an herbivore initiates feeding on plant tissue, amino acid polypeptides such as systemin can enhance the production of lipase enzyme in the receptor cell membrane leading to release of linolenic acid. Linolenic acid then acts as precursor of jasmonic acid signaling pathway, which ultimately produce peroxidase (PO), Polyphenol oxidase (PPO) and proteinase inhibitors. They oxidize phenols to form reactive oxygen species (H_2O_2) and quinones (Thipyapong et al., 2007; Mahanil et al., 2008; Seram, 2019). Quinones act as anti-nutritional proteins interfering with digestibility and nutrient uptake of insects (Merino et al., 2018) Figures 3 and 4, causing significant reduction in herbivore fitness. These proteinase inhibitors also cause starvation in insects as they bind with the digestive enzymes inside insect midgut, reducing digestibility and release of nutrients and minerals required to perform essential metabolic functions for survival (War et al., 2012).

Polyphenols can also be toxic to insect herbivores by causing oxidative damage in the midgut through the following mechanisms. They readily bind with thiols, thereby reducing non-protein thiols and ascorbic acid both in plants as well as in the midgut epithelial tissue of midgut of herbivore when they consume polyphenols while feeding on plant as examined during foliar feeding on soybean by *H. zea* (Bi and Felton, 1995). The effect of binding of the polyphenols with the digestive enzymes of insects is reflected by delay in the development, molting and consequently, reduction in fitness of insect herbivore. Rehman et al. (2012) reported the delay in development of mites due to the binding of phenolics to the digestive enzymes when fed on plant cultivars with high catechol content (Rehman et al., 2012). Flavonoids (apigenin, chrysin, luteolin and quercetin) have been also found to inhibit the EcR (ecdysone receptor) dependent gene expression in insects which affect their molting activity (Oberdorstera et al., 2001). Stilbenes can inhibit the crocin and DPPH (Diphenyl picrylhydrazyl; insect growth regulatory enzymes) activity in *Spodoptera frugiperda* J. E. Smith (Torres et al., 2003). Flavonoids and phenolic acids (ferulic acid, vanillic acid and 4-hydroxybenzoic acid) have been also found to inhibit acetylcholinesterase (enzyme involved in molting) in rice weevil (*Sitophilus oryzae* L.) (Maazoun et al., 2017). Tannins are also reported to bind with the proteins and digestive enzymes in the gut of insect larvae causing similar effects. Similarly, binding of quinione to the dietary proteins has been found to be cause anti-nutritive in *M. sexta* (Felton and Duffey, 1991), and quinones also undergo addition reaction with thiols and amino groups in digestive system of herbivores, which drastically reduces the availability of dietary protein (Duffey and Felton, 1990). Flavonoids such as taxifolin have been found to inhibit the activity of glutathione S-transferases enzyme (which detoxify insecticides) thereby, enhancing insecticidal properties (Wang et al., 2014, 2016). Flavonoids have also been found to affect gustatory sensilla and their neuronal responses affecting food choice and consequently reducing consumption (Harborne and Williams, 2000; Hoffmann et al., 2001; Simmonds, 2003). For example, rutin and quercetin 3-glucosylgalactoside present in soybean (*Glycine max* L.) leaves reduce the food consumption of cabbage looper (*Trichoplusia ni* Hubner) after detection (Harborne and Williams, 2000; Hoffmann et al., 2001). And finally, in addition to inhibitory effects on digestion, stilbenes have been also reported to have anti-molting activity by acting as ecdysteroid receptor antagonist leading to premature induction of molting or even failure in molting (Dinan et al., 1999; Sarker et al., 1999; Lv et al., 2014).

Antixenosis or non-preference is the reduced preference for a host plant by herbivores, primarily due to the defense responses in plants that can affect their growth and development. For example, proteinase inhibitors produced after herbivory makes plants unpalatable and hence are not preferred by herbivores. Green and Ryan were the first to report the induction of proteinase inhibitors upon herbivory in promoting resistance in plants (Green and Ryan, 1972). And Dreyer and Jones (1981) demonstrated that flavonoids such as dihydrochalcones and polar phenolic compounds in wheat has strong anti-deterrent activity for green peach aphid (*Myzus persicae* Sulzer) and wheat aphid (*Shizaphis graminum* Rondani) (Dreyer and Jones, 1981). Resistance to herbivory by antixenosis is also achieved by the morphological adaptations such as, hairiness, wax on leaves, color and by emitting foul-smelling volatile organic compounds such as terpenes (Kariyat et al., 2014; Xing et al., 2017). Collectively, this reduces host location, oviposition activity, colonization, or have adverse post ingestive effects on insects (Shoorooei et al., 2013). Additionally, peroxidase (PO) enzyme regulates the defense signaling in plants leading to hypersensitive response, which also increases the lignification of cell wall, thereby reducing the digestibility of plant tissue. For example, peroxidase enzyme can modify the structure of polyphenols; peroxidase enzyme converts chlorogenic acid into chloroquinone, which binds to amino acids significantly reducing their availability (Kundu and Vadasserv, 2019), similar to quinones that attach to proteins and reduce their availability. Taken together, insect feeding on plants enhance the production of PO and PPO activity, which ultimately oxidize polyphenols and they act as either physical or chemical barriers or as signaling molecules providing resistance to plants against insect pests (Mahanil et al., 2008).

Antisymbiosis, on the other hand, is an example of the plant defense mechanism that indirectly affects growth of insect herbivores by affecting the growth and development of beneficial microbes associated with insects. Polyphenols have been shown to have antimicrobial activity on microbial symbionts of insect herbivores, thereby indirectly impacting herbivores. For example, polyphenols (condensed tannins) were reported to repel leaf cutter ants (*Atta* spp.)

by affecting the activity of wood rotting basidiomycete fungi in symbiosis with leaf cutter ants Schultz et al., 1992). Tannins from Eurasian watermilfoil (*Mtriophyllum spicatum* L. Family: Haloragaceae) have been found to have allelochemical affect on the gut symbiont of water veneer (*Acentria ephemerella* Denis and Schiffermüller), thereby affecting their larval growth (Walenciak et al., 2002). Although these examples provide an insight into the highly diverse and tightly regulated species-specific effects of polyphenols, investigating how different polyphenolic molecules act inside the insect body, their targets, and consequently their cellular and ecological effects is still a black box and needs further investigation.

Buffer-Storage of Polyphenols for Future Responses

Plants have also been found to sequester phenolic compounds in the cell vacuole, to swiftly combat any future attack (Wink, 1997; Beckman, 2000; Brillouet et al., 2014). These compounds are not only toxic to herbivores but are also found to be toxic to plants as well. Consequently, plants tend to store them in special compartments known as phenyloplasts; the cells of thylakoid membrane which are produced via redifferentiation of primary cells so to store polyphenolic compounds. In order to store polyphenols in these cells, they are first detoxified by conjugating it with glycosides to form phenylglycoside, making them hydrophilic to remove their toxicity (Gachon et al., 2005). These phenyloplasts are progressively filled with phenylglycosides until they become mature enough to be released outside the chloroplast (Gachon et al., 2005). Once filled with polyphenolic compounds, they shift themselves to move inside the vacuoles. At the onset of herbivory, signaling molecules such as ROS (Reactive Oxygen Species) are produced by insect oral secretions (Gandhi et al., 2020) leading to oxidative stress in cell, forcing phenyloplasts to break their outer protective layer, thus releasing various polyphenolic compounds (Gachon et al., 2005). These compounds released from the vacuole, cross-link and/or polymerize cell wall, which imparts mechanical strength and rigidity to the plants, posing a harder barrier for herbivores to continue feeding by chewing and biting. PPO also oxides the secondary metabolites to form polymerized quinones (Kessler and Baldwin, 2002) that act as proteinase inhibitors which bind with several essential enzymes inside the insect body, obstructing several essential physiological processes, digestive ability and nutritional uptake (Kessler and Baldwin, 2002).

Defense Fitness Trade-Offs in Response to Insect Herbivory

Under continuous herbivory, plants reprogram their cellular machinery to allocate their energy resources among defense, growth and reproduction, in line with the predictions of resource allocation theory (Neilson et al., 2013). The theory predicts when plants possess limited resources to carry diverse functions, they reallocate their resources in a way that optimizes their overall performance, efficiency, vigor, and fitness (Simms and Rausher, 1987; Neilson et al., 2013; Zaynab et al., 2018). As expected, polyphenolic secondary metabolites also mediate such trade-offs. For example, *T. ni* Hubner) herbivory on wild parsnip (*Pastinaca sativa* L.; Apiaceae) leads to furanocoumarin production on cost of its seed fitness lowering seed mass (Zangerl et al., 2002). And, in another example., *Psychotria horizontalis* (Rubiaceae) plants exposed to pyralid and ctenuchid caterpillars induce the production of tannins leading to herbivore defenses at the cost of reduced growth of plants (Sagers and Coley, 1995). Post-herbivory, plants tend to overcome losses incurred during herbivory by enhancing metabolism and photosynthesis at the damaged site to invest in regrowth with possible fitness effects (Zhou et al., 2015). However, this leads to the diversion of resources towards defenses effectively reducing available resources-leading to shorter lifecycle and differences in root/shoot ratio. Even with all the recent developments in molecular genetics and metabolomics, we are still in our infancy on understanding the mechanisms underlying transgenerational effects (e.g., epigenetics) of herbivory, and how the intensity of herbivory influence allocation of resources in offspring. Being primarily mediated through polyphenols, studies on such trade-offs in resource reallocation between growth and defense examining single and groups of phenolic compounds can be used to explore more in this area, with an eye for potential application for crop improvement programs and pest management.

Recent Developments in Secondary Metabolites Research

It is clear that recent emphasis in this field is to elucidate the underlying molecular mechanisms involved in polyphenol biosynthesis. More recently, microRNA's (non-coding, 21–24 nucleotides long RNA strands regulating gene expression) have been reported to be involved in the biosynthesis of PSM (Gupta et al., 2017). For instance, 4-coumarate-CoA ligase gene involved in flavonoid biosynthesis have been targeted by miR172i and caffeoyl-CoA O-methyl transferase involved in lignin biosynthesis targeted by miR1438 (Biswas et al., 2016). Also, by modifying the expression of such genes involved in biosynthetic pathway, methods to enhance their synthesis can be identified. Although exploration at molecular level to alter the pathways to regulate the synthesis of polyphenolic compounds is still a work in progress, most of such research has been carried out to extract specific PSM for pharmaceutical and food industry with less focus on plant insect interactions. More advancement in this area can potentially assist in breeding plants that are naturally and sustainably resistant to various biotic and abiotic stresses.

Re-focusing to extract such compounds by developing inexpensive, simple, environmental and farmer friendly methods to combat the losses incurred due to biotic stressors. Recently, polyphenol rich pericarp extract, a byproduct of corn processing industry, extracted by inexpensive techniques has been found to negatively affect the growth and development of specialist insect herbivore *M. sexta* (Tayal et al., 2020a; Kariyat et al., 2019); Table 1 as well as against generalist herbivore fall armyworm (*Spodoptera frugiperda*) (Singh and Kariyat, 2020) Table 1. Such waste byproducts of food industry and other waste plant sources should be further explored under different systems and herbivores with different feeding behavior. Such developments do have the potential to become an alternative to the over reliance on synthetic pesticides in pest management.

Future Directions

Plant insect interactions and chemical ecology has benefitted greatly from understanding and quantifying secondary metabolites and examining their role in insect traits. Recent advances in molecular biology and metabolomics has taken this to the next level by allowing scientists to tease apart individual metabolites, genes and enzymes to target these specifically. Large number of enzymes and genes have been identified, which are mostly linked to different polyphenol pathways induced during plant defense responses to herbivory. While polyphenols have gained a lot of attention in parts- their use in food chemistry, they have also been an area of interest for studies in insect plant interactions. However, in this review we show how interspecific variation has an immense effect on the distribution and mode of action of different polyphenol compounds. Also, it is quite clear that a defensive compound in one plant system can be beneficial in another reinforcing their species specificity. Theories of resource allocation and trade-offs in plants are still debated and requires better understanding to answer questions; when plants invest either in defense or in growth, when they start back investing in growth after threat from herbivory is over, and how various class of metabolites play a role in these tradeoffs' decisions. The lack of studies in developing the methodologies of economically extracting these compounds to test them as potential biopesticide and to replace synthetic pesticides for sustainable crop production also warrants further investigation. Research in these areas will provide plant ecologists to further explore into defense mechanisms of plants and give insights to plant breeders for crop breeding. We urge our fellow scientists to move beyond model organisms and explore wild and native plant species and their interacting insects to understand, quantify, and extract PSM's and examine in detail their role in mediating these interactions both in vivo and in vitro.

Tables

a. Polyphenols mediated defense interactions with insect herbivores

Compound	***Plant***	***Insect herbivore***	***Mode of action***	***Reference***
Anthocyanin and tannins (flavonoids)	Purple corn (*Zea mays*)	Fall armyworm (*Spodoptera frugiperda*)	Feeding deterrent	Singh and Kariyat, 2020
Genistein and rutin (flavonoids)	Soybean (*Glycine max)*	Stink bug (*Piezodorus guildinni)*	Antibiosis	Bentivenha et al., 2017
Anthocyanin and tannins (flavonoids)	Purple corn (*Zea mays*)	Tobacco hornworm *(M. sexta)*	Ovipositional and feeding deterrent	Tayal et al., 2020a,b
Chlorogenic acid (Phenolic acids)	Chrysanthemum (*Dendranthema grandiflora*)	Thrips	Pro-oxidant effect	Leiss et al., 2009
p-coumaric acid (Phenolic acids)	Yellow maize (*Zea mays)*	Pink stalk borer *Sesamia nanogriodes*	Antibiosis	Santiago et al., 2005

Chlorogenic acid (Phenolic acids)	Yellow maize *Z. mays*	European corn borer *(Ostrinia nubilalis)*	Anti-feedant	Mao et al., 2007
Chlorogenic acid (Phenolic acids)	Honeysuckle (*Lonicera maackii)*	Beet armyworm *(Spodoptera exigua)*	Feeding deterrent	Cipollini et al., 2008
Phenolic acids	European filbert *(Corylus* L).	Hazel aphid (*Myzocallis coryl)i*	Anti-feedant	Gantner et al., 2019
Isoflavonoids (flavonoids)	Lupinus (*Lupin* spp.)	Grass grub (*Costelytra zealandica) and* African black beetle (*Heteronychus arator)*	Feeding deterrent	Lane et al., 1987
Piceid, isorhapontin, astringin.	Sakhalin spruce (*Picea glehnii)*	Japanese termite (*Reticulitermes speratus)*	Feeding deterrent	Shibutani et al., 2004

Syringic, coumaric, vanillic acid (phenolic acids)	Castor bean (*Ricinus communis* L.)	Castor semi-looper (*Achaea janata* L.)	Anti-feedant	Rani and Pratyusha, 2014
Secoisolariciresinol, secoisolariciresinol diglucoside and (Lignans)	Linseed (*Linum usitatissimum)*	Green peach aphid (*Myzus persicae)*	Toxic causing mortality	Saguez et al., 2012
3Deoxyanthocyanid-in (flavonoid)	Sorgum (*Sorghum bicolor)*	Corn leaf aphid (*Rhopalosiphum maidis)*	Toxic causing mortality	Kariyat et al., 2019
Pisatin (flavonoid)	Pea (*Pisum sativum)*	Peaaphid (*Acyrthosiphon pisum)*	Feeding-deterrent	Morkunas et al., 2015
Quercetin dehydrate and rutin hydrate (flavonoid)	Apple (*Malus domestica)*	Wooly apple aphid (*Eriosoma lanigerum)*	Aphicidal	Ateyyat et al., 2012

Vitisin B (Stilbene)	Grape vine *(Vitis vinifera)*	African cotton leafworm (*Spodoptera littoralis)*	Chronic toxicity, anti-feedant.	Pavela et al., 2017
Vanillic acid, syringic acid, cinnamic acid, and p-coumaric acids (Phenolic acid)	Rice (*Oryza sativa*)	Yellow stem borer (*Scirpophaga incertulas),* leaf roller *(Cnaphalocrosis medinalis),* and brown plant hopper *(Nilaparvata lugens)*	Toxic	Rani and Jyothsna, 2010
Ferulic acid	Rice (*Oryza sativa*)	Resistance against brown planthopper (*Nilaparvata lugens)*		Yang et al., 2017
Burchellin, podophyllotoxin, pinoresinol,	Sesame (*Sesamum indicum*), *Aniba burchelli,*	Triatomid bug (*Rhodnius prolixus)*	Anti-molting	Garcia et al., 2000

sesamin, licarin A, or nordihydroguaiaretic acid (Lignans)	chinaberry (*Melia azedarach*), *Licaria aritu*, chaparral (*Larrea divaricate*) and Mayapple (*Podophyllum peltatum)*			
Pinoresinol + podophyllotoxin derivatives (Lignans)	Chinaberry (*Melia azedarach)*	Milkweed bug (*Oncopeltus fasciatus)*	Anti-molting	Cabral et al., 1999
combretastatin A-4, 4,4′-dihydroxystilbene, resveratrol and 3,3′,5,5′-tetrahydroxy-4-methoxystilbene	*)* Izote (*Yucca persicola)*	Fall armyworm (*Spodoptera frugiperda)*	Toxin	Torres et al., 2003

Caffeic acid and chlorogenic acid	Cotton (*Gossypium hirsutum*)	Corn earworm (*Helicoverpa zea)*	Arrest the larval growth and development	Bi and Felton, 1995
Vitisin A and vitisin B (Stilbene)	Grapes *(Vitis vinifera)*	Colorado potato beetle *(Leptinotarsa decemlineata)*	Inhibit larval growth, chronic toxicity and anti-feedant,	Gabaston et al., 2018
b. Polyphenols mediated interactions with insect herbivores that enhance herbivore traits				
Phenolic glucosides and tannins	Almond willow *(Salix triandra* L.)	Shrank leaf beetle (*Gonioctena linnaeana)*	Feeding stimulant	Niemi et al., 2005
Phenolic glucoside (tremulacin 1.5%)	Willow*(Salix. rosmarinifolia)*	Shoot gallow sawfly *(Euura lasiolepis)*	Oviposition stimulant	Roininen et al., 1999
Isoquercitrin, Quercetin and	Chickpea *(Cajanus cajan)*	Cotton bollworm *(Helicoverpa armigera)*	Feeding stimulant	Green et al., 2003

quercetin-3-methyl ether				
Flavonoids	Milkweed (*Ascelpias curassavica* L.)	Monarch butterfly *(Daunus plexippus*)	Oviposition stimulant	Baur et al., 1998
Flavonoid glycoside, rutin (pentahydroxy-flavone-3-rutinoside	Lettuce (*Lactuca sativa)*	American grasshopper *(Schistocerca Americana)*	Feeding stimulant	Bernays et al., 1991
Quercitrin, iso-quercitrin and rutin (Flavonoid)	Cotton (*Gossypium hirsutum)*	Corn earworm *(Heliothis zea)*	Feeding stimulant	Shaver et al., 1969
Flavanol glycosides and quercetin	Narrow leaf wedge (*Vicia angustfolia* L.)	Bean aphid (*Megoura crassicauda*)	Stimulate probing	Takemura et al., 2002
Flavonoids (aglycones, quercetin and myricetin	Crown vetch *(Coronilla varia)* and Alfalfa *(Medicago sativa)*	Blue butterfly *(Polyommatus icarus)*	Sequestration in wings (mate recognition)	Schittko et al., 1999

Flavonoids	Mulberry (*Morus alba)*	Silk moth *(Bombyx mori)*	Sequestration in pupae	Fujimoto et al., 1959
Flavone C-glycosides	Crown vetch *(Coronilla varia)*	Larvae of lycaenid butterfly (*Polyommatus bellargus)*	Sequestration in wings	Geuder et al., 1997
Flavone glycoside, luteolin glycoside	Carrot *(Daucas carota)*	Black swallowtail butterfly (*Papilio polyxenes)*	Oviposition stimulant	Feeny et al., 1988
Quercetin and rutin	Milkweeds (*Asclepias curassavica*)	Female monarch butterfly (*Danaus plexippus)*	Oviposition stimulant	Haribal and Renwick, 1996
Flavonoid glycosides	St John’s Wort (*Hypericum* Spp.)	*Tenthredo zonula*	Sequester compounds in larval body.	Crockett and Boeve, 2011
Flavonoids	Kale (*Brassica oleracea* var. *acephala*)	*Pieris brassica*	Sequestration	Ferreresa et al., 2009

Trans-chlorogenic acid	Wild parsnip, (*Pastinaca sativa*) (Apiaceae),	*Papilio polyxenes*	Oviposition stimulant	Carter et al., 1998

Table 1: Major polyphenolic compounds present in plants mediating insect plant interactions. These compounds are widely distributed in different plant parts, defending plants from insect herbivores and in some cases, increasing the survival of insect herbivores through multiple modes of action.

Plant	***Plant part***	***Types of compounds***	***Reference***
Rice (*Oryza sativa*)	Rice straw	Phenolic acids (*p*-hydroxybenzoic, vanillic, coumaric, syringic, ferulic acid)	Kuwatsuka and Shindo, 1973
Soybean (*Glycine max*)	Seed	Phenolic acids (Syringic, ferulic and vanillic acids)	Maga and Lorenz, 1974
Cotton *(Gossypium hirsutum)* L.	Leaves	Phenolic acid (Gallic acid, catechin and caffeic acid)	Rani and Pratyusha, 2013

Sunflower (*Helianthus annus*)	Seed	Phenolic acid (Chlorogenic acid)	Mikolajczak and Smith, 1970
Citrus fruits, apple, berries, peaches, fruits, nuts, berries, tea, red wine	Fruit	Flavonoids (Flavanols)	Ross and kasum, 2002; Basli et al., 2012
Red rose (*Rosa indica),* China rose (*Hibiscus rosachinensis*),	Flowers	Flavonoids (Anthocyanins)	Khoo et al., 2017
Rice bran	Flowers	Flavonoids (Flavone)	Cai, 2005
Soybean, alfalfa, red clover, chickpeas, peanut	Seeds and vegetables	Flavonoids (Isoflavones)	Panche et al.,
Tea leaves (black tea and oolong tea)	Leaves	Flavonoids (Catechins)	Leung et al., 2001
Sesame *(Sesamum indicum)*	Seed	Lignan (Furofuran lignan)	Moazzami et al., 2007
Tea (*Thea* sp.)	Leaves	Lignans (Matairesinol and secoisolariciresinol)	Mazur et al., 1998

Conifers	Roots, bark and needles	Stilbene (Trans-astringin and trans-isorhapontin)	Underwood et al., 1991

Table 2: Main classes of polyphenols and their localization in different plant parts.

Figures

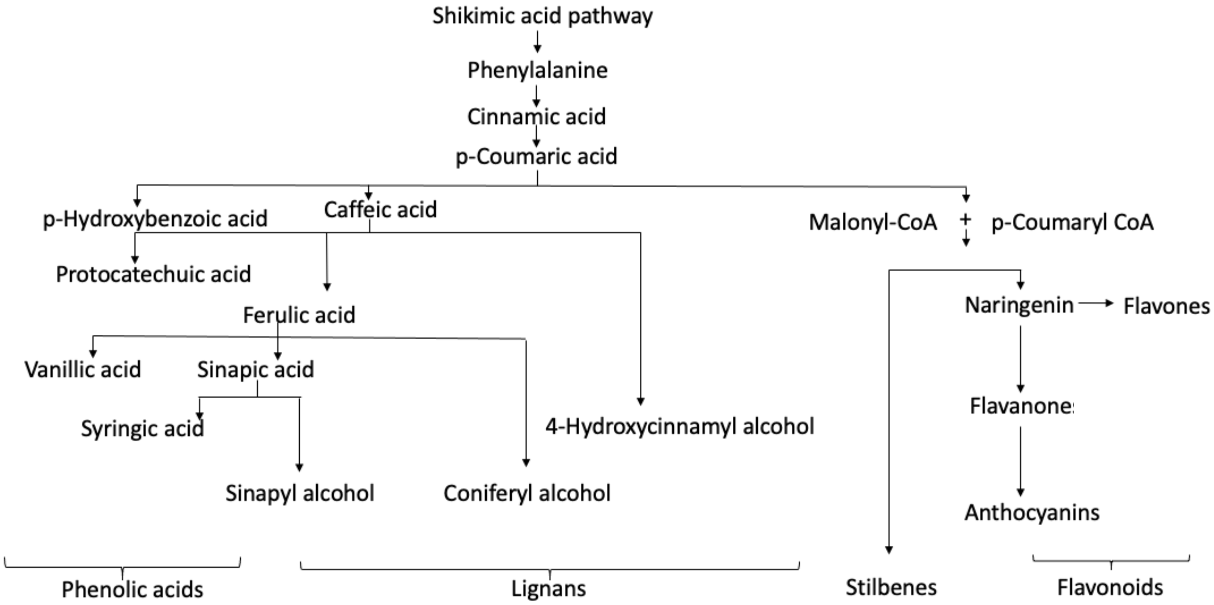


Figure 1: Basic classification and synthesis outline of major polyphenol classes in plants.

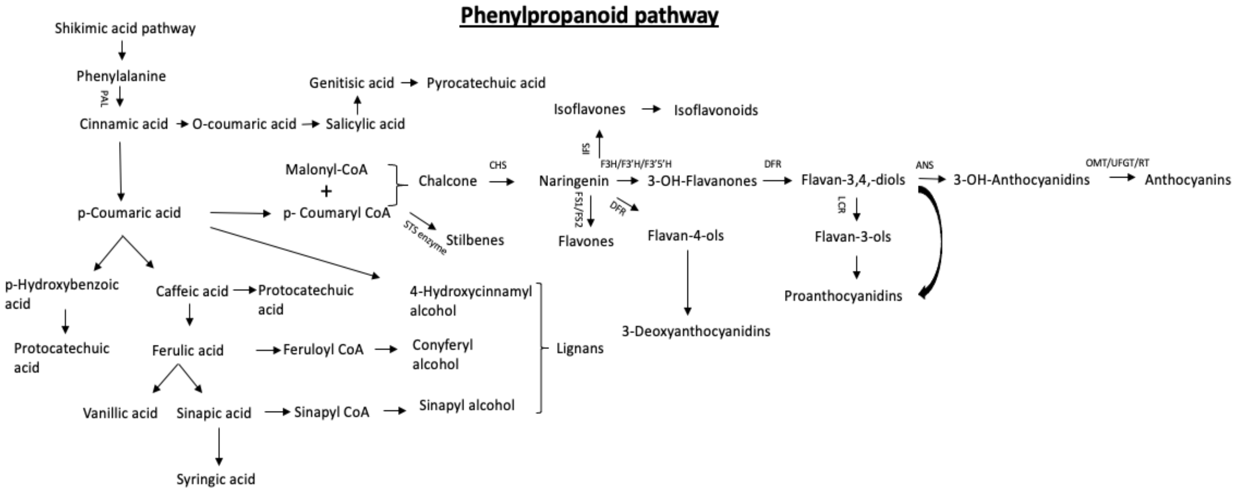


Figure 2: . Schematic of phenylpropanoid pathway leading to synthesis of different polyphenols i.e., phenolic acids, flavonoids, stilbenes and lignans by the action of various enzymes.

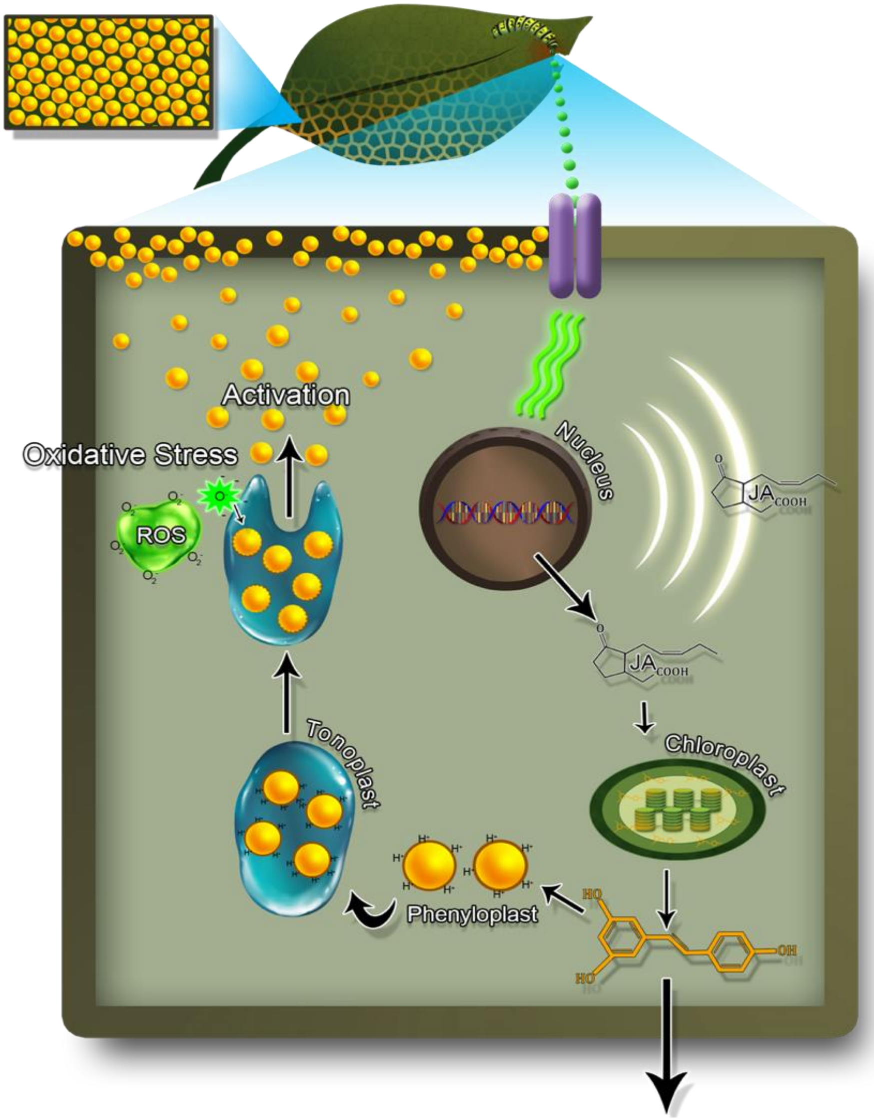


Figure 3: Schematic representation of signaling cascade after insect herbivory at the cellular level inside a plant cell. The regurgitant of caterpillar that includes contents from salivary gland and gut consists of fatty acid conjugates, β-glucose oxidase, peroxidase that acts as elicitors. Elicitors binds with the receptors on cell membrane and cause biochemical changes in the cell culminating in gene expression and the activation of octa-decanoid pathway (Louis et al., 2012) which upregulates defense- related genes followed by down-regulation of photosynthesis genes. The upregulation of defense genes that encodes proteins can be broadly classified into three categories- defense genes which produce anti-nutritional proteins and the enzymes involved in shikimate-phenylpropanoid pathway producing secondary metabolites, proteinase inhibitors which are involved in cross-linking and polymerization of cell walls and the third includes phytohormone signaling pathway genes for i.e., jasmonic acid, salicylic acid and ethylene. Jasmonic acid moves to plastid/chloroplast to activate the chief enzyme of shikimate

pathway i.e., Phenylalanine Ammonia Lyase (PAL). Most of the polyphenol biosynthesis takes place in plastids, however flavonoid production occurs either in the cytoplasm or the cytoplasmic surface of endoplasmic reticulum (Eigenbrode and Trumble, 1993). PAL in the stomata which diverts amino acids from primary metabolism toward the formation of secondary metabolites including a diverse set of polyphenols (Seram, 2019). Some polyphenols are shuttled outside the cell to act as anti-feedant or anti-deterrent to ward-off the herbivory, while others are stored inside the tonoplast of cells for quick-future action. These polyphenols are compartmentalized by converting them into inert and reduced state called phenyloplast, protected inside the tonoplast. During the successive herbivore attack, the regurgitant of herbivores that activates reactive oxygen species generates oxidative stress in the cell, leading to dissolution of compartments and release of polyphenol oxidase. Polyphenol oxidase can form quinones which act as anti-nutritional proteins interfering with digestibility and nutrient uptake of insects or produce proteinase-inhibitors leading to cross-linking and polymerization of cells leading to herbivore defense. Illustration by Annette Diaz, conceptualized by Ishveen Kaur and Japneet Kaur.

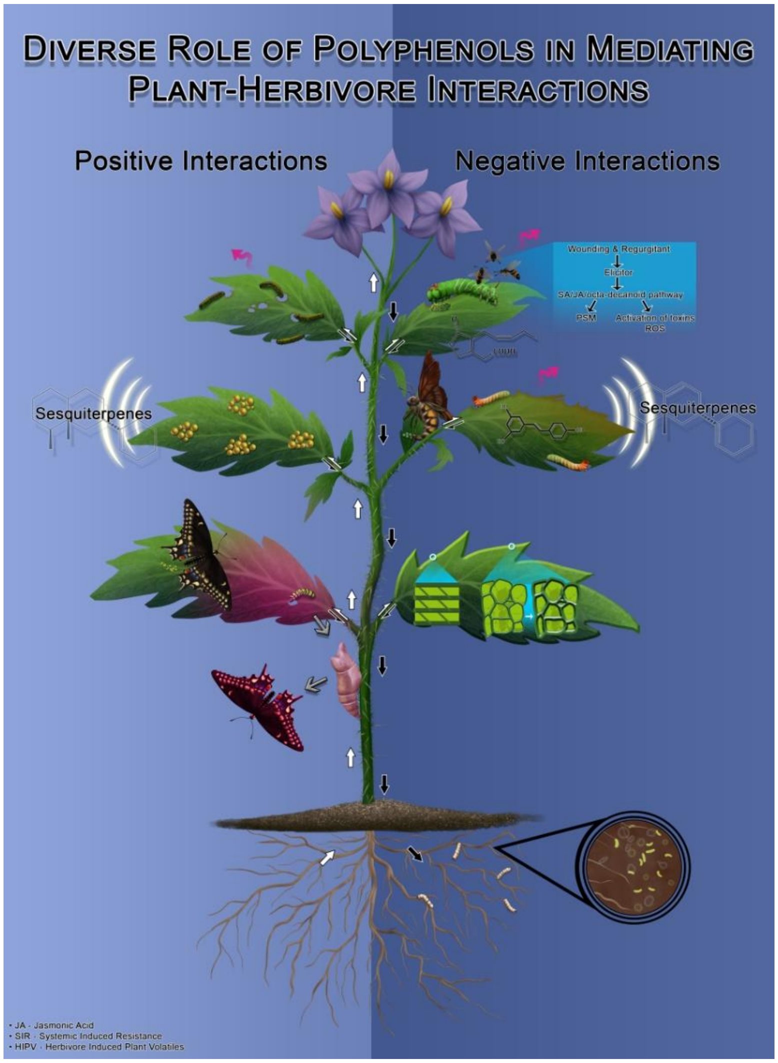


Figure 4: Schematic illustrating the wide gamut of herbivory related functions performed by polyphenols in plants. Plants produce polyphenols at the advent of adverse conditions such as biotic and abiotic stresses. Herbivory causes abrasions, wounds, and tissue loss which act as signal for the production of polyphenols. Moreover, the saliva or regurgitant from herbivores contain peroxidases which act as elicitors for the activation of different signaling pathways (Tian et al., 2013). These secretions activate different plant hormones and signaling pathways such as jasmonic acid, salicylic acid and octadecanoid pathway (Seram, 2019) which generate and transmit signals to all the parts of plants which is depicted by bi-directional arrows running throughout the plant leading to generation of Systemic Induced Resistance (SIR) in the plants (Lagrimini et al., 1993). The production of polyphenols also leads to synthesis of sesquiterpenes for defense priming of the neighboring plants. Both positive and negative impacts are being illustrated on the plant with left and right sides of the schematic respectively. Polyphenols generally have anti-feedent and anti-deterrent effect on most of the insects. Flavonoids (class of polyphenols) and tannins have cascading effects on the feeding and oviposition activity of tobacco hornworm caterpillar (*Manduca sexta* L.; Tayal et al., 2020a,b), also protects plants

against the damaging herbivores by releasing herbivore-induced plant volatiles (HIPV) attracting their predators and parasitoids (Schultz et al., 1992). Activation of defense mechanisms also leads to the production of reactive oxygen species (ROS) which ultimately lead to the formation of polyphenol oxidase and subsequent synthesis of compounds such as proteinase inhibitors preventing the digestibility of tissues by cross-linking and polymerizing the cells walls with alkylated amino acids. Polymerization of cinnamyl alcohol into lignin by polyphenol oxidase (formed due to activation and synthesis of polyphenols) deposits lignin in leaves and fruits which also confers resistance to the plants (Green et al., 1972). These chemical toxins are also observed to have negative impacts on activity and functionality of microbes, thus indirectly affecting their symbiotic insects as well (Hoffmann-Compo et al., 2001). Polyphenols are also observed to affect the herbivores positively; thus, playing dual role in plant-insect relationship dynamics. Flavanone glycosides present in carrot (*Daucus carota* L.; Apiaceae) acts as oviposition stimulant for black swallowtail butterfly (*Papilio polyxenes* Fabricius) by releasing volatiles which attract the insects to lay eggs (Lv et al., 2014), and sequestration of flavone glucosides in the wings of lycaenid butterfly (*Polyommatus bellargus* Rottemburg) aiding them in visual communication and mate recognition. Illustration by Annette Diaz, conceptualized by Ishveen Kaur and Japneet Kaur**.**

CHAPTER II

EXPOSURE TO POLYPHENOL-RICH PURPLE CORN PERICARP EXTRACT RESTRICTS FALL ARMYWORM *(SPODOPTERA FRUGIPERDA)* GROWTH

This chapter has been previously published as ‘Exposure to Polyphenol-Rich Purple Corn Pericarp Extract Restricts Fall Armyworm *(Spodoptera frugiperda)* Growth’ in ‘Plant Signaling and Behavior’ journal. Below is the link to the paper:

Sukhman Singh & Rupesh R. Kariyat (2020) Exposure to polyphenol-rich purple corn pericarp extract restricts fall armyworm *(Spodoptera frugiperda)* growth, Plant Signaling & Behavior, 15:9, DOI: 10.1080/15592324.2020.1784545

Figure 5: This figure was selected as cover photo for the Issue number 9 (2020) in 'Plant Signaling and Behavior' Journal. Fall armyworm caterpillar image (*Spodoptera frugiperda*). Link to Volume and Issue:

https://www.tandfonline.com/toc/kpsb20/15/9?nav=tocList

Abstract

Bioactive compounds such as polyphenols in plants have been well studied for their potential insecticidal activities. These are considered as safe alternatives against chemical pesticides because of their lower persistence in environment, lower toxicity to humans and other organisms. However, they are present constitutively in lower amounts in plants and have to undergo complicated extraction methods – hampering their commercial exploitation in pest management. Using an inexpensive extraction method developed to recover polyphenol-rich liquid extract from purple corn pericarp, we recently documented that this extract has anti-feeding effects that cascade from larval to adult stages in a model herbivore tobacco hornworm (*Manduca sexta*). However, *M. sexta* does not feed on corn or any other major crops other than the species in the nightshade family (Solanaceae). In this study, we explored the same idea but using a generalist and common herbivore on corn, the fall armyworm (*Spodoptera frugiperda*). We found that purple corn pericarp extract inhibited the larval growth and development as well as negatively affected the pupal stages of *S. frugiperda*. However, unlike on *M. sexta*, time to complete larval life cycle was unaffected. Our findings confirm the toxicity of this extract on a generalist, economically important herbivore, but also suggest potential species-specific effects that should be explored further

Main Text

Insect herbivory is ubiquitous in both natural and agricultural ecosystems (Sharma et al., 2009; Vandenborre et al., 2011). Annually, arthropod pests are estimated to reduce crop yield by ~15%, making it a key concern in agriculture, and hence food security (Mitchell et al., 2016). Advances in organic and analytical chemistry have provided us with a tremendous variety of synthetic pesticides, that have improved crop yield across the world, in multiple cropping systems. However, the excessive use of such pesticides has also led to collateral damage in the form of contamination of water bodies, biomagnification, pesticide residue in organisms leading to sub-lethal and lethal effects (Portmann et al., 1975; Dubey, 2011; Mitra et al. 2011; Chaudhary, 2017). For example, recent meta-analyses have revealed that maternal parent exposure to pesticides contributes as a risk factor for leukemia (Han et al., 2019; Yang et al. 2020). In addition, the advent of organic agriculture and its documented benefits for human health has warranted a renewed interest in finding natural and sustainable methods for pest management (Kaur et al., 2020), with bioactive plant products being a key player (Gupta and Dikshit, 2010; Dubey, 2011).

Employing bioactive plant compounds against pests is nothing new. From the early discoveries of the potential use of nicotine as an effective pest deterrent, scientists have made huge strides in using plant extracts in pest control (Yamamoto, 1999). Polyphenols, a major group of secondary metabolites in plants has been well documented to have insect deterrent properties (Shibutani and Samejima, 2004; Morkunas et al., 2015; Kariyat et al., 2019; Tayal et al., 2020a). For example, chlorogenic acid in yellow maize (*Zea mays* Family: Gramineae) has been found to have anti-feeding properties against European corn borer *(Ostrinianubilalis*;

Crambidae) (Mao et al., 2007). Additionally, secondary metabolite compounds present in arruda (*Ruta graveolens* Family: Rutaceae) leaves have been reported to have insect repellent properties against maize weevil (*Sitophilus zeamais*; Curculionidae) (Perera et al., 2017).

However, the relatively low amounts of polyphenols present in plants, and tedious and complicated methods of extraction have hampered commercial exploitation of these compounds in pest management. Recently Li et al. 2017, devised an inexpensive method to extract polyphenols from purple corn pericarp (*Zea mays* Family: Gramineae), a byproduct of corn processing (Li et al., 2017). Purple corn is native to Andes region of Peru and has been found to be rich in anthocyanins, a family of polyphenolic compounds that imparts purple, red or blue pH-dependent pigmentation in corn. Recently, atotal of ~4710.08 ± 43.13 mg cyanidin-3-O-glucoside (anthocyanin) per kg dry corn was quantified from purple corn (Tayal et al., 2020a). Using the pericarp recovered through dry milling and extracted through this method, we recently showed that feeding on this extract infused artificial diet can severely impact the growth and development of model herbivore tobacco hornworm caterpillar (*Manduca sexta*; Sphingidae) (Tayal et al., 2020a). More specifically, we found that feeding on this extract added diet inhibited egg hatching, caterpillar growth and development (Tayal et al., 2020a). In addition, these larval effects can cascade to pupal and adult stages, affecting their pupal mass and adult oviposition (Tayal et al., 2020b). Moreover, eggs hatched from oviposition of purple corn extract fed adults gained less mass compared to the adults fed on control diet. Collectively, these results show that a byproduct of pigmented corn processing has the potential to be an effective pest deterrent both in vitro (diet experiments) and in vivo (sprayed on plants).

A drawback of these experiments was regarding the herbivore choice. While *M. sexta* is an excellent model system to study dietary effects of plant defenses (Kariyat et al., 2017b; Kariyat et al., 2019), and provides ample opportunity to examine toxic effects specific to instars and different life stages (Portman et al., 2015), the species is also a specialist herbivore on Solanaceae (night shade) family. And, there are no reports on *M. sexta* successfully feeding on corn or other important members of Gramineae. The rationale for using *M. sexta* for those experiments was to prove the concept of polyphenol-rich pericarp extract toxicity on herbivores in general, so that further detailed experiments can be followed up using multiple herbivores that differ in their feeding habits (generalist vs. specialist) and feeding type (chewing vs. biting).

To test this, we repeated the growth and development experiments to test the effects of polyphenol-rich pericarp toxicity on fall armyworm (FAW) (*Spodoptera frugiperda*; Noctuidae), a common herbivore of corn and other Gramineae species that cause significant damage. Additionally, FAW also feeds on other numerous plant families and therefore is considered as one of the most important generalist herbivores causing significant economic losses (Padhee and Prasanna, 2019). The caterpillars feed on leaf whorls and deposit frass causing both foliar damage and microbial infection (Ray et al., 2015). Similar to the previous experiment, we made pericarp extract by steeping 5 g pericarp in 100 ml deionized water and incubated at 52°C for 24 h at 100 rpm. After steeping, extracts were centrifuged at 5000 rpm for 5 min and filtrate obtained were used to prepare artificial diet to rear insect pest under study, i.e. *S. frugiperd*a (Tayal et la., 2020a). We used a wheat germ-based FAW diet and FAW caterpillars were purchased as eggs from Benzon Research Inc., laboratory in the Cumberland county, PA, USA. The eggs were incubated at 78°F and 65% relative humidity (Perkins, 1979).

Once hatched, the caterpillars were first allowed to grow on artificial diet without extract until they were 5–7 d old. This was done to ensure that while managing the caterpillars, they do not die of other causes due to their fragility since they had to be handled individually every day for mass measurements. To examine the insecticidal properties of corn pericarp extract on *S. frugiperda* we fed newly molted third instar caterpillars on artificial diet mixed with purple corn pericarp extract. To prepare 1 kg diet, 875 ml water was boiled by adding 19 gagar and blended with 144 g wheat germ-based diet and 40 ml purple corn pericarp extract (for details, see Tayal et al., 2020b). Following the same methodology, we prepared control diet without the extract. Twenty individual caterpillars were placed on 1 cm^3 cube of artificial diet in plastic cups (Product #9091, Frontier Agriculture Sciences, Newark, DE, USA) covered with lids. To test the effects of two different treatments, data on caterpillar mass (in grams) was collected daily using a digital weighing balance (Accuris Dx W3101A-220, Mid Sci, Valley Park, MO, USA) until they pupated, and this was used to calculate mass gain using the equation: mass gain = (final mass – initial mass)/initial mass (Kariyat et al., 2017b). Cups were cleaned daily by removing frass and replacing old diet with new diet pellets to ensure infection-free hygienic conditions for caterpillar growth and development. After they pupated, data of time to pupate (in days), and pupal mass using weighing balance (Accuris Dx W3101A-220, Mid Sci, Valley Park, MO, USA) (in mg) and pupal length using manual Vernier caliper (in cm) was also collected.

In total, we did eight mass measurements of 19 *S. frugiperda* caterpillars, until they pupated. Out of total 20 caterpillars initially kept on diet, one caterpillar died in each treatment during first mass gain and we excluded them from the analyses. Remaining 19 caterpillars successfully pupated. We used this data to compute two types of mass gains; computing each mass measurement with the previous mass to determine variation in per day mass gain and comparing each mass with initial mass to determine gain relative to starting mass. This helped us to eliminate any confounding mass variation in the starting population of caterpillars. Those mass gains in which data was normally distributed were analyzed using t-test while in which was not normally distributed, were analyzed using Kruskal–Wallis test. After analysis of mass gains over previous mass and comparing each mass with initial mass, we found that there were no significant differences in mass gain between instars (Figure 1a). However, there was a general trend that caterpillars on control diet were gaining more mass than on purple corn extract. The trend became much stronger and significant when we compared mass gain of each mass with the first mass measurement (Table 1; Figure 1b). It was clear that the extract negatively impacted early mass gain and these differences cascaded through the late instars, a trend we have also observed in *M. sexta* (Tayal et al., 2020a).

Further, to examine whether these differences translate into pupal stage we also measured pupal mass and pupal length, and time in days to pupate. We found that pupal mass of purple corn pericarp extract diet-fed caterpillars was significantly lower than those on control diet [T-test T = 2.08; *P* value = .04; Figure 2a)]. Also, pupal length was significantly lower in purple corn pericarp extract-fed caterpillars compared to caterpillars fed on control diet (Kruskal–Wallis test H = 5.68; *P* value = .017; Figure 2b). However, both set of caterpillars use similar number of days to pupate from the start of the experiment (Kruskal–Wallis test H = 0.12; *P* value = .73; Figure 2c). Taken together, our results clearly show that purple corn pericarp extract had a negative effect on the larval and pupal stages of *S. friguperda*. We have previously documented that these inhibitory effects are primarily driven by the polyphenol-rich pericarp that mainly has anthocyanins, flavonoids, and tannins. We also found that these effects cascade into pupal stages affecting pupal mass.

It is well-understood that the quality of larval diet affect insect growth and development (Bauerfeind and Fischer, 2005a; 2009) not only in larval but also in subsequent stages (Bauerfeind and Fisher, 2005b). From these results, we can speculate that it will also affect the adult eclosion, mass, and fecundity as well because it is directly correlated with pupal mass (Gilbert, 1984), which we observed in *M. sexta* with similar treatments (Tayal et al., 2020b). Increased concentration of secondary metabolites in insect diet has been found to effectively reduce larval growth rate (Smilanich et al., 2011; Mao et al., 2007). Additionally, Torres et al., 2003 reported high mortality in *S. frugiperda* caused by polyphenol-rich extracts obtained from *Yucca persicola* (Family: Asparagaceae), while the extracts obtained from *Reynoutria spp*. (Family: Polygonaceae) inhibited the growth of *S.littoralis* (Noctuidae) (Torres et al., 2003; Pavela et al., 2017). Several studies have reported that polyphenolic compounds present in plants negatively affects the growth and development of insect herbivores (Lane et al., 1987; Santiago et al., 2005; Tayal et al., 2020a), despite the fact that their respective mode of action varies from compound to compound based on the origin, structure, biosynthesis, and concentration in different plants. Our results suggest that either the compounds present in purple corn pericarp act as an antifeedant or toxic against insects, but actual underlying molecular mechanisms and mode of action still need to be explored.

In conclusion, the results from our previous studies (Tayal et al., 2020a,b) and present study signify the importance of purple corn pericarp as a potential biopesticide against specialist as well as generalist insect herbivores. Furthermore, we are planning field experiments to check the persistence and efficiency of spray application of purple corn extract and we speculate that both purple corn and extract sprayed plants in general will have an impact on multi-trophic interactions. A major take away from the experiment is that we were able to confirm the negative effects observed in the model herbivore *M. sexta* on FAW, a common and a devastating pest that causes huge economic losses (Ray et al., 2015). However, we also found that there are species-specific differences, clearly suggesting possible physiological modifications in play. Identifying these mechanisms and targeting them would be an additional line of research for the development of cheap, efficient, and innovative ways of pest management.

Tables

Larval mass gain over initial mass	***Test***	***Test statistics***	***P value***
Mass gain 1	Kruskal-Wallis test	1.19698	0.2313
Mass gain 2	t-test	-0.69648	0.4906
Mass gain 3	t-test	-2.1196	0.0418
Mass gain 4	t-test	-1.49914	0.1428
Mass gain 5	t-test	-2.59089	0.014
Mass gain 6	t-test	-3.28658	0.0023
Mass gain 7	t-test	-3.08766	0.0039

Table 3: Kruskal–Wallis and t-test results of larval mass gains over initial mass. Values in bold denotes statistical significance at *P<0.05*.

Figures

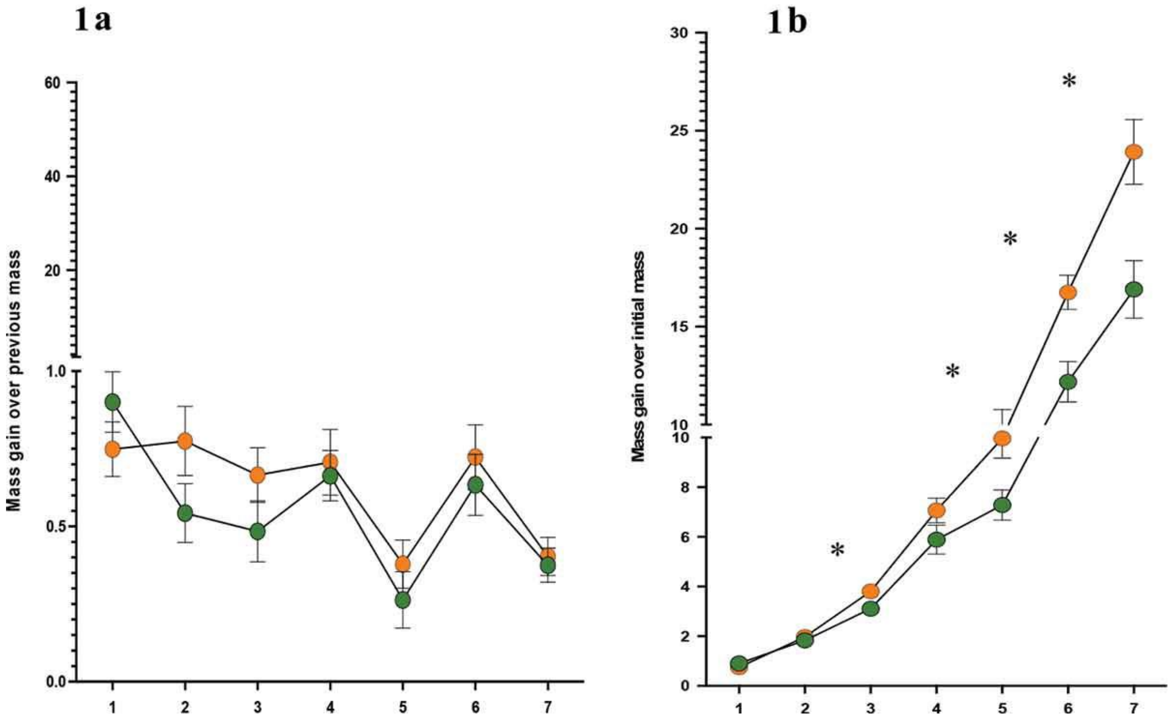


Figure 6: Results of Kruskal–Wallis/t-tests showing effects of purple corn pericarp extract on: (1a) the larval mass gain over previous mass and (1b) mass gain over initial mass in *S. frugiperda*. Means are shown by different colors. Green and orange dots for larval mass gain in caterpillars fed on purple corn pericarp extract and control diet, respectively. Means shown by asterisk in figure are significantly different ($p < .05$). X-axis denotes number of times mass gain was calculated. Nineteen is the sample size to calculate the mass gain.

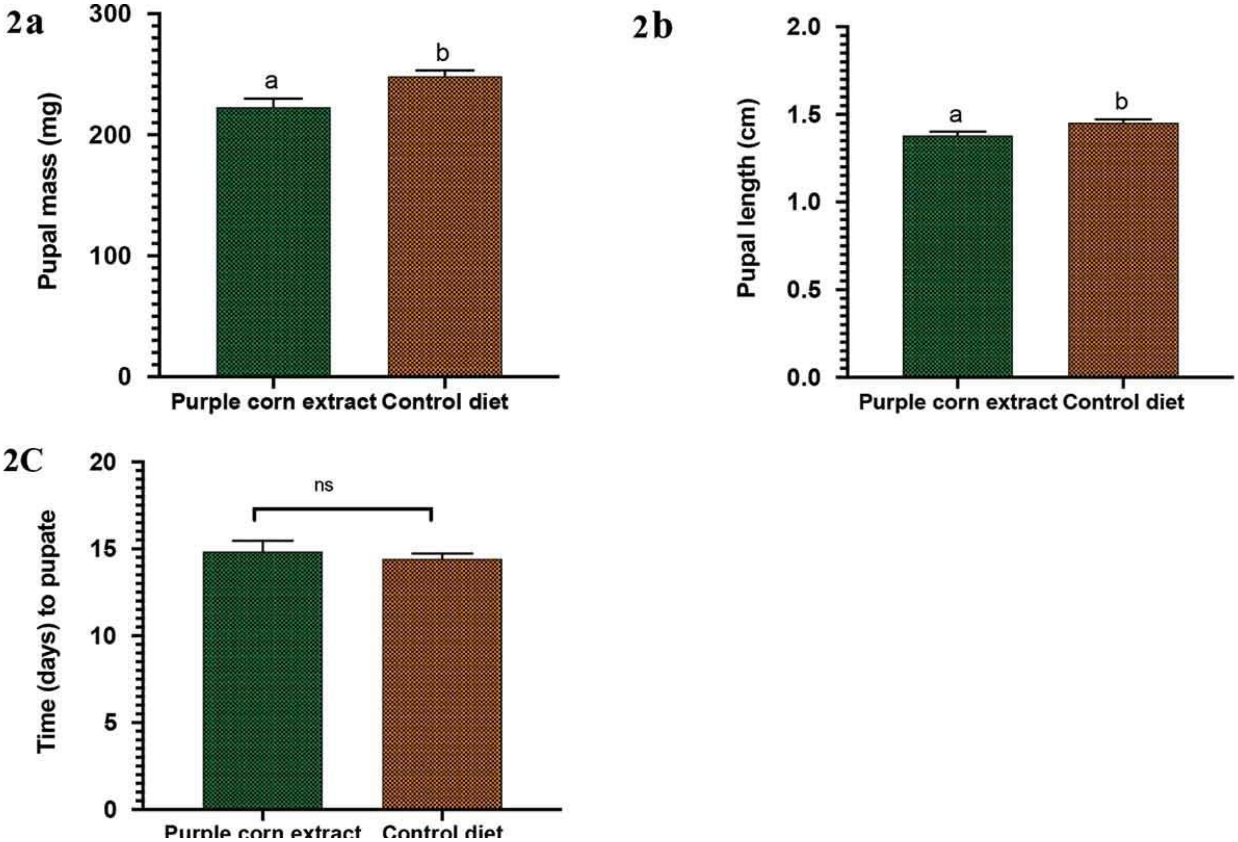


Figure 7: Results showing effects of purple corn pericarp extract on: (2a) the pupal mass (t-test), (2b) pupal length (Kruskal–Wallis test) and (2c) time to pupate in *Spodoptera frugiperda* (Kruskal–Wallis test). Means shown by different letters are significantly different at $P < .05$, while means shown by same letters are not significantly different at $P < .05$. Nineteen is the sample size to calculate the pupal mass and length and time to pupate.

CHAPTER III

OVIPOSITION SUCCESS IS INFLUENCED BY LARVAL EXPOSURE TO HOST DEFENSE VARIATION IN TOBACCO HORNWORM (*MANDUCA SEXTA*)

Abstract

Oviposition is critical for insect success but also signals the threat of imminent herbivory to their host plants. However, research on plant-herbivore interactions have been disproportionally focused on larval stages, and whether variation in plant defenses can affect an insect's oviposition success warrants more attention. To test this, tobacco hornworm (*Manduca sexta*), a specialist on Solanaceae, was reared on three different diets: a combination of four *Solanum* species (*S. retroflexum*, *S. melanocerasum*, *S. aethiopicum* and *S. melongena*), tomato (*S. lycopersicum*), and a wheat germ based artificial diet (control; AD), and we examined whether diet treatments affect mass, life span, oviposition, and egg hatching. These experiments were followed up by also examining plant defenses using a spectrophotometer based polyphenol oxidase (PPO) quantification, a key enzyme in plant defense against herbivores, and a scanning electron microscope based assessment of leaf trichome density. Our results show that *M. sexta* reared on tomato gained less pupal, as well as adult, mass and had a significantly shorter life cycle when compared to AD and the four *Solanum* species. However, more number of eggs were laid per day by *M. sexta* reared on tomato followed by AD and four *Solanum* species. Additionally, egg hatching rate was also higher on tomato than both AD and four *Solanum*

species. And, both PPO activity and trichome density were significantly higher in four *Solanum* spp., when compared to tomato, suggesting plant defense traits can also have delayed effects, in this case on adults traits. Taken together, our results suggest that defense variation in diet plays a significant but differential role in development, oviposition as well as progeny success

Introduction

Oviposition is critical to insect fitness and is key to their success (Rosenheim et al., 1999 a,b). On the other hand, oviposition is a warning to host plants on imminent herbivory (Voirol et al., 2020), leading to a suite of defenses ranging from necrosis to defense gene expression, and the release of volatile organic compounds that attract predators and parasitoids (Meiners and Hilker, 2000; Desurmont and Weston, 2011; Fatouros et al., 2012; Hilker and Fatouros, 2015; Bertea et al., 2020). For instance, oviposition by plant hopper species (*Nilaparvata lugens, Sogotella furcifera and Laodelphax striatellus*) on rice plants (*Oryza sativa,* Family: Poaceae) lead to formation of watery lesions which produce ovicidal compounds (Seino et al., 1996; Suzuki et al., 1996). Additionally, production of oviposition-induced plant volatiles has been reported in many species including maize (*Zea mays*, Family: Poaceae) against lepidopteran insects, which attract *Trichogramma sp.,* an egg parasitoid (Romeis et al., 2005; Tamiru et al., 2012). However, since larval stages are the chief destructors of plant tissue, research on plant defenses and herbivores has been disproportionately focused on larvae and larval traits (Shukle and Murdock, 1983; Tumlinson and Engelberth, 2008; Kariyat et al., 2016; 2017 a,b) when compared to oviposition.

To defend against herbivores, plants employ an array of indirect and direct defenses. Indirect defenses include the production of volatile organic compounds, which attract parasitoids and predators of insect herbivores (Moraes et al., 1998; Mccormick et al., 2012; Kaur and Kariyat; 2020). Direct defenses include trichomes, spines and waxy cuticle, which are structural defenses, and toxic chemical compounds such as alkaloids, flavonoids, and many other secondary metabolites, which are chemical defenses (Howe and Jander, 2008; Hauser, 2014). For instance, Kariyat et al., (2017) reported that feeding of tobacco hornworm (*Manduca sexta*) in carolina horsenettle (*Solanum carolinense*; Solanaceae) was negatively affected by the presence of stellate trichomes, which when ingested also led to the tearing of their peritrophic matrix (Kariyat et al., 2017b). Additionally, we recently found the inhibitory effects of polyphenols on the growth and development of *M. sexta*, and *Spodoptera frugiperda* (fall armyworm; Noctuidae), not only in larval stages but also in pupal and adult stages (Tayal et al., 2020 a,b; Singh et al., 2020). Taken together, it is clear that plants have a tightly regulated herbivore-specific defense system that can negatively impact herbivore growth and fitness, and possibly cascades from larval to adult stages. However, most of these studies on larval stages tend to ignore the consequences or such effects of these defenses on the oviposition success of adults.

It has been well understood that the quality of the parental diet is important for the growth of their progeny (Azevedo et al., 1997; Mousseau, 1998; Vijendravarma et al., 2009; Portman et al., 2020). Poor nutritional quality of diet can negatively impact the growth and development not only of the parents, but also their progeny (Tayal et al., 2020b). Vijendravarma et al., (2010) reported that one generation of *Drosophila melanogaster* that fed on poor quality diet lead to eggs heavier but smaller in size (Vijendravarma et al., 2009). Portman et al., (2015; 2020) showed that intraspecific variation in host plant quality can lead to reduced flight muscle development in adults, with possible impacts on adult dispersal (Portman et al., 2015; 2020).

Therefore, it is reasonable to expect that plants with a wide range of defenses including direct and indirect, constitutive and induced, against insect herbivores (Howe and Jander, 2008) could negatively impact the growth and fitness of the next generation of herbivores.

In general, most studies show that adult size positively correlates with insect fecundity (Gilbert, 1984; Wasserman and Mitter, 1978; Deseo, 1971). However, the proximate reasons for size variation can be heavily influenced by various factors including host plant quality (Leather, 1988), and can in many cases produce offsprings that vary in their functional traits. For example, in sawfly (*Neodiprion sertifer*; Diprionidae), heavier adults produced more number of eggs but are less fertile than the smaller adults (Heliovarra et al., 1990). On the other hand, in aphids such as the black bean aphid (*Aphis fabae*; Aphididae), larger aphids have slower rate of reproduction but more fertile young ones than the smaller aphids (Taylor, 1975). And, age of adult is also correlated with fertility of eggs they lay, and fitness of their next generation, and it has been found that in Lepidoptera, older females lay eggs having lower fertility when compared to young females (Wiklund and Persson, 1983; Leather, 1984; Gordon and Stewart, 1988). For example, in almond moths (*Carda cautella*; Pyralidae) eggs laid on day 1 were found to be more fertile (80% fertile eggs) as compared to eggs laid on day 8 (20% fertile eggs) (Gordon and Stewart, 1984). The same was observed in the speckled wood butterfly (*Pararge aegeria*; Nymphalidae) (Wiklund and Persson, 1983). Again, when compared to larval traits, not much is known about the effects of host plant quality on the fecundity of insect eggs.

Taken together, examining oviposition success and progeny growth is critical to understanding plant defense response and herbivore fitness. To test this, we conducted a set of experiments using *M. sexta* caterpillars (specialist herbivore in the Solanaceae family) by allowing them to feed on three different diets; tomato (*Solanum lycopersicum)*, a wheat germ based artificial diet (control; AD), and a short exposure (detailed in methods) of 48 hours to a combination of four *Solanum* species; wonderberry (*S. retroflexum*)*,* huckleberry (*S. melanocerasum*)*,* Turkish orange eggplant (*S. aethiopicum*) and white eggplant (*S. melongena*). All these plant species (tomato and other four *Solanum* species) belong to the Solanaceae family, which are known to have a wide range of physical and chemical defenses against insect herbivores (Kariyat et al., 2017a; Flanders et al., 1992; Kant et al., 2004; Kaplan et al., 2009; Kariyat et al., 2019). Tomato has well defined physical and chemical defenses (Stout et al., 1998; Fowler et al., 2009; Tian et al., 2012), and so are the other four other *Solanum* species. For example, *S. retroflexum* is rich in alkaloids, flavonoids and cinnamic acid derivatives (Dlamini and Madala, 2017), as these compounds are known to inhibit larval growth reported in several studies Tayal et al., 2020a; Singh et al., 2020; Mao et al., 2007; Bentivenha et al., 2017). Additionally*, S. aethiopicum* have glandular and nonglandular trichomes and *S. melongena* has been found to elicit volatile organic compounds against *M. sexta* (Alborn et al., 2003; Mcdowell, 2010; Yoshinaga et al., 2014; Taher et al., 2019). Leaf trichomes have been found to significantly affect insect herbivore growth (War et al., 2012) and can have toxic compounds such as terpenoids, flavonoids and alkaloids in them. Additionally, high density of trichomes restrict the movement of caterpillars in their early growth stages. Also, insect growth inhibitor enzymes such as polyphenol oxidase (PPO) and peroxidase are known to oxidize polyphenols and leads to formation of quinones, which reduces the protein digestion in insect herbivores and significantly affects their growth and development (War et al., 2012; Singh et al., 2021). Therefore, to examine whether physical (trichomes) and chemical (PPO) defenses can also play a role in oviposition success, we estimated these defenses in host plants, in addition to *M. sexta* traits.

We hypothesized that *M. sexta* will perform poorly on tomato, and even worse on the four *Solanum* species, two wild species (*S. retroflexum and S. melanocerasum*), and two cultivated species (*S. aethiopicum* and *S. melongena*)], due to their wide variety of plant defenses (Dlamini and Madala, 2017; Mcdowell, 2010; Yoshinga et al., 2014; Taher et al., 2019). On the other hand, artificial diet (AD) is rich in antibiotics, nutrients, and without any toxic chemicals would be best fit for *M. sexta* adult moths, their reproduction and survival of offspring.

Materials and Methods

Plant Material

Hybrid F1 tomato (Variety: Valley girl, Product ID 741; Johnny's selected), *S. retroflexum, S. melanocerasum, S. aethiopicum* and *S. melongena* seeds used in the experiment were purchased from Johnny's Selected Seeds (ME, USA), plant world seeds (Newton Abbot, Devon, U.K.) and amazon.com respectively. Seeds were sown in plastic trays (51.435 cm * 25.4 cm) in potting mixture (Sunshine professional growing mix: Sun Gro Horticulture Canada Ltd., MA, USA). After sowing trays were watered and kept under controlled conditions at 27° C (16 hours light and 8 hours dark) and 65% relative humidity (RH). Emerged seedlings were transplanted at 2-3 true leaf stage into plastic pots. After transplanting they were kept at 27°C (16 hours light and 8 hours dark) and 65% RH. Plants were watered daily to provide optimum moisture conditions. Plants were fertilized after 10 days with organic fish fertilizer (NPK 5:1:1; Alaska Fish Fertilizer, Pennington Seed, Inc., GA, USA). Four to six weeks old tomato and four *Solanum* species were used for experiments. For egg laying, only tomato plants were used to reduce any variation in olfactory or visual cues in oviposition by *M. sexta* (Kariyat et al., 2013).

Artificial diet (AD)

Soy-wheat germ diet was used to prepare artificial diet (AD) for feeding *M. sexta* caterpillars. Artificial diet is composed of the following ingredients: sucrose, soy flour (50%), wheat germ, salt mix (Wesson; rich in Ca, Fe and Na), USDA vitamin premix, fibre, sorbic acid, methyl paraben and ascorbic acid. To prepare 1 liter of general lepidopteran diet, 875 ml water was boiled by adding 19-gram agar and blended with 144-gram soy-wheat germ-based diet (for details see Tayal et al., 2020a; Singh et al., 2020).

Insect colony

Tobacco hornworm (*M. sexta*) eggs were purchased from Great Lakes Hornworm Ltd. Romeo, Michigan, USA and reared under laboratory conditions. We had also established a lab colony with wild caught *M. sexta* periodically introgressed into the colony, used in previous and current work (Tayal et al., 2020a,b; Kariyat et al., 2019). Adult moths obtained from the colony reared on AD were kept for mating in pop-up cages (32cm*28cm*28cm, Popup rearing cage: #1466AB, BioQuip Products, Inc., CA, USA) with tomato plants as host for egg laying. Eggs collected were then allowed to grow and develop on respective treatments (16 hours light and 8 hours dark).

Feeding of *M. sexta* caterpillars on tomato and four *Solanum* species

One hundred newly hatched first instar caterpillars were transferred to tomato plants. Two caterpillars were placed on the leaves of each plant. They were left to feed on plants and were monitored daily to ensure that they are feeding and have enough plant material to eat. After all the leaves from each plant were eaten, caterpillars were transferred to new plants. They were left to feed on plants until late 4th instar and afterwards transferred to AD in plastic boxes (36.6cm*20.3cm*12.4cm), Walmart Inc, Edinburg, TX). *M. sexta* caterpillars tend to voraciously feed until they are in the fifth instar and then tend to wander and in many cases die in this process. To avoid any confounding data of caterpillar death c due to wandering and not diet toxicity, we decided to remove the caterpillars from the plant treatment (tomato) when they became fourth instars and moved them into artificial diet, and allowed them to pupate. In addition, we have recently documented that diet effects on *M. sexta* caterpillar growth is significant in early instars and not in late instars using a set of manipulative and reciprocal experiments (Tayal et al., 2020a; Singh et al., 2020).

A similar procedure was employed for feeding on four *Solanum* species, ensuring that the caterpillars had equal availability of all the species. Thirty second instar caterpillars were placed on equal number of similar sized *Solanum* species, allowing them to freely move around and feed. We have previously observed that the caterpillars have no specific choice among these species, and were able to feed. However, we only allowed the caterpillars to feed on four *Solanum* spp diet for 48 hours. This was because although *M. sexta* caterpillars feed and develop on these species, our preliminary observations showed that late instars have higher mortality, and death by starvation due to wandering on these species. Since our experiment was focused on oviposition and progeny success, we decided to only give a short exposure on these species. In addition, we have previously documented that diet effects are more severe during the early stages of caterpillar growth (Kariyat et al., 2019; Tayal et al., 2020a; Singh et al., 2020) and thus only allowed second instar caterpillars on the four *Solanum spp* diet. Afterwards, they were transferred to AD for rest of their larval period to pupate and eclose.

Feeding of *M. sexta* on artificial diet

Newly hatched first instar caterpillars were fed on AD for their whole life cycle. First and second instar caterpillars were fed on AD placed on round cut paper towel in petri dishes (8.8 cm diameter, Mid Sci, Valley Park, MO, USA). Petri dishes were cleaned daily (replacing paper towel and AD) to ensure clean and hygienic conditions for caterpillar growth. Caterpillars at 3rd instar stage were transferred to plastic boxes (36.6cm*20.3cm*12.4cm, Walmart Inc, Edinburg, TX) to provide enough space for caterpillar growth. Boxes were cleaned daily by changing paper towel and diet. They were continuously fed until they were ready to pupate.

Pupation of caterpillars and placement of adult moths for mating

When the caterpillars start wandering and were no longer feeding on their diet, they were transferred to pop-up cages with wooden shavings, to mimic dark conditions for their pupal burrowing. After they pupated, pupae were separated by sex (male /female) and were kept in different pop-up cages. These cages were covered with woolen blanket, and a heat lamp (no direct light) was placed aside to replicate dark and warm (28°C) conditions. Pupae were monitored daily. As moths started eclosing, we monitored the cages containing pupae, to have at least n=20 number of male/female adult pairs. All pairs were weighed separately (male/female) and transferred into new pop-up cages with one 4 weeks old tomato plant placed at the center of the cage. A conical flask (250 ml) with a paper towel dipped in honey solution (90:10; water: honey) was also placed for egg laying and feeding moths. Paper towels were changed daily, and new paper towels were dipped in a honey solution and placed in flasks to avoid any fungal growth and to provide clean feeding conditions.

Egg collection

The day after adult eclosion, moths (one male and female) were kept in cages, each cage was tracked daily for egg laying. As they started laying eggs, eggs were collected from each cage (on the tomato plant) and kept separately on artificial diet placed in petri dishes. Petri dishes were labeled in a similar manner as was done for pair recognition along with date, pair number and treatment mentioned on each petri dish. Using the same procedure, eggs were collected daily after every 24 hours and kept on diet in labeled petri dishes to keep track of eggs laid on each day. We continued egg collection until each pair stopped laying eggs and died.

Egg hatching

Collected eggs were stored at 27°C to provide optimum condition for their hatching. They were monitored daily to collect data on their hatching rate and data of daily hatched eggs from eggs laid by each pair on each separate day. Newly hatched caterpillars were daily removed from each petri dish to record number of eggs hatched on next day. Hatched caterpillars were transferred to separate petri dishes and kept on AD. AD and paper towel from the petri dishes containing eggs were also changed daily. Data collection of hatching was terminated after five continuous days of no egg hatching.

Polyphenol Oxidase (PPO) quantification in leaves of tomato and 4 *Solanum* species:

Leaf samples from 11 tomato plants and 7 samples of 4 *Solanum* species (one leaf each from all four species pooled to form one sample) were collected and stored in -80°C for PPO quantification. Samples were powereded in liquid nitrogen using a pestle and mortar. 0.1 gram samples were mixed with 1ml assay buffer (4°C) for extraction and kept on ice for detection. Afterwards, tubes were centrifuged at 8000g for 10 minutes at 4°C and extract was transferred into new tubes. Extract obtained was used for PPO quantification using general Polyphenol Oxidase Assay Kit (Catalog# MBS822343; MyBioSource; Wang et al., 2016). Absorbance was measured using multiskan sky spectrophotometer at 410 nm (details). Calculations for PPO quantification was done in U/gram per sample.

Trichomes: morphology and density estimation:

Total leaf trichome density of *Solanum lycopersicum, S. melanocerasum, S. aethiopicum* and *S. melongena* (n = 3-6) was determined using Desktop Scanning Electron Microscope (SNE-4500 Plus Tabletop Scanning Electron Microscope; Nanoimages LLC, Pleasanton, California, USA; 5KV voltage; SE detector). Circular discs (0.63 cm in diameter) of fresh leaf samples were excised using hole punctures and fixed on the aluminum stubs using double-sided carbon tape. The images for trichome density count were captured at 60X magnification which corresponds to 5.32 mm^2 of leaf area. After obtaining the images, the trichome density was manually counted as:

Trichome density = Number of trichomes in the image taken at 60X magnification (leaf area= 5.32 mm^2*)*

Statistical analysis:

Pupal mass of *M. sexta* was analysed using non parametric Kruskal-Wallis test (non-normal distribution of data even after data transformation) followed by Dunn's multiple comparison test to compare all treatments i.e. tomato, four *Solanum* species and AD. Adult mass data of *M. sexta* was normally distributed and thus analysed by using ANOVA and post-hoc pairwise comparisons were carried out by Tukey tests. Furthermore, to analyse the number of days to complete whole life cycle and number of days adults survived we also used ANOVA as assumptions were met. We also used similar tests for analyzing the variation in oviposition due to different diets on number of eggs laid per pair, egg hatching rate per pair. Average number of days to first egg hatch and days to first hatch from pooled days data was not normally distributed. Therefore, we used Kruskal-Wallis test followed by Dunn's multiple comparison test. We also analyzed the percent of eggs hatched respective to the day eggs were laid using two way random mixed effects ANOVA. Finally, we also ran a spearman correlation analysis to see if there is any correlation for egg laying and hatching with adult mass of *M. sexta*. We ran separate analyses for male mass with female mass, pair mass, eggs laid and hatching rate; female mass with pair mass, eggs laid and hatching rate; pair mass with eggs laid, and hatching rate, and eggs laid with hatching after pooling all treatments. Similar analysis was also done for each treatment i.e. tomato, four *Solanum* species and AD. PPO data was non-normal, and was analyzed with Mann-Whitney test, and trichome density data was anayzed with an unpaired t-test.

Results

Pupal and adult mass:

Pupal and adult mass data were analysed to examine the affect of different diet treatments on *M. sexta* caterpillars. We found that *M. sexta* grown on different diets affected pupal mass (Kruskal-Wallis test; Kruskal-Wallis statistic: 17.54; P = 0.0002). More specifically, pupal mass of AD fed *M. sexta* and those that fed on four *Solanum* species were not significantly different (Dunn's multiple comparison; P value = 0.3418; figure 1A). However, pupae from caterpillars that fed on tomato plants gained significantly lower mass than both AD fed and *Solanum* fed pupae (Dunn's multiple comparison; P = 0.0092; AD vs tomato; P = 0.0001; four *Solanum* species vs. tomato; figure 1A). We also separately analyzed the male and female adult mass based on the three treatments. We found that, pair mass (combination of male + female mass) of all the treatments was significantly different from each other i.e. lowest in tomato followed by four *Solanum* species and AD (two way ANOVA; F = 22.13; P = 0.000; figure 1B). In addition, irrespective of the treatment, sex i.e. male (combined males of all treatments) and female (combined females of all treatments) was also significantly different from each other (two way ANOVA; F = 0.000; P = 0.000; figure 1B). But, treatment X sex interaction was not significantly different (two way ANOVA; F = 0.57; P = 0.568; figure 1B).

Time to complete life cycle and adult survival of *M. sexta*:

Analyses of the effect of different diets on the complete life cycle of *M. sexta* and survival of adult moths showed that diet variation affected the time to complete the whole life cycle of *M.sexta* (one way ANOVA, F = 28.28; P <0.0001; figure 2A). *M. sexta* caterpillars fed on AD and four *Solanum* species completed their life cycle in similar number of days (Tukey's multiple comparison; P = 0.9644; figure 2A). However, tomato fed *M. sexta* completed their life cycle significantly faster than both AD and four *Solanum* species [Tukey's multiple comparison; P <0.0001(AD vs tomato); P <0.0001 (four *Solanum* species vs. tomato); figure 2A]. Further, adult lifespan also varied significantly in three different treatments (one way ANOVA; F = 14.77; P <0.0001; figure 2B). Results indicate that adults of *M. sexta* fed on four *Solanum* species and tomato survived for similar number of days (Tukey's multiple comparison; P = 0.9351; figure 2B). However, their adult lifespan (in days) was significantly lower than the AD fed *M. sexta* (Tukey's multiple comparison; P <0.0001(AD vs tomato); P <0.0001 (AD vs. four *Solanum* species; figure 2B).

Oviposition:

Additionally, we explored the oviposition behavior of *M. sexta* that fed on different diets. Our results indicate that mean number of eggs laid per pair by treatment were not different [one way ANOVA ; F = 2.074; P = 0.1356; Tukey's multiple comparison: P = 0.3362 (AD vs. four *Solanum* species), P = 0.8227 (AD vs. tomato) and P = 0.1232 (four *Solanum* species vs. tomato); figure 3A]. However, the number of days eggs laid w.r.t. treartment were significantly different with variation in diet (one way ANOVA test; F = 9.229; P = 0.0004; figure 3B). More specifically, they were similar in the case of four *Solanum* species and tomato fed *M. sexta,* but for both these treatments they laid eggs for significantly less number of days than AD fed *M. sexta* adult moths [Tukey's multiple comparisons test: P = 0.0012 (AD vs. four *Solanum* species), P =0.0019 (AD vs. tomato) and P = 0.9764 (four *Solanum* species vs. tomato); figure 3B]. Further, we analysed the mean number of eggs laid per day for each treatment and found that in tomato fed *M. sexta* for the first five days mean number of eggs laid per day was higher than both four *Solanum* species and AD fed *M. sexta,* except for the sixth day there was no significant difference between all three treatments (figure 4). On the other hand, mean number of eggs laid for first two days were lower in four *Solanum* species fed than AD fed *M. sexta* and for other days they were similar (figure 4). Our correlation analyses using pooled data from all three treatments did not find any significant correlation between adult mass and egg laying capacity [r=0.186, P = 0.171 (egg laying vs female mass); r=-0.223, P=0.099 (egg laying vs male mass); r=-0.046, P=0.171 (egg laying vs pair mass); figure 5]. However, a strong positive correlation was observed for female mass with egg laying capacity of *M.sexta* adult moths in tomato diet treatment [r=0.498, P = 0.035 (egg laying vs female mass); figure 6], but not in AD treatment [r=0.166, P=0.471 (egg laying vs female mass); r=-0.234, P=0.308 (egg laying vs male mass); r=-0.045, P=0.845 (egg laying vs pair mass); figure 7]. We also found that female mass and pair (male and female) mass had a significant correlation with egg laying capacity of adult moths in four *Solanum* species diet treatment [r=0.487, P=0.048 (egg laying vs female mass); r=0.437, P=0.080 (egg laying vs pair mass) figure 8].

Egg hatching:

Results from our egg hatching analyses shows that hatching percent per pair was significantly different in three diet treatments (one way ANOVA; F = 6.883; P = 0.0022; figure 9A) i.e. more in both tomato and four *Solanum* species than AD [Tukey's multiple comparison; P = 0.0394 (AD vs four *Solanum* species) and P = 0.0020 (AD vs tomato); figure 9A]. However, it was similar for tomato and four *Solanum* species (Tukey's multiple comparison; P = 0.6585; figure 9A). Additionally, there was no significant difference between the treatments for average number of days to first hatch [(Kruskal-Wallis test; Kruskal-Wallis statistic: 4.107; P = 0.1283; figure 9B); Dunn's multiple comparison; P = 0.3469 (AD vs four *Solanum* species), P = 0.1704 (AD vs tomato) and P >0.9999 (four *Solanum* species vs tomato); figure 9B]. When we pooled the days data first hatch, they were found to be significantly different (Kruskal-Wallis test; Kruskal-Wallis statistic: 14.40; P = 0.0007; figure 9C). These results indicates that egg hatching in four *Solanum* species and AD were significantly different from tomato fed *M. sexta* and took longer in tomato (Dunn's multiple comparison; P = 0.0007; figure 9C), but there was no significant difference between egg hatching between AD and four *Solanum* species fed *M. sexta*

(Dunn's multiple comparison; P = 0.1305; figure 9C) and AD and four *Solanum* species (Dunn's multiple comparison; P = 0.3058; figure 9C) fed adults. More specifically, we found that for eggs laid on first day, the number of days it took to hatch for eggs laid was significantly different from each other for all treatments i.e. more number of days it took to hatch for four *Solanum* fed *M. sexta* followed by tomato and AD (figure 10), but for the second day in tomato fed *M. sexta* it took less number of days to hatch than both four *Solanum* species and AD fed *M. sexta* and there was no significant difference between both latter treatments (figure 10). For third day eggs laid there was no significant difference between all three (figure 10). But for day four and five it took less number of days to hatch in tomato fed *M. sexta* tna both other treatments, but not significantly different between latter ones (figure 10). Moreover, our results from percent eggs hatching w.r.t. the day eggs were laid shows that higher percentage of eggs were hatched in tomato fed than AD and four *Solanum* species (Random Mixed effects ANOVA; F= 12.61; P=0.00) but was similar in AD and four *Solanum* species (Tukey pairwise comparisons; see figure 9D). Furthermore, we found that there was no significant correlation between egg hatching with adult mass and egg laying for individual diet treatments, but egg laying was positively correlated to egg hatching in all pooled treatmnts [r=0.371, P=0.006 (egg laying vs egg hatching; supplementary figure 4, 5, 6 and 7].

PPO quantification in tomato and 4 *Solanum* species:

Results from our PPO estmation clearly demonstrated that 4 *Solanum* species have significantly higher amount of PPO present in their leaves in comparison to tomato plants (Mann Whitney test; P=0.034; figure 11A).

Trichome density on tomato and four *Solanum* species:

Our results on trichome density shows that four *Solanum* species have more trichome density than tomato plants (Unpaired t-test; t=2.344; P=0.0223; figure 11B and 12).

Discussion

In this study, we examined how variation of diet affects the life cycle of *M. sexta*. We also examined how diet affected progeny success and found rather surprising results. We then correlated these results with physical and chemical defenses of host plants. We found that variation in diet caused alterations in successful completion of parental life cycle, oviposition pattern, and egg hatching rates.

Our results show the mass of *M. sext*a pupae that fed on tomato plants was lower in comparison to both four *Solanum* species and AD, but not different on both latter ones. Also, mass of adults that were fed on tomato was lower than four *Solanum* species, and was highest when fed on AD. This shows that plant defenses (chemical and structural) present in tomato might have caused larval stress, which cascaded to other stages of its lifecycle. Tomato has a wide range of defenses such as trichomes (glandular and non glandular) and chemical defenses (jasmonic acid induction on herbivory and also present in glandular trichomes) (Peiffer et al., 2009). These defenses may be constitutive, or induced upon an herbivory attack (Karban and Baldwin, 1997; Agrawal et al., 1999; Mccormick et al., 2012; Kaur and Kariyat, 2020), which could have restricted the growth and development (Bi and Felton, 1995; Mitchell et al., 2016; Paudel et al., 2019).

The cascading effects of larval diet has been also found to affect flight capacity of adults (Portman et al., 2020), with possible consequences for dispersal (Portman et al., 2015) as observed in the case of *M. sexta* on inbred and outbred horsenettle (*Solanum carolinense*) (Portman et al., 2015) and on wild and JA mutant tomato for fall armyworm (*Spodoptera frugiperda*) and southern armyworm (*Spodoptera erdania*) (Portman et al., 2020). Various studies have also reported the effects of diet on the post larval stages of insect herbivores, thus reducing pupal as well as adult mass (Kaitaniemi et al., 1999; Bauerfiend and Fisher, 2005; 2009; Kehl and Fischer, 2012; Tayal et al., 2020a,b). Kaitaniemi et al., (1999) reported lowered pupal and adult mass in autumnal moth (*Epirrita autumnata*) due to the variation in host quality (Kaitaniemi et al., 1999). However, effects on mass of pupal and adult stages in *M. sexta* fed on four *Solanum* species were not significant, possibly due to exposure of caterpillars for just two days to these plants, nullifying any possible effects of defense induction, although we have previously found in the same caterpillar species, that exposure to toxins during early stages can cause severe developmetal delays that are unable to be repaired later (Tayal et al., 2020a; Kariyat et al., 2019).

Interestingly though, we found that PPO activity (figure 11A) and trichome density (figure 11B and 12) was higher in four *Solanum* species, which could have affected feeding of caterpillars during their early growth stages (48 hours feeding period). PPO is known to interfere with the protein availability of insects and reduce digestibility. Furthermore, larval nutritional quality and availability of proteins have been found to be correlated with investment of adults in their reproduction (Boggs and Freeman, 2005; Vande Velde et al., 2013; Nestel et al., 2016). Low nutritional quality during larval stages have been correlated with lower reproductive capacity (Nestel et al., 2016). And, later after moving them to artificial diet made them to invest more into their growth and development and nullify the effects of these plant defenses (although they had higher PPO activity). We speculate that this investment would have aided them to regain their mass in pupal and adult stages and invest more in growth. It is also possible that due to growth fitness trade-offs caterpillars reared on 4 *Solanum* spp gained more mass in pupal and adult stages at the cost of their reproductive fitness. Taken together, our data clearly shows that stress caused by plant defenses at larval stages can linger to the pupal and adult stages.

Our results on lifespan show that tomato fed *M. sexta* survived less number of days than both four *Solanum* species and AD fed ones, while their survival on four *Solanum* species and AD were similar. This is indeed a possible spillover result from larval traits, as it has been shown that insects feeding on lower quality host take longer for their growth and development (Fathipour et al., 2020), clearly confirming the effects of host quality on the fitness of insects. Additionally, higher amount of PPO in four *Solanum* species (figure 11A) and, their exposure to high amount of PPO could have lowered their rate of growth and it took longer for caterpillars to develop. Insects fed with nutrient rich and good quality host tend to complete their life cycle faster than those fed on lower quality host (Singh and Parihar, 1988; Kariyat et al., 2019). Moreover, adult longevity was also affected by diet effects and our results indicate that adults from tomato and four *Solanum* species fed *M. sexta* were found to survive less number of days than adults from AD. Interestingly here, even a brief exposure of *M. sexta* caterpillars for just two days to four *Solanum* species leads to shorter life span of adults. Clearly, these defenses act disproportionately at different life stages, since no effect was observed on life span on four *Solanum* species diet, but observed in adult life. It has been shown that poor quality diet in larval stages extend their overall life span and adults produced from them tend to live for short period of time (Runagall-Mcnaull, 2015; Fathipour et al., 2020).

A significant part of our experiment was focused on oviposition rate and success. Previous studies reported negative correlations of the insect longevity with their reproduction success (Lanteren and Noldus, 1990; Fathipour et al., 2020). Insects tend to reproduce more and live short life cycle on the more suitable host (Singh and Parihar, 1988). For instance, cotton bollworm (*Helicoverpa armigera*) fed on corn (*Zea mays*) survived for more number of days but had lower egg laying capacity and vice-versa when they were fed on cowpea (*Vigna unguiculata*) (Fathipour et al., 2020). We also found similar pattern in our diet treatments where tomato fed *M. sexta* laid more number of eggs per day while longevity was lower as compared to AD treatment but similar to four *Solanum* species. However, it was opposite in four *Solanum* fed *M. sexta* (figure 4), where adult longevity was also lower than AD, but laid less number of eggs per day when compared to both other treatments (figure 4). Taken together, this shows that four *Solanum* species is a poor quality host for *M. sexta* for oviposition success, in comparison to tomato and tomato is better for *M. sexta* oviposition success. We speculate that this is because, the four *Solanum* species have high amount of PPO and high density of trichomes when compared to tomato plants.

Previous studies have reported the variations in secondary metabolite profiles of different plant species within same genus (Mason et al., 2015; Meyer et al., 2015; Burdziej et al., 2019; Lopez-Palacios and Pena-Valdivia, 2020). Mason et al. (2015) reported interspecific variation in abundance of secondary metabolites in genus *Helianthus* spp (Mason et al., 2015). Additionally, domesticated grapevine (*Vitis vinifera*; Vitaceae) have been found to have reduced amount of triterpenoid compounds in it as comparison to wild species (Burdziej et al., 2019). More specifically, from the species we used, *S. retroflexum* have been found to have wide range of secondary metabolites (~30) such as flavonoids, cinnamic acid, alkaloids etc. (Dlamini and Madala, 2017). *S. aethiopicum* leaves also have many such metabolites present (alkaloids, flavonoids, saponins and cytogenic glycosides) (Ono et al. 2006). Similarly, *S. melongena* leaves have alkaloids, saponins, tannins, flavonoids and terpenoids present in it (Shrivastava et al., 2012). *S. melanocerasum* and *S. melongena* also found to have ecdysteroid activity in their leaves, which control growth and development of insects by disrupting their hormonal system (kariyat et al., 2013). Clearly, these defenses can play a significant negative role in herbivore development. On the other hand, tomato leaves have been found to have flavonoids, tannins, terpenoids and saponins. As PPO activity is one such measure, we speculate that could have possibly affected the growth and development of parental generation of *M. sexta* and their reproductive capacity.

Although PPO activity relates to defense proteins that negatively affect the growth and development of insect herbivores (Singh et al., 2021), more detailed profiling of secondary metabolites needs to be carried out (Singh et al., 2021) to explore the mechanisms of diet effects on parental generation, oviposition and egg hatching capacity. Our data suggests that intrageneric variation leads to variation in plant defenses and consequently differentially affecting the herbivore growth and oviposition. Regardless of treatment we observed the general trend of egg laying, ~65% eggs were laid in first three days of egg laying (approximately for nine days egg laying occurred regardless of treatment) and continuously reduced in following days.

Additionally, we found that altering diet not only affected the parental generation but also their off spring. Our results show that the tomato fed *M. sexta* also had higher hatching rate than other treatments. This is a further indication of enhanced fitness of *M.sexta* on tomato plants, although their larval stages suffered more on tomato. It has been reported that longer development time in insects is related to higher food consumption to maintain metabolism (Mehrkhou et al., 2015), reduced efficiency in digestive ability in adults, which leads to reduced fertility (egg hatching percent) (Fathipour et al., 2018; Ismail, 2020). As we found that PPO amount is higher in four *Solanum* species in comparison to tomato plants (figure 5A) and PPO is known to reduce the digestibility in insects as well as palatability and nutritional quality of food against them (Bhonwong et al., 2008; Mahanil et al., 2008; Singh et al., 2021). An interesting follow up would be to do secondary metabolic profiling on underlying mechanisms related to host quality and insect capacity to produce fertile eggs. We also observed that it took longer for eggs from tomato and AD fed *M. sexta*, to hatch when compared to eggs from four *Solanum* species fed *M. sexta*. Interestingly, we not found any correlation for male, female and pair mass with egg hatching rate. Collectively, effects of parental diet on egg hatching rate shows both similar and dissimilar patterns when compared growth, development and oviposition, an area that has been poorly understood, and clearly warrants further research.

In conclusion, tomato fed *M. sexta* had higher egg laying and hatching capacity, but was negatively affected in their growth and development, at all stages of life cycle. On the other hand, exposure of *M. sexta* for such short period of time to four *Solanum* species has cascading effects on their oviposition suggesting possible dose dependency of plant defenses, possibly also due to the higher amounts of PPO and trichomes, and the presence of a broad range of toxic secondary metabolites, differentially affecting their oviposition.

Figures

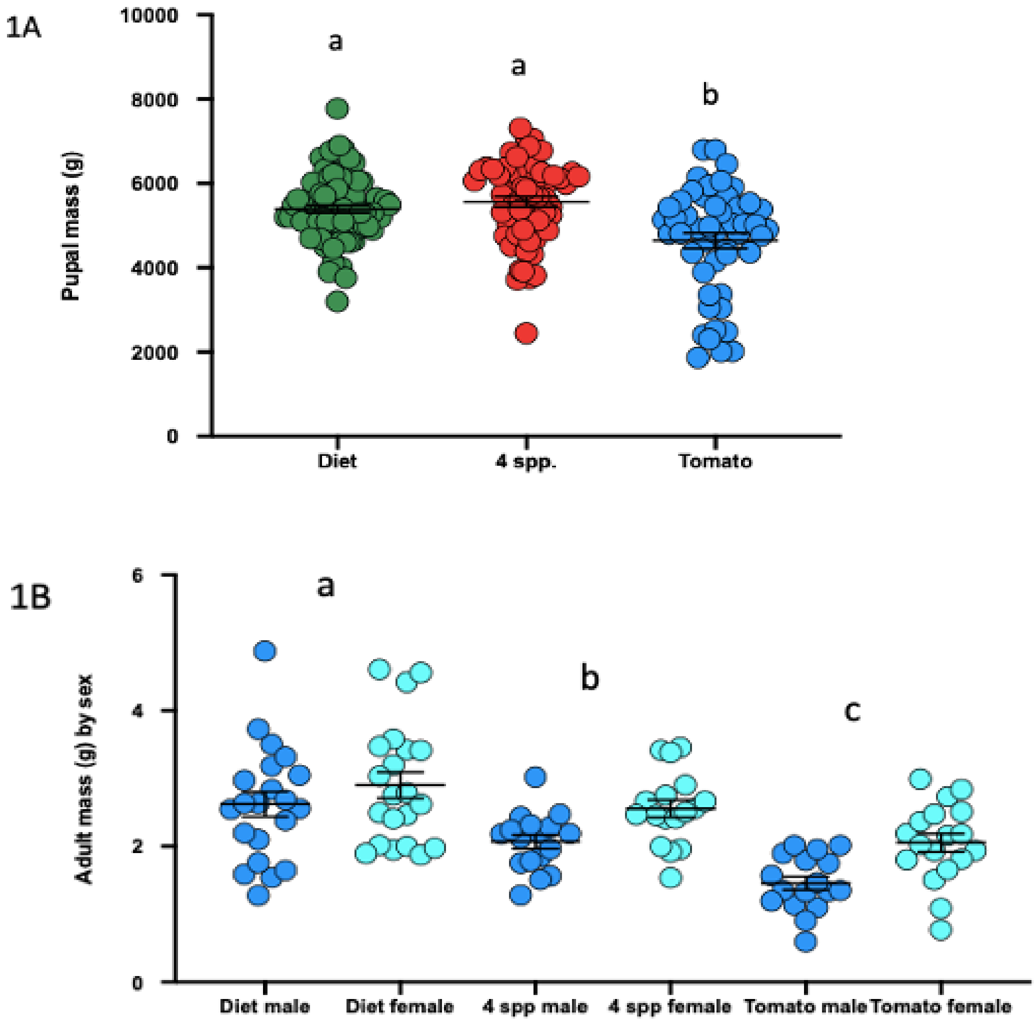


Figure 8: Graphs represents growth trait results of *M. sexta* fed on three different diet treatments i.e. tomato, four *Solanum* species and artificial diet (AD). Average *M. sexta* (A) pupal mass (Kruskal-Wallis test; Dunn's multiple comparison test; P value = 0.0002; Y-axis – pupal mass in milligram (mg) and (B) adult mass [ANOVA test; treatment P value = 0.000, sex (male/female) P value = 0.000 and Interaction of treatment and sex P value = 0.568; Y-axis – adult mass in grams (g)] of three diet treatments i.e. tomato, four *Solanum* species and AD. Means shown by different letters are significantly different. 4 spp. represents four *Solanum* species and diet represents AD. X-axis – different diet treatments.

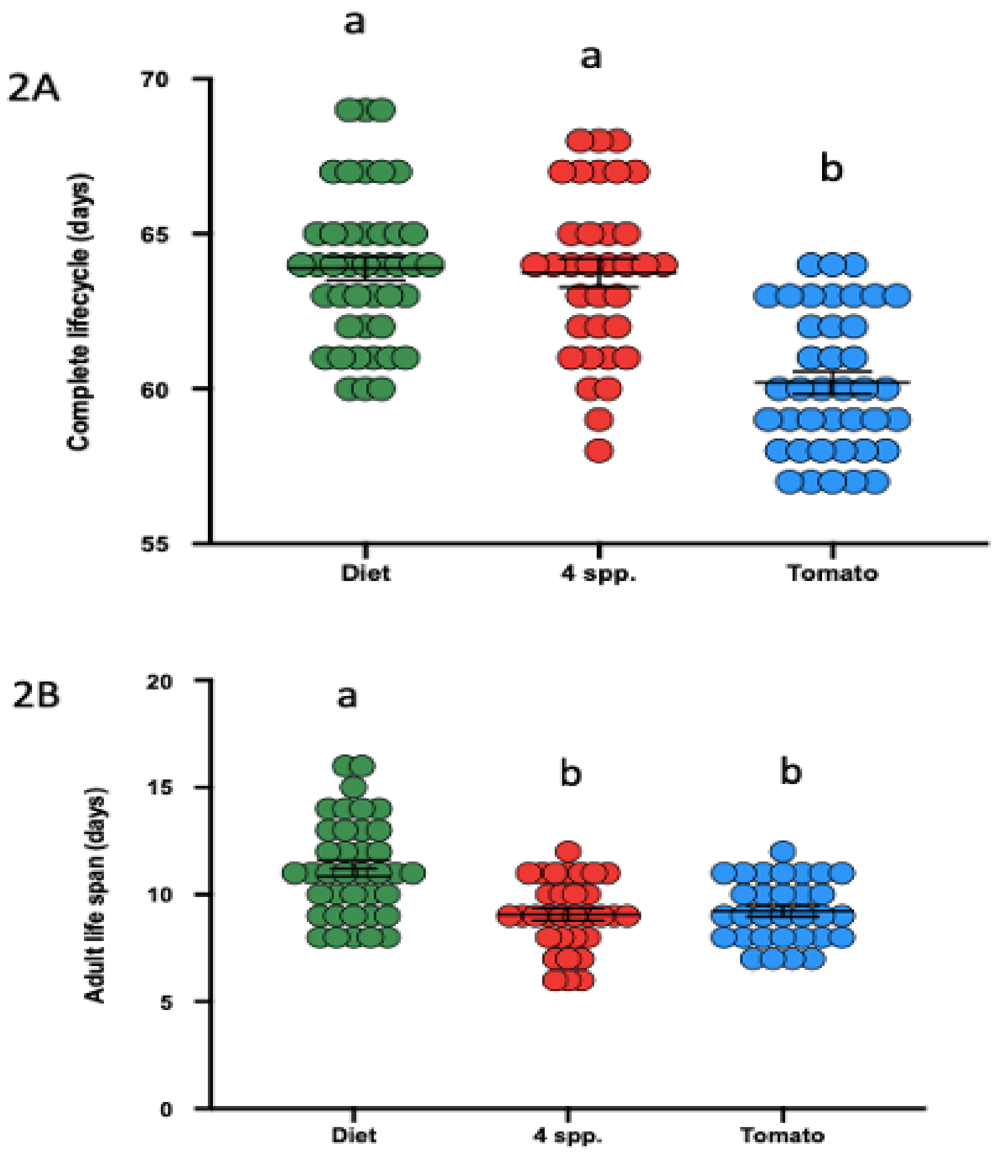


Figure 9: Graphs represents life cycle traits results of *M. sexta* fed on three different diet treatments i.e. tomato, four *Solanum* species and artificial diet (AD). Average number of days taken by *M. sexta* to (A) complete life cycle (ANOVA test; Tukey's multiple comparison test; P value <0.0001; Y-axis – number of days took to complete whole life cycle) (B) adult life span (ANOVA test; Tukey's multiple comparison test; P value <0.0001; average number of days adult survived). Means represented by different letters are significantly different. 4 spp. represents four *Solanum* species and diet represents AD. X-axis – different diet treatments.

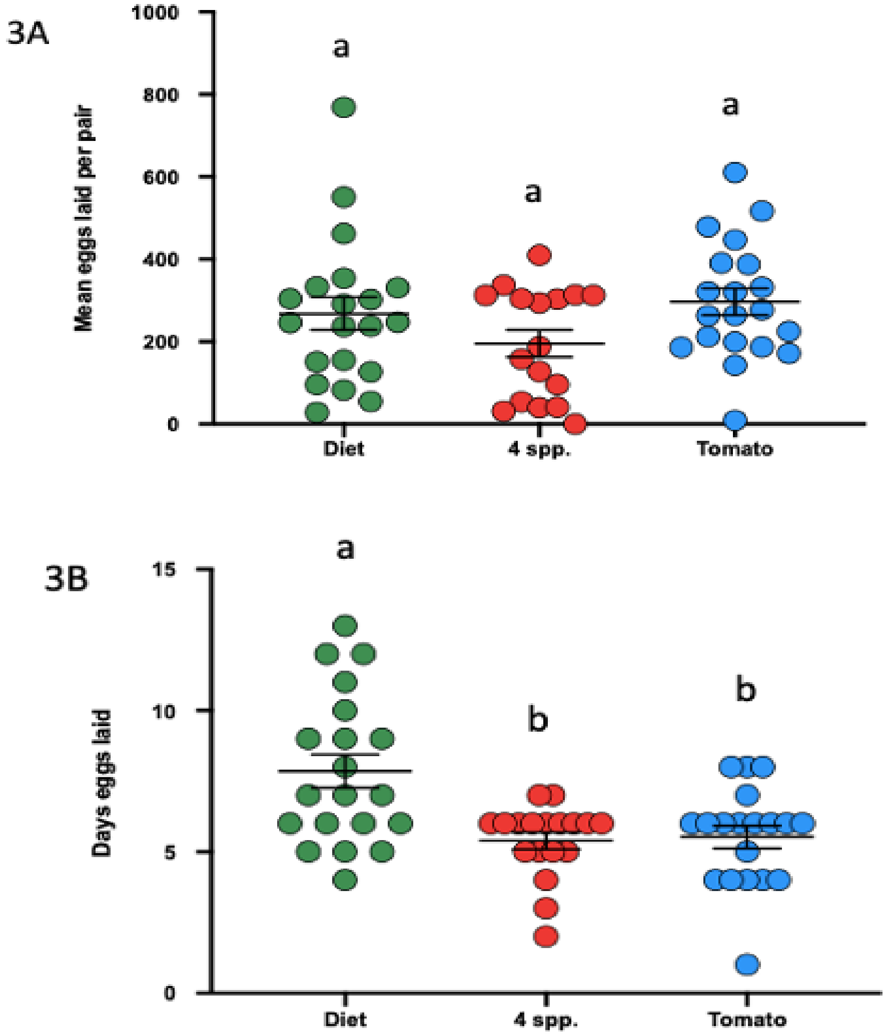


Figure 10: Graphs represents oviposition results of *M. sexta* fed on three diet treatments i.e. tomato, four *Solanum* species and artificial diet (AD). (A) mean number of eggs laid per pair (ANOVA test; Tukey's multiple comparison test; P value = 0.1356; Y-axis – mean number of eggs laid per pair) (B) average number of days eggs laid (ANOVA test; Tukey's multiple comparison test; P value = 0.0004; Y-axis – average number of days eggs were laid). Means shown by different letters are significantly different. 4 spp represents four *Solanum* species and diet represents AD. X-axis – different diet treatments.

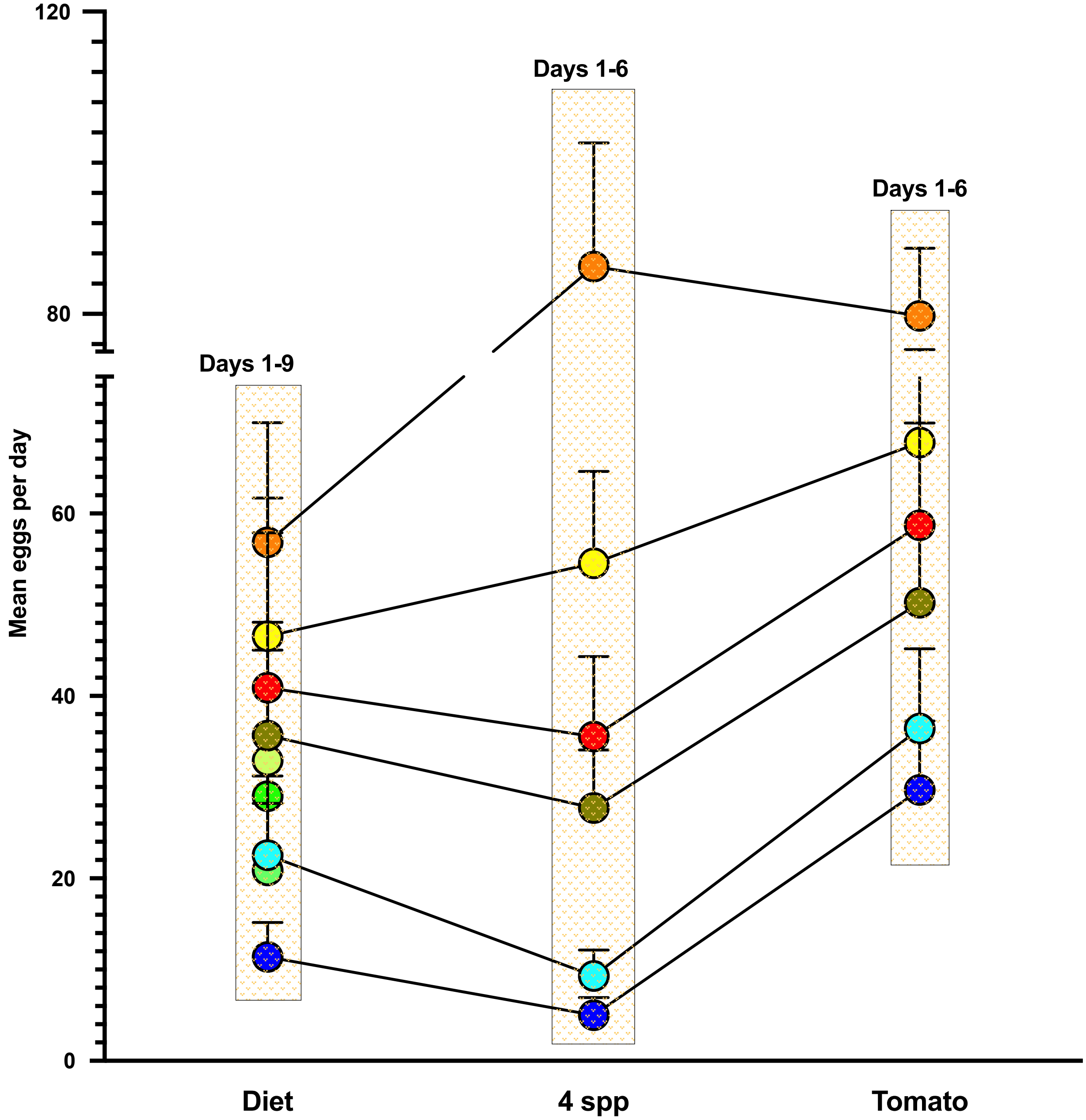


Figure 11: Mean number of eggs laid per day in all three treatments i.e. tomato, four *Solanum* species and artificial diet (AD). Y-axis represents average number of eggs laid per day and X-axis represents different diet treatments.

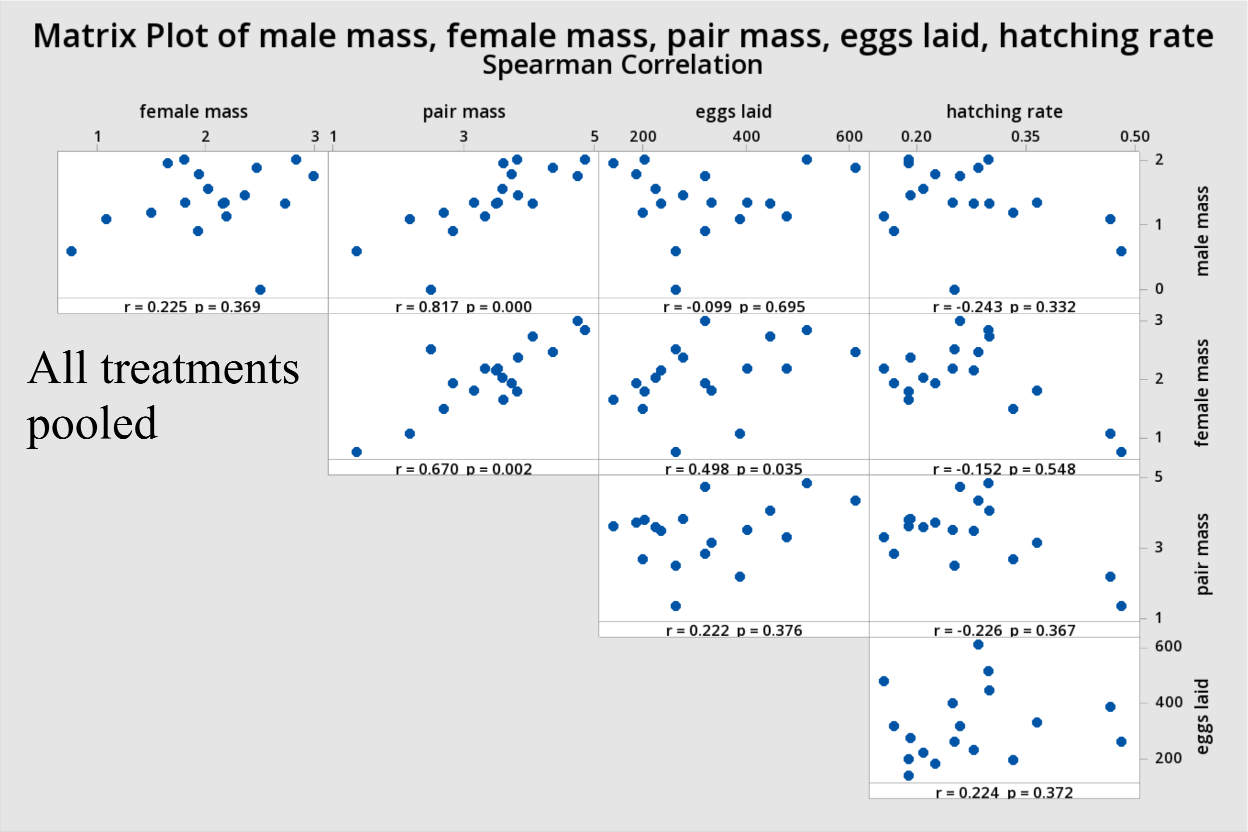


Figure 12: Correlation analysis of *M. sexta* on all three treatments pooled together. Correlation of male mass (left vertical line) with female mass, pair mass, eggs laid and hatching rate (upper horizontal line); female mass (left vertical line) with pair mass, eggs laid and hatching rate (upper horizontal line); pair mass (left vertical line) with eggs laid and hatching rate (upper horizontal line); and eggs laid (left vertical line) with egg hatching (upper horizontal line) after pooling all treatments. Red rectangular box shows significant positively correlation between egg hatching and egg laying (spearman correlation; r=0.371, P=0.006).

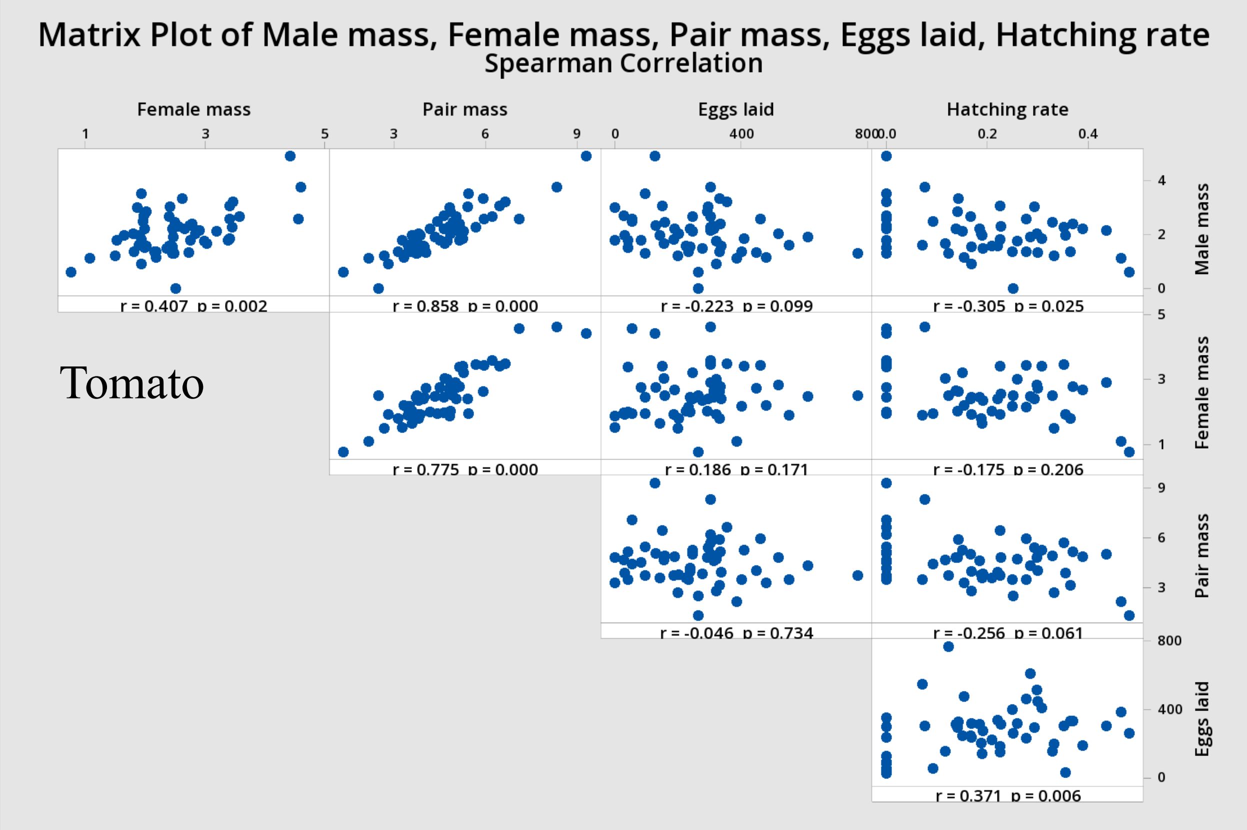


Figure 13: Correlation analysis of *M. sexta* on tomato diet treatment. Correlation of male mass (left vertical line) with female mass, pair mass, eggs laid and hatching rate (upper horizontal line); female mass (left vertical line) with pair mass, eggs laid and hatching rate (upper horizontal line); pair mass (left vertical line) with eggs laid and hatching rate (upper horizontal line); and eggs laid (left vertical line) with egg hatching (upper horizontal line). Red rectangular box shows significant positively correlation between egg laying and female mass (spearman correlation; r=0.498, P=0.035).

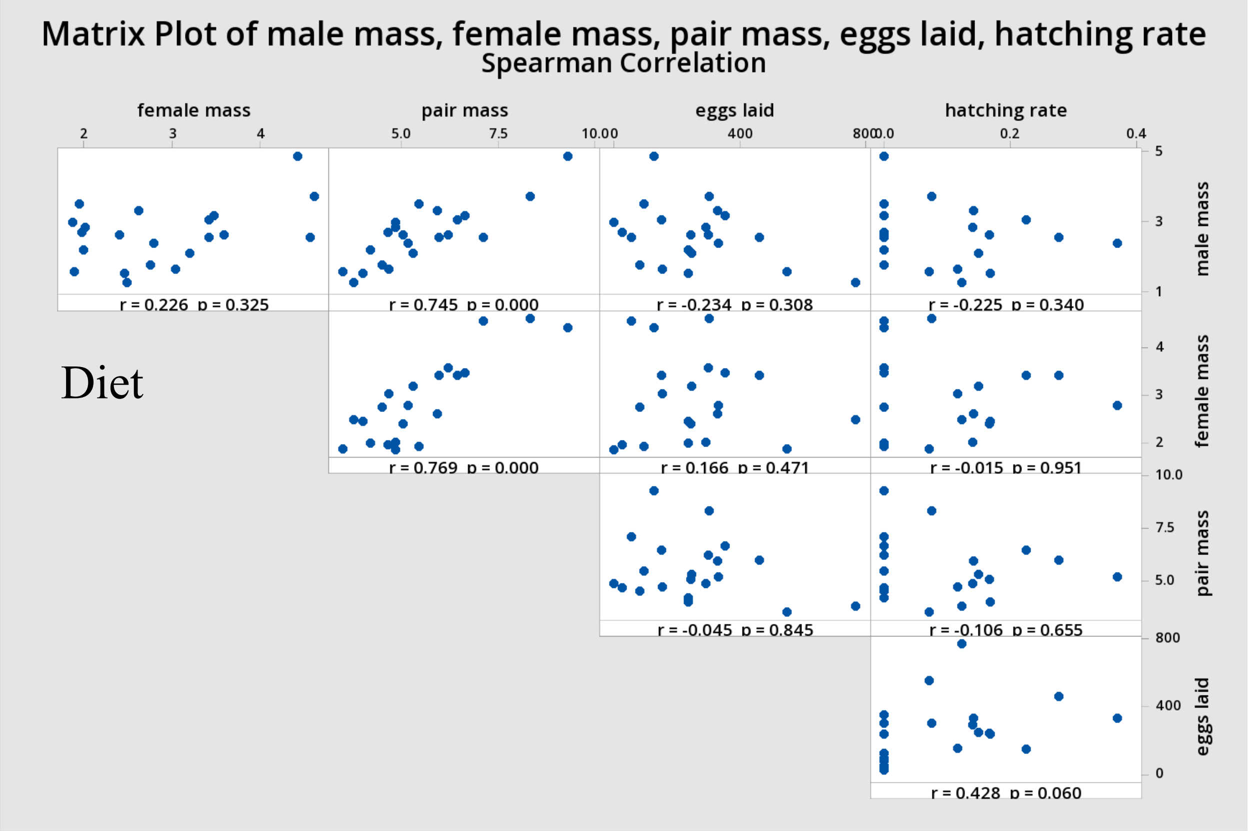


Figure 14: Correlation analysis of *M. sexta* on AD diet treatment. Correlation of male mass (left vertical line) with female mass, pair mass, eggs laid and hatching rate (upper horizontal line); female mass (left vertical line) with pair mass, eggs laid and hatching rate (upper horizontal line); pair mass (left vertical line) with eggs laid and hatching rate (upper horizontal line); and eggs laid (left vertical line) with egg hatching (upper horizontal line).

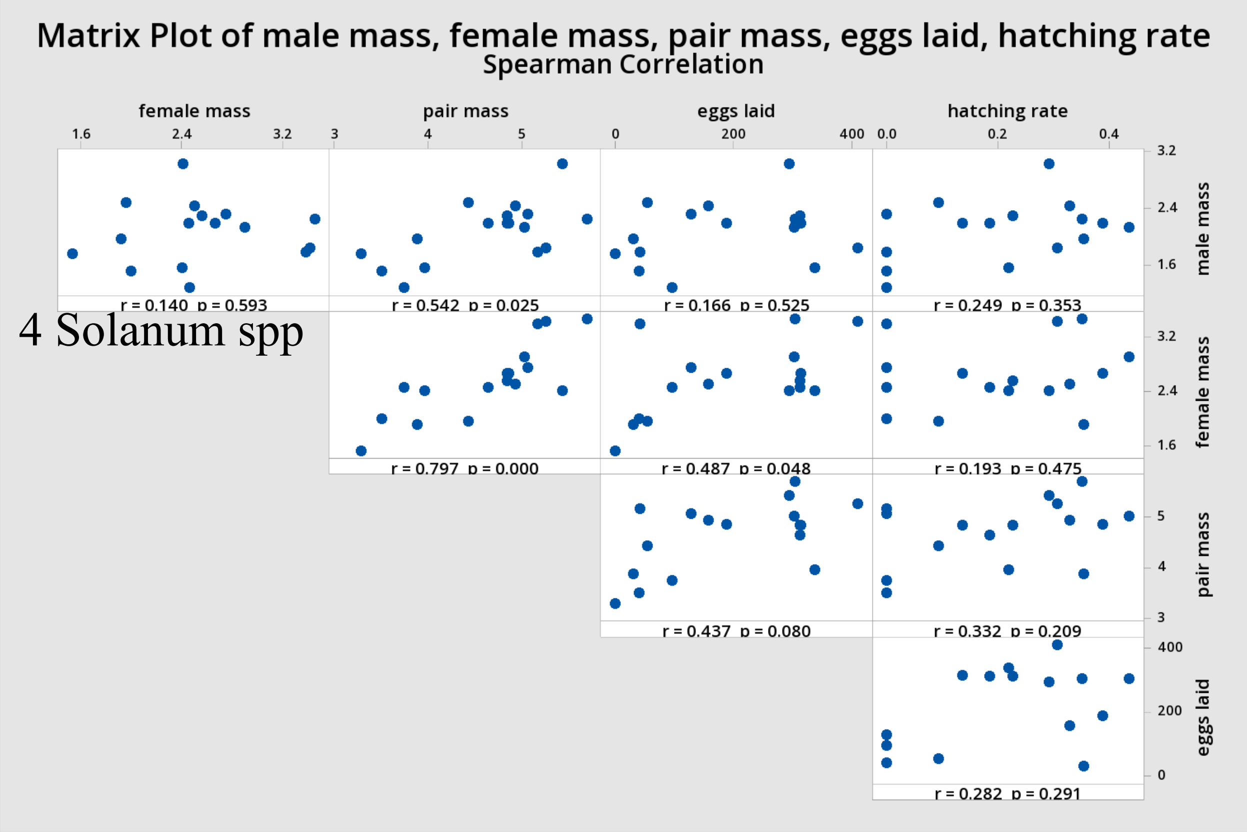
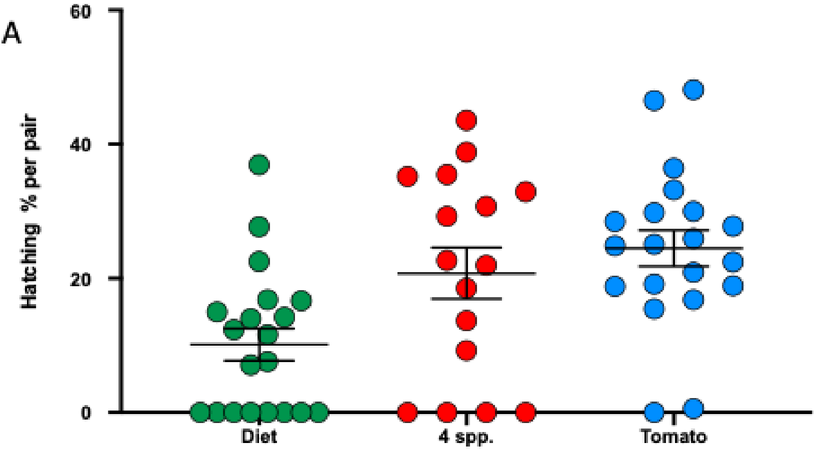
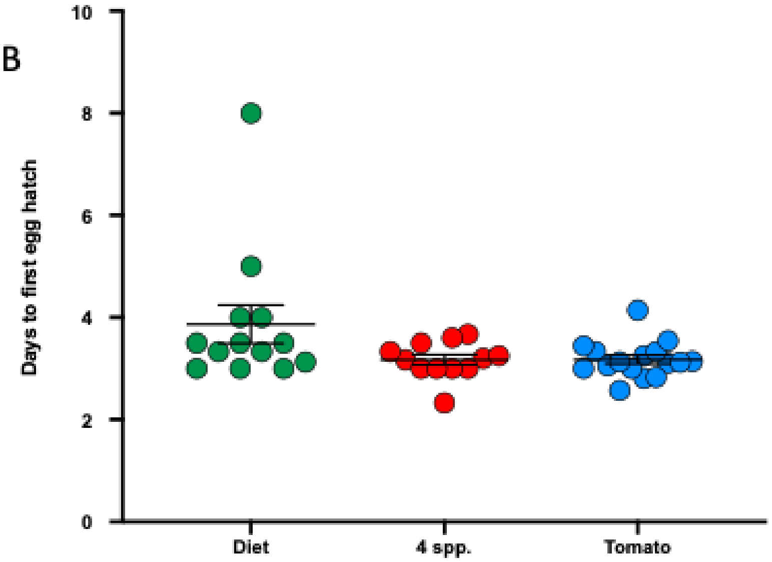


Figure 15: Correlation analysis of *M. sexta* on four *Solanum* species diet treatment. Correlation of male mass (left vertical line) with female mass, pair mass, eggs laid and hatching rate (upper horizontal line); female mass (left vertical line) with pair mass, eggs laid and hatching rate (upper horizontal line); pair mass (left vertical line) with eggs laid and hatching rate (upper horizontal line); and eggs laid (left vertical line) with egg hatching (upper horizontal line). Red rectangular boxes show significant positively correlation between egg laying and adult mass [spearman correlation; r=0.487, P=0.048 (egg laying vs female mass); r=0.437, P=0.080 (egg laying vs pair mass)].

9A


Hatching % per pair
60
40
20
0
Diet
4 spp.
Tomato

9B


Days to first egg hatch
10
8
6
4
2
0
Diet
4 spp.
Tomato

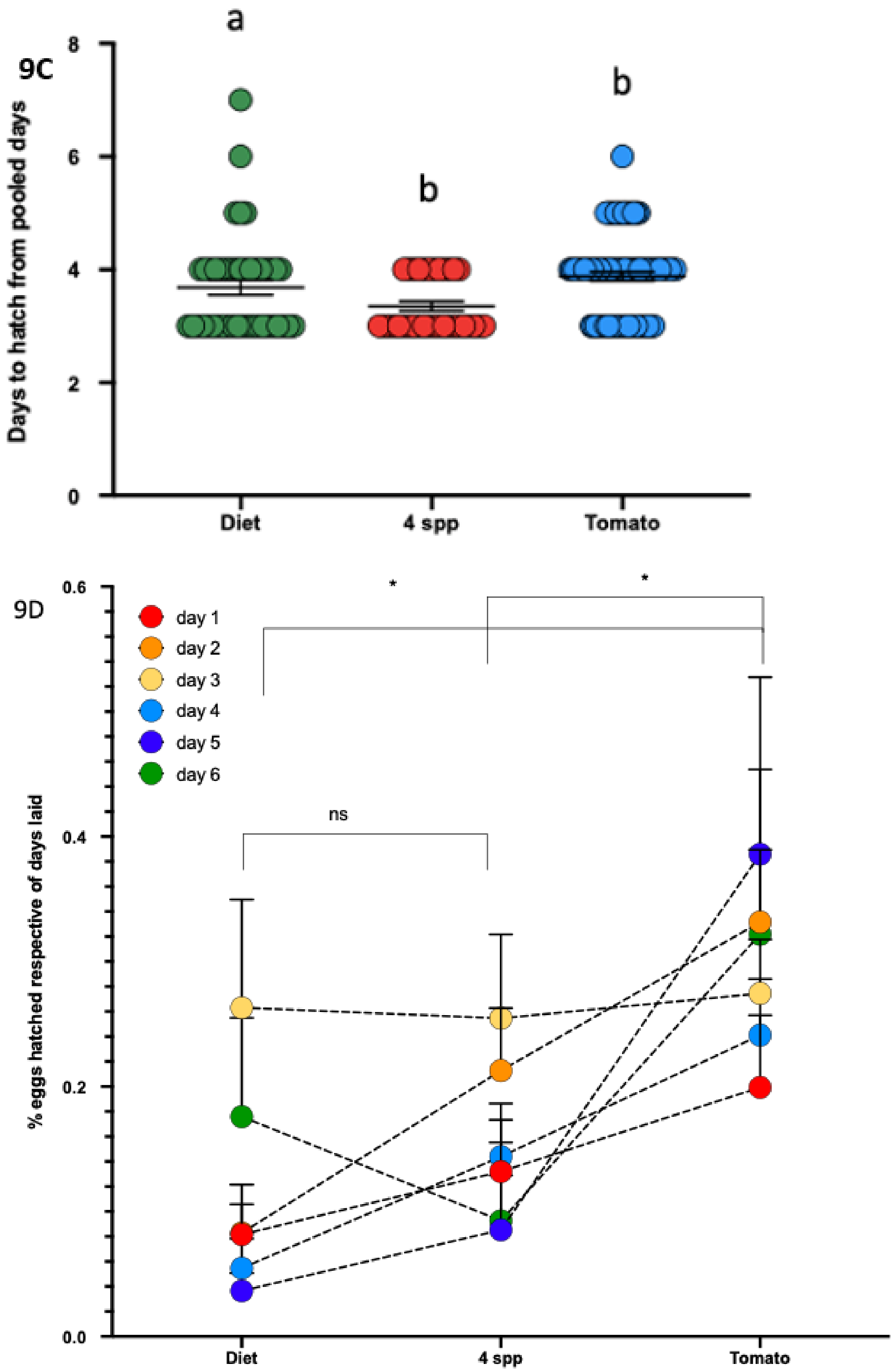
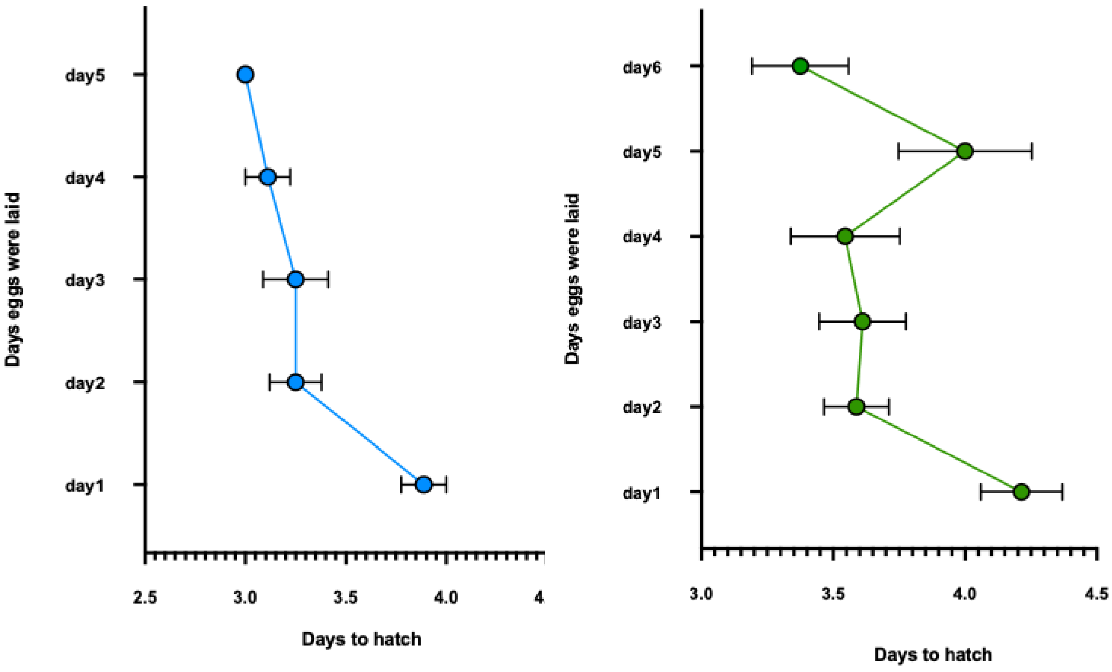


Figure 16: Graphs represents egg hatching results of *M. sexta* fed on three diet treatments i.e. tomato, four *Solanum* species and artificial diet (AD). (A) hatching percent per pair

(ANOVA test; Tukey’s multiple comparison test; P value = 0.0022; Y-axis – egg hatching % per adult pair of M. sexta)) (B) average number of days took to first hatch (Kruskal-Wallis test; Dunn’s multiple comparison test; P value = 0.1283; Y-axis – average number of days it took to first hatching of eggs for eggs laid on first day). (C) number of days to hatch from pooled days (Kruskal-Wallis test; Dunn’s multiple comparison test; P value = 0.0007; Y-axis – average number of days it took to hatch eggs from all pooled days of eggs). Means represented by same letters are not significantly different and those by different letters are significantly diferent. (D) percent eggs hatched w.r.t. the day eggs were laid (mixed effects ANOVA model; Y-axis - % eggs hatched w.r.t. the day eggs were laid). Asterik in (D) represents significant difference. 4 spp represents four *Solanum* species and diet represents AD. X-axis represents different diet treatments.



Tomato

4 Spp.

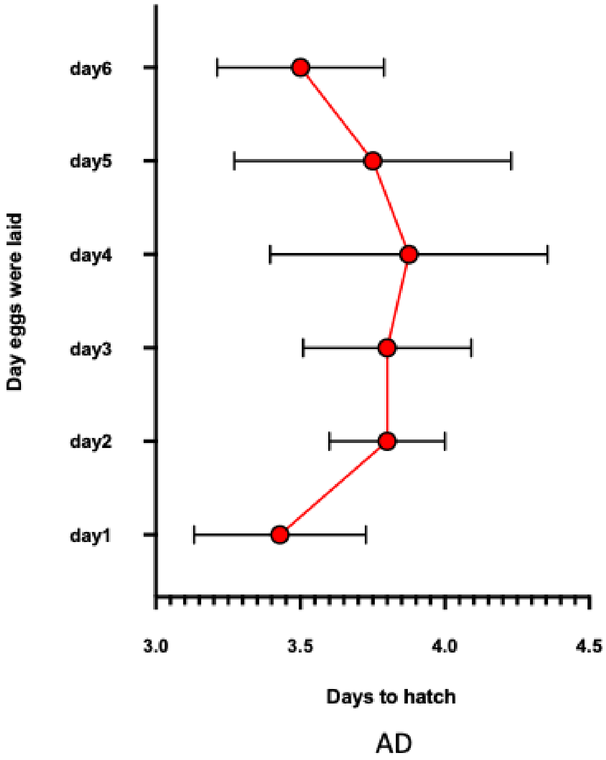


Figure 17: Average number of days it took for hatching eggs in relation to the day eggs were laid in all three treatments i.e. tomato, four *Solanum* species and artificial diet (AD). Y-axis represents day on which eggs were laid and X-axis represents average number of days it took to hatch.

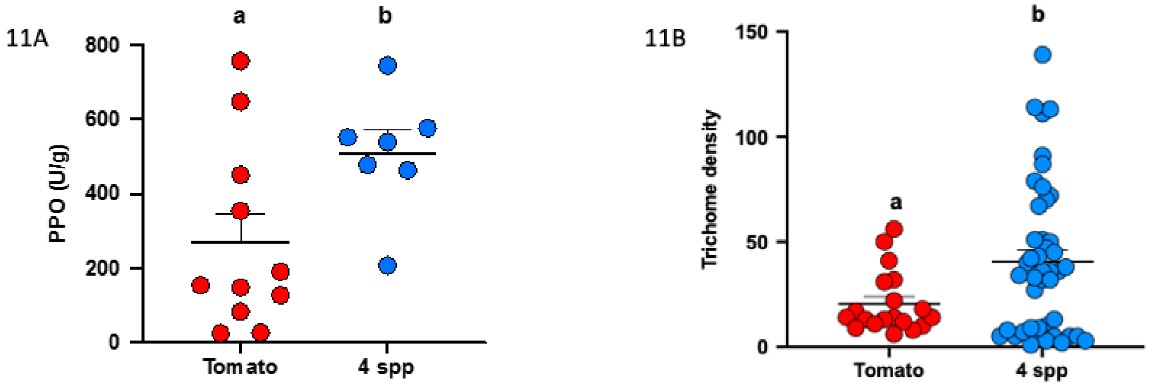


Figure 18: Graph represent (A) PPO amount (U/gram; Mann-Whitney test; p=0.0346) and (B) trichome density (t-test; P=0.0223) in tomato and four *Solanum* species. a and b represent the significant difference. Y-axis represents PPO (U/gram) and X-axis represents diet treatments.

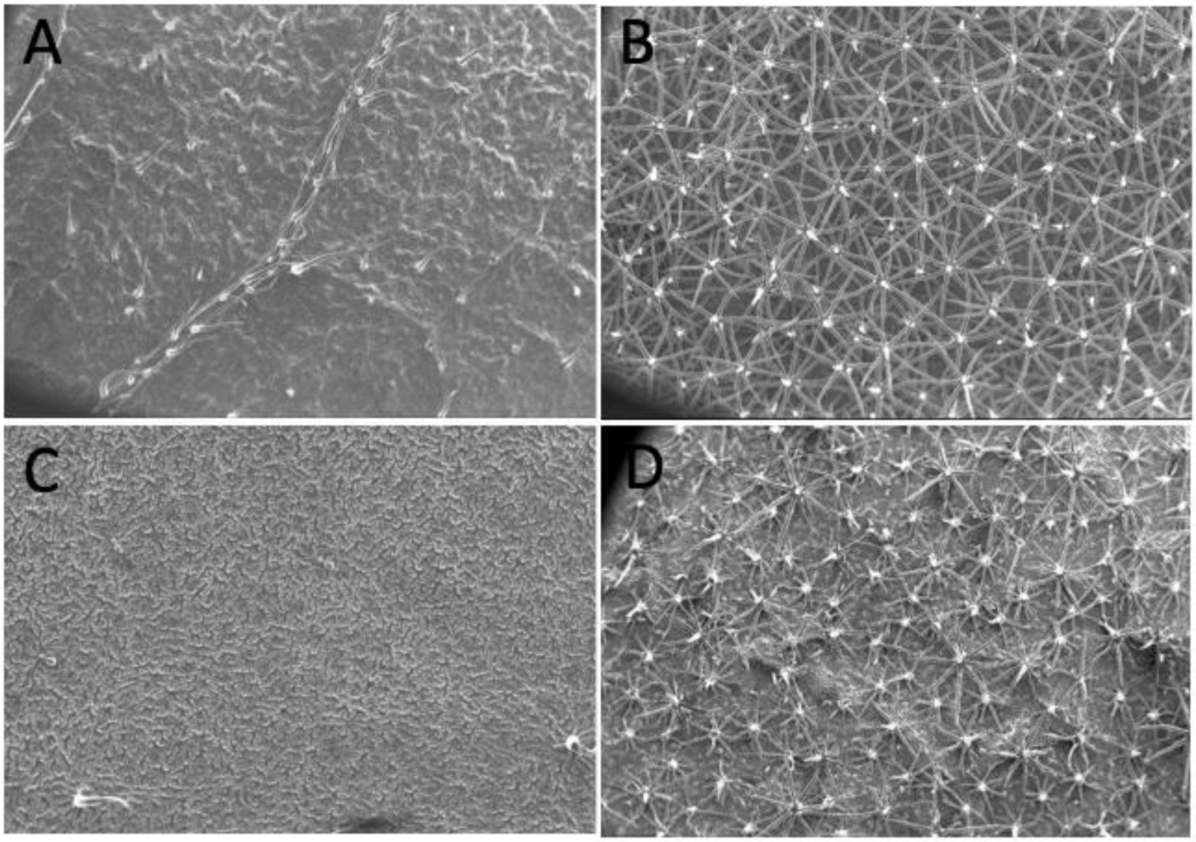


Figure 19: Scanning Electron Microscopy images of abaxial leaf surface of (A) *Solanum lycopersicum* (B) *S. aethiopicum* (C) *S. melanocerasum* (D) *S. melongena*, captured at 60X magnification.

CHAPTER IV

CONCLUSIONS AND FUTURE DIRECTIONS

Through an extensive literature review, I conclude and reinforce the point that plant secondary metabolites plays significant role in mediating plant-insect interactions. A tremendous amount of research has been done to explore the various mode of action of these compounds against insect herbivores. Underlying mechanisms on molecular level, different genes and enzymes involved in biosynthesis and induction of these compounds during plants under stress conditions have been explored. However, there still exista a major gap and need to study different plant defense and growth trade-off's between primary and secondary metabolism. More targeted research need to be done in resource allocation mechanisms of plants during biotic and abiotic stress conditions. Furthermore, there is need to develop cheap and simple methods of extraction of these metabolites from plants due to their potential to be used as an alternative to synthetic insecticides. More specifically, we should focus more on finding simple methods of secondary metabolite extraction from plant parts which are not of economic use and considered as waste.

Through experiments detailed in second chapter, we conclude that polyphenol rich purple corn pericarp negatively affect the growth and development of fall armyworm (*S. frugiperda*). We found that it not only effect the larval stages but also the pupal stage. Mass gain of *S.*

frugiperda caterpillar and pupal stage was reduced indicating the potential cascading effects in their adult stages. Our findings suggest that there is potential to develop commercial product from purple corn pericarp that could be used as bioinsecticide. Future work, should be focused on testing the efficacy under field conditions, actual underlying mechanisms of polyphenols on *S. frugiperda* and exploring more potential plant based sources for their insecticidal properties using simple methods of extraction. This is an area our lab is currently focusing on.

From our third chapter, we tested whether diet variation has any affect on oviposition success and progeny fitness of insects. Finally, we conclude that variation in insect diet during their larval stages have significant role in their reproductive fitness. Plant defenses acts differentially on the growth and development of tobacco hormworm (*M. sexta*), their oviposition and progeny success. *M. sexta* fed on four *Solanum* species for short period of time reduced their capacity of egg laying and hatching, but *M. sexta* fed on tomato had higher egg laying and hatching capacity. This could be possibly due to higher amount of PPO amount and higher trichome density in four *Solanum* species than tomato plants. There might be wide range of toxic secondary metabolites present in them, which might have affected their oviposition. Future work should be focused on detailed secondary metabolic profiling of different *Solanum* species, which can provide insight to underlying mechanisms affecting oviposition and progeny success. Another area of interest is exploring structural defenses such as trichomes, spines that could also affect egg laying and egg hatching.

REFERENCES

Agrawal, A. A.; Strauss, S. Y.; Stout, M. J. Costs of Induced Responses and Tolerance to Herbivory in Male and Female Fitness Components of Wild Radish. *Evolution* **1999**, *53*, 1093.

Ahmad, S.; Veyrat, N.; Gordon-Weeks, R.; Zhang, Y.; Martin, J.; Smart, L.; Glauser, G.; Erb, M.; Flors, V.; Frey, M.; et al. Benzoxazinoid Metabolites Regulate Innate Immunity against Aphids and Fungi in Maize. *Plant Physiol.* **2011**, *157*, 317–327.

Alborn, H. T.; Brennan, M. M.; Tumlinson, J. H. *Journal of Chemical Ecology* **2003**, *29*, 1357–1372.

Aljbory, Z.; Chen, M.-S. Indirect plant defense against insect herbivores: A review. *Insect Sci.* **2017**, *25*, 2–23.

Ateyyat, M.; Abu-Romman, S.; Abu-Darwish, M.; Ghabeish, I. Impact of Flavonoids against Woolly Apple Aphid, Eriosoma lanigerum (Hausmann) and Its Sole Parasitoid, Aphelinus mali (Hald.). *J. Agric. Sci.* **2012**, *4*, doi:10.5539/jas.v4n2p227.

Austin, M.B.; Noel, J.P. The Chalcone Synthase Superfamily of Type III Polyketide Synthases. *ChemInform* **2003**, *34*.

Azevedo, R. B. R.; French, V.; Partridge, L. Life-History Consequences of Egg Size inDrosophila Melanogaster. *The American Naturalist* **1997**, *150*, 250–282.

Basli, A.; Soulet, S.; Chaher, N.; Mérillon, J.-M.; Chibane, M.; Monti, J.-P.; Richard, T. Dietary Polyphenols and Their Effects on Cell Biochemistry and Pathophysiology. *Oxidative Med. Cell. Longev.* **2012**.

Bauerfeind, S. S.; Fischer, K. Effects of adult-derived carbohydrates, amino acids and micronutrients on female reproduction in a fruit-feeding butterfly. *Journal of Insect Physiology* **2005**, *51*, 545–554.

Bauerfeind, S. S.; Fischer, K. Effects of food stress and density in different life stages on reproduction in a butterfly. *Oikos* **2005**, *111*, 514–524.

Bauerfeind, S. S.; Fischer, K. Effects of larval starvation and adult diet-derived amino acids on reproduction in a fruit-feeding butterfly. *Entomologia Experimentalis et Applicata* **2009**, *130*, 229–237.

Baur, R.; Haribal, M.; Renwick, J.A.A.; Stadler, E. Contact chemoreception related to host selection and oviposition behaviour in the monarch butterfly, Danaus plexippus. *Physiol. Entomol.* **1998**, *23*, 7–19.

Beckman, C.H. Phenolic-storing cells: Keys to programmed cell death and periderm formation in wilt disease resistance and in general defence responses in plants? *Physiol. Mol. Plant Pathol.* **2000**, *57*, 101–110.

Bentivenha, J. P. F.; Canassa, V. F.; Baldin, E. L. L.; Borguini, M. G.; Lima, G. P. P.; Lourenção, A. L. Role of the Rutin and Genistein Flavonoids in Soybean Resistance to Piezodorus guildinii (Hemiptera: Pentatomidae). *Arthropod-Plant Interactions* **2017**, *12*, 311–320.

Bernays, E. A.; Howard, J. J.; Champagne, D.; Estesen, B. J. Rutin: a phagostimulant for the polyphagous acridid Schistocerca americana. *Entomol. exp. appl* **1991**, *60*, 19–28.

Bertea, C. M.; Casacci, L. P.; Bonelli, S.; Zampollo, A.; Barbero, F. Chemical, Physiological and Molecular Responses of Host Plants to Lepidopteran Egg-Laying. *Frontiers in Plant Science* **2020**, *10*.

Bhonwong, A.; Stout, M. J.; Attajarusit, J.; Tantasawat, P. Defensive Role of Tomato Polyphenol Oxidases against Cotton Bollworm (Helicoverpa armigera) and Beet Armyworm (Spodoptera exigua). *Journal of Chemical Ecology* **2008**, *35*, 28–38.

Bi, J. L.; Felton, G. W. Foliar oxidative stress and insect herbivory: Primary compounds, secondary metabolites, and reactive oxygen species as components of induced resistance. *Journal of Chemical Ecology* **1995**, *21*, 1511–1530.

Bi, J. L.; Murphy, J. B.; Felton, G. W. Antinutritive and Oxidative Components as Mechanisms of Induced Resistance in Cotton to Helicoverpa zea. *Journal of Chemical Ecology* **1997**, *23*, 97–117.

Biswas, S.; Hazra, S.; Chattopadhyay, S. Identification of conserved miRNAs and their putative target genes in Podophyllum hexandrum (Himalayan Mayapple). *Plant Gene* **2016**, *6*, 82–89.

Boggs, C. L.; Freeman , K. D. Larval food limitation in butterflies: effects on adult resource allocation and fitness. *Oecologia* **2005**, *144*, 353–361.

Brillouet, J.-M.; Verdeil, J.-L.; Odoux, E.; Lartaud, M.; Grisoni, M.; Conéjéro, G. Phenol homeostasis is ensured in vanilla fruit by storage under solid form in a new chloroplast-derived organelle, the phenyloplast. *J. Exp. Bot.* **2014**, *65*, 2427–2435.

Burdziej, A.; Pączkowski, C.; Destrac-Irvine, A.; Richard, T.; Cluzet, S.; Szakiel, A. Triterpenoid profiles of the leaves of wild and domesticated grapevines. *Phytochemistry Letters* **2019**, *30*, 302–308.

Cabral, M.; Kelecom, A.; Garcia, E. Effects of the lignan, pinoresinol on the moulting cycle of the bloodsucking bug Rhodnius prolixus and of the milkweed bug Oncopeltus fasciatus. *Fitoterapia* **1999**, *70*, 561–567, doi:10.1016/s0367-326x(99)00089-1.

Cai, H. The rice bran constituent tricin potently inhibits cyclooxygenase enzymes and interferes with intestinal carcinogenesis in ApcMin mice. *Mol. Cancer Ther.* **2005**, *4*, 1287–1292.

Campos, M.L.; Yoshida, Y.; Major, I.T.; Ferreira, D.D.O.; Weraduwage, S.M.; Froehlich, J.E.; Johnson, B.F.; Kramer, D.M.; Jander, G.; Sharkey, T.D.; et al. A. Rewiring of jasmonate and phytochrome B signalling uncouples plant growth-defense tradeoffs. *Nat. Commun.* **2016**, *7*, DOI: 10.1038/ncomms12570

Carter, M.; Sachdev-Gupta, K.; Feeny, P. Tyramine from the leaves of wild parsnip: A stimulant and synergist for oviposition by the black swallowtail butterfly. *Physiol. Entomol.* **1998**, *23*, 303–312.

Chamarthi, S.K.; Sharma, H.C.; Sahrawat, K.L.; Narasu, L.M.; Dhillon, M.K. Physico-chemical mechanisms of resistance to shoot fly, Atherigona soccata in sorghum, Sorghum bicolor. *J. Appl. Entomol.* **2010**, *135*, 446–455.

Chaudhary, S. Progress on Azadirachta indica Based Biopesticides in Replacing Synthetic Toxic Pesticides. *Frontiers in Plant Science* **2017**, *8*.

Chen, S.; Lin, R.; Lu, H.; Wang, Q.; Yang, J.; Liu, J.; Yan, C. Effects of phenolic acids on free radical scavenging and heavy metal bioavailability in kandelia obovata under cadmium and zinc stress. *Chemosphere* **2020**, *249*, 126341.

Cheynier, V.; Comte, G.; Davies, K.M.; Lattanzio, V.; Martens, S. Plant phenolics: Recent advances on their biosynthesis, genetics, and ecophysiology. *Plant Physiol. Biochem.* **2013**, *72*, 1–20.

Chrzanowski, G.; Leszczyński, B. Induced accumulation of phenolic acids in winter triticale (Triticosecale Wittm.) under insects feeding. *Herba Polonica* **2008**, *54*.

Cipollini, D.; Stevenson, R.; Enright, S.; Eyles, A.; Bonello, P. Phenolic Metabolites in Leaves of the Invasive Shrub, Lonicera maackii, and Their Potential Phytotoxic and Anti-Herbivore Effects. *J. Chem. Ecol.* **2008**, *34*, 144–152.

Crockett, S.L.; Boevé, J.-L. Flavonoid Glycosides and Naphthodianthrones in the Sawfly Tenthredo zonula and its Host-Plants, Hypericum perforatum and H. hirsutum. *J. Chem. Ecol.* **2011**.

Deseo, K. V. Study of factors influencing the fecundity and fertility of codling moth (Laspeyresia pomonella L., Lepidoptera, Tortricidae). *Acta Phytopathol. Acad. Sci.* **1971**, *6*, 243–252.

Desurmont, G. A.; Weston, P. A. Aggregative oviposition of a phytophagous beetle overcomes egg-crushing plant defences. *Ecological Entomology* **2011**, *36*, 335–343.

Dinan, L.; Savchenko, T.; Whiting, P.; Sarker, S.D. Plant natural products as insect steroid receptor agonists and antagonists. *Pestic. Sci.* **1999**, *55*, 331–335.

Dlamini, B. C.; Madala, M. E. Phytochemical composition and antioxidant and antimicrobial activities of Solanum retroflexum leaf extracts. . **2017**.

Dreyer, D.L.; Jones, K.C. Feeding deterrency of flavonoids and related phenolics towards Schizaphis graminum and Myzus persicae: Aphid feeding deterrents in wheat. *Phytochemistry* **1981**, *20*, 2489–2493.

Dubey, N. K. Natural products in plant pest management. *CABI* **2011**.

Duffey, S.S.; Felton, G.W. ChemInform Abstract: Plant Enzymes in Resistance to Insects. *ChemInform* **1990**, *21*.

Eigenbrode, S.D.; Trumble, J.T. Antibiosis to Beet Armyworm (Spodoptera exigua) in Lycopersicon Accessions. *HortScience* **1993**, *28*, 932–934.

El-Basyouni, S. Z.; Chen, D.; Ibrahim, R. K.; Neish, A. C.; Towers, G. H. N. Biosynthesis of hydroxybenzoic acids in higher plants. *Phytochemistry* **1964**, *3*, 485–492.

Erb, M.; Reymond, P. Molecular Interactions Between Plants and Insect Herbivores. *Annu. Rev. Plant Biol.* **2019**, *70*, 527–557.

Farmer, E.E.; Ryan, C.A. Octadecanoid Precursors of Jasmonic Acid Activate the Synthesis of Wound-Inducible Proteinase Inhibitors. *Plant Cell* **1992**, 129–134.

Fathipour, Y.; Baghery, F.; Bagheri, A.; Naseri, B. Development, reproduction and life table parameters of Helicoverpa armigera (Lepidoptera: Noctuidae) on five main host plants. *Journal of Crop Protection* **2020**, *9*, 551–561.

Fathipour, Y.; Chegeni, E.; Moharramipour, S. Genotype-Associated Variation in Nutritional Indices of Helicoverpa armigera (Lepidoptera: Noctuidae) Fed on Canola. *Journal of Agricultural Science and Technology* **2018**, *20*, 83–94.

Fatouros, N. E.; Lucas-Barbosa, D.; Weldegergis, B. T.; Pashalidou, F. G.; Loon, J. J. A. V.; Dicke, M.; Harvey, J. A.; Gols, R.; Huigens, M. E. Plant Volatiles Induced by Herbivore Egg Deposition Affect Insects of Different Trophic Levels. *PLoS ONE* **2012**, *7*.

Feeny, P.; Sachdev, K.; Rosenberry, L.; Carter, M. Luteolin 7-O-(6”-O-malonyl)-β-d-glucoside and trans-chlorogenic acid: Oviposition stimulants for the black swallowtail butterfly. *Phytochemistry* **1988**, *27*, 3439–3448.

Felton, G.W.; Duffey, S.S. Protective action of midgut catalase in lepidopteran larvae against oxidative plant defenses. *J. Chem. Ecol.* **1991**, *17*, 1715–1732.

Ferreresa, F.; Fernandesb, F.; Oliveirac, J.M.A.; Valentãob, P.; Pereirad, J.A.; Andradeb, P.B. Metabolic profiling and biological capacity of Pieris brassicae fed with kale (*Brassica oleracea* L. var. acephala). *Food Chem. Toxicol.* **2009**, *47*, 1209–1220.

Flanders, K. L.; Hawkes, J. G.; Radcliffe, E. B.; Lauer, F. I. Insect resistance in potatoes: sources, evolutionary relationships, morphological and chemical defenses, and ecogeographical associations. *Euphytica* **1992**, *61*, 83–111.

Fowler, J. H.; Narváez-Vásquez, J.; Aromdee, D. N.; Pautot, V.; Holzer, F. M.; Walling, L. L. Leucine Aminopeptidase Regulates Defense and Wound Signaling in Tomato Downstream of Jasmonic Acid. *The Plant Cell* **2009**, *21*, 1239–1251.

Fraenkel, G.S. The Raison d’Etre of Secondary Plant Substances: These odd chemicals arose as a means of protecting plants from insects and now guide insects to food. *Science* **1959**, *129*, 1466–1470.

Freeman. An Overview of Plant Defenses against Pathogens and Herbivores. *Plant Health Instr.* **2008**.

Fujimoto, N.; Hayashiya, K.; Nakajima, K. Studies on the pigments of cocoon. (IV) The formation and translocation of the pigments of green cocoon in the silkworm larvae. *J. Seric Sci Jpn.* **1959**, *28*, 30–32.

Fürstenberg-Hägg, J.; Zagrobelny, M.; Bak, S. Plant Defense against Insect Herbivores. *Int. J. Mol. Sci.* **2013**, *14*, 10242–10297.

Gabaston, J.; Khawand, T.E.; Waffo-Teguo, P.; Decendit, A.; Richard, T.; Mérillon, J.-M.; Pavela, R. Stilbenes from grapevine root: A promising natural insecticide against Leptinotarsa decemlineata. *J. Pest Sci.* **2018**, *91*, 897–906.

Gachon, C.M.; Langlois-Meurinne, M.; Saindrenan, P. Plant secondary metabolism glycosyltransferases: The emerging functional analysis. *Trends Plant Sci.* **2005**, *10*, 542–549.

Gandhi, A.; Kariyat, R. R.; Chappa, C.; Tayal, M.; Sahoo, N. Tobacco Hornworm (Manduca sexta) Oral Secretion Elicits Reactive Oxygen Species in Isolated Tomato Protoplasts. *International Journal of Molecular Sciences* **2020**, *21*, 8297.

Gantner, M.; Najda, A.; Piesik, D. Effect of phenolic acid content on acceptance of hazel cultivars by filbert aphid. *Plant Prot. Sci.* **2019**, *55*, 116–122.

Garcia, E. S.; Cabral, M. M. O.; Schaubb, G. A.; Gottlieb, O. R.; Azambuja Patrícia Effects of lignoids on a hematophagous bug, Rhodnius prolixus: feeding, ecdysis and diuresis. *Phytochemistry* **2000**, *55*, 611–616.

Geuder, M.; Wray, V.; Fiedler, K.; Proksch, P. Sequestration and Metabolism of Host-Plant Flavonoids by the Lycaenid Butterfly Polyommatus bellargus. *J. Chem. Ecol.* **1997**, *23*, 1361–1372.

Gilbert, N. Control of Fecundity in Pieris rapae: I. The Problem. *The Journal of Animal Ecology* **1984**, *53*, 581.

Gordon, D. M.; Stewart, R. K. Demographic Characteristics of the Stored-Products Moth Cadra cautella. *The Journal of Animal Ecology* **1988**, *57*, 627.

Green, P. W. C.; Stevenson, P. C.; Simmonds, M. S. J.; Sharma, H. C. Phenolic Compounds on the Pod-Surface of Pigeonpea, Cajanus cajan, Mediate Feeding Behavior of Helicoverpa armigera Larvae. *Journal of Chemical Ecology* **2003**, *29*, 811–821.

Green, T.R.; Ryan, C.A. Wound-Induced Proteinase Inhibitor in Plant Leaves: A Possible Defense Mechanism against Insects. *Science* **1972**, *175*, 776–777.

Grover, S.; Agpawa, E.; Sarath, G.; Sattler, S.E.; Louis, J. Interplay of phytohormones facilitate sorghum tolerance to aphids. *Plant Mol. Biol.* **2020**.

Gupta, O.P.; Karkute, S.G.; Banerjee, S.; Meena, N.L.; Dahuja, A. Contemporary Understanding of miRNA-Based Regulation of Secondary Metabolites Biosynthesis in Plants. *Front. Plant Sci.* **2017**, *8*.

Gupta, S.; Dikshit, A. Biopesticides: an ecofriendly approach for pest control. *J Biopest* **2010**.

Han, M. A.; Kim, J. H.; Song, H. S. Persistent organic pollutants, pesticides, and the risk of thyroid cancer. *European Journal of Cancer Prevention* **2019**, *28*, 344–349.

Harborne, J.B. The Flavonoids: Advances in Research since **1980**; Chapman & Hall: London, 1988.

Harborne, J.B.; Williams, C.A. Advances in flavonoid research since 1992. *Phytochemistry* **2000**, *55*, 481–504.

Haribal, M., & Renwick, J. A. (1996). Oviposition stimulants for the monarch butterfly: Flavonol glycosides from Asclepias curassavica. *Phytochemistry, 41*(1), 139-144. doi:doi.org/10.1016/0031-9422(95)00511-0

Hauser, M.-T. Molecular basis of natural variation and environmental control of trichome patterning. *Frontiers in Plant Science* **2014**, *5*.

Heliovaara, K.; Vaisanen, R.; Varama, M. Fecundity and egg viability in relation to female body size in Neodiprion sertifer (Hymenoptera: Diprionidae). *Ecography* **1990**, *13*, 166–172.

Hilker, M.; Fatouros, N. E. Plant Responses to Insect Egg Deposition. *Annual Review of Entomology* **2015**, *60*, 493–515.

Hoffmann-Campo, C.; Harborne, J.; Mccaffery, A. Pre-ingestive and post-ingestive effects of soya bean extracts and rutin on Trichoplusia ni growth. *Entomol. Exp. Et Appl.* **2001**, *98*, 181–194.

Howe, G. A.; Jander, G. Plant Immunity to Insect Herbivores. *Annual Review of Plant Biology* **2008**, *59*, 41–66.

Hu, Q.; Min, L.; Yang, X.; Jin, S.; Zhang, L.; Li, Y.; Ma, Y.; Qi, X.; Li, D.; Liu, H.; et al. Laccase GhLac1 Modulates Broad-Spectrum Biotic Stress Tolerance via Manipulating Phenylpropanoid Pathway and Jasmonic Acid Synthesis. *Plant Physiol.* **2017**, *176*, 1808–1823.

Huot, B.; Yao, J.; Montgomery, B.L.; He, S.Y. Growth–Defense Tradeoffs in Plants: A Balancing Act to Optimize Fitness. *Mol. Plant* **2014**, *7*, 1267–1287.

Ismail, S. Influences of Different Host Plants on Biological and Food Utilization of the Cotton Leafworm, Spodoptera littoralis. *Progress in Chemical and Biochemical Research* **2020**, *3*, 229–238.

Jiani, L.; Yuan, S.; Wei, W.; Yu, Z.; Zebin, C.; Lei, Y. Effects of Nicotine, a Plant Secondary Metabolite, on Protective Enzyme and Detoxification Enzyme of Frank linie lla occ ide ntalis. *Plant Dis. Pests* **2019**, *10*, 7–10.

Jun, S.-Y.; Sattler, S. A.; Cortez, G. S.; Vermerris, W.; Sattler, S. E.; Kang, C. Biochemical and Structural Analysis of Substrate Specificity of a Phenylalanine Ammonia-Lyase. *Plant Physiology* **2017**, *176*, 1452–1468.

Kaitaniemi, P.; Neuvonen, S.; Nyyssönen, T. Effects Of Cumulative Defoliations On Growth, Reproduction, And Insect Resistance In Mountain Birch. *Ecology* **1999**, *80*, 524–532.

Kant, M. R.; Ament, K.; Sabelis, M. W.; Haring, M. A.; Schuurink, R. C. Differential Timing of Spider Mite-Induced Direct and Indirect Defenses in Tomato Plants. *Plant Physiology* **2004**, *135*, 483–495.

Kaplan, I.; Dively, G. P.; Denno, R. F. The costs of anti-herbivore defense traits in agricultural crop plants: a case study involving leafhoppers and trichomes. *Ecological Applications* **2009**, *19*, 864–872.

Karban, R. The ecology and evolution of induced resistance against herbivores. *Funct. Ecol.* **2010**, *25*, 339–347.

Karban, R.; Baldwin, I. T. Induced Responses to Herbivory. **1997**.

Kariyat RR, Scanlon SR, Moraski RP, Stephenson AG, Mescher MC, Moraes CMD. Plant inbreeding and prior herbivory influence the attraction of caterpillars (Manduca sexta) to odors of the host plant Solanum carolinense (Solanaceae). American Journal of Botany 2014;101:376–80. doi:10.3732/ajb.1300295

Kariyat, R. R.; Gaffoor, I.; Sattar, S.; Dixon, C. W.; Frock, N.; Moen, J.; Moraes, C. M. D.; Mescher, M. C.; Thompson, G. A.; Chopra, S. Sorghum 3-Deoxyanthocyanidin Flavonoids Confer Resistance against Corn Leaf Aphid. *Journal of Chemical Ecology* **2019**, *45*, 502–514.

Kariyat, R. R.; Hardison, S. B.; Moraes, C. M. D.; Mescher, M. C. Plant spines deter herbivory by restricting caterpillar movement. *Biology Letters* **2017**, *13*, 20170176.

Kariyat, R. R.; Mauck, K. E.; Balogh, C. M.; Stephenson, A. G.; Mescher, M. C.; De Moraes, C. M. Inbreeding in horsenettle (Solanum carolinense) alters night-time volatile emissions that guide oviposition by Manduca sexta moths. *Proceedings of the Royal Society B: Biological Sciences* **2013**, *280*, 20130020.

Kariyat, R. R.; Portman, S. L. Plant-herbivore interactions: Thinking beyond larval growth and mortality. *American Journal of Botany* **2016**, *103*, 789–791.

Kariyat, R. R.; Raya, C. E.; Chavana, J.; Cantu, J.; Guzman, G.; Sasidharan, L. Feeding on glandular and non-glandular leaf trichomes negatively affect growth and development in tobacco hornworm (Manduca sexta) caterpillars. *Arthropod-Plant Interactions* **2019**, *13*, 321–333.

Kariyat, R. R.; Smith, J. D.; Stephenson, A. G.; Moraes, C. M. D.; Mescher, M. C. Non-glandular trichomes of Solanum carolinense deter feeding by Manduca sexta caterpillars and cause damage to the gut peritrophic matrix. *Proceedings of the Royal Society B: Biological Sciences* **2017**, *284*, 20162323.

Kariyat, R.R.; Mena-Alí, J.; Forry, B.; Mescher, M.C.; Moraes, C.M.; Stephenson, A.G. Inbreeding, herbivory, and the transcriptome of Solanum carolinense. *Entomol. Exp. Et Appl.* **2012**, *144*, 134–144.

Kariyat, R.R.; Mauck, K.E.; Moraes, C.M.D.; Stephenson, A.G.; Mescher, M.C. Inbreeding alters volatile signalling phenotypes and influences tri-trophic interactions in horsenettle (Solanum carolinense L.). *Ecol. Lett.* **2012**, *15*, 301–309.

Kaur, I.; Kariyat, R. R. Eating barbed wire: Direct and indirect defensive roles of non-glandular trichomes. *Plant, Cell & Environment* **2020**, *43*, 2015–2018.

Kaur, J.; Chavana, J.; Soti, P.; Racelis, A.; Kariyat, R. Arbuscular mycorrhizal fungi (AMF) influences growth and insect community dynamics in Sorghum-sudangrass (Sorghum x drummondii). *Arthropod-Plant Interactions* **2020**, *14*, 301–315.

Kaur, J.; Kariyat, R. Role of trichomes in plant-stress biology. In *Evolutionary Ecology of Plant-Herbivore Interactions*; Valverde, P., Nunez-Farfan, J., Eds.; Springer International Publishing, Cham, Switzerland: 2020.

Kehl, T.; Fischer, K. Larval starvation reduces responsiveness to feeding stimuli and does not affect feeding preferences in a butterfly. *Journal of Insect Physiology* **2012**, *58*, 1028–1035.

Kessler, A.; Baldwin, I.T. Plantresponses Toinsectherbivory: The Emerging Molecular Analysis. *Annu. Rev. Plant Biol.* **2002**, *53*, 299–328.

Khoo, H.E.; Azlan, A.; Tang, S.T.; Lim, S.M. Anthocyanidins and anthocyanins: Colored pigments as food, pharmaceutical ingredients, and the potential health benefits. *Food Nutr. Res.* **2017**, *61*, 1361779.

Koornneef, A.; Pieterse, C.M. Cross Talk in Defense Signaling: Figure 1. *Plant Physiol.* **2008**, *146*, 839–844.

Kovalikova, Z.; Kubes, J.; Skalicky, M.; Kuchtickova, N.; Maskova, L.; Tuma, J.; Vachova, P.; Hejnak, V. Changes in Content of Polyphenols and Ascorbic Acid in Leaves of White Cabbage after Pest Infestation. *Molecules* **2019**, *24*, 2622.

Kundu, A.; Vadassery, J. Chlorogenic acid-mediated chemical defence of plants against insect herbivores. *Plant Biol.* **2019**, *21*, 185–189.

Kuwatsuka, S.; Shindo, H. Behavior of phenolic substances in the decaying process of plants: I. Identification and Quantitative Determination of Phenolic Acids in Rice Straw and Its Decayed Product by Gas Chromatography. *Soil Sci. Plant Nutr.* **1973**, *19*, 219–227.

Lagrimini, L.M.; Vaughn, J.; Erb, W.A.; Miller, S.A. Peroxidase Overproduction in Tomato: Wound-induced Polyphenol Deposition and Disease Resistance. *Hort. Sci.* **1993**, *28*, 218–221.

Lambert, C.; Richard, T.; Renouf, E.; Bisson, J.; Waffo-Téguo, P.; Bordenave, L.; Ollat, N.; Mérillon, J.-M.; Cluzet, S. Comparative Analyses of Stilbenoids in Canes of Major Vitis vinifera L. Cultivars. *J. Agric. Food Chem.* **2013**, *61*, 11392–11399.

Lane, G. A.; Sutherland, O. R. W.; Skipp, R. A. Isoflavonoids as insect feeding deterrents and antifungal components from root ofLupinus angustifolius. *Journal of Chemical Ecology* **1987**, *13*, 771–783.

Lanteren, J. V.; Noldus, L. Whitefly-plant relationships: behavioural and ecological aspects. *Whiteflies: their bionomics, pest status and management* **1990**.

Lattanzio, V. Phenolic Compounds: Introduction. *Nat. Prod.* **2013**, 1543–1580.

Leather, S. R. Size, Reproductive Potential and Fecundity in Insects: Things aren't as Simple as They Seem. *Oikos* **1988**, *51*, 386.

Leather, S. R. The effect of adult feeding on the fecundity, weight loss and survival of the pine beauty moth, Panolis flammea (D&S). *Oecologia* **1984**, *65*, 70–74.

Leiss, K.A.; Maltese, F.; Choi, Y.H.; Verpoorte, R.; Klinkhamer, P.G. Identification of Chlorogenic Acid as a Resistance Factor for Thrips in Chrysanthemum. *Plant Physiol.* **2009**, *150*, 1567–1575.

Leung, L.K.; Su, Y.; Chen, R.; Zhang, Z.; Huang, Y.; Chen, Z.-Y. Theaflavins in Black Tea and Catechins in Green Tea Are Equally Effective Antioxidants. *J. Nutr.* **2001**, *131*, 2248–2251.

Li N, Han X, Feng D, Yuan D, Huang L-J. Signaling Crosstalk between Salicylic Acid and Ethylene/Jasmonate in Plant Defense: Do We Understand What They Are Whispering? International Journal of Molecular Sciences 2019;20:671. doi:10.3390/ijms20030671.

Li, A.-N.; Li, S.; Zhang, Y.-J.; Xu, X.-R.; Chen, Y.-M.; Li, H.-B. Resources and Biological Activities of Natural Polyphenols. *Nutrients* **2014**, *6*, 6020–6047.

Li, Q.; Somavat, P.; Singh, V.; Chatham, L.; Mejia, E. G. D. A comparative study of anthocyanin distribution in purple and blue corn coproducts from three conventional fractionation processes. *Food Chemistry* **2017**, *231*, 332–339.

López-Palacios, C.; Peña-Valdivia, C. B. Screening of secondary metabolites in cladodes to further decode the domestication process in the genus Opuntia (Cactaceae). *Planta* **2020**, *251*.

Louis, J.; Singh, V.; Shah, J. Arabidopsis thaliana—Aphid Interaction. *Arab. Book* **2012**, *10*.

Luteyn, J.L.; Harborne, J.B.; Williams, C.A. A Survey of the flavonoids and simple phenols in leaves of Cavendishia (*Ericaceae*). *Brittonia* 1980, *32*, 1–16.

Lv, X.-Q.; Feng, G.; Liu, Y.-Q.; Nan, X.; Yang, L. CA-4, a natural cis-stilbene compound with potential insecticidal activity. *Med. Chem. Res.* **2014**, *23*, 3347–3352.

Maazoun, A.M.; Hlel, T.B.; Hamdi, S.H.; Belhadj, F.; Jemâa, J.M.B.; Marzouki, M.N. Screening for insecticidal potential and acetylcholinesterase activity inhibition of Urginea maritima bulbs extract for the control of Sitophilus oryzae (L.). *J. Asia-Pac. Entomol.* **2017**, *20*, 752–760.

Macdonald, M.J.; D'Cunha, G.B. A modern view of phenylalanine ammonia lyase. *Biochem. Cell Biol.* **2007**, *85*, 273–282.

Maga, J.A.; Lorenz, K. Gas-liquid chromatography separation of the free phenolic acid fractions in various oilseed protein sources. *J. Sci. Food Agric.* **1974**.

Mahanil, S.; Attajarusit, J.; Stout, M. J.; Thipyapong, P. Overexpression of tomato polyphenol oxidase increases resistance to common cutworm. *Plant Science* **2008**, *174*, 456–466.

Mao, J.; Burt, A. J.; Ramputh, A.-I.; Simmonds, J.; Cass, L.; Hubbard, K.; Miller, S.; Altosaar, I.; Arnason, J. T. Diverted Secondary Metabolism and Improved Resistance to European Corn Borer (Ostrinia nubilalis) in Maize (Zea maysL.) Transformed with Wheat Oxalate Oxidase. *Journal of Agricultural and Food Chemistry* **2007**, *55*, 2582–2589.

Mao, Y.-B.; Cai, W.-J.; Wang, J.-W.; Hong, G.-J.; Tao, X.-Y.; Wang, L.-J.; Huang, Y.-P.; Chen, X.-Y. Silencing a cotton bollworm P450 monooxygenase gene by plant-mediated RNAi impairs larval tolerance of gossypol. *Nature Biotechnology* **2007**, *25*, 1307–1313.

Marciniak, P.; Kolińska, A.; Spochacz, M.; Chowański, S.; Adamski, Z.; Scrano, L.; Falabella, P.; Bufo, S.A.; Rosiński, G. Differentiated Effects of Secondary Metabolites from Solanaceae and Brassicaceae Plant Families on the Heartbeat of Tenebrio molitor Pupae. *Toxins* **2019**, *11*, 287.

Mason, C. M.; Bowsher, A. W.; Crowell, B. L.; Celoy, R. M.; Tsai, C.-J.; Donovan, L. A. Macroevolution of leaf defenses and secondary metabolites across the genusHelianthus. *New Phytologist* **2015**, *209*, 1720–1733.

Matsuda, H.; Tewtrakul, S.; Morikawa, T.; Yoshikawa, M. Anti-allergic activity of stilbenes from Korean rhubarb (Rheum undulatum L.): structure requirements for inhibition of antigen-induced degranulation and their effects on the release of TNF-α and IL-4 in RBL-2H3 cells. *Bioorganic & Medicinal Chemistry* **2004**, *12*, 4871–4876.

Mazur, W.M.; Wähälä, K.; Rasku, S.; Salakka, A.; Hase, T.; Adlercreutz, H. Lignan and isoflavonoid concentrations in tea and coffee. *Br. J. Nutr.* **1998**, *79*, 37–45.

Mccormick, A. C.; Unsicker, S. B.; Gershenzon, J. The specificity of herbivore-induced plant volatiles in attracting herbivore enemies. *Trends in Plant Science* **2012**, *17*, 303–310.

Mcdowell, E. T.; Kapteyn, J.; Schmidt, A.; Li, C.; Kang, J.-H.; Descour, A.; Shi, F.; Larson, M.; Schilmiller, A.; An, L.; Jones, A. D.; Pichersky, E.; Soderlund, C. A.; Gang, D. R. Comparative Functional Genomic Analysis of Solanum Glandular Trichome Types. *Plant Physiology* **2010**, *155*, 524–539.

Mehrkhou, F.; Musavi, M.; Talebi, A. A. Effect of different Solanaceous host plants on nutritional indices of Spodoptera exigua (Lepidoptera: Noctuidae). *Journal of Crop Protection* **2015**, *4*, 329–336.

Meiners, T.; Hilker, M. *Journal of Chemical Ecology* **2000**, *26*, 221–232.

Meriño-Cabrera Y, Zanuncio J, Silva RD, Solis-Vargas M, Cordeiro G, Rainha F, et al. Biochemical response between insects and plants: an investigation of enzyme activity in the digestive system of Leucoptera coffeella (Lepidoptera: Lyonetiidae) and leaves of Coffea arabica (Rubiaceae) after herbivory. Annals of Applied Biology 2018;172:236–43. doi:10.1111/aab.12416.

Meyer, R. S.; Whitaker, B. D.; Little, D. P.; Wu, S.-B.; Kennelly, E. J.; Long, C.-L.; Litt, A. Parallel reductions in phenolic constituents resulting from the domestication of eggplant. *Phytochemistry* **2015**, *115*, 194–206.

Mikolajczak, K.L.; Smith, C.R. Phenolic and sugar components of Armavireo variety sunflower (*Helianthus annuus*) seed meal. *J. Agric. Food Chem.* **1970**, *18*.

Mitchell, C.; Brennan, R. M.; Graham, J.; Karley, A. J. Plant Defense against Herbivorous Pests: Exploiting Resistance and Tolerance Traits for Sustainable Crop Protection. *Frontiers in Plant Science* **2016**, *7*.

Mitchell, C.; Brennan, R. M.; Graham, J.; Karley, A. J. Plant Defense against Herbivorous Pests: Exploiting Resistance and Tolerance Traits for Sustainable Crop Protection. *Frontiers in Plant Science* **2016**, *7*.

Mitchell, C.; Brennan, R.M.; Graham, J.; Karley, A.J. Plant Defense against Herbivorous Pests: Exploiting Resistance and Tolerance Traits for Sustainable Crop Protection. *Front. Plant Sci.* **2016**, doi: 10.3389/fpls.2016.01132.

Mitra, A.; Chatterjee, C.; Mandal, F. B. Synthetic Chemical Pesticides and Their Effects on Birds. *Research Journal of Environmental Toxicology* **2011**, *5*, 81–96.

Moazzami, A.A.; Haese, S.L.; Kamal-Eldin, A. Lignan contents in sesame seeds and products. *Eur. J. Lipid Sci. Technol.* **2007**, *109*, 1022–1027.

Moraes, C. M. D.; Lewis, W. J.; Paré, P. W.; Alborn, H. T.; Tumlinson, J. H. Herbivore-infested plants selectively attract parasitoids. *Nature* **1998**, *393*, 570–573.

Morkunas, I.; Woźniak, A.; Formela, M.; Mai, V. C.; Marczak, Ł.; Narożna, D.; Borowiak-Sobkowiak, B.; Kühn, C.; Grimm, B. Pea aphid infestation induces changes in flavonoids, antioxidative defence, soluble sugars and sugar transporter expression in leaves of pea seedlings. *Protoplasma* **2015**, *253*, 1063–1079.

Mousseau, T. The adaptive significance of maternal effects. *Trends in Ecology & Evolution* **1998**, *13*, 403–407.

Naikoo, M.I.; Dar, M.I.; Raghib, F.; Jaleel, H.; Ahmad, B.; Raina, A.; Khan, F.A.; Naushin, F. Role and Regulation of Plants Phenolics in Abiotic Stress Tolerance. *Plant Signal. Mol.* **2019**, 157–168.

Neelam; Khatkar, A.; Sharma, K.K. Phenylpropanoids and its derivatives: Biological activities and its role in food, pharmaceutical and cosmetic industries. *Crit. Rev. Food Sci. Nutr.* **2019**, *60*, 2655–2675.

Neilson, E.H.; Goodger, J.Q.; Woodrow, I.E.; Møller, B.L. Plant chemical defense: At what cost? *Trends Plant Sci.* **2013**, *18*, 250–258.

Nestel , D.; Papadopoulos, N. T.; Pascacio-Villafán , C.; Righini , N.; Altuzar-Molina , A. R.; Aluja , M. Resource allocation and compensation during development in holometabolous insects. *Journal of Insect Physiology* **2016**, *95*, 78–88.

Niemi, L.; Wennström, A.; Ericson, L. Insect feeding preferences and plant phenolic glucosides in the system Gonioctena—Salix triandra. *Entomol. Exp. Et Appl.* **2005**, *115*, 61–66.

Oberdörstera, E.; Clay, M.A.; Cottamb, D.M.; Wilmotb, F.A.; McLachlanac, J.A.; Milnerb, M.J. Common phytochemicals are ecdysteroid agonists and antagonists: A possible evolutionary link between vertebrate and invertebrate steroid hormones. *J. Steroid Biochem. Mol. Biol.* **2001**, *77*, 229–238.

Ono, E.; Hatayama, M.; Isono, Y.; Sato, T.; Watanabe, R.; Yonekura-Sakakibara, K.; Fukuchi-Mizutani, M.; Tanaka, Y.; Kusumi, T.; Nishino, T.; et al. Localization of a flavonoid biosynthetic polyphenol oxidase in vacuoles. *Plant J.* **2006**, *45*, 133–143.

Padhee, A. K.; Prasanna, B. M. The emerging threat of fall armyworm in India. Indian Farming. *Indian Farming* **2019**, *69*, 51–54.

Panche, A.N.; Diwan, A.D.; Chandra, S.R. Flavonoids: An overview. *J. Nutr. Sci.*

Pandey, K.B.; Rizvi, S.I. Plant Polyphenols as Dietary Antioxidants in Human Health and Disease. *Oxidative Med. Cell. Longev.* **2009**, *2*, 270–278.

Paudel, S.; Lin, P.-A.; Foolad, M. R.; Ali, J. G.; Rajotte, E. G.; Felton, G. W. Induced Plant Defenses Against Herbivory in Cultivated and Wild Tomato. *Journal of Chemical Ecology* **2019**, *45*, 693–707.

Pavela, R.; Waffo-Teguo, P.; Biais, B.; Richard, T.; Mérillon, J.-M. Vitis vinifera canes, a source of stilbenoids against Spodoptera littoralis larvae. *Journal of Pest Science* **2017**, *90*, 961–970.

Peiffer, M.; Tooker, J. F.; Luthe, D. S.; Felton, G. W. Plants on early alert: glandular trichomes as sensors for insect herbivores. *New Phytologist* **2009**, *184*, 644–656.

Perera, A.; Karunaratne, M.; Chinthaka, S. Secondary Metabolite Profile and Maize Weevil Repellent Activity of the Leaves of Ruta graveolens. *Proceedings of International Forestry and Environment Symposium* **2017**, *21*.

Perkins, W. D. Laboratory Rearing of the Fall Armyworm. *The Florida Entomologist* **1979**, *62*, 87.

Portman, S. L.; Felton, G. W.; Kariyat, R. R.; Marden, J. H. Host plant defense produces species-specific alterations to flight muscle protein structure and flight-related fitness traits of two armyworms. *The Journal of Experimental Biology* **2020**, *223*.

Portman, S. L.; Kariyat, R. R.; Johnston, M. A.; Stephenson, A. G.; Marden, J. H. Cascading effects of host plant inbreeding on the larval growth, muscle molecular composition, and flight capacity of an adult herbivorous insect. *Functional Ecology* **2015**, *29*, 328–337.

Portmann, J. E. The bioaccumulation and effects of organochlorine pesticides in marine animals. *Proceedings of the Royal Society of London. Series B. Biological Sciences* **1975**, *189*, 291–304.

Preston, C.A.; Lewandowski, C.; Enyedi, A.J.; Baldwin, I.T. Tobacco mosaic virus inoculation inhibits wound-induced jasmonic acid-mediated responses within but not between plants. *Planta* **1999**, *209*, 87–95.

Quideau, S.; Deffieux, D.; Douat-Casassus, C.; Pouységu, L. Plant Polyphenols: Chemical Properties, Biological Activities, and Synthesis. *Angew. Chem. Int. Ed.* **2011**, *50*, 586–621.

Rani, P. U.; Pratyusha, S. Defensive role of Gossypium hirsutum L. anti-oxidative enzymes and phenolic acids in response to Spodoptera litura F. feeding. *Journal of Asia-Pacific Entomology* **2013**, *16*, 131–136.

Rani, P.U.; Jyothsna, Y. Biochemical and enzymatic changes in rice plants as a mechanism of defense. *Acta Physiol. Plant.* **2010**, *32*, 695–701.

Rani, P.U.; Pratyusha, S. Role of castor plant phenolics on performance of its two herbivores and their impact on egg parasitoid behaviour. *BioControl* **2014**, *59*, 513–524.

Ray, S.; Gaffor, I.; Acevedo, F. E.; Helms, A.; Chuang, W.-P.; Tooker, J.; Felton, G. W.; Luthe, D. S. Maize Plants Recognize Herbivore-Associated Cues from Caterpillar Frass. *Journal of Chemical Ecology* **2015**, *41*, 781–792.

Rehman, F.; Khan, F.A.; Badruddin, S.M.A. Role of phenolics in plant defense against insect herbivory. *Chem. Phytopotentials: Health Energy Environ. Perspect.* **2012**, 309–313.

Reymond, P.; Bodenhausen, N.; Poecke, R.M.V.; Krishnamurthy, V.; Dicke, M.; Farmer, E.E. A Conserved Transcript Pattern in Response to a Specialist and a Generalist Herbivore. *Plant Cell* **2004**, *16*, 3132–3147.

Reymond, P.; Farmer, E.E. Jasmonate and salicylate as global signals for defense gene expression. *Curr. Opin. Plant Biol.* **1998**, *1*, 404–411.

Roininen, H.; Price, P. W.; Julkunen-Tiitto, R.; Tahvanainen, J.; Ikonen, A. Oviposition Stimulant for a Gall-Inducing Sawfly, Euura lasiolepis, on Willow is a Phenolic Glucoside. *Journal of Chemical Ecology* **1999**, *25*, 943–953.

Romeis, J.; Babendreier, D.; Wäckers, F. L.; Shanower, T. G. Habitat and plant specificity of Trichogramma egg parasitoids—underlying mechanisms and implications. *Basic and Applied Ecology* **2005**, *6*, 215–236.

Rosenheim, J. A. Characterizing the cost of oviposition in insects: a dynamic model. *Evolutionary Ecology* **1999**, *13*.

Rosenheim, J. A. The Relative Contributions of Time and Eggs to the Cost of Reproduction. *Evolution* **1999**, *53*, 376.

Ross, J.A.; Kasum, C.M. Dietary Flavonoids: Bioavailability, Metabolic Effects, and Safety. *Annu. Rev.* **2002**, *22*, 19–34.

Runagall-Mcnaull, A.; Bonduriansky, R.; Crean, A. J. Dietary protein and lifespan across the metamorphic boundary: protein-restricted larvae develop into short-lived adults. *Scientific Reports* **2015**, *5*.

Sagers, C.L.; Coley, P.D. Benefits and Costs of Defense in a Neotropical Shrub. *Ecology* **1995**, *76*, 1835–1843.

Saguez, J.; Attoumbré, J.; Giordanengo, P.; Baltora-Rosset, S. Biological activities of lignans and neolignans on the aphid Myzus persicae (Sulzer). *Arthropod Plant Interact.* **2012**, *7*, 225–233.

Santiago, R.; Malvar, R. A.; Baamonde, M. D.; Revilla, P.; Souto, X. C. Free Phenols in Maize Pith and Their Relationship with Resistance to *Sesamia nonagrioides* (Lepidoptera: Noctuidae) Attack. *Journal of Economic Entomology* **2005**, *98*, 1349–1356.

Sarker, S.D.; Whiting, P.; Dinan, L.; Šik, V.; Rees, H.H. Identification and ecdysteroid antagonist activity of three resveratrol trimers (suffruticosols A, B and C) from Paeonia suffruticosa. *Tetrahedron* **1999**, *55*, 513–524.

Schittko, U.; Burghardt, F.; Fiedler, K.; Wray, V.; Proksch, P. Sequestration and distribution of flavonoids in the common blue butterfly Polyommatus icarus reared on Trifolium repens. *Phytochemistry* **1999**, *51*, 609–614.

Schultz, J.C.; Hunter, M.D.; Appel, H.M. Antimicrobial Activity of Polyphenols Mediates Plant-Herbivore Interactions. *Plant Polyphen.* **1992**, 621–637.

Seino, Y.; Suzuki, Y.; Sogawa, K. An Ovicidal Substance Produced by Rice Plants in Response to Oviposition by the Whitebacked Planthopper, Sogatella furcifera (HORVATH) (Homoptera: Delphacidae). *Applied Entomology and Zoology* **1996**, *31*, 467–473.

Seram, D. Polyphenol Oxidase in Plants Vis-À-Vis Insect And Pathogen Attack. *Think India J.* **2019**, *22*.

Shadle, G. L.; Wesley, S.; Korth, K. L.; Chen, F.; Lamb, C.; Dixon, R. A. Phenylpropanoid compounds and disease resistance in transgenic tobacco with altered expression of l -phenylalanine ammonia-lyase. *Phytochemistry* **2003**, *64*, 153–161.

Sharma, A.; Shahzad, B.; Rehman, A.; Bhardwaj, R.; Landi, M.; Zheng, B. Response of Phenylpropanoid Pathway and the Role of Polyphenols in Plants under Abiotic Stress. *Molecules* **2019**, *24*, 2452.

Sharma, H. C.; Sujana, G.; Rao, D. M. Morphological and chemical components of resistance to pod borer, Helicoverpa armigera in wild relatives of pigeonpea. *Arthropod-Plant Interactions* **2009**, *3*, 151–161.

Shaver, T.N.; Lukefahr, M.J. Effect of Flavonoid Pigments and Gossypol on Growth and Development of the Bollworm, Tobacco Budworm, and Pink Bollworm123. *J. Econ. Entomol.* **1969**, *62*, 643–646.

Shibutani, S.; Samejima, M.; Doi, S. Effects of stilbenes from bark of Picea glehnii (Sieb. et Zucc) and their related compounds against feeding behaviour of Reticulitermes speratus (Kolbe). *Journal of Wood Science* **2004**, *50*, 439–444.

Shoorooei, M.; Lotfi, M.; Nabipour, A.; Mansouri, A.I.; Kheradmand, K.; Zalom, F.G.; Madadkhah, E.; Parsafar, A. Antixenosis and antibiosis of some melon (Cucumis melo) genotypes to the two-spotted spider mite (*Tetranychus urticae*) and a possible mechanism for resistance. *J. Hortic. Sci. Biotechnol.* **2013**, *88*, 73–78.

Shrivastava, A.; Shrivastava, N.; Kumar, N. PHYTOCHEMICAL SCREENING AND STUDY OF ANALGESIC ACTIVITY OF BRINJAL LEAVES. *Pharma Science Monitor* **2012**, *3*, 3028–3033.

Shukle, R. H.; Murdock, L. L. Lipoxygenase Trypsin Inhibitor, and Lectin from Soybeans: Effects on Larval Growth of Manduca sexta (Lepidoptera: Sphingidae)1. *Environmental Entomology* **1983**, *12*, 787–791.

Simmonds, M.S.J. Flavonoid–insect interactions: Recent advances in our knowledge. *Phytochemistry* **2003**, *64*, 21–30.

Simms, E.L.; Rausher, M.D. Costs and Benefits of Plant Resistance to Herbivory. *Am. Nat.* **1987**, *130*, 570–581.

Singh, O. P.; Parihar, S. B. B. Effect of different hosts on the development of Heliothis armogera Hub. *Bulletin of Entomological Research* **1988**, *29*, 168–172.

Singh, S.; Kariyat, R.R. Exposure to polyphenol-rich purple corn pericarp extract restricts fall armyworm (Spodoptera frugiperda) growth. *Plant Signal. Behav.* **2020**, *15*, 1784545.

Singh, S.; Kaur, I.; Kariyat, R. The Multifunctional Roles of Polyphenols in Plant-Herbivore Interactions. *International Journal of Molecular Sciences* **2021**, *22*, 1442.

Smilanich, A. M.; Vargas, J.; Dyer, L. A.; Bowers, M. D. Effects of Ingested Secondary Metabolites on the Immune Response of a Polyphagous Caterpillar Grammia incorrupta. *Journal of Chemical Ecology* **2011**, *37*, 239–245.

Spiteller, D. Plant Defense Strategies. *Encycl. Ecol.* **2008**, 2798–2811.

Spoel, S.H.; Johnson, J.S.; Dong, X. Regulation of tradeoffs between plant defenses against pathogens with different lifestyles. *Proc. Natl. Acad. Sci.* **2007**, *104*, 18842–18847.

Srinivasulu, C.; Ramgopal, M.; Ramanjaneyulu, G.; Anuradha, C.; Kumar, C.S. Syringic acid (SA) – A Review of Its Occurrence, Biosynthesis, Pharmacological and Industrial Importance. *Biomed. Pharmacother.* **2018**, *108*, 547–557.

Stam, J.M.; Kroes, A.; Li, Y.; Gols, R.; Loon, J.J.V.; Poelman, E.H.; Dicke, M. Plant Interactions with Multiple Insect Herbivores: From Community to Genes. *Annu. Rev. Plant Biol.* **2014**, *65*, 689–713.

Steinbrenner, A.D.; Muñoz-Amatriaín, M.; Chaparro, A.F.; Aguilar-Venegas, J.M.; Lo, S.; Okuda, S.; Glauser, G.; Dongiovanni, J.; Shi, D.; Hall, M.; et al. A receptor-like protein mediates plant immune responses to herbivore-associated molecular patterns. *Proc. Natl. Acad. Sci. USA* **2020**.

Stout, M. J.; Brovont, R. A.; Duffey, S. S. *Journal of Chemical Ecology* **1998**, *24*, 945–963.

Suprun, A.R.; Ogneva, Z.V.; Dubrovina, A.S.; Kiselev, K.V. Effect of spruce PjSTS1a, PjSTS2, or PjSTS3 gene overexpression on stilbene biosynthesis in callus cultures of Vitis amurensis Rupr. *Biotechnol. Appl. Biochem.* **2019**, *67*, 234–239.

Suzuki, J.; Tanji, I.; Ota, Y.; Toda, K.; Nakagawa, Y. QSAR of 2,4-diphenyl-1,3-oxazolines for ovicidal activity against the two-spotted spider mite Tetranychus urticae. *Journal of Pesticide Science* **2006**, *31*, 409–416.

Swain, T.; Bate-Smith, E. Flavonoid Compounds. *Comp. Biochem.* **1962**, 755–809.

Taher, D.; Rakha, M.; Ramasamy, S.; Solberg, S.; Schafleitner, R. Sources of Resistance for Two-spotted Spider Mite (Tetranychus urticae) in Scarlet (Solanum aethiopicum L.) and Gboma (S. macrocarpon L.) Eggplant Germplasms. *HortScience* **2019**, *54*, 240–245.

Takemura, M.; Nishida, R.; Mori, N.; Kuwahara, Y. Acylated flavonol glycosides as probing stimulants of a bean aphid, Megoura crassicauda, from Vicia angustifolia. *Phytochemistry* **2002**, *61*, 135–140.

Tamiru, A.; Bruce, T. J. A.; Midega, C. A. O.; Woodcock, C. M.; Birkett, M. A.; Pickett, J. A.; Khan, Z. R. Oviposition Induced Volatile Emissions from African Smallholder Farmers' Maize Varieties. *Journal of Chemical Ecology* **2012**, *38*, 231–234.

Tayal, M.; Somavat, P.; Rodriguez, I.; Martinez, L.; Kariyat, R. Cascading effects of polyphenol-rich purple corn pericarp extract on pupal, adult, and offspring of tobacco hornworm (Manduca sexta L.). *Communicative & Integrative Biology* **2020**, *13*, 43–53.

Tayal, M.; Somavat, P.; Rodriguez, I.; Thomas, T.; Christoffersen, B.; Kariyat, R. Polyphenol-Rich Purple Corn Pericarp Extract Adversely Impacts Herbivore Growth and Development. *Insects* **2020**, *11*, 98.

Taylor, L. R. Longevity, Fecundity and Size; Control of Reproductive Potential in a Polymorphic Migrant, Aphis fabae Scop. *The Journal of Animal Ecology* **1975**, *44*, 135.

Thaler, J.S.; Stout, M.J.; Karban, R.; Duffey, S.S. Exogenous jasmonates simulate insect wounding in tomato plants (Lycopersicon esculentum) in the laboratory and field. *J. Chem. Ecol.* **1996**, *22*, 1767–1781.

The Effect of Fungi Associated with Leaf Blight of Solanum aethiopicum L. in the Field on the Nutrient and Phytochemical Composition of the Leaves and Fruits of the Plant. *Journal of Plant Pathology & Microbiology* **2013**, *04*.

Thipyapong, P.; Stout, M.; Attajarusit, J. Functional Analysis of Polyphenol Oxidases by Antisense/Sense Technology. *Molecules* **2007**, *12*, 1569–1595.

Tian, D.; Peiffer, M.; Moraes, C.M.D.; Felton, G.W. Roles of ethylene and jasmonic acid in systemic induced defense in tomato (Solanum lycopersicum) against Helicoverpa zea. *Planta* **2013**, *239*, 577–589.

Tian, D.; Tooker, J.; Peiffer, M.; Chung, S. H.; Felton, G. W. Role of trichomes in defense against herbivores: comparison of herbivore response to woolly and hairless trichome mutants in tomato (Solanum lycopersicum). *Planta* **2012**, *236*, 1053–1066.

Tohge, T.; Perez de Souza, L.; Fernie, A.R. Current understanding of the pathways of flavonoid biosynthesis in model and crop plants. *J. Exp. Bot.* **2017**, *68*, 4013–4028.

Torres, P.; Avila, J. G.; Vivar, A. R. D.; García Ana M.; Marín Juan C.; Aranda, E.; Céspedes, C. L. Antioxidant and insect growth regulatory activities of stilbenes and extracts from Yucca periculosa. *Phytochemistry* **2003**, *64*, 463–473.

Tumlinson, J. H.; Engelberth, J. Fatty Acid-Derived Signals that Induce or Regulate Plant Defenses Against Herbivory. *Induced Plant Resistance to Herbivory* 389–407.

Umezawa, T. Diversity in lignan biosynthesis. *Phytochem. Rev.* **2003**, *2*, 371–390.

Underwood, C.D.T.; Pearce, R.B. Astringin and isorhapontin distribution in Sitka spruce trees. *Phytochemistry* **1991**, *30*, 2183–2189.

Vande Velde, L.; Schtickzelle, N.; Van Dyck, H. Effect of larval food stress on male adult behaviour, morphology and reproductive investment in the butterfly Pararge aegeria. *Evolutionary Ecology* **2012**, *27*, 221–234.

Vandenborre, G.; Smagghe, G.; Damme, E. J. V. Plant lectins as defense proteins against phytophagous insects. *Phytochemistry* **2011**, *72*, 1538–1550.

Vijendravarma, R. K.; Narasimha, S.; Kawecki, T. J. Effects of parental larval diet on egg size and offspring traits in Drosophila. *Biology Letters* **2009**, *6*, 238–241.

Voelckel, C.; Weisser, W.W.; Baldwin, I.T. An analysis of plant-aphid interactions by different microarray hybridization strategies. *Mol. Ecol.* **2004**, *13*, 3187–3195.

Voirol, L. R. P.; Valsamakis, G.; Lortzing, V.; Weinhold, A.; Johnston, P. R.; Fatouros, N. E.; Kunze, R.; Hilker, M. Plant responses to insect eggs are not induced by egg-associated microbes, but by a secretion attached to the eggs. *Plant, Cell & Environment* **2020**, *43*.

Walenciak, O., Zwisler, W., & Gross, E. M. (2002). Influence of Myriophyllum spicatum-Derived Tannins on Gut Microbiota of Its Herbivore Acentria ephemerella. *Journal of Chemical Ecology, 28*(10), 2045-2056. doi:10.1023/a:1020754012785

Walling, L.L. The Myriad Plant Responses to Herbivores. *J. Plant Growth Regul.* **2000**, *19*, 195–221.

Wang, J.; Chung, S. H.; Peiffer, M.; Rosa, C.; Hoover, K.; Zeng, R.; Felton, G. W. Herbivore Oral Secreted Bacteria Trigger Distinct Defense Responses in Preferred and Non-Preferred Host Plants. *Journal of Chemical Ecology* **2016**, *42*, 463–474.

Wang, Z.; Zhao, Z.; Abou-Zaid, M.M.; Arnason, J.T.; Liu, R.; Walshe-Roussel, B.; Waye, A.; Liu, S.; Saleem, A.; Cáceres, L. Aet al. Inhibition of Insect Glutathione S-Transferase (Gst) By Conifer Extracts. *Arch. Insect Biochem. Physiol.* **2014**, *87*, 234–249.

Wang, Z.; Zhao, Z.; Cheng, X.; Liu, S.; Wei, Q.; Scott, I.M. Conifer flavonoid compounds inhibit detoxification enzymes and synergize insecticides. *Pestic. Biochem. Physiol.* **2016**, *127*, 1–7.

War, A. R.; Paulraj, M. G.; Ahmad, T.; Buhroo, A. A.; Hussain, B.; Ignacimuthu, S.; Sharma, H. C. Mechanisms of plant defense against insect herbivores. *Plant Signaling & Behavior* **2012**, *7*, 1306–1320.

War, A.R.; Sharma, H.C.; Paulraj, M.G.; War, M.Y.; Ignacimuthu, S. Herbivore induced plant volatiles: Their role in plant defense for pest management . *Plant Signal. Behav.* **2011**, *6*, 1973–1978.

Wasserman, S. S.; Mitter, C. The relationship of body size to breadth of diet in some Lepidoptera. *Ecological Entomology* **1978**, *3*, 155–160.

Wiklund, C.; Persson, A. Fecundity, and the Relation of Egg Weight Variation to Offspring Fitness in the Speckled Wood Butterfly Pararge aegeria, or Why Don't Butterfly Females Lay More Eggs? *Oikos* **1983**, *40*, 53.

Wink, M. (1997). Compartmentation of Secondary Metabolites and Xenobiotics in Plant Vacuoles. *Advances in Botanical Research The Plant Vacuole,* 141-169. doi:10.1016/s0065-2296(08)60151-2

Winkel-Shirley, B. Flavonoid Biosynthesis. A Colorful Model for Genetics, Biochemistry, Cell Biology, and Biotechnology. *Plant Physiol.* **2001**, *126*, 485–493.

Wouters, F.C.; Blanchette, B.; Gershenzon, J.; Vassão, D.G. Plant defense and herbivore counter-defense: Benzoxazinoids and insect herbivores. *Phytochem. Rev.* **2016**, *15*, 1127–1151.

Xing, G.; Liu, K.; Gai, J. A high-throughput phenotyping procedure for evaluation of antixenosis against common cutworm at early seedling stage in soybean. *Plant Methods* **2017**, *13*.

Yamamoto, I. Nicotine to Nicotinoids: 1962 to 1997. *Nicotinoid Insecticides and the Nicotinic Acetylcholine Receptor* **1999**, 3–27.

Yang, J.; Sun, X.-Q.; Yan, S.-Y.; Pan, W.-J.; Zhang, M.-X.; Cai, Q.-N. Interaction of Ferulic Acid with Glutathione S-Transferase and Carboxylesterase Genes in the Brown Planthopper, Nilaparvata lugens. *J. Chem. Ecol.* **2017**, *43*, 693–702.

Yang, X.; Zhang, M.; Lu, T.; Chen, S.; Sun, X.; Guan, Y.; Zhang, Y.; Zhang, T.; Sun, R.; Hang, B.; Wang, X.; Chen, M.; Chen, Y.; Xia, Y. Metabolomics study and meta-analysis on the association between maternal pesticide exposome and birth outcomes. *Environmental Research* **2020**, *182*, 109087.

Yao, C.-S.; Lin, M.; Liu, X.; Wang, Y.-H. Stilbene derivatives from Gnetum cleistostachyum. *J. Asian Nat. Prod. Res.* **2003**, 131–137.

Yeats, T.H. Setting and Diffusing the Cyanide Bomb in Plant Defense. *Plant Physiol.* **2018**, *178*, 956–957.

Yoshinaga, N.; Ishikawa, C.; Seidl-Adams, I.; Bosak, E.; Aboshi, T.; Tumlinson, J. H.; Mori, N. N-(18-Hydroxylinolenoyl)-l-Glutamine: A Newly Discovered Analog of Volicitin in Manduca sexta and its Elicitor Activity in Plants. *Journal of Chemical Ecology* **2014**, *40*, 484–490.

Zanella, I.; Biasiotto, G.; Holm, F.; Lorenzo, D. di Cereal lignans, natural compounds of interest for human health? *Nat. Prod. Commun.* **2017**, *12*.

Zangerl, A.R.; Hamilton, J.G.; Miller, T.J.; Crofts, A.R.; Oxborough, K.; Berenbaum, M.R.; Lucia, E.H.D. Impact of folivory on photosynthesis is greater than the sum of its holes. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 1088–1091.

Zaynab, M.; Fatima, M.; Abbas, S.; Sharif, Y.; Umair, M.; Zafar, M.H.; Bahadar, K. Role of secondary metabolites in plant defense against pathogens. *Microb. Pathog.* **2018**, *124*, 198–202.

Zhou, S., Lou, Y., Tzin, V., & Jander, G. (2015). Alteration of plant primary metabolism in response to insect herbivory. *Plant Physiology*. doi:10.1104/pp.15.01405

Zunjarrao, S.S.; Tellis, M.B.; Joshi, S.N.; Joshi, R.S. Plant-Insect Interaction: The Saga of Molecular Coevolution. *Ref. Ser. Phytochem. Co-Evol. Second. Metab.* **2020**, 19–45, doi:10.1007/978-3-319-96397-6_42.

BIOGRAPHICAL SKETCH

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