Nanotechnology-Based Bioactive Antifeedant for Plant Protection

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An antifeedant approach for insect control in crop management has been comprehensively studied by many researchers, though it has only been restricted to plant-based compounds and to the laboratory level at least. Nano-delivery formulations of biopesticides offer a wide variety of benefits, including increased effectiveness and efficiency with the improved properties of the antifeedant. An antifeedant nano-delivery system can increase their bioactivities, such as increasing sublethal bioactivity or reducing toxicity levels in both crude extracts/essential oils (EOs) and pure compounds.

Keywords: biopesticides ; antifeedant ; nano-delivery system ; nanotechnology

1. Insect Pest Control Strategies Using Antifeedant Plant-Derived Pesticides: Antifeedant Management, Resources, and Reserve

The concept of pest control today has developed on the principles of integrated pest control that considers economic threshold aspects, application of biopesticides from natural products, and biocontrol using natural enemies or agencies entomopathogenic [1][2][3]. Certainly, Integrated Pest Management (IPM) is a combination of the conventional approach and the adoption of various technological developments, which plays an important role in achieving sustainable agriculture goals [4]. Bioinsecticides are part of the strategies that significantly contribute to IPM [1]. The multi-active role of plant-based bioinsecticides has been studied, which has included toxicity and growth inhibitory effects, and the role of antifeedant on preventing insect resistance [5][6]. Moreover, the environmentally friendly nature of preventive approaches such as antifeedant makes them good alternatives for insect pest control strategies.

An antifeedant received from the secondary metabolite active compounds of plants revealed phytophagous insect protection [1][7]. These active compounds belong to a group of allomones, which are interspecific compounds needed to mediate the interaction with phytophagous insects [7]. The groups of metabolite active antifeedant compounds that have been reported are limonoids, chromenes, polyacetylenes, saponins, flavonoids, quassinoids, cucurbitacins, cyclopropane acids, phenolics, alkaloids, various types of terpenes, monoterpenoids, diterpenoids, sesquiterpenes, and their derivatives [8][9][10]. There are two fundamental mechanisms of antifeedant; the first being the deterrent effect due to taste receptors, and the second being due to disruption of the midgut of the insects. The deterrent effect is due to taste receptors being stimulated by the phagostimulant compound interfering with the normal function of neurons [11][5][8]. Meanwhile, Isman [12] has stated that deterrent effect activities caused by chemicals serve to accelerate the roles of the central nervous system in preventing ingestion or absorption of substances and, subsequently, creating sublethal toxicity and disruption of the midgut.

The investigations of potential antifeedants have been extensively studied in the field of crop protection. The order Lepidoptera dominates as the main insect pest on crops due to its shorter life cycle characteristic and higher fecundity capacity, among others [13]. In addition, antifeedants explore stored grain insect pest control and play a small part in oil palm plantation insect pest management. Meanwhile, the majority of grain-stored insect pests is dominated by the order Coleopteran [14], where their feeding activities on crushing grains into powder caused them to be easily contaminated by fungi and bacteria. In addition, carcasses, secretions, eggs, and fecal remains cause allergic reactions in humans. To overcome this problem, the use of synthetic insecticides and fumigation turned out to leave residues on grains that are harmful to consumers. However, these insect pests tend to be adaptable and more resistant to synthetic chemical insecticides by inheriting resistant generations. As an alternative, bioinsecticide antifeedant provides a variety of compositions of phytochemical compounds, allowing various modes of action to prevent such resistance problems from occurring [1]. Therefore, this encourages researchers to use antifeedants as prospective alternatives for crop protection and stored pest management.

Regarding plant-source bioactivity on stored grain insect pests, semiochemical repellents provide excellent performance compared to antifeedants. Thus, semiochemical repellents are more rapidly developed in stored pest control strategies [15]. On the other hand, the use of antifeedants to control oil palm pests is driven by the importance of maintaining natural enemies to prevent a resurgence due to the irresponsible overuse of synthetic insecticides [16]. The damage of oil palm plantations is due to the activity of the polyphagous insect pest that defoliates young palm plantations. Although antifeedants play an important role in controlling feeding activity and maintaining the existence of natural enemies, their role in oil palm pest control strategies seems unexplored at an intensive level.

Antifeedant plant resources are mainly obtained from plant extracts and essential oil compounds. These resources are investigated in various forms, such as the active fractions of crude extract or essential oil (EO), and also in further processing screening steps to obtain isolation of pure active compounds. Essential oils are usually used as antifeedant resources in the stored and palm oil pest management, while crude plant extract is used as an antifeedant resource in crop management. Active compounds are not always more effective than crude extracts or essential oils; thus, choosing antifeedant resources is determined by the specificity and characteristics of the target insect pest. The active fractions of crude extract or essential oil (EO) may provide synergistic functional activity to the target insect pest. In addition, the utilization of antifeedant from crude extracts or essential oils offers a simpler process. In contrast, the application of pure active compounds has required sophisticated and high-cost production [17][18]. Therefore, the use of crude extracts or essential oils is interesting to explore in providing antifeedant plant resources.

It is known that grain insect pests are effectively controlled by EO due to their sensitivity to volatile semiochemicals [15][19]. Thus, antifeedant from essential oils is a preferable choice in stored grain pest management compared to plant extract. Contrary to this, antifeedant from plant extract shows higher efficacy for crop pest management compared to essential oils that are targeted against phytophagous insect pests [20]. Moreover, plant extract provides the possibility to form a solid paste extract that is suitable for residual application in oral targeting, allowing a great amount of residual antifeedant substance and persisting long enough to deter feeding activities [13]. Therefore, crude plant extract preparation has more opportunities to be applied for antifeedants in crop management.

The research progress of antifeedants on improving efficacy against target insect pests includes reservation and preparation techniques from conventional methods to the latest nanoformulas. Many studies have reported on the advanced development of EO nanoformulation applied in stored pests and oil palm pest management. In contrast, rarely reported are studies on the nanoformulation of crude plant extract applied for insect pest crop management. Generally, before formulation, crude plant extracts are isolated to obtain pure active compounds. However, this route of preparation needs sophisticated and longer steps and, consequently, a reduced economic process. Few researchers propose to prepare a nanoformulation from a crude extract. However, the majority of reported studies are still in laboratory-scale production; only a few studies have reported on pilot-scale studies and field applications. Thus, given the great potential and abundant resources, the development of a nano-based formulation is promising in accelerating the applications of antifeedant; this is in line with the recommendations from Isman [21] on the prospect of antifeedant from plant resources. Despite many determining factors, the concern of relevant stakeholders is needed for the successful implementation of an antifeedant strategy for sustainable agriculture.

2. The Role of Nanotechnology in Plant-Derived Pesticide Formulations

Currently, nanotechnology is the breakthrough of various innovations in the development of bioinsecticide formulas [22][23]. Biopesticide formulas established through nanotechnology improve delivery performances and enhance their application efficiencies. It is well known that the smaller size of particles serves to increase the surface of the active ingredient and, consequently, improve the solubility. Moreover, the challenges involved are preparing the synthesis of the water-based medium, formula stability, mobility, and ensuring the delivery target system [24]. A broad variety of natural materials are used in the assembly of pesticide nanoformulations. There are two types of formulations—nano-particle pesticides and nano-carrier systems—to allow delivering active compounds to the target site. The structure of the delivery system includes the encapsulation of active compounds inside, a nanoparticulate polymeric shell, adsorption onto the nanoparticle surface, attachment onto the nanoparticle core via ligands, and entrapment within the polymeric matrix [25]. The properties of these various types of nanocarrier formulations are known to enhance the efficacy and efficiency of biopesticides against insect pests, i.e., a nanoemulsion loaded with essential oil from various plants products [26][27][28], plant extracts loaded in micelle with a hydrophobic core [29] and liposome with a hydrophilic core [30]. Recently, materials from natural polysaccharides, proteins, alginates, silica, and other types of polymers have been utilized as nanoparticle encapsulants, such as chitosan, zein, gum arabic, and silica nanoparticles [31][26][32].

Botanical active compounds have also been reported to be successfully loaded in a nanocapsule and being mesoporous for the slow-release system as well as being entrapped in the matrix polymer and the cross-linked nanoparticles mediated by specific ligands [33][34][35][36]. It is well known that the characteristic content of organic active compounds inherent in botanical ingredients is that they are easily degraded and, consequently, have a lower long-term potency [37]. The various types of nanocarrier systems offer the appropriate properties to improve the efficacy and efficiency performance of plant-derived nano-pesticides' delivery.

Nano-emulsified carriers are emerging as the most intensively investigated of plant-derived pesticides. This system is suitable to be adapted to EO and crude extracts of plant-derived pesticides by applying a simple emulsification method, requiring low energy and with suitable surfactants [38][39]. Emulsion-based formulations are designed to increase dispersion or solubility of ingredients, improve stability, and increase bioactivity and efficiency, especially in controlling insect crop pests [31]. Nanoemulsion formulas are extensively investigated for EO plant-derived nano-pesticides' delivery to obtain desired properties due to the nano-sized droplet dispersion uniformity and the stability into two liquid phases by the fundamental role of the surfactants. Thus, the engineering characteristic and the properties of the delivery system can provide a slow-release performance [38]. Micelles are ideal nanocarriers for encapsulating, especially for insoluble-organic compounds such as plant extracts [40]. This allows the nano-sized insoluble-organic suspension dispersed in the water system that enhances the wettability and bioefficacy toward targeted insect pests [22]. Liposomes are vesicular to nanoscale structures, and which consist of a lipid bilayer covering an aqueous phase in the core [40]. The preparation of a liposomal nano-carrier has emerged as a promising aspect of nano-delivery biopesticides due to separate compartments that can encapsulate both the hydrophilic and hydrophobic active compounds that are effective against targeted insect pests [30].

The encapsulation involves a vesicular composed of the biodegradable matrix/polymer that encloses the active compounds in the inner core [22]. Nanocapsule and nanoparticle encapsulation increase the targeting delivery, and shell degrades slowly by environmental conditions, thus improving the chemical stability of organic compounds, such as volatile compounds commonly containing types of EO [40]. Mesoporous nanoparticles with hollow silica were adapted for water-soluble and lipid-dispersed controlled release biopesticide delivery systems. While nanospheres are designed as dense spherical vesicular systems in which active compounds are evenly distributed via adsorption or trapping in the nano-matrix/polymer, the cross-linked nanoparticles of the entrapped active compounds are mediated by ligands that act as sensors or markers for specific receptor molecules in targeted delivery. These efficient encapsulations and smart entrapped nano-carrier systems were confirmed to load the EO or pure active compounds with quite a high loading capacity with lethal and sublethal bioactivities due to a controlled slow-release mechanism [26][34][35][36][41].

Plant-derived nano-pesticides have been tailored for desired properties, involving the use of matrix types [42]. Studies have reported carrier systems prepared by organic and inorganic matrices/polymers and suitable surfactants as a means of delivering various extracts, EO, and their active compounds [41][42]. The utilization of nature/organic matrices' resources matter is growing rapidly to compete with the non-organic matrices, such as chitosan, gum arabic, and zein. This carrier system maintains the susceptibility of active organic compounds to degradation so that they can be persistent for a longer period. Thus, these efficiently increase toxicity, fumigants, repellency, attractants, antifeedant, growth development, and oviposition inhibition [41][43].

The evaluation of studies shows that a compatible nanocarrier adopted in crude EO can even outperform or be comparable with the effectiveness of pure active compounds [26][44]. Nanocarrier biopesticide formulas can also enhance the effectiveness of pure active compounds to be comparable or more effective than synthetic insecticides in an in vitro bioassay test [30]. The performance of nanocarrier formulas of EO and plant extract can reduce the level of toxicity, indeed enhancing sublethal bioactivities such as the impact of antifeedant and repellency, and inhibiting growth regulation [29][41][45]. The advantages of the nanocarrier formula compared to conventional or synthetic insecticide formulas are determined through increased efficiency performance, such as the solubility and dispersion, formula stability, and release control mechanism offered by the nano-delivery system. This factor has a significant impact on increasing its efficacy against target insect pests. Plant-derived pesticides from abundant plant extracts resources are the most studied pesticides in the investigation of crop pest management. However, the potential compatibility of nanocarrier formulas for application is less explored.

Furthermore, the prominent role of the nano-delivery plant-derived pesticides formula is to reduce the level of toxicity so that the antifeedant and other potent sub-lethal bioactivities can be enhanced due to nano-delivery reserves. Especially for safety products in crop management, a plant-derived pesticides formula is hindered by toxicant residues and resistance problems. The challenges are compatibility with nanocarriers and resources for appropriate bioactivity on target insect pests and cost-effective formulation to allow the filed or practical application of recent advanced technological development.

3. Nano-Delivery System of Antifeedant Formulation

As antifeedant is potentially received from plant-derived bioactivity, it becomes an interesting object as an important component of integrated pest management, especially in crop pest insect control [1][46]. Further noted is that the antifeedant mode of action is determined by a feeding mechanism, which is induced by special taste receptors in insects that stop feeding activity. Antifeedants are generally obtained from the resources of plant extracts or essential oils that contain ingredients sensitive to insect taste receptors [8][47]. The biodiversity of potentially bioactive phytochemicals is the main source in formulating nanobiopesticides. Nanobiopesticides have been shown to have a significant impact on improving plant-derived pesticide properties, including antifeedant performance [20][23]. The efficiency and effectiveness of nanobiopesticides including antifeedants are enhanced by using nanoformulation polymers, metal oxides, active particles combined with micelles, etc. [23].

Nanoparticle (NP) biopesticide formulas are currently in great demand for sublethal dose testing, including for antifeedant bioactivity [48]. As an example, the biosynthesis of silver nanoparticles using plant extracts [49][50][51] produces silver nanoparticles (AgNPs) through a simple and low-energy process. In general, the research purpose for metal nanoparticles is to find safer and lower concentration levels of cost-effective toxicants. Notably, only a few studies have reported the progress of a nanobiopesticide impacting on the formula's efficiency, which is one of the important properties in the biopesticide nano-based formulation for application. It is emphasized that among those three examples [49][50][51] of inorganic nano-carriers (AgNPS) for the delivery of crude extract, generally, a nano-sized delivery system enhances bioactivity and suppresses toxicity compared to the control.

Another antifeedant nano-based formulation relies on a slow-release control designed to entrap the EO compounds by specific polymers, such as polymeric or chitosan nanoparticles [52][53][54]. The active biopesticide-based nanoparticle generally improves the efficiency of NPs in a controlled manner and shows prolonged bioactivity. However, the controlled activity established by the encapsulated structure does not necessarily contribute to any significant feed-deterrent activity of insect pests. By the treatments of EO-bergamot and EO-geranium, it displays antifeedant activities better than EO-PEG nanoparticles where the role of PEG encapsulation can improve loading efficacy by up to 75% against *Tribolium castaneum* [52]. This is in line with the treatments of the encapsulated neem oil in poly(ε-caprolactone) (PCL), poly (β–hydroxy-butyrate) (PHB), and poly (methylmethacrylate) (PMMA) polymeric nanoparticles compared to the broth neem oil against Spodoptera frugiperda. The observation result shows that only neem oil still provides antifeedant activity with a phagostimulant index < 1 at 7 days after spraying [53]. This is reasonable when considering that antifeedant activity is stimulated by a series of taste receptors as an impulse input to the insect feeding regulator. The encapsulation of the active ingredient must consider a matrix or polymer that accommodates the stimulate of the antifeedant compound when the polymer-enclosed material enters the oral and insect digestive system of the insect. This can be explained through the application of the chitosan-nanoparticle cross-linking agent formula studied by Zheng et al. [55]. The degree of polymeric encapsulant swelling is determined based on the pH value corresponding to the acidity level in the digestive system of *Solenopsis invicta* in correlation with the consuming activities. The cross-linked structure of polymers is not only appropriate for the slow-release of NP biopesticide but also for enhancing the efficacy and efficiency of the formula. Moreover, a clear explanation of the active ingredients' absorption mechanism has been explored and reported. Interestingly, the advantage of this smart nanobiopesticide is that it can predict the impact, including the prolonged activity of active ingredients. Unfortunately, the practicality and cost of production constrain the large-scale field application of this kind of nanobiopesticide. Thus, improving the scale-up of production to meet field application remains a challenge.

A more practical and cost-effective antifeedant role model formula was displayed by a nano-based antifeedant formulation obtained from crude plant extract nanoparticle resources [56][29]. The neem gum nanosuspension can be prepared by a simple stirring method adding $TiCl_4$ as a stabilizing agent on a certain composition, and has even tested as having a higher 100% antifeedant activity on *H. armigera* and *S. litura* larvae at a low concentration treatment (100 ppm) [56]. The insoluble organic extracts of *L. Camara* ethyl acetate nano-fraction can be dispersed in a water system by a simple reverse emulsion method with the composition of Tween 80 ratios as an appropriate surfactant [29]. The results show a significantly enhanced antifeedant activity in a strong category at LC_{50} value 0.39% concentration treatments against *Crocidolomia larvae*. However, the weakness of both formulas is easily agglomerated, hence it requires handling and agitation before application.

Despite the advantageous features of non-volatile active antifeedant resources, they are usually hindered by the characteristics of plant extract antifeedants to dissolve in water [22][57]. Furthermore, not all extracts are easy to dry to obtain a desirable nanopowder. Moreover, dispersing insoluble organic plant extract into nanosuspensions in the water system by the emulsification method is a breakthrough for obtaining nanosuspensions. Generally, micelles are formed due to the natural assembly properties of amphiphilic blocks' surfactant in an aqueous medium; when the hydrophilic portion of the surfactant is added to the solution over the critical micelles concentration (CMC), the inner spherical micelles are formed into water [58]. Thus, insoluble compounds are trapped in the core of micelle formation, which is called spontaneous emulsification. The emulsion with micelle formation, is also effective as a protective system of active ingredients with a one-layer surfactant. This formation does not require time for the encapsulant to dissolve when exposed to insect pests. Therefore, it can directly induce the phagostimulant deterrent receptors of phytophagous insect pests.

The nano-delivery-based antifeedant is aimed at increasing the effectiveness and efficiency of active ingredients that are targeted and are safe for the environment. The inversion process that occurs during emulsification with the appropriate surfactant is known to disperse nano-sized suspensions in fine emulsion droplets [57][59][60]. The nanobiopesticide, which includes the antifeedant nano-delivery system, forms a stable dispersion, improves the efficacy and efficiency, and improves the wetting and spreading on the leaf surface [22]. In addition, antifeedant nanoparticles need to deposit and spread uniformly on the foliage surface, leading to increased retention rates and decreased spraying doses. Moreover, it is in line with that recommended by Zhao et al. [22] and Lade et al. [23], who state that the important aspects needed in the development of nanobiopesticides, especially in antifeedant nano-delivery strategies, are: (i) development of a water-based dispersion system, (ii) leaf-targeted deposition and dose transfer mechanism of nano-delivery, (iii) increased bioavailability mechanism of nano-based formulations, (iv) natural degradation and biosafety of residues. Moreover, advances in the application of nanomaterial formulation in pesticides have indicated that utilizing nanotechnology to design and prepare targeted pesticides with an environmentally responsive controlled release via chemical modifications and compounds offers great potential for creating new formulations [61][62].

This antifeedant delivery by micelle formulation is still considered premature to accommodate the abovementioned desired properties. There are still many limitations within the study on the efficiency that need to be investigated. The challenges are how to evaluate the effectiveness of its efficiency when interacting with UV exposure, the material persistence, the stability of efficacy performance during field application, as well as the side effects on non-target organisms. However, the development of this antifeedant formula offers a bright prospect for alternative formulas received from plant extract resources. Fortunately, there are abundant available resources of plant extracts and they can be prepared with a simple method, low costs, and easy handling, creating a forthcoming insight for the field-scale application of this nano-delivery antifeedant. Considering another important aspect of integrated pest management, antifeedant bioactivity plays an important part and should be integrated with other approaches in phytophagous insect pest control. It allows the anticipation of insect resistance with multiple modes of action such as antifeedant activity, growth and development inhibition, anti-oviposition, reduced fecundity, and repellency.

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