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RELEASE OF SEMIOCHEMICALS: NATURAL POLYMERS

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Abstract: Semiochemicals are substances involved in chemical communication between individuals and can alter the behavior and physiology of individuals. The use of semiochemicals in pest control has grown and today it is an important tool in pest control and constitutes an interesting alternative to pesticides, reducing environmental risks, to farmers, consumers and pest resistance. This study addresses the types of semiochemical releasers currently used and the polymers in their compositions. This is a descriptive study, of the literature review type, with searches on the Capes journal portal, the SciELO, Elsevier, Web of Science and PubMed databases. Incorporating semiochemicals into controlled release devices is necessary to optimize their applicability as pest control agents, providing adequate release that meets the needs of the environment. Therefore, semiochemical releasers must meet some specifications, such as biodegradability and constant release kinetics. Biodegradable matrices are preferred for modified release, with starch, chitosan and sodium alginate being some of the materials of choice for this.
Keywords: pest control; biodegradable matrices; controlled release.

INTRODUCTION

In recent decades, the increase in agricultural activity has occurred with the use of insecticides as they are a more commercially viable control tactic in Brazil, since the products are available and easy to apply, and provide control of insect pests of crop crops. fast and very effective way. However, the large-scale use of these substances can cause environmental contamination and lead to the establishment of resistance to these chemical agents by insect pests, with negative effects on non-target organisms such as pollinators and natural enemies (Koul, 2020; Pavela et al., 2019).

Behavioral pest control, based on the application of semiochemicals for the management of agrosystems, is a tool that can be used with or in place of pesticides, reducing risks to the environment, farmers and consumers (Brezolin et al., 2018; Ramos et al., 2017; Silva et al., 2018).

Semiochemicals are molecules used in intraspecific and interspecific communication and are increasingly included in Integrated Pest Management (IPM) strategies, as a tool for monitoring and controlling pests. As advantages to insecticides, they do not have an adverse effect on beneficial organisms and do not generate a risk of insect resistance (Goulart et al., 2015; Pålsson et al., 2022).

Semiochemicals are classified according to the involvement between individuals of the same species, pheromones are of intraspecific action, and allelochemicals are those that are involved in communication between different species, interspecific action. Pheromones are classified according to the action they trigger: aggregation pheromone, alarm pheromone, oviposition deterrent pheromone (deterrent), domestic recognition pheromone, sexual pheromone, trail pheromone, royalty pheromone and recruitment pheromone. Allelochemicals are divided into five categories: allomones, kairomones, synomones, antimonies and apneumonium (El-Ghany, 2019).

Most semiochemicals are volatile and very unstable in terms of the action of ultraviolet light, temperature and oxidizing agents, due to their chemical structure, thus indicating their incorporation into devices that can provide protection and carry out a controlled release, allowing them to remain in field for a prolonged and constant period, without interference from environmental conditions (Stipanovic et al., 2004) and in order to protect them from degradation caused by oxygen and light in the ultraviolet region (Heuskin et al., 2011).

To be efficient in IPM techniques, the semiochemical releaser must be stable, inert, and release in a controlled manner (Goulart et al., 2015) and, to this end, must have particular specifications:

I. The amount of semiochemical released must not vary depending on its concentration, that is, the release kinetics must be of zero order;

II. The releaser must meet the semiochemical needs in relation to the type of treatment and climatic conditions, and must be resistant to oxidation and degradation by abiotic factors;

III. The emission of semiochemical mixtures must be given in appropriate proportions throughout the application period, considering that most of these are complex mixtures of compounds, with different volatilities;

IV. The releaser must be biodegradable.

For semiochemical releasers to be efficient and used in the field, the device must allow storage, protection and adequate release of substances (Abd El-Wahab et al., 2021; Y. Chen et al., 2018; Lemos et al., 2021)

Compounds from natural sources are desirable as controlled release devices for semiochemicals, biodegradable, biocompatible, with the ability to adhere and form non-toxic hydrogels, with natural polysaccharides being the materials of first choice.

Natural polymers such as starch, chitosan, gelatin, dextran, albumin, lignin, chitin, cellulose and alginate are extensively researched as modified release devices for many bioactive molecules, here we will discuss the application in the controlled release of semiochemicals (Nuruzzaman et al., 2019; Valladares et al., 2016).

The present review aims to describe the main types of semiochemical releasing systems of interest in Integrated Pest Management, as well as present some of the main natural polymers used to obtain these dispensers.

METHODOLOGY

This is a narrative-descriptive literary review article, which researched semiochemicals, their use and form of application in the field. We did not use publication time limits when choosing articles, however, the most recent publications were sought to have an overview of the types of releasers currently used, and the natural polymers that are candidates for the production of these releasers.

Only scientific articles published in English, Spanish and Portuguese, available on the Periódicos Capes platform in the SciELO, Elsevier, Web of Science and PubMed databases, were included in the research. The key words used in the research were semiochemicals, controlled release, chitosan, starch, maltodextrin, arabic gum, sodium alginate and natural polymers. Articles that were unavailable in full and review articles were excluded. The results were expressed in a descriptive way.

RESULTS AND DISCUSSION

CLASSIFICATION OF LIBERATORS

The different types of releasers can be classified into three types of systems: solid matrix dispensers, liquid spray formulations and reservoir formulations.

The reservoir system releasers (Figure 1) are made up of two layers: a core, which contains the semiochemical inside, and a coating layer, normally made up of polymers, which acts by isolating the active ingredient from the external environment through a layer or membrane, allowing its diffusion through its walls (Heuskin et al., 2011)

Reservoir-type releasers, such as hollow fibers, “twisted rope”, bags and microcapsules, "bottle" type polyethylene tubes and the *eppendorf®* type microtube are the most used for releasing pheromones.

In reservoir system releasers (Figure 1), the release kinetics of the substance depend on the filling level of the reservoir, making zero-order kinetics difficult. As a result, a non-linear release behavior occurs, due to the decrease in the release rate as a function of time (CONCENTRATION, QUANTITY OF PRODUCT) and then a first-order kinetic is considered, in which half of the sample will evaporate in a time t1 /2 which is the half-life of the compound (Heuskin et al., 2011).

Figure 1: Eppendorf type reservoir system releaser®

In matrix system releasers, also called solid matrix, the semiochemicals are adsorbed in a network formed by chains of one or several polymerized chemical substances, called matrix, which acts as a release modulating agent. The release rate of the adsorbed semiochemical will depend on the geometric parameters of the matrix, and it is possible to achieve the desired release kinetics through modulation of these parameters. Therefore, the release rate of the same pheromone can differ considerably from one device to another, depending on the material it is made of, and its useful life can vary between 60 and 140 days (Heuskin et al., 2011)

The rubber or plastic septum (Figure 2), considered the first semi-chemical releasing system AND STILL VERY IN USE, is a better-known matrix system releaser (Hummel et al., 2013). The active substance impregnated in the septum is released over days or weeks, with first-order release kinetics. In addition to the rubber septum, membranes, polymer films and gel-type dispensers are also part of this delivery system.

Figure 2: Rubber septum

In microencapsulated or sprayable systems, semiochemicals in the form of microparticles (1-1000 µm) are encapsulated by a polymeric wall, generally consisting of polyamide, polyurea, gelatin, gum arabic, cellulose ester and others (Figure 3). Releasers of this class protect the pheromone from oxidation and light during the storage period and release it at a controlled rate (Kong et al., 2009). The release time and efficiency of these formulations are directly linked not only to the chemical properties of the pheromone, but also to environmental factors, size of the microspheres and their release capacity, which can vary from days to weeks.

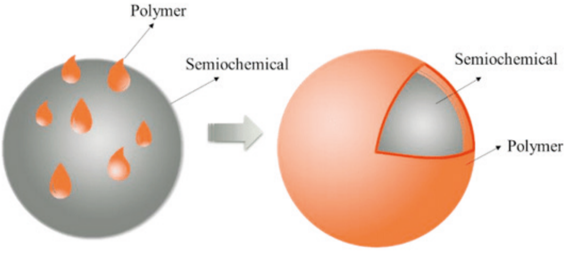

Figure 3: Microencapsulated reservoir system

Atterholt et al. (1999)adheres to tree bark or foliage, releases pheromone for an extended period of time, and will slowly erode from bark and biodegrade in soil. Pheromone emulsions can be applied with simple spray equipment. Pheromone release-rates from paraffin were measured in laboratory flow-cell experiments. Pheromone was trapped from an air stream with an adsorbent, eluted periodically, and quantified by gas chromatography. Pheromone release from paraffin was partition-controlled, providing a constant (zero-order used a spray system consisting of a paraffin emulsion and observed a zero-order release rate for the pheromone of the peach pest, the oriental moth, *Grapholita molesta* (Lepidoptera: Tortricidae). Later, Chen et al., (2007) used gelatin and gum arabic to microencapsulate the *Plutella xylostella* pheromone, and compared the effectiveness of this system with that of rubber septa impregnated with the pheromone for a period of six weeks. They observed that the microcapsules proved to be superior because they are easily prepared, promote the protection of the pheromone against oxidation and irradiation during storage and release in the field, in addition to promoting the controlled release of the pheromone, and can be adopted as a new method for releasing the pheromone. pheromone of the pest in question.

Sprayable formulations were also evaluated to control the corn borer, *Sesamia nonagroides*, by disrupting the mating of the pest. These formulations were tested in large-scale field experiments by spraying using a helicopter in 5-hectare maize fields in Spain, Greece and France and the release of the pheromone was observed for a period of more than 30 days (De Vlieger, 2008). SPLAT verb® technology, composed of a wax emulsion matrix to dispense pheromones, is used to control *Dendroctonus ponderosae* (Fettig et al., 2015). Several SPLAT® (Specialized Pheromone & Lure Application Technology) formulations are currently marketed in Brazil against different insect pests.

The advantages of using polymeric materials when compared to other ceramic or metallic materials as a device to store bioactive molecules include the ease in manufacturing films, membranes, nanoparticles, among other forms, the low production cost and availability of finding materials with properties mechanics and physics desired for specific applications (Ramos et al., 2017). The polymers used in the manufacture of controlled release systems for bioactive molecules can be of natural or synthetic origin.

Polyamides, polyethylene, polypropylene, polyacrylates, fluorocarbons, polyesters, polyurethanes are some of the synthetic polymers used to transport bioactive molecules, mainly in the pharmaceutical industry, being easily adaptable to exert a wide variety of functional properties, which makes it possible to manipulate, for example, the shape and size of the devices, as well as their mechanical properties.

NATURAL POLYMERS

Biodegradable matrices are the materials of choice as devices for the modified release of semiochemicals, and natural polysaccharides are the materials of first choice due to their ease of obtaining and versatility (Valladares et al., 2016). Unlike synthetic polymers, natural polymers have non-toxic degradation products, are affordable to obtain, are obtained from renewable sources and can mimic the components of the extracellular matrix.

However, they present complexity in their purification, which leads to differences in characteristics from one batch to another, as they are extracted from living organisms such as algae, plants, animals and microorganisms, as occurs with chitosan, which is extracted from insect carcasses and starch that comes from vegetable origin.

Natural polymers such as starch, alginate, chitosan, gelatin, maltodextrin and gum arabic (Figure 4) are useful and receive a lot of attention in the search for preparing modified release devices for many bioactive molecules (Nuruzzaman et al., 2019).

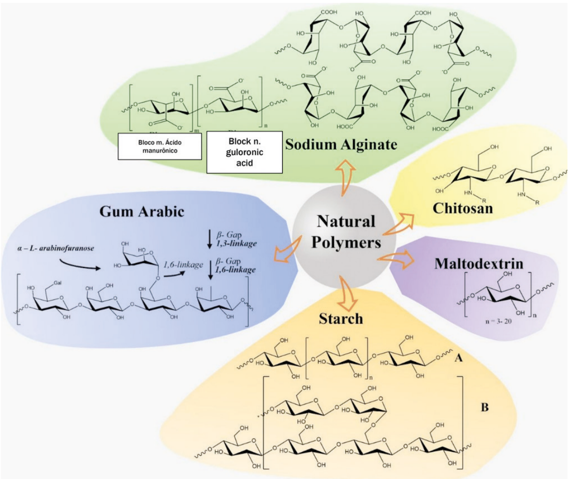

Figure 4 – Chemical structures of natural polymers presented in this study. Starch: Chemical structure of amylose with α-(1,4) (A) and amylopectin with α-(1,6) (B); Chemical structure of chitosan, where R = H(GlcN) or COCH3(GlcNAc); Monomer forming maltodextrin with α-(1,4) and α-(1,6).

STARCH

Starch is a natural, biodegradable polymeric carbohydrate originating from renewable sources, it can be obtained from roots and tubers, such as cassava and potatoes, in cereal grains, such as rice, wheat and corn, as well as in stems and seeds of various plants.

Its structure is formed by two main polysaccharides: amylose and amylopectin, both composed of repeating α-D-glucose units connected by glycosidic bonds (Bertoft, 2017). Amylose is an essentially linear polymer, formed by glycosidic bonds in α-(1→4) (Figure 4A), with a tendency to present a helical conformation and corresponds to 15-25% of the composition of native starches. Amylopectin, in addition to the α-(1→4) bonds between its main chain glycosidic units, also has α-(1→6) bonds, giving it a branched structure (Figure 4B) (Garcia et al., 2016)

The different proportions of amylose and amylopectin in the composition of a starch make it possible to distinguish the natural source from which it was extracted, in addition to giving a semi-crystalline character to this polymer. The hydrogen bonds that stabilize the amylopectin chains result in a crystalline region, whereas the amorphous regions originate from the branch points of amylopectin and amylose.(Garcia et al., 2016).

In addition to its wide application in the food industry, starch is also widely used in the microencapsulation of pharmaceutical compounds and bioactive molecules, in order to protect them against photo-oxidation, thermal decomposition and also enable controlled release (Hoyos-Leyva et al., 2018).

CHITOSAN

Chitosan (Figure 4) is a naturally occurring heteropolysaccharide found in the cell walls of some fungi, especially *Aspergillus niger* and species of the genera *Mucor* and *Zygomicetes* (Laranjeira et al., 2011; Regattieri et al., 2016). It is presented in the form of a linear copolymer composed of monomers of 2-amino-2-deoxy-D-glucopyranose (GlcN) and 2-acetamido-2-deoxy-D-glucopyranose (GlcNAc) with different degrees of polymerization arranged in a linear chain similar to that of cellulose (with the exception of the substitution of the hydroxyl groups in position 2), whose composition varies depending on the degree of acetyl group residue, however, with the GlcN unit always in a greater proportion (Gonçalves et al., 2011). In the formation of the polymer chain, these two units remain linked by β-type glycosidic bonds (1→4).

The largest source of obtaining chitosan is from the N-deacetylation reaction of chitin, the second most abundant biopolymer in nature, after cellulose and which can be extracted from carapaces and exoskeletons of crustaceans, cuticles of various invertebrates, cell walls fungi and some algae. As a rule,

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the N-deacetylated product of chitin only becomes considered chitosan when the degree of deacetylation becomes equal to or greater than 60%, the percentage from which the polysaccharide becomes soluble in dilute acidic solutions; Chitin, on the other hand, does not have this property and remains insoluble in acidic environments. (Assis & Valmir L. da, 2003; Novaes et al., 2020)

The presence of a high percentage of reactive amino groups distributed in its polymeric matrix makes it possible to carry out numerous chemical modifications, such as the introduction of chelating functional groups and metal complexation, allowing chitosan to have different applications.

Chitosan has been widely used in different areas due to its versatility, mainly in the preparation of controlled and prolonged release systems of bioactive molecules in the pharmaceutical and biomedical industry. Due to its versatility and properties, this polymer has aroused special interest in agriculture in the release of pheromones, and the literature has recorded its use in the protection of fruits and seeds in the form of a coating, it is used in agriculture to protect fertilizers and fungicides. (Godínez-Garrido et al., 2021)

The functionality of chitosan is dependent on its chemical structure, such as the presence of amino groups, but also on the molecular size, which define the physicochemical and functional properties of a polymer chain.

The presence of pores, without a doubt, is one of its most promising characteristics for use as a carrier of bioactive molecules. The porous structures of the polymer, when in acidic solutions and coagulated in NaOH solution, have been the subject of many review articles.(Borba Da Cruz et al., 2016; Souza et al., 2014)

When used as a molecule releaser, it is interesting that chitosan becomes inert and for this it uses bifunctional agents, crosslinking agents or intercrossing agents such as glutaraldehyde. Crosslinking is normally achieved using an excess of the bifunctional agent that will provide the surface of the chitosan matrix with groups different from the initial amines. The covalent bond between the amino group and the terminal aldehyde group of glutaraldehyde is irreversible, generating polymeric networks and resists extremes in pH and temperature, which makes the application of chitosan more versatile (Gonsalves et al., 2011)

Abd El-Wahab et al., (2021) evaluated the influence of using chitosan nano-gels containing the Rhynchophorus *ferrugineus pheromone* in traps distributed in the field. A 20% increase in insect capture was found with the use of the pheromone in the form of nano-gel, compared to the application of the pheromone in current use.

SODIUM ALGINATE

Alginate is a natural, unbranched polysaccharide extracted from the cell walls of brown algae (*Phaeophyceae)*, and corresponds to up to 40% of their dry matter, being, for this reason, quite abundant in nature.

This anionic biopolymer is soluble in water and formed by two types of polyuronic acids: β-D-mannuronic acid and α-L-guluronic acid (Figure 4). The organization of these acids in the alginate structure can be observed in three fractions, two of which are monomeric, composed only of β-D-mannuronyl (M block) or only α-L-guluronyl (G block), and a third fraction of dimers of M and G (MG block), interspersing the previous two and joined through glycosidic bonds between their carbons 1 and 4(Karoyo & Wilson, 2021).

The ability of alginate to retain water, forming high viscosity gels or colloidal solutions, whose characteristics depend on the ratio of M/G blocks and the number of cross-links between polymer chains, as well as their gelling, stabilization and non-toxic properties, allow a wide range of industrial applications such as the prolonged release of various active ingredients in the pharmaceutical, medical and agricultural areas and has diverse uses in the food and cosmetic areas.

Gels are formed through a process called ionotropic gelation, which is the result of the interaction between divalent cations, such as calcium (Ca^2+), barium (Ba^2+), strontium (Sr^2+) and zinc (Zn^2+), with the residues of guluronic acid, which has interchangeable sodium ions (Na+) coupled to its structure.

When sodium ions are exchanged for divalent cations, junction zones are formed, with the cations being trapped inside electronegative cavities, causing the polymeric network to assume a conformation called "egg-box". (Figure 4) (Hecht & Srebnik, 2016).

The simple ionotropic gelation method leads to obtaining an inert and hydrophilic matrix, with its high-water absorption capacity resulting from the hydrophilic groups in its structure, such as -OH, -COOH, -CONH, -SO3H

The study of a solid matrix with slow release of semiochemicals for behavioral control of the pest Megaplatypus mutatus, Valladares et al. (2015) IT WAS CARRIED OUT WITH alginate and chitosan beads with the encapsulation of the sexual pheromone Sucatol (6-methyl-5-hepten-2-ol). The polymeric matrix was efficient in releasing the active ingredient at an adequate level to obtain an efficient attraction response from the female M. mutatus, at a concentration of 4% alginate.

MALTODEXTRIN

Maltodextrin (Figure 4) is a polymer produced by the partial hydrolysis of starch with acids or enzymes and composed of a molecule of 3 to 1 D-glucose (dextrose), linked by alpha (1-4) and α- (1,6) bonds. It contains 2–3% glucose and 5–7% maltose and can be made into a spray-dried white hygroscopic powder. The extent of starch degradation in maltodextrin is indicated by the dextrose equivalent (DE) value that evaluates the content of reducing end groups, which is the inverse value of the average degree of polymerization (DP) of dehydrated glucose units. The DE value of maltodextrin is in the range of 3 to 20, indicating that its carbohydrate chain is long and is a complex mixture of high and low molecular weight substances(Du et al., 2021; Saavedra-Leos et al., 2015; Xiao et al., 2022).

Maltodextrin is soluble in water and has low viscosity, due to these characteristics it is commonly used as a wall material in the microencapsulation of food ingredients. It can be used as a fast-dissolving film, due to its strong hydrophilic characteristic and poor mechanical and barrier properties. It can be used as packaging film after mixing with other polymers that reinforce its films.

GUM ARABIC

Gum Arabic is produced by some species of the genus Acacia, especially the *Acacia senegal* tree, and is the oldest known gum exudate. Its use has been reported for more than 5000 years by the Egyptians in paintings as it is an adhesive mineral pigment and today it is used as a thickener for writing inks. Currently, its application extends to the areas of food, pharmaceuticals, cosmetics, textiles, adhesives, paints, printing and ceramics. Its production is mostly in the arid and semi-arid region of Africa and in smaller quantities in the Arabian Peninsula and South Asia (Prasad et al., 2022).

Its chemical structure comprises β-D-galactopyranosyl units linked in the 1,3 form. The side chains are made of two to five 1,3-linked β-D-galactopyranosyl units, linked to the primary chain by 1,6 linkages. Both the main and side chains contain the pyranosidic hexose units of L-raminose, D-glucuronic acid and D-galactose, and the pentose furanosidic unit L-arabinose (Figure 4) (Mariod, 2018).

The attributes of gum arabic can change fundamentally depending on the geological origin and age of the trees, climatic conditions, soil condition and even the exudation location on the tree. Gum Arabic is biodegradable and soluble in water, which allows it to stabilize oil-in-water emulsions, turning them into concentrated solutions of low consistency. This characteristic gives the gum the ability to act as an encapsulating agent in microencapsulation processes of volatile bioactive compounds such as aromas and also medicines (Bhushette & Annapure, 2017; Point & Point, 2019; Prasad et al., 2022).

APPLICATIONS OF POLYMERS WITH SEMIOCHEMICALS AND/OR IN PEST MANAGEMENT

Maltodextrin and gum arabic were used as encapsulating agents in the microencapsulation of *Capsicum annum* L. essential oil and the microencapsulated product showed inhibitory activity against *Staphylococcus aureus*, *Pseudomonas aeruginosa* and *Enterococcus faecalis*, and antimicrobial activity only against *Staphylococcus aureus*.

Microencapsulation resulted in significant preservation of the essential oil against oxidation during the storage period, which optimized its use. (Karaaslan et al., 2021).

Another microencapsulation produced for pest control is the bacteria *Bacillus thuringiensis* with chitosan and gum arabic to control *Helicoverpa armigera* (Lepidoptera: Noctuidae) caterpillars in cotton. The microcapsules obtained with an average size of 32 μm, provided an increase in the solubility of the toxin in the alkaline fluid of the insect's midgut, which, upon entering the gastrointestinal tract of the larva, caused the inactivity of proteins in the gastrointestinal tract, and as it was not metabolized, it increased larval mortality (Murthy et al., 2014).

Chitosan was also used to microencapsulate the bacteria *Streptomyces fulvissimus* together with gellan gum, and the product obtained increased the efficiency of probiotic bacterial agents in adverse laboratory conditions, providing better control of take-all wheat disease caused by *Gaeumannomyces graminis* var. tritici (Saberi-Riseh & Moradi-Pour, 2021).

More recently, Lemos et al. (2021) studied the effectiveness of amylose inclusion complexes associated with the aggregation pheromone Rincophorol (S(-)2-methyl-5(E)-hepteno-4-ol) (Figure 2), finding that the release rate of semiochemistry is influenced by the molecular weight of the polymer. The recovered Rincophorol content was suitable for attracting insects, concluding that the application of amylose to retain the studied pheromone is appropriate.

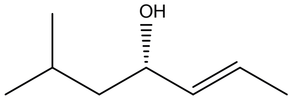

Figure 5- Chemical structure of Rincophorol (S(-)2-methyl-5(E)-heptene-4-ol)

FINAL CONSIDERATIONS

The use of polymers, essentially natural ones, as a modified pheromone release system appears to be a viable and efficient alternative, becoming the target of many studies of interest to the agricultural environment. By incorporating pheromones into a polymer matrix, the pheromones can be released slowly over a longer period of time, ensuring a more effective and efficient delivery system. This can be particularly important in agricultural environments where pheromones can be used to control pest populations, as a sustained release can increase the effectiveness of the pheromones while reducing the amount of material needed to achieve the desired effect.

Additionally, polymers can be tailored to specific release rates and mechanisms, allowing greater control over pheromone delivery. For example, polymers can be designed to release pheromones in response to changes in temperature or humidity, or to release pheromones more slowly in colder environments to ensure a longer shelf life.

Overall, the use of polymers in controlled pheromone release systems can provide a more efficient, effective, and customizable way to deliver pheromones for a variety of applications. Characteristics such as controlled release, non-toxicity, low cost of obtaining and ease of manufacturing place these compounds at the top of the preferred materials to compose pheromone release systems.

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