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## Semiochemicals: The future of pest management

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### Abstract

The Revolution of chemical pesticides in industry and agricultural production which began with the discovery of DDT insecticidal properties by Paul Hermann Muller in 1939 (Noble Prize in medicine 1948) started its decline (As a false revolution) in 1962 with the deceleration of Rachel Carson in her magnificent book " The Silent Spring " about the harmful effects of chemical pesticides on both the environment and human health. The true revolution – from the aspect of pest control – began in 1959 (20 years after the false one) with the discovery and identification of the first insect pheromone, Bombykol, the silkworm *Bombyx mori* sex – pheromone by Adolf Friedrich Johann Butenandt (The Noble Prize in Chemistry 1939, discovery of human female sex – hormones, estrone and other primary female sex hormones, received in 1949). Since then, Semiochemicals (especially pheromones and Kairomones) have been pointed out as the future tool of integrated pest management (IPM). By the beginning of the 21st century, the era of chemical pesticides started their end in the industry (Many pesticide companies closed or converted to Semiochemicals manufacturing) and agriculture production (Too many pesticides proved to be environmental pollutants), while the era of Semiochemicals has begun to take its role in human development and civilization, as a clean industry and clean pest management tools. Semiochemicals are very important to the whole world, to African countries and especially to The Nile Basin countries not only in industry and agricultural production, but in public health also, that is because of its multiple advantages which will be mentioned in this review.

### Introduction

Insecticides are used in agriculture, medicine, industry and the household. The use of insecticides is believed to be one of the major factors behind the increase in agricultural

productivity in the 20<sup>th</sup> century. Nearly all insecticides have the potential to significantly alter ecosystems, many are toxic to humans, and others are concentrated in the food chain.

### Semiochemicals:

A semiochemical (Semeon means a signal in Greek) is a generic term used for a chemical substance or mixture that carries a message. These chemicals act as messengers within or between species. It is usually used in the field of chemical ecology to encompass pheromones, allomones, kairomones, attractants and repellents. Probably all insects use semiochemicals; natural chemicals released by an organism that affect the behaviors of other individuals. Pheromones are intraspecific signals that aid in finding mates, food and habitat resources, warning of enemies, and avoiding competition. Interspecific signals known as allomones and kairomones have similar functions. The goals of using semiochemicals in pest management are:

- To monitor pest populations to determine if control is warranted.

- To alter the behavior of the pest or its enemies to the detriment of the pest.

In general, the advantages of using semiochemicals are:

- They have adverse effects only on target pests.

- They are relatively nontoxic and required in low amounts.

- They are non-persistent and environmentally safe.

- They appear difficult for insects to develop resistance against.

## **1. Definitions: Structure**

### **1.1. Pheromones:**

A pheromone (From Greek phero "to bear" + hormone from Greek - "impetus") is a secreted or excreted chemical factor that triggers a social response in members of the same species. Pheromones are chemicals capable of acting outside the body of the secreting individual to impact the behavior of the receiving individual. There are alarm pheromones, food trail pheromones, sex pheromones, and many others that affect behavior or physiology. Their use among insects

has been particularly well documented. In addition, some vertebrates and plants communicate by using pheromones. The term "pheromone" was introduced by Peter Karlson and Martin Lüscher in 1959, based on the Greek words pherein (To transport) and hormone (To stimulate). They are also sometimes classified as ecto-hormones. German Biochemist Adolf Butenandt characterized the first such chemical, Bombykol (A chemically well-characterized pheromone released by the female silkworm to attract mates.

### **1.2. Allomones:**

An allomone is any chemical substance produced and released by an individual of one species that affects the behaviour of a member of another species to the benefit of the originator but not the receiver. Production of allomones is a common form of defense, particularly by plant species against insect herbivores. "Allomone" was proposed by Brown and Eisner 1968 to denote those substances which convey an advantage upon the emitter.

### **1.3. Kairomones:**

A kairomone is a semiochemical, emitted by an organism, which mediates interspecific interactions in a way that benefits an individual of another species which receives it, without benefitting the emitter. Two main ecological cues are provided by kairomones, they generally either indicate a food source for the receiver or give warning of the presence of a predator.

### **1.4. Pheromones applications:**

The concept of integrated pest management (IPM) is based on the recognition that no single approach to pest control offers a universal solution, and that the best crop protection can be provided by a fusion of various tactics and practices based on sound ecological principles. Pheromones are a commonly used component of many insect IPM programs.

The existence of pheromones has been known for centuries, apparently originating in observations of a mass bee stinging in response to a chemical released by the sting of a single bee. The first isolation and identification of an insect pheromone (Silkworm moth) occurred in 1959 by German scientists. Since then, hundreds, perhaps thousands of insect pheromones have been identified by increasingly sophisticated equipment. Today we have a much clearer view of the limitations and possibilities associated with insect pheromones in IPM programs. The two primary uses of insect pheromones are for the detection and monitoring of populations and for mating disruption. These uses take advantage of sex pheromones on which a vast majority of insect pests rely to mediate reproduction.

## **2. Uses of pheromones in IPM:**

### **2.1. Detection and monitoring:**

The principal use of insect sex pheromones is to attract insects to traps for detection and determination of temporal distribution. In most instances, it is the males who are responders to female-produced sex pheromones. Trap baits, therefore, are designed to closely reproduce the ratio of chemical components and the emission rate of calling females. Ideally, a trap bait should uniformly dissipate its pheromone content over time and not permanently retain or degrade the pheromone in the process. Trap baits of many designs have been tested over the years, but the hollow polyvinyl plastic fiber (Emit from open ends), closed hollow fiber and bag (Emit through walls) and laminated plastic flake (Emit through walls and exposed edges) are commonly used today. Trap design is also critical to the effective use of traps for monitoring insect populations. Traps vary in design and size depending on the behavior of the target insects. Consistent trapping

protocols are essential for population evaluations, spray thresholds, and year to year comparisons. The information from trap catches can be very useful for decision making on insecticide applications or other control measures. For example, trap catches may indicate a loss of effect of pheromone on mating disruption and the need to reapply a pheromone treatment. Careful monitoring and experience in interpreting collected data are important for success. Traps may also be placed with the objective of destroying males for population control. Male annihilation is trapping carried to a seemingly logical conclusion. Place enough traps, catch enough males, and leave the females of the species without mates. This approach has been used against pink bollworms in an isolated area of Arizona with low numbers of overwintering moths. A rate of 5 traps per acre was used and the traps were composed of Styrofoam cups containing oil to provide larger capacity for dead moths. These traps were placed on row centers to avoid the cultivator and were never serviced again. The growing community paid for this program for a few years, but the results were difficult to prove because a control area was not available. Calculations by Dr. Edward Knipling (USDA retired) indicated that almost all (95%+) male pink bollworms would have to be destroyed before they could mate in order to exert significant population control. Any untrapped males simply mate more frequently. Mating disruption does not depend on traps for control, although traps are frequently used to monitor the extent of mating disruption in the population. Failure to trap males is taken as an indication that males are unable to find females which may or may not be true. Thus, trap data must always be related to actual levels of crop infestation.

### **2.2. Mating disruption:**

With the commercial availability of insect sex pheromones for several agricultural pests in the 1970s, scientists and entrepreneurs turned their attention to mating disruption as a "rational" approach to insect control. In theory, mating disruption may be accomplished in two principal ways: false trail following or confusion. False trail following results from placing many more point sources of pheromone (Hollow fibers, flakes or other point sources) per acre than the anticipated numbers of females in the crop. The odds of males finding females at the end of the pheromone trail must be greatly reduced. The emission of pheromone is relatively low from each source such that a downwind trail is created and not lost in a background of released pheromone. Males following these trails are thought to spend their mating energies in pursuit of artificial pheromone sources. Pink bollworm males were early observed trying to mate with hollow fiber pheromone sources in treated fields. Thereafter, commercial pink bollworm pheromone products were applied in stickers containing small amounts of contact insecticide. The resulting attract-and-kill formulations (Another form of male annihilation) were viewed as a subversion of the pheromone by purists, but in practice the damage was limited to the target species. However, the effectiveness of the added insecticide is largely unknown under field conditions. Growers endorsed the idea that a dead male is better than a confused one. A further combination of pheromones and insecticides is occasionally encountered. Dual applications of pheromone and full-strength insecticides (Either separately or in tank mixes) are applied with the idea of increasing insect flight activity and thus increasing the chance of insecticide exposure. Full-strength applications of pheromones are generally used for this

method. The greater the amount of pheromone applied and the greater the release rate, the more likely males are to be confused in the fog of ambient pheromone. Male confusion is thought to be the result of ambient pheromone concentrations sufficient to hide the trails of calling females (Large doses from diffuse sources such as microcapsules or larger doses of pheromone in point source dispensers such as tie-on polyethene ropes). Added to the effect, or indeed the effect, is the adaptation of antennal receptor sites and/or habituation of the insect's central nervous system. Specific receptor sites on the antennae respond to only the pheromone molecules (Individual component molecules appear to have individual receptor sites on antennae). When a receptor site is continually activated by high ambient concentrations of pheromones, the resulting electrical signal diminishes (Measured by an electroantennogram). The receptor site becomes unresponsive, and the insect becomes navigationally blind. When the insect's central nervous system is inundated with signals from the receptor sites it becomes habituated: no longer able to provide the directed behavior. All the above are, to some degree, based on known neurophysiology, but exactly what proportion of each occurs in each situation can only be guessed. The net result of confusion is that the male is unable to orient to any pheromone source and follow the upwind trail to a mate. For a current summary of the theory and application of pheromones for the control of Lepidopterous pests. Present commercial formulations of pheromones for both trap baits and mating disruption mimic the natural chemical blends of females as clearly as possible. Most insect sex pheromones are multicomponent with precise ratios of components which may be expensive to manufacture. Thus, insect sex

pheromones and products containing pheromones, are commercially available primarily for insects of economic importance. Fortunately, there are hardly any insect species of agricultural importance, among the Lepidoptera at least, for which there are not some pheromone products available.

### **3. Different pheromone tactics applied in Egypt:**

The pheromone strategy differs completely in its tactics from the insecticide strategy (Because of their different aims and targets). In Egypt, the pheromone strategy was used widely for some time (1991-1998) with many different tactics as an important part of the IPM program conducted then. Some of these tactics could be useful to be used in the Nile Basin countries, some of these tactics are:

#### **3.1. Pheromone traps for monitoring and detection technique:**

**3.1.1.** The use of pheromone traps, of different types and shapes, for monitoring insect pest field population density and dynamics over place (Village, district, Governorate, region and countrywide) (Albeltagy *et al.*, 1991a).

**3.1.2.** The use of pheromone traps, of different types and shapes, for monitoring insect pest field population density and dynamics over time (Day, week, month, season, year) (Albeltagy *et al.*, 1993a).

**3.1.3.** The use of pheromone traps, especially delta traps, as a control indicator to differentiate between different kinds of control actions as a means of IPM (Albeltagy *et al.*, 1996a).

**3.1.4.** The use of pheromone traps, especially delta traps, as a control trigger for insect pest control decisions for different kinds of control actions as means of IPM (Albeltagy, 1999).

**3.1.5.** The use of pheromone traps, especially delta traps to evaluate the

pheromone release rates and its corresponding effect on crop infestations (Albeltagy *et al.*, 1993 c).

**3.1.6.** The use of pheromone traps, especially delta traps, to indicate the relationship between trap catches and crop infestation (Albeltagy *et al.*, 1995 a).

**3.1.7.** The use of pheromone traps, especially delta traps, to build up computer simulation models for different insect pest control strategies and tactics (Albeltagy *et al.*, 1995b).

#### **3.2. Pheromone traps for mass trapping technique:**

The use of many different pheromone trap types (Delta, funnel and / or water) as a mass trapping technique against many different insect pest field strains (Albeltagy *et al.*, 1991b and Hamid and Albeltagy, 1995).

#### **3.3. Pheromone disruption technique:**

**3.3.1.** Pink bollworm (PBW) rope gossypylure (The sex pheromone of PBW) formulation was used against pink bollworm on large scale applications (Thousands of acres) in cotton fields for many years (Albeltagy, 1993 and Albeltagy *et al.*, 1993 b) .

**3.3.2.** The use of pheromone disruption technique as a part of IPM program against cotton insect complex pests (Albeltagy *et al.*, 1993d).

**3.3.3.** The use of pheromone disruption technique as a part of IPM program to enhance the role of biological control agents in cotton fields (Mostafa *et al.*, 1994).

**3.3.4.** The use of different pheromone confusion techniques, disruption – lure and kill, in different formulation types (Dispensers, rubbers, microencapsulated) (Abdo *et al.*, 1991 and Albeltagy and Haroun, 1996).

#### **3.4. Attracticide resistance monitoring technique (ARMT):**

The use of pheromone traps in the attracticide resistance monitoring

technique as a simple, easy, effective, accurate, and quick tool for monitoring and detecting insecticide resistance in insect pest field populations (Albeltagy *et al.*, 1996 b; Albeltagy *et al.*, 2000 and Albeltagy *et al.*, 2010).

### 3.5. Advantages of pheromone applications:

3.5.1. Decreases the number of insecticide applications.

3.5.2. Rationalizes insecticide usage.

3.5.3. Keeps the susceptibility of insect pest field populations.

3.5.4. Keeps the efficiency of insecticides.

3.5.5. Increases pollinators.

3.5.6. Increases crop production.

3.5.7. Decreases environmental pollution.

3.5.8. Enhances biological control agents.

3.5.9. Increases honey- bee populations and honey production.

3.5.10. Increases farmer benefits.

3.5.11. Increases National income.

### 4. Pheromones and kairomones for control of pest control:

The solid-phase micro extraction (SPME) technique has been successfully used for identification of the main sex pheromone components of *Cydia* and *Bonagota* species (Lepidoptera: Tortricidae). Synthesis of a series of dodecadienols, tetradecadienols, and their corresponding aldehydes and acetates have been performed to be used for testing inhibitory and synergistic effects on pest insects of these species. Behaviorally active volatile compounds emitted from aphids and aphid-infested plants have been identified by SPME-technique, synthesized, and used in olfactometer tests. Methyl salicylate is shown to act in interplant communication released by plants infested by insects. In the presence of the compound, the colonization density of aphids in the crop is reduced. Methyl salicylate is a common multifunctional

compound, which is active in several biological systems. The action of this compound as an anti-aphrodisiac will be presented. The compound is transferred at mating from the male pierid butterfly *Pieris rapi* to the female and makes the female unattractive for mating. The chemo diversity in Nature is most fascinating. There are more than 100, 000 different low-molecular compounds described in the literature. Many more are to come since there is rapid development in the field of organic natural product chemistry and ecological chemistry. A compound in a living organism is produced (Biosynthesized) because it serves a specific function or several functions. Some compounds have functions which are common to all living organisms or to certain groups of organisms.

They are essential and are directly involved in life's processes (e.g., hormones and cofactors). A compound may also occur because once in the earlier evolution of the organism, it served a specific function but now remains a "metabolic fossil" with potential for a function. Most organic natural products have functions that are species-specific or specific to certain classes or groups of living organisms. They have evolved because they play a part in biological interactions such as defense, protection, signal transduction, or other specific functions essential for life processes or beneficial for the organism.

To obtain selectivity, Nature has applied different strategies for the evolution of chemicals (Signals) for specific functions. Either a very specific and unique chemical signal has evolved or, more commonly, nature has used a combinatorial approach using a mixture of compounds with a unique composition. When considering these evolutionary aspects, one has also to consider the parallel evolution of

suitable and selective receptors for the signals.

Chemo diversity is essential for chemical communication between organisms in Nature and is demonstrated by research on volatile compounds, which are active in insect–insect, insect–plants relationships (semiochemicals such as pheromones and allomones). The biological effects of the complex insect and plant scents are evaluated by tests in the field and in the laboratory. The identified insect behavior releasing compounds may find or have found applications in the monitoring and control of insect pest populations.

The chemo diversity in Nature very often rests on stereochemistry. Most of the asymmetric natural products occur in an optically active form. The pheromone field offers excellent examples where chirality and stereochemistry plays an important role for bioactivity. In this context I wish to bring forward a particular case which has been studied in our laboratories. It deals with the very active sex pheromones of sawflies, *Neodiprion* and *Diprion* species. There is a very delicate tuning of the diastereomeric, and chiral compositions of the sex pheromone components released by these insects.

This tuning provides species specificity and proper biological effects among sympatric species. Minor alterations of the composition inhibit the pheromonal effect. This case also demonstrates the importance of having access to enantiomerically and diastereomeric ally pure compounds for biological studies.

The pheromones emitted from several lepidopteran pest insects are currently being investigated. Solid phase microextraction (SPME) techniques in combination with electro-antennographic (EAG) measurements are most useful for such studies.

Lepidoptera pheromone constituents are usually long-chain (C10–C18) saturated or unsaturated alcohols, aldehydes, or esters, and the active signal is usually a mixture of constituents of narrowly defined composition.

### **5. Semiochemicals for insect pest management:**

Semiochemicals determine insect life situations such as feeding, mating, and egg-laying (Ovipositing). Semiochemicals are thus potential agents for selective control of pest insects (For definitions of terms used for various chemical signals (Figure 2). Biological control with pheromones or kairomones can be used for detection and monitoring of insect populations. Monitoring is important for the efficient use of conventional insecticides. Mating disruption by use of pheromones is a promising and, in many cases, a successful strategy for control (Confusion strategy). The use of semiochemicals as feeding deterrents is another strategy. The most common strategy for control using semiochemicals is to attract, trap, and kill the pest insects.

Since the first identification of a pheromone over 40 years ago, chemical signals have received much attention from scientists in biology, chemistry, and agriculture / forestry. Many of the findings have come into practical use for monitoring or suppression of insect pests. Crop protection based on semiochemicals has advantages over conventional insecticides but is not yet widely used. Also, need more efficient technology transfer for those who will benefit by applications of control methods based on semiochemicals. Also, need to learn more about the chemical language of insects and plants. The olfactory system of insects is very sensitive, and limited amounts of semiochemicals are needed for control.

This is demonstrated by the current application of pheromones for control (Mating disruption by confusion strategy) of codling moth (*Cydia pomonella*) in apple orchards. A dispenser for insect control emits about 1 g/ha, and the amounts of pheromone needed for control using the confusion strategy are only about 1 g/ha. On the other hand, the amount of insecticide needed for a conventional treatment is in this case about 1 kg/ha. Furthermore, the use of nonselective insecticides is questioned because of ecological and environmental reasons.

Synthetic organic chemistry is important for the successful identification of active compounds. Synthesis is also important for preparing compounds for biological tests to confirm the chromatographic and spectroscopic identification of a chemical signal and for field tests. The chemical signals are either one single compound or a mixture of compounds in specific proportions. The signal may be a rather common and structurally simple compound. Very often, such a common compound can have different biological functions on different species. In this presentation, you will find examples of such simple chemical signals.

Recently, it was found that water is an aggregation signal for the almond moth, *Ephestia cautella*, an insect that may cause problems in chocolate and candy production units. Water seems also useful for the aggregation of other pest insects (The pyralid moths *Ephestia kuehniella* and *Plodia interpunctella*) that cause damage in the food industry and to stored food products. Water traps in combination with pheromones for mating disruption seem to be an efficient method for control. Chocolate volatiles are powerful attractants for both sexes of *E. cautella* and *P. interpunctella*. Important volatile

constituents are ethyl vanillin, nonanal, and phenylacetaldehyde (Figure 3). Control methods based on these findings are under investigation.

Impurities of isomeric compounds may completely change the biological response. Selective synthetic methods are therefore essential for successful work. This is demonstrated in our work on the pheromone constituents of the pine sawfly, the larvae of which feed on fresh pine needles. The active pheromone composition was shown to be an intricate mixture of diastereomers of diprinyl acetate (Figure 4). The presence of very small amounts of one minor component is essential for biological activity. The development of selective asymmetric synthetic methods was essential and led to samples of more than 99.9 % isomeric and enantiomeric purity.

Synthesis has also been essential for the development of pheromone-based control methods of many Lepidopteran insect pests. Common Lepidopteran pheromone constituents are long-chain saturated or unsaturated alcohols and their derivatives (Acetates and aldehydes). The double bonds are conjugated or nonconjugated. The positions and configurations of the double bonds are important. Efficient and selective syntheses of such compounds have been part of the development of pheromone-based control methods such as in our study of the pheromone communication of the codling moth, *Cydia pomonella*. The importance of the composition of the pheromone blend is clearly shown by a comparative study involving some closely related species.

Host volatiles are of importance for the aggregation of many insects. A combination of host plant volatiles and pheromones has been shown to be efficient for the control of the apple



fruit moth, *Argyresthia conjugella*. The preferred hosts for this moth are the fruits of mountain ash (rowan), *Sorbus aucuaria*, and apple (*Malus domestica*) with a slight preference for the fruits of mountain ash. We investigated the volatile constituents of apple and rowan berries and found some similarities. Some simple and common compounds were found to be particularly attractive to both males and females as shown by electrophysiological recordings in combination with gas chromatography (GC). The compounds are now used in a field test in Norway for a strategy based on attract and kill. An advantage is that both males and females are trapped. A common ecological observation is that many pest organisms detect dead or weakened host plants for feeding or egg-laying. At an early stage of our research on chemical signals, we were involved in a study of some forest pest insects that exhibit this behavior. To our surprise, some simple compounds were responsible for the aggregation of these pest insects. In fact, the mixture of ethanol and (-)- $\alpha$ -pinene is now used for monitoring of these and some other forest pest insects.

#### **6. Role of kairomones in integrated pest management:**

The seminal role of chemical ecology in regulating the attacks of insect pests on cultivated plants was delineated by Fraenkel in 1969: "There can hardly be an entomologist today who does not know that host selection is the very heart of agricultural entomology and that secondary plant substances are the clues to the problem." Twenty-five years later we are able to state with conviction that progress in integrated pest management (IPM) will be closely meshed with the use of semiochemicals that modify insect behavior. These semiochemicals include pheromones that regulate intraspecific communication of alarm, aggregation, trail-following and mating

behavior; and kairomones that regulate interspecific communication of appropriate host selection for feeding, oviposition, and shelter. For use in insect control, semiochemicals have the important advantages of physiological and ecological selectivity and are often of extremely high biological activity (Expressed in picograms to nanograms at the target antennal receptor site). Appropriate uses for semiochemicals in insect pest management include (a) monitoring for pest density in relation to the economic threshold, (b) detection of outlying infestations, (c) mass removal trapping, (d) incorporation as attractants and phagostimulants in toxic baits or trap crops, and (e) adverse modification of sexual or social behavior.

Despite these manifold advantages and substantial scientific enthusiasm for chemical ecology, the use of semiochemicals in insect control has progressed at a slow pace. A recent survey suggested that sales of insect pheromone technology in 1990 were only about \$6 x 10<sup>6</sup> compared with \$7 x 10<sup>9</sup> for insecticide technology.

For use in IPM programs, plant kairomones have certain major advantages over insect pheromones. Many effective kairomones such as geraniol, eugenol and phenethanol for the Japanese beetle; methyl eugenol and raspberry ketone for *Dacus* spp. fruit flies; and cinnamaldehyde, cinnamyl alcohol, 4-methoxycinnamaldehyde and 4-ethoxyphenethanol for *Diabrotica* spp. rootworms, are simple inexpensive chemicals costing only a few cents a gram in contrast to the approximately 100-fold greater cost of the corresponding pheromones of these insects. The kairomones are often effective as lures for both male and female insects in contrast to the sex pheromones which typically mostly attract male insects only. However, the kairomones methyl eugenol and

raspberry ketone of the *Dacus* spp. fruit flies are notable exceptions, attracting only males. The plant kairomones are highly specific for individual insect pests and generally have little or no attraction to beneficial parasites and predators. The plant kairomones, like the sex pheromones, are attractive in minute quantities. For example, methyl eugenol, which is a kairomone for at least 58 closely related species of *Dacus* spp., is attractive to the oriental fruit fly, *Dacus dorsalis*, when applied to filter paper at  $10^{-10}$  g and causes arrest and phagostimulation at  $10^{-9}$  g. Raspberry ketone or 4-(4-hydroxyphenyl)-2-butanone, which is a kairomone for at least 176 closely related species of *Dacus*, is similarly attractive and phagostimulatory to the male melon fly, *Dacus cucurbitae*, over the range of  $10^{-10}$  to  $10^{-8}$  g.

In field trapping, male *D. dorsalis* are caught in delta sticky traps with as little as  $10^{-6}$  g of methyl eugenol and male *D. cucurbitae* with as little as  $10^{-5}$  g of raspberry ketone. A kairomone lure for the adult western corn rootworm, *Diabrotica virgifera virgifera*, 4-methoxycinnamaldehyde is effective in field trapping with cylindrical sticky traps at 30 micro-g. per trap; and 4-methoxyphenethanol, a kairomone for the northern corn rootworm, *Diabrotica barberi*, is attractive at 100 micro-g. per trap. Although it is essentially non-volatile, the tetracyclic triterpenoid cucurbitacin B from the bitter Curcubitaceae, which is a kairomone for many species of *Diabroticites* and *Aulacophorites*, is an arrestant for the rootworm adults at  $5 \times 10^{-12}$  g and a phagostimulant at  $1 \times 10^{-9}$  g.

Role of kairomones in IPM. The preponderance of semiochemical research and development for insect control relates to the use of sex pheromones. There has been little appreciation in recent literature of the

possible uses of host kairomones important in host selection and feeding stimulation (phagostimulants). However, the first identification of an insect behavior modifying chemical was Howlett's characterization in 1915 of the plant kairomone methyl eugenol as an attractant for male fruit flies (*Dacus diversus*, *D. zonatus* and *D. dorsalis*). This discovery antedated the first identification of an insect pheromone bombykol of the female silkworm moth, *Bombyx mori*, by 44 years.

Geraniol, a volatile kairomone attractant for the Japanese beetle, *Popillia japonica*, was patented by Smith *et al.* in 1926. In 1935, Riley and Hepburn demonstrated that terpineol acetate from a variety of essential oils was a specific attractant for the male Mediterranean fruit fly, *Ceratitidis capitata*, and for the Natal fruit fly, *Ceratitidis rosae*.

Robust IPM technology has emerged from these discoveries in the employment of methyl eugenol and raspberry ketone for the monitoring of incipient infestations of several hundred species of Dacini fruit flies, including the oriental fruit fly, the Queensland fruit fly, *Dacus tryoni*, and the melon fly. The 'male annihilation' technology developed by Steiner *et al.* in 1965 has led to the use of these kairomone lures in multiple-source toxic baits for the complete control and even eradication of these fruit flies in insular infestations.

The extensive investigations of kairomone attractants for the Japanese beetle by the U.S. Department of Agriculture have resulted in the development of synergistic lure combinations such as geraniol, eugenol and phenethyl propanoate, presently used in hundreds of thousands of simple 'bag traps' for the control of this insect in suburban and isolated locations. The three lure components are widely

distributed among the very large host plant resources of the Japanese beetle. Investigations of kairomone lures for the Mediterranean fruit fly have identified the terpenoid *ot-copaene* from *Archangelica officinalis* as an exceptionally active lure, attractive to males at dilutions as low as 1 ppb. Angelica oil containing *ct-copaene* has been used to monitor incipient infestations of the Medfly since 1957. Thus, the employment of kairomone lures for insect control was solidly established well before the potentialities of pheromones became evident.

More recent milestones in kairomone technology include the identification of the tetracyclic triterpenoids cucurbitacin B and cucurbitacin E from bitter Cucurbitaceae, as phagostimulants for the Chrysomelidae beetles, Aulacophorini and Diabroticini.

The incorporation of these phagostimulants in 'attracticide' baits has produced specific control of adult rootworms when applied at about 1-2 g of cucurbitacin and 10-20 g of insecticide per ha. It has shown that the plant kairomone hypericin from *Hypericum* spp. is a powerful phagostimulant for many species of *Chrysolina* beetles, explaining the remarkable effectiveness of these beetles as biological control agents for the control of the rangeland weed *Hypericum perforatum*. Analogously, the identification of 1-octene-3-ol as a powerful kairomone attractant for the tse-tse flies, *Glossina* spp., has revolutionized the control of these vectors of African trypanosomiasis. Recent identification of oviposition kairomones for *Heliothis* budworms and the sweet potato weevil, *Cylas formicarius*, may provide other avenues for the exploitation of kairomone technology.

Parakairomones as lures. Parakairomones are structurally optimized analogues of natural kairomones with similar behavior-modifying properties. In general, the semiochemical structural limitations for insect receptor depolarization are less rigorous for kairomones than for pheromones (Figure 1). Parakairomones may have simpler chemical structures than natural kairomones and are therefore cheaper to produce. For example, trimedlure or tert-butyl 4-(or 5)-chloro-2-methylcyclohexane carboxylates, widely used in monitoring for Medfly infestations, is a parakairomone of *tx-copaene*. Parakairomones may have more favorable physical and chemical properties than natural kairomones. Thus, the parakairomone cue-lure or (4-p-acetoxyphenyl)-2-butanone is about 17-fold more volatile than the kairomone raspberry ketone of (4-hydroxyphenyl)-2-butanone and is a more effective lure for the melon fly, although raspberry ketone is more persistent. Similarly, the Japanese beetle lure, phenethyl propanoate, is a parakairomone of the natural kairomone phenethanol, and 4-methoxycinnamitrile is a parakairomone of the lure for the western corn rootworm, 4-methoxycinnamaldehyde.

Parakairomones may have more favorable toxicological properties than kairomones; for example, the parakairomone of the oriental fruit fly, 3,4-dimethoxy-1-propylbenzene, as compared with the kairomone methyl eugenol or 3,4-dimethoxy-1-allylbenzene. Thus, parakairomones may have important roles in IPM.

Conclusions. Intensive study of the role of kairomones in host selection by insect pests is highly rewarding in furthering the basic and applied aspects of IPM. Kairomone attractants already provide inexpensive lures for more than

300 insect pests. Combining these lures with disposable traps provides the simplest means for monitoring incipient pest infestations in geographically isolated areas, and for quantitative estimation of pest populations to evaluate economic thresholds for pest control. Kairomone lures are presently used in millions of 'removal traps' to control low-level pest infestations, as for fruit flies, scarab beetles and tsetse flies. Incorporation of volatile kairomone lures and kairomone arrestants and phagostimulants into bait sprays and granulars, 'twist-ties', and fiberboard squares, containing minimal quantities of insecticides -- can provide areawide insect control free from hazards to beneficial insects and pollinators. This use of 'attracticides' can reduce the amount of insecticide applied to as little as 1% of that required for conventional sprays, and thus almost eliminate the hazards of insecticide residues on edible produce. Attracticides have exceptional promise for exposing insect pests to insect growth regulators and to microbial insecticides. Knowledge of the chemical ecology of kairomones

present in cultivars provides elegant opportunities for selective plant breeding to remove host attractants from the cultivars. This antixenotic approach has already been shown to be effective in the amelioration of herbivory of Cucurbitaceae devoid of cucurbitacin phagostimulants for *Luperini* beetles (*Diabroticites* and *Aulacophorites*) and of *Hypericum* spp. devoid of hypericin phagostimulants for *Chrysolina* beetles. The most rewarding product of kairomone research, however, may well be the fundamental insights that it provides about insect behavior and the coevolution of plants and insects.

This short review of some current work on semiochemicals demonstrates the importance of fundamental and interdisciplinary research dealing with the chemistry of biologically active compounds in combination with biological studies on their action. Such studies provide tools for future applications of the compounds for the benefit of mankind. Research efforts in organic chemistry, both analytical and synthetic, play an essential role in such research efforts.

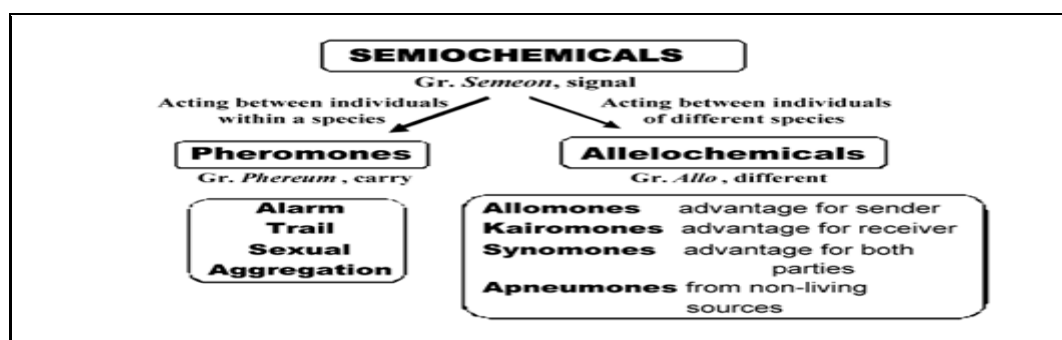
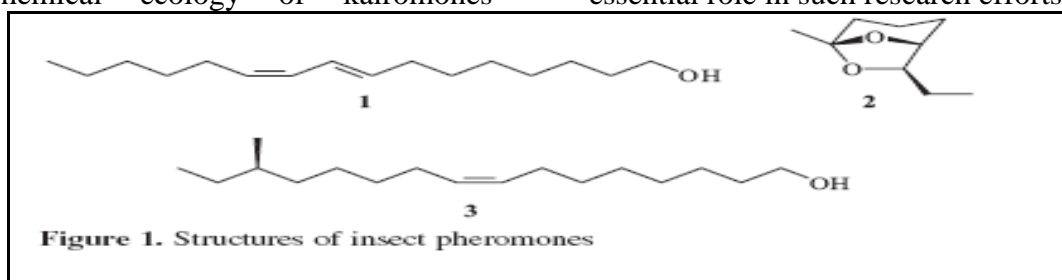


Figure (2): Terms commonly used for various semiochemicals (Chemical signals) .

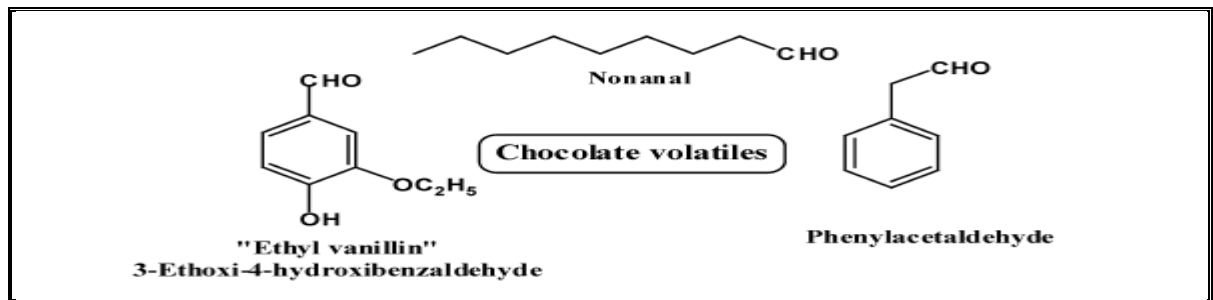


Figure (3) : Chocolate flavors are attractants for *E. cautella* and *P. interpunctella*.

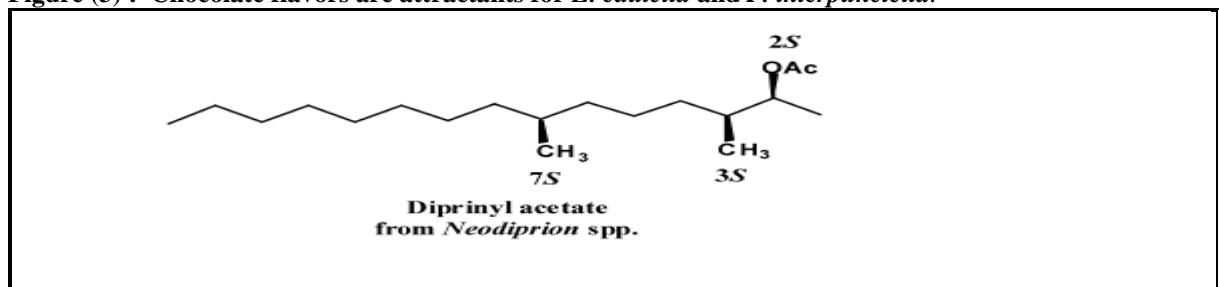


Figure (4) : Diprinyl acetate, (2S,3S,7S)-3,7-dimethylpentadecanyl acetate—one of several isomeric sex pheromone constituents of pine saw-flies, Diprinoide family.

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