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Chapter 8

Biorational Approaches in Pest Management

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Abstract

Most of the commercially available conventional and synthetic insecticides have broad range toxicity as they target those insect's systems which have physiology exactly like the higher mammals including man. That why they are imposing serious health hazard threats (mutagenic, carcinogenic and teratogenic effects) on human being due to possessing very high mammalian toxicity, long-term residual persistency and high magnification potential. They are also creating many other serious problems like ecological backlashes in pest species, environmental pollution and degradation, threat to biodiversity conservation and loss of beneficial fauna (predators, parasites pollinators etc.). There is a need to explore and develop biorational molecules/products which would tackle most of the issues associated with conventional insecticides. Need is to develop analogues of such biorational and highly target specific biomolecules through modern biotechnological molecular approaches. Biorational products/approaches are based on the growth and development as well as communication system of insects which is quite different from higher animals and human being. These products have great potential for

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replacing the persistent conventional insecticides, confirming effective cost-benefit-ratio, tackling ecological backlashes and ensuring food security with safe environment and enhanced exports. In the new era of biotechnology, most of the issues associated with these biorational products have been solved and these products are not only winning the reliability of the market and end user; but also demonstrating their worth and potential in sustainable IPM program. This chapter focuses on the perspectives and prospects of biorational approaches in sustainable Integrated Pest Management (IPM) program of economic crops.

Key words: IGRs; Semiochemicals; Biorationals; Pheromones; Allelochemicals; pest management

8.1. Introduction

The term “Integrated Control” was introduced by Stern et al. (1959). This was the era characterized by insect pest control with broad-spectrum, conventional insecticides including organochlorines (OCs), organophosphates (OPs), pyrethroids and carbamates, which were mostly neurotoxic. The use of these broad-spectrum insecticides led to environment degradation, problems of ecological backlashes and public health associated issues and the public criticism demanding alternative pest control tactics. Then there came the concept of IPM approaches for the pest management. The concept of IPM, later on, experienced a paradigm shift towards “risk reduction approaches” reducing impacts of pests and pest management tactics on human possessions and ecology. Such reduced risk agents and approaches are crucial and fundamental means of strengthening IPM strategies to address the challenges of a society (Ishaaya 2003; Ishaaya et al. 2005).

Nutritional requirements of insects and vertebrates are almost similar. Likewise, physiology and biochemistry of digestive and nervous systems as well as metabolic processes and reactions involved in biosynthesis of proteins and nucleic acids of insects also fundamentally similar to vertebrates. However, the aspects of insects’ physiology and the anatomy that are different from those of vertebrates include the structure of their integument and their endocrine and communication systems. Majority of the insecticides belonging to different classes for managing insect pests are neurotoxicants and highly non-selective; because they impose same toxic effects on higher animals including man as they have on insects (Dhaliwal and Arora 2003). This emphasizes on the development of selective insecticides from those molecules which block, disrupt or inhibit any of the pathway bridging their biosynthesis, storage, release, transport and reception in insects’ cuticle, endocrine and chemical communication systems. The biochemics, which are involved in other pharmacokinetics and detoxification mechanisms of insecticides in insects and are different from those of vertebrates can be used to develop insecticide molecules. Such molecules when synthesized in form of insecticide formulation will highly be lethal and target specific affecting the growth, behavior and chemical communication systems of insects.

The pesticides have been classified on the basis of their chemical structure [e.g., carbamate, Organochlorines (OCs), Organophosphates (Ops), Pyrethroids], mode of

action [e.g., narcotic, synaptic, axonic, muscles, and physical poisons; IGRs (Insect Growth Regulators), antifeedants, etc], mode of entry (e.g., stomach, contact, systemic, translaminar fumigant insecticides), source of origin (e.g., 'natural', botanical, animal, synthetic, analog etc.). However, the authorities are still unable to decide the actual definition, fate and place of term "biorational pesticides". The term "biorationals" has been derived from two words, biological and rational and denote to such pesticides that have been derived from some natural source and impose minimum or no adversarial threats on the environment or beneficial organisms (Ware 1989). Historically, Carl Djerassi (Djerassi et al. 1974) used the term "biorationals" for the first time for pheromones, insect hormones, and hormone antagonists. However, he did not proposed any particular definition of "biorationals" except describing their properties like their species-specificity, active lethality at low concentrations and low persistency or toxicity to non-target vertebrates. Since then, the term "Biorational pesticides" is still ambiguous and confusing. Some consider microbial or plant origin molecules as "biorational pesticides"; a few speciously contemplate organic pesticides as "biorational pesticides"; while others categorize plant or insect oriented natural biochemicals and their synthetic analogs as "biorational pesticides". Some define biorationals as biologicals or botanicals which are highly compatible with living systems of human being. According to a viewpoint, insecticides are termed as biorationals if they denote pragmatic and empirical compatibility in one system but categorically do not impose such effects in another system (Ellsworth and Martinez-Carrillo 2001; Naranjo et al. 2003, 2004). Still there is a group that emphasizes that biorational agents should have limited or no affect on non-target organisms, including humans and their domestic plants and animals (Diver and Hinman 2008). Another term "reduced-risk pesticides" synonym to "biorationals" was introduced in 1997 for those pesticides that augment and accelerate the effectiveness of IPM program economically imposing least or no toxic jeopardies to human health, non-target organisms or environmental resources (Uri 1998). No established definition of "biorationals" exists in literature. Different scientists define the term "biorational pesticides/biorationals" in different way. For example, according to Environmental Protection Agency (EPA) the term "biorationals" is practically synonym to term "biopesticides" which have low risk, are derived from natural sources including plants, animals, bacteria and certain minrals and are divided into "microbials", plant-incorporated protectants (PIPs) and biochemical (Rosell et al. 2008). Stern et al. (1959) introduced the term "Selective insecticide" and defined it as "an insecticide which kill the pest individuals but spares much or most of the other fauna, including beneficial species.". Plimmer (1985) introduced process-oriented definition of "biorational" and explicated that "biorational is the exploitation of knowledge about plant or animal biochemistry in order to synthesize a new molecule which acts at a particular site or blocks a key step in a biochemical process". Bowers (2000) modified and improved process-oriented definition and concept of "biorational" by incorporating the concept of selectivity. According to him, "biorational is the exploitation of knowledge about plant or animal biochemistry in order to synthesize a new molecule designed to act at a particular site or to block a key step in a biochemical process; however, these pest-suppressive molecules and their associated methodologies should disturb those discrete evolutionary aspects of pest biology and behavior that separate invertebrate and

microorganism from human biology.” According to Ware (1989), biorational pesticides include derivative of a variety of biological origin (including bacteria, viruses, fungi and protozoa) and chemical analogues of natural biochemicals (like pheromones and insect growth regulators) that are environmental-friendly and meticulously resemble to chemicals of insects and plants origin. According to Pathak and Dhaliwal (1986) and Dhaliwal and Arora (2003), “Biorational Control” involves the utilization of chemicals that suppress insect populations in a control system by modifying behavior, disrupting growth and impeding reproduction of the insects populations. Generally and operationally, the biorational pest management involves the substances or processes that execute diminutive or no adverse consequences to the environment and non-target organisms (humans, beneficial fauna and flora etc.); however, impose lethal, suppressive or behavior modifying effects on a target organism and augment the specific control system. A brief categorization of the biorational pesticides is illustrated in Figure 8.1.

This chapter focuses on the discussion of safer, ecofriendly and target-specific biorational insecticides based on neuropeptides, neurotransmitters and growth hormone in insects, venom-peptides of parasitoids and natural-enemy-, plant- and herbivore-derived semiochemicals, which have been developed by using modern biotechnological approaches.

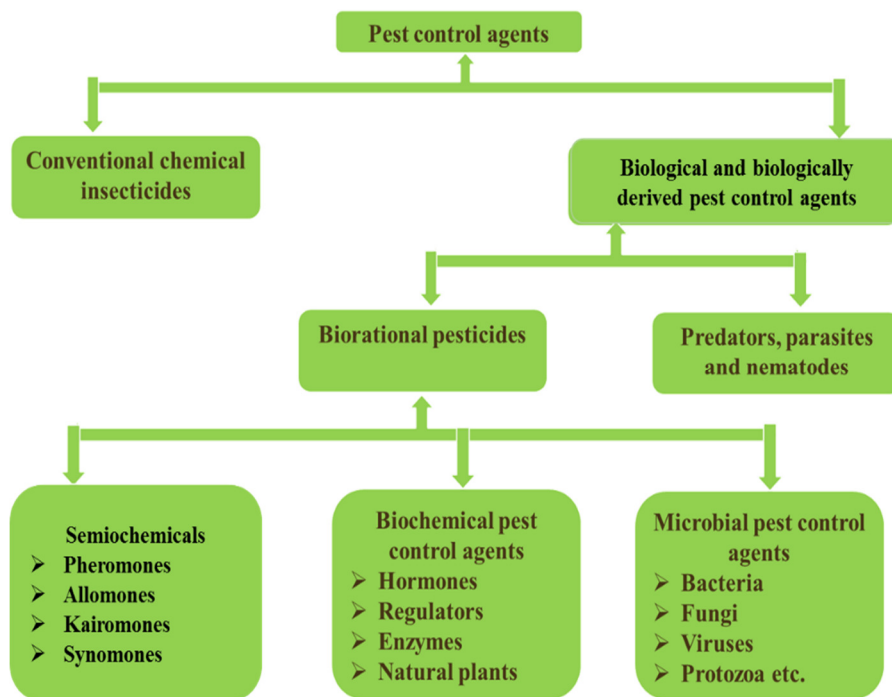


Fig. 8.1 Categories of biorational pesticides

8.2. Insect growth based approaches

These approaches include utilization of IGRs (Insect Growth Regulators) which do not have direct lethal or deadly effects on insects; rather, they disrupt the normal mechanisms of insects' growth and development. These biorational insecticides affects the growth and development in two ways: they either; 1) interrupt with the mechanism of normal cuticle formation by inhibiting or accelerating chitin synthesis, chitin degradation or sclerotization process in insects; or 2) inhibit or accelerate the secretion and action of insects' growth hormones. IGRs are generally categorized into two major classes (Dhaliwal et al. 2006) on the basis of their mode of action.

- 1) IGRs interfering with the cuticle formation mechanisms (e.g., Chitin synthesis inhibitors, chitin degradation inhibitors, cuticle sclerotization disrupters etc.)
- 2) IGRs interfering with the secretion and actions of insect growth hormones (e.g., Brain hormones, Juvenile hormones, Molting hormones, etc.)

8.2.1. Insect cuticle targeting insecticides

Main structural component of insect cuticle is the chitin which is composed of many units of N-acetyl-D-glucosamine. The mechanisms of biosynthesis and biodegradation of cuticle and cuticular sclerotization are considered perfect targets for idealizing any insecticide as highly target specific and safe for human (Dhaliwal and Arora 2003; Dhaliwal et al. 2006). A large number of natural molecules or their analogues possessing such mode action have been developed and commercialized as insecticides (Table 1). Insect cuticle based biorational IGRs are categorized into following types:

8.2.1.1. Chitin synthesis inhibitors

Chitin synthesis inhibitors (CSI) belong to that class of biorational insecticides which were unexpectedly developed in 1970 when insecticidal property of benzyolphenyl urea (BPU) analogues was confirmed by Philips-Duphar Company. The first most CSI analogue (DU 19.111) was developed by combining two herbicides (dichlobenil and diuron) (Dhaliwal et al. 2006). The target site of CSIs is the polymerization step of chitin-biosynthesis catalyzed by chitin-synthase. At this site, they modify the permeability of membrane and block the availability of substrate at the active site of membrane bound enzyme (chitin synthase) (Mayer et al. 1990; Dhaliwal and Arora 2003). CSI disrupts the biosynthesis of chitin which makes a 30-60% portion of the insect exoskeleton (cuticle) and impairs the development of new exoskeleton in larval instars at molting stage. The insects without normal or with abnormal exoskeleton cannot survive and die within short period of time due to rapid desiccation or excessive dehydration from larval body. The major groups of CSI biorationals include benzoylureas, triazine/pyrimidine derivatives, buprofezin and plumbagin. CSIs do not induce toxicity until or unless these are ingested with food. That's why, most of the CSIs are innocuous and safe for bees, predators and parasitoids (Tomlin 2000) because these insects do not ingest the CSI-treated foliage. Rest of the properties and characteristics of CSIs are illustrated in Table 2.

8.2.1.2. Chitin degradation inhibitors

Steps of chitin degradation and enzymes involved are reported as source of target specific biorational IGRs or preparation of their analogues which may act as chitin degradation inhibitors (CDIs). In insect's growth, specifically at the time of ecdysis, chitin degradation is as much important as the chitin biosynthesis because degradation process not only makes the old cuticle more frail and delicate along epistomal suture (ecdysal cleavage line) to facilitate the rapturing of old cuticle and emergence of insect but also provides degradative products which, after their recycling, are used in the synthesis of new cuticle. If chitin degradation is inhibited, the old cuticle remains hard enough not to facilitate rupturing, ecdysis does not occur and insect dies inside the old skin (exuvium). Similarly, synthesis and deposition of new cuticle is not possible that leads to the death of new instar due to excessive desiccation and dehydration. All the process of chitin biodegradation is regulated by chitinolytic enzymes (chitinase and chitobiase) which seem to be striking target for developing CDI analogues with enough biological activity quite similar to those natural biomolecules which regulate chitin degradation in insects. Similarly, the genes translating chitinolytic enzymes during chitin degradation process are also promising targets for genetic engineering of crops against phytophagous insects (Pedigo 2003; Chapman 2013). However, no bio-molecule or analogue has been developed, synthesized or commercialized as insecticide yet that possess chitin degradation inhibiting properties (Dhaliwal and Arora 2003; Dhaliwal et al. 2006). Some laboratory studies documented the identification of some molecules having CDI activity. For example, Shahabuddin et al. (1993) reported allosamidin as a specific chitinase inhibitor.

8.2.1.3. Sclerotization inhibitors or accelerators

In insect's cuticle, about twenty (20) different types of proteins, phenolic compounds and other constituents are covalently stabilized by sclerotization mechanism (Hopkins and Kramer 1992) which is a very complicated and intricate process regulated by a hormone "Bursicon" in insects during postecdysal processes (Pedigo 2003). The inhibition or acceleration in this process leads to abnormalities (failure of sclerotization or unusual and infrequent hardening) in larval or pupal cuticle making it more vulnerable to desiccation. In this situation the insect die due to excessive dehydration. Different types of neurosecretory enzymes are involved that accelerate and inhibit the process of sclerotization when required in the insect growth stage. These postecdysal processes and associated enzymes are the appropriate target for developing target specific biorational analogues as IGRs with sufficient sclerotization inhibiting or accelerating activities. The examples of insecticides having sclerotization disrupting properties include MON-0585 (only commercialized sclerotization inhibitor developed by Monsanto), α -methyl DOPA and Cryomazine (Dhaliwal et al. 2006). The detailed properties and other characteristics have been illustrated in Table 2.

8.2.2. Insect growth hormones based insecticides

All growth and developmental processes in insects are controlled by a variety of hormones secreted by ductless glands of endocrine system. The insect's growth

regulating hormones are secreted from various neurosecretory cells (ductless glands) of different parts of nervous system and have specific role in postembryonic growth and metamorphosis. These hormones include Brain Hormone (BH) or Prothoracicotropic Hormone (PTTH), Moulting Hormones (MH), Juvenile Hormones (JH), Eclosion Hormone (EH) and Tanning Hormone (TH) (Pedigo 2003). BH or PTTH is produced by the neurosecretory cells of brain and triggers the prothoracic glands which resultantly secrete ecdysone (a molting hormone). MH controls the molting process of immatures (larvae, nymphs or naiads). JH is secreted by corpora allata (gland) that control the juvenile characters and type of molt in insects. A high concentration of JH in haemolymph triggers the larval molting into next larval instar, its low concentration elicits larval molting to pupation and absence of JH in haemolymph stimulates pupal stage to molt into adult (eclosion). JH is almost absent in the pupae, but present in adults where it persuades vitellogenesis and controls reproduction during the reproductive stage of the insect (Eto 1990). EH is secreted by neurosecretory cells of brain; whereas, TH by neurosecretory cells of brain or abdominal ganglia. EH and TH are responsible for process of eclosion and sclerotization in insects, respectively. This endocrine system and associated hormones are promising biochemical specific-sites for developing biorational biochemical-agents that, when interfere with the actions of these biochemical specific-sites, disrupt the physiology of growth processes, induce abnormalities in growth and bring mortality in insects (Ishaaya and Horowitz 1998; Ishaaya 2001; Dhaliwal et al. 2006). The biomolecules of these hormones and their analogues are safe and insect-specific; but their utilization in pest management is limited because of: 1) their linear nature and high vulnerability to proteolytic degradation, 2) problems of their penetration into biological tissues, 3) vulnerability to quick photo-degradation and 4) complications in designing their antagonists (Altstein et al. 2000; Horowitz et al. 1995). However, these limitations are addressable by the exploitation of modern biotechnological approaches; for examples, i) synthesis of simpler peptide analogues with high photostability, penetration and agonistic or antagonistic properties to cuticle and target tissues of insects, ii) Insertion of neuropeptide regulating genes into host-plant's tissues by genetic engineering to produce GM-crops resistant to insects like Bt-crops, iii) large-scale economical production of neuropeptides by vector-mediated and vectorless gene transfer technology (Dhaliwal et al. 2006).

8.2.2.1. Brain hormones based insecticides

Brain hormones are neuropeptides which are also called neurohormones. These neuropeptides are produced by central nervous systems (CNS) in form of chemical signals for controlling various metabolic events in the body of insects (Dhaliwal and Arora 2003; Pedigo 2003; Dhaliwal et al. 2006). As these neuropeptides secreted from insect's brain regulate many of the physiological functions of insect's life like development, growth, reproduction, behavior, metabolism etc., so their agonistic or antagonistic analogues can be exploited commercially for the development of biorational insecticides. Proctolin was originally an insect's brain hormone which was isolated from *Periplaneta americana* (American cockroach) in 1975 and has broad range of physiological functions (Dhaliwal and Arora 2003; Dhaliwal et al. 2006). It acts as a putative neurotransmitter and neuromodulator on oocytes for

uptake of vitellogenin during oogenesis inside the reproductive system and performs neurohormonal role in insect's growth and development (Goudey-Perriere et al. 1994; Lange 2002). More than 65 such neuropeptides have been isolated and identified from different types of insects belonging to Dictyoptera, Lepidoptera, Hymenoptera and Diptera (Dhaliwal et al. 2006).

Different kinds of brain hormones are produced by the CNS and stored as well as released from neurohaemal sites in the insect's brain like corpora cardiac and corpora allata (Coast et al. 2002). A little bit detail of these brain hormones is as under:

Diuretic and antidiuretic brain hormones

The diuretic and antidiuretic hormones are diuresis controlling antagonistic hormones which promote and inhibit water loss, respectively (Spring et al. 1988). These two hormones are produced by neurosecretory cells of insect's brain and stored and released from corpora cardiac. They regulate the excretion metabolism, urine balance, water balance, postprandial diuresis, post-eclosion diuresis, excretion of excess metabolic water, clearance of toxic wastes and restricting metabolites loss by their regulated-interactive and antagonistic action on malpighian tubules and hindgut (Furuya et al. 2000; Holtzhausen and Nicolson 2007). Diuretic hormones are grouped into three main families including calcitonin (CT)-like peptides, corticotropin-releasing factor (CRF)-related peptides, and the insect kinins (Coast et al. 2002).

Eclosion hormone

Eclosion hormone is a neuropeptide secreted either by the neurosecretory cells of brain or by ventral ganglia of insects depending upon the growth and development stage of insect. It initiates a cascade of pre- and post-eclosion actions and regulates the sequence of events of eclosion (process of adult's emergence from the pupa) in insects. It is also involved, with other hormones (e.g. ecdysone), in moulting of the cuticle by immature stages (Chapman 2013).

Allatostatins

The term "allatostatins" describes those allatostatic neuropeptides which are secreted from the neurosecretory cell of brain and inhibit the biosynthesis of juvenile hormone by corpora allata. These brain hormones were isolated for the first time from the brain cells of pacific beetle cockroach, *Diploptera punctate* (Tobe 1980) and belong to Allatostatins-A (are stage/sex or species specific), Allatostatin-B (neither stage/sex nor species specific) and Lepidopteran-allatostatins families. Many researchers have isolated various members of allatostatins-A from different insects including cockroaches, crickets, grasshoppers, locust, stick-insects, blowflies, mosquitoes, lepidopteran species (*Helicoverpa* sp., *Cydia* sp. etc.), honey bees etc. and documented varying capability of inhibiting JH biosynthesis by these allatostatins depending on the donor-receiver physiological differences and development stages of insects. On the basis of their sequence homology, allatostatins-A are discussed as callatostatins (flies), helicostatins (bees), cydiastatins (moths), schistostatins (locusts) and carausiustatins (stick-insects) (Hoffmann et al. 1999). Allatostatin-B includes all non-peptides that exhibit sequence resemblance to myoinhibiting peptides and cause 50% inhibitions of JH biosynthesis (Blackburn et al. 1995; Lorenz

and Hoffman 1998). Lepidopteran allatostatins are amidated peptides (Kramer et al. 1991)

Allatotropins

These are neuropeptides which are secreted by neurosecretory cell of brain and stimulate the corpora allata to produce JH (Bogus and Scheller 1994). They belong to family of myoactive peptides and exhibits manifold neural, endocrine, myoactive and JH-stimulating role in insects (Elekonich and Horodyski 2003). The only allatotropin isolated from the brain of pharate adults of *M. sexta* moth is Mas-AT (Hoffmann et al. 1999)

Prothoracicotropic hormone

Prothoracicotropic hormone (PTTH) is a neuropeptide which is secreted by neurosecretory cells of insect's brain and triggers prothoracic gland to produce ecdysone (molting hormone) (Chapman 2003; Klowden 2007). There is need to explore or synthesize highly photostable and penetrable antagonistic analogues of PTTH having disruptive effects on ecdysone production by prothoracic gland. Some examples of such analogues are commercially available which have been discussed under heading "Molting hormone based insecticides".

Pheromone biosynthesis activating brain hormones

Pheromone biosynthesis activating hormones (PBAH) are pheromone biosynthesis activating neuropeptides (PBAN) which are produced by neurosecretory cells of insect's brain or suboesophageal ganglia near brain and triggers the pheromone glands for pheromone biosynthesis in insects. PBAH or PBAN belongs to PK (Pyrokinin)/PBAN family including Pheromonotropin (PT) and Myotropin (MT) peptides (Altstein 2004) and their quantitative production depends on the sexual form of the insects because of the differences in gene expression and functional responses of different sexual forms. Their chemical nature varies from insect to insect species; for example, in *Helicoverpa zea*, *Pseudaletia (Mythimna) separate*, *Leucophaea maderae* and *Locusta migratoria* Hez-PBAN (33-aminoacid peptides) (Raina et al. 1989), *Pss*-PT (18-aminoacid peptides) (Matsumoto et al. 1992), *Lem*-PK (8-aminoacid peptides) and *Lom*-MT-II (8-aminoacid peptides) (Choofs et al. 1990) were identified as PK/PBAN peptides, respectively (Heriton et al. 2009). The aminoacid sequence as well as chemical and biological activities of PBAH or PBAN have been reported to vary consistently with the insect's species and their phylogenetic associations (Choi and Meer 2009; Choi et al. 2011).

This multifunctional PK/PBAN family of neuropeptides controls many behavioral and developmental processes in insect (Heriton et al. 2009), including mating behavior (sex pheromone biosynthesis) (Altstein et al. 1995), feeding (contraction of gut muscles) (Schoofs et al. 1991), diapause (Zhang et al. 2004; Sun et al. 2005), cuticular melanization (Altstein et al. 1996) and pupariation (Nachman et al. 1997). Using INAI (Insect Neuropeptides Antagonist Insecticide) technique, several highly potent, selective and metabolically stable backbone cyclic (BBC) antagonists of Pyrokinin/Pheromone Biosynthesis Activating Neuropeptide (PK/PBAN) were discovered. These BBC antagonists of PK/PBAN lack of agonistic role and possess sex pheromone biosynthesis inhibition properties in female insects, especially moths

(Altstein 2004; Heriton et al. 2009). Such antagonists of PK/PBAN have been reported to cause sex pheromone biosynthesis inhibition effects in females of a variety of insects (Heriton et al. 2009). For example, *Helicoverpa peltigera* females and *Spodoptera littoralis* larvae exhibited 70% inhibition in biosynthesis of sex pheromone and 100% inhibition of cuticular melanization, respectively, when treated with antagonists of PK/PBAN. Biosynthesis of pheromone in Indian meal moth (*Plodia interpunctella*) was inhibited by its *in vitro* treatment with Arylaldehyde semicarbazones and 5-aryloxazoles. Some other bioagent amine like tyramine, dopamine and octopamine act on pheromone glands disturbing sex-pheromone production (Hirashima et al. 2007). However, the potential of these agonists in pest control are not yet achieved due to many problems in commercial exploitation of these neuropeptides.

8.2.2.2. Molting hormones based insecticides

Prothoracic glands secrete hydrophilic Molting Hormones (MH) which are steroidal peptides comprising of mainly ecdysone (20-hydroxyecdysone, 26-hydroxyecdysone, 20, 26-dihydroxyecdysone), ecdysteroids and ecdysterone (Makisterone-A, 20-deoxymakisterone). These steroidal peptides regulate various physiological metabolisms of molting, growth, maturation and reproduction in insects (Dhaliwal and Arora 2003; Dhaliwal et al. 2006).

MHs or their analogues cannot be efficient molecules for development of insecticides due to their hydrophilic nature that make these molecules non-penetrable through insect cuticle. The biosynthesis of MHs in insect body is a very complex process. In the presence of desmosterol, phytosteroids are converted into cholesterol which is then converted into MH (ecdysone). Phytoecdysteroids also play a vital role in developing MHs imbalance in insect body, promoting abnormal growth and ultimately causing death of the insect (Dhaliwal et al. 2006).

Phytoecdysteroids (steroids extracted from plants), through desmosterol-cholesterol-ecdysone conversion reaction, enhance the titer of ecdysone in the haemolymph of insects. The ecdysone produced by this conversion reaction is metabolized and excreted out of insect body very slowly creating hormonal imbalance. Some phytoecdysteroids having insecticidal activity have been isolated from different parts of plants. Triaparanol, diazacholesterol, azasterol, azasteroids, nitrogen containing steroids, and non-steroidal amines or amides inhibits the action of sterol-reductase enzyme, interrupt the desmosterol-cholesterol- ecdysone conversion reaction and biosynthesis of ecdysone leading to disruption of growth and development of insects. Phytoecdysteroids extracted from the seed of *Diploclisia glaucescens* Diels and phytoecdysterone isolated from mature stems of *D. glaucescens* exhibit insecticidal activity against *Ostrinia nubilalis* (Hubner) larvae (European corn borer) and *Aphis craccivora* Koch. (Groundnut aphids). Similarly, ecdysteroids isolated from dried parts of *Ajuga reptans* L. and *A. remota* act as MH mimic and demonstrate strong disrupting effects on the growth and metamorphosis of Mexican bean beetle, *Epilachna varivestis* Mulsant. However, such phytosteroids are not available commercially due to high cost required for their production and commercialization, quick photo-degradation and many other problems already mentioned (Dhaliwal et al. 2006).

Exploration or synthesis of MH Agonists/antagonists or Phytoecdysteroids can lay the foundation of biorational biomolecules for ecofriendly management of various insect pests. The MH agonists/antagonists can be potential biomolecules for developing new insecticides having activity of disrupting the ecdysteroid receptor and normal growth in insects (Dhadialla et al. 1998; Harada et al. 2011). MH-agonists are mimics of MH and forcefully trigger the molting insects towards premature molting leading to feeding cessation and finally death of molting insects. They also enhanced mortality of eggs and reduce fecundity as well as rate of reproduction. The commercially available MH-agonists include Tebufenozide, Chromafenozide, Halofenozide and Methoxyfenozide which are Bisacyllhydrazines (BSH). MH-Antagonists (MHA) are those MHA-analogues which disrupt the production of PTTH and inhibit the effects of MH (Ecdysone). So far, two MHA based insecticides, i.e. Diofenolan and azadirachtin, are available commercially (Table 8.4).

8.2.2.3. Juvenile hormones based insecticides

Juvenile hormones (JHs) belong to acyclic sesquiterpenoids (class of terpenes having the molecular formula $C_{15}H_{24}$) that regulate many physiological and metabolic aspects of insect life like diapause, development, reproduction, polyphenisms (Wyatt and Davey 1996; Li et al. 2007; Parthasarathy et al. 2008), embryogenesis, molting and metamorphosis, pigmentation, caste differentiation, communication, migration/dispersal, silk production, and phase transformation with main function of maintaining larval status (Tunaz 2004). JHs isolated and identified in insects so far are categorized into JH_0 , JH_I , JH_{II} and JH_{III} (Table 8.1). JH_{III} is the most commonly found juvenile hormone in most of the insects (Judy et al. 1973). However, JH_0 , JH_I and JH_{II} are the juvenile hormones which have specifically been isolated and identified from butterflies and moths. Another bisepoxide form of JH_{III} has been isolated and identified from dipterans (true flies) and categorized as JHB_3 (Richard et al. 1989). Because of their selective morphogenetic effects, these JHs have been focused as impending stand-ins for synthetic non-selective insecticides. As compared to natural JHs, JHA (Juvenile Hormone Analogue) are more stable. Examples of such MHAs which have been commercialized include methoprene, hydroprene, kinoprene, triprene, fenoxycarb, pyriproxyfen, epofenonane and dayoutong (Table 8.4). Some plant products also have JH activity. For example, juvabione (methyl ester of todomatuic acid) and its analogue, dehydrojuvabione (isolated from balsam fir tree, *Abies balsamea* L.) both have JHA activity against various insects (Dhaliwal and Arora 2003; Dhaliwal et al. 2006).

There are also some other chemicals which block the synthesis of natural JHs, facilitate JH degradation, or destroy corpus allatum in insects (Leighton et al. 1981; Dhaliwal et al. 2006). These chemicals are antiallatotropins, or precocenes and are referred as Anti-Juvenile Hormone Agents (AJHAs) or JH antagonists. Some of the initial examples of AJHAs include precocene-I, precocene-II and precocene-III which were isolated from *Ageratum houstonianum* Mill. and *A. conyzoides* L., respectively. These precocenes are metabolized inside the body of insects into cytotoxic compounds (cytotoxins) which selectively disrupt the functions of corpus allatum, promote precocious metamorphosis, induction of sterilization in female adults, initiation of diapause and impediment of biosynthesis of sex pheromone.

Table 8.1 List of Juvenile hormones and their associated details

Category of JH	(Insect from which it was isolated for the first time)	Chemical formula (chemical name)	Chemical structure
JH-0	Tobacco hornmoth, <i>Manduca sexta</i> (Judy et al. 1973)	C ₁₉ H ₃₂ O ₃ (methyl (2E,6E)-10R,11S-(oxiranyl)-3,7-diethyl-11-methyl-2,6-tridecadienoate)	
JH-I	♀ Cecropia moth, <i>Hyalophora cecropia</i> (Roller et al. 1969)	C ₁₈ H ₃₀ O ₃ (methyl (2E,6E)-10R,11S-(oxiranyl)-7-ethyl-3,11-dimethyl-2,6-tridecadienoate)	
JH-II	Cecropia moth, <i>H. cecropia</i> (Meyer et al. 1968)	C ₁₇ H ₂₈ O ₃ (methyl (2E,6E)-10R,11S-(oxiranyl)-3,7,11-trimethyl-2,6-tridecadienoate)	
JH-III	Tobacco hornmoth, <i>Manduca sexta</i> (Bowers et al. 1965; Judy et al. 1973)	C ₁₆ H ₂₆ O ₃ (methyl (2E,6E)-10R-(oxiranyl)-3,7,11-trimethyl-2,6-dodecadienoate)	
JH-B3	<i>Drosophila</i> spp. (Richard and Gilbert 1991)	C ₁₆ H ₂₆ O ₄ (methyl (2E,6E)-6S,7S,10R-(dioxiranyl)-3,7,11-trimethyl-2-dodecaenoate)	
Methyl farnesoate	Insects and crustaceans (Nagaraju (2007))	C ₁₆ H ₂₆ O ₂ (methyl (2E,6E)-3,7,11-trimethyl-2,6,10-dodecatrienoate)	

Later, some new compound with like compactations (vertebrate hypocholesterolemic agents), fluoromevalonate (vertebrate hypocholesterolemic agents), Piperonyl butoxide (PBO), imidazole, acetylenic compounds, cyclopropyl amines, furanyl compounds, ETB (ethyl 4-(2- pivaloyloxybutyloxy)-benzoate) and EMD act as JH-receptor antagonists and AJHAs (Staal 1986; Dhaliwal et al. 2006).

8.3. Insect communication based approaches

In an environment surrounding insect's population, different kinds of olfactory, gustatory, visual, auditory or/and tactile stimuli are present. Such stimuli modify the insect's behavior partially or completely. Insects respond to these stimuli detecting them by the chemo- or mechano-receptors present on different parts/organs of insect's body. However, fundamental and crucial mode of communication is chemical signaling/messaging. Insect's communication may be interspecific (communication between two different species) or intraspecific (communication between two same species). Such types of communications elicit various behavioral changes and are accomplished by sending various communicational signals like stridulatory-noise, flashing-light, chemical-cues etc. The purposes of these communication signals are: i) communicate one's presence; ii) defense, deception or camouflage; iii) locate the host-plants by pests and prey or host by entomophagous insects; iv) establish territoriality; v) locate and recognize sexmates, nestmates or kins; vi) facilitate courtship, copulating and mating; vii) panic the invader; viii) warning the population of danger; ix) regulate ecological behavior of insects like migration, trivial movements, dispersal, aggregation etc.; x) provide clues for exact location of food and other sources. These purposes are achieved using five sensory modalities including contact or tactile senses (taste and touch) and remote senses (vision, olfaction and hearing) (Dhaliwal and Arora 2003; Dhaliwal et al. 2006).

Tactile communication is used in the insects with poor sound perception and vision. Antennal tapping by male blister beetle [*Mylabris* and *Lytta* species (Coleoptera: Meloidae)] on all sides of body of female blister beetle stimulate her for courtship and mating. Dance language of honey bees inside the colony in form of "Round Dance" (a series of circular turns with recurrent changes in direction) and "Waggle Dance" (a series of abdominal waggles on a straight run after each half-circle turn on pattern of figure eight) is also types of tactile communication to signal the other nestmates about distance, location and quality of food source. Tactile signals are generated by whirligig beetles [*Gyrinus* species (Coleoptera: Gyrinidae)] in form of ripples to keep away the members of same species and detect the presence of any predator or prey in its vicinity. Vibrations generated in the host-plant tissues by treehoppers (Hemiptera: Membracidae) are tactile mode of communication to elicit alarming or protective-maternal behavior (Meyer 2006).

Acoustic communication is very well developed in some insects especially in orthopteran which have well developed stridulatory and auditory organs on abdomen (grasshoppers) and tibia (crickets). The sounds generated by these organs or by different ways in various insects may be a mating call for opposite sex and alarming call for other individuals or invaders (Meyer 2006).

Visual communication involves the clues stimulated from colored patterns, body movements and light-flashes in different insects. For examples, colored patterns in adults and larvae of butterflies and moths are used to scare away the natural enemies; whereas, light-flashes in fireflies serve as mating communication between opposite sexes. For examples, males of *Photinus consumilis* generate 3-5 short flashes, while in response, females produce double flash (Meyer 2006).

Chemical communication is major mode of inter- or intra-specific dialogue in insects. Insects are more momentarily dependent on chemical communication than other modes of communication. The chemicals involved in inter- or intra-specific communication are termed as “Semiochemicals” or “infochemicals” which have been and still are being targeted for the development of biorational insecticides that are exploited in sustainable management of insect pests of various economical crops (Dhaliwal and Arora 2003; Meyer 2006).

8.3.1. Semiochemicals: concepts and categories

The word “semiochemical” is a combination of two words i.e. semio and chemicals which have been derived from a Greek word “semeon” referring to sign or signal and chemical, respectively. Some scientists have deployed semiochemicals as infochemicals because these convey only information between two same or different organisms. These semiochemicals may be of natural origin including various parts of plants (flowers, leaves, roots or stem barks), microbial secretions, insects’ glands, excretory products, reproductive organs etc., non-living origin (apneumones) or of synthetic nature. Semiochemicals elicit coded or decoded chemical messages which may be advantageous for emitter, receiver or both. The chemical messages evoked by semiochemicals stimulate two types of changes in receiver’s behavior i.e., short-term and reversible behavioral change in response (releaser effect) or long-term irreversible physiological and/or biochemical change in response (primer effects). The most important of short-term and reversible behavioral responses include aggregation, attraction and repellence elicitation (Pedigo 2003; Chapman 2003).

The study of semiochemicals is a part of chemical ecology of any organism. Semiochemical is a chemical or mixture of chemicals that elicit some behavioral responses in form of chemical messages/communications between two same (intraspecific) or two different species (interspecific) for accomplishment of various aims including finding mates, food and habitate resources, cautioning natural enemies, avoiding competition (Ayasse 2010). They are classified into two major groups intraspecific semiochemicals (pheromones) and interspecific semiochemicals (allelochemicals). The interspecific semiochemicals (allelochemicals are further classified into allomones, kairomones, synomones, apneumones and antimones (Cork 2004; Dhaliwal et al. 2006) (Fig. 8.2).

8.3.1.1. Pheromones

The word pheromone originates from two Greek words “*phero* or *pherein*” means “to bear or transport” and “*hormone*” means “impetus or stimulate” and introduced by Peter Karlson and Martin Luscher in 1959. Pheromones are also called ectohormones and “*Bombykol*” was first most of such ectohormone which was isolated and characterized from female *Bombyx mori* by Adolf Butenandt. Pheromones are those intraspecific chemical factors which are excreted out of the body of emitters and trigger social responses in receivers of same species. Pheromones are categorized into following two general classes on the basis of their

mode of action or responses stimulated (Matthews and Matthews 1979; Jutsum and Gordon 1989).

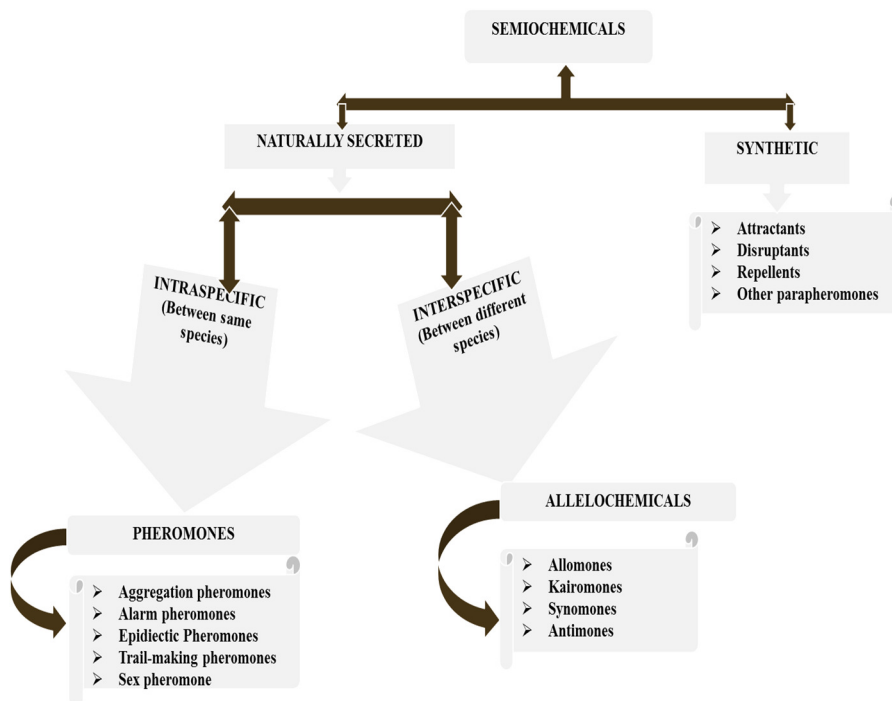


Fig. 8.2 Schematic diagram of the categories of semiochemicals (Dhaliwal and Arora 2003; Dhaliwal et al. 2006)

i) Pheromones exhibiting primer effects (Primer Pheromones)

These pheromones trigger off a series of physiological changes in the receiver without stimulating any immediate change in its behavior. The physiological changes triggered by these pheromones are not reversible. They provoke responses in the receivers through gustatory sensilla. The best known examples of such pheromones are produced by social insects like ants, bees, wasps, termites. Such pheromones stimulate gustation, mediate reproduction and regulate caste determination in these insects. The practical importance of such pheromones in IPM program is negligible and insignificant (Pedigo 2003; Cork 2004).

ii) Pheromones exhibiting releaser effects (Releaser Pheromones)

These pheromones induce instantaneous and reversible change in the behavior of the receiver. Such pheromones are characteristically odorous, redolent and evocative. They stimulate behavior communications and responses in the receivers through olfactory sensilla and act directly on the central nervous system of receiver. They are used as potential and successful biomolecules in pest management program due to

their practical importance in IPM program of insect pests. On the basis of variety of behavior modification induced by pheromonal communication, releaser pheromones are further classified as sex pheromones, alarm pheromones, epideictic pheromones, trail pheromones and aggregation pheromones (Jutsum and Gordon 1989; Cork 2004).

Sex pheromones

Sex pheromones are those intraspecific semiochemicals which are mostly secreted by females of a species to attract males of the same species for mating. However, in *Bicyclus anynana*, male butterflies produce sex pheromones to trigger courtship responses in female butterflies (Nieberding et al. 2008). Such pheromones are mainly emitted by Lepidoptera, Diptera species. Sex pheromones may be monocomponent pheromones (composed of one chemical compound) or multicomponent pheromones (composed of more than one chemical compounds in specific ratio). The species specificity to sex pheromone is due to variation in the ratio of different chemical compounds in multicomponent pheromones though these chemical compounds have same chemical nature for two or more different insect species (Table 8.3).

Aggregation pheromones

Aggregation pheromones are intraspecific semiochemicals which are released by one gender of a species to attract both sexes of the same species for exploiting a specific resource like food, appropriate mating or hiding site, etc. These are mainly emitted by Coleopterous species (Heuskin et al. 2011).

Alarm pheromones

Alarm pheromones are intraspecific semiochemicals which make the conspecifics vigilant and trigger behavioral change or response in conspecific population to get dispersed. Such types of pheromones are conspecific features of social or gregarious insects and some insect pests belonging to Aphididae and Thripidae. Alarm pheromones have great potential in IPM program of many insect pests of economical crops, fruits, vegetables, ornamentals etc., (Verheggen et al. 2010).

Trail pheromones

Trail pheromones are mostly secreted by workers members of social insects. The worker cast of the colonies of social insects drop these pheromones inform of trail which indicate the track to be followed by the scout insects for locating food resource. These kinds of pheromones are typical characteristic of ants and termites (Tschinkel and Close 1973).

Host-marking pheromones

Host marking pheromones are those intraspecific semiochemicals which are secreted to diminish intraspecific competition for oviposition, space etc. Host-marking pheromones are mostly secreted by female parasitoids for marking the host (Heuskin et al. 2011).

8.3.1.2. Allelochemicals

Allelochemicals are interspecific semiochemicals which elicit chemical-signals based communication in some members of different species. Allelochemicals include repellent, attractants, antifeedants and a gigantic group of other compounds/molecules that regulate interspecific behaviors. Herbivory evolved on the basis of two types of interactions between plants and herbivores. These interaction may be mutualistic or/and antagonistic. The existence of antagonism between plants and herbivores is justified when host plants fed on by herbivores try to repel or kill herbivore by some endogenous obnoxious, noxious and lethal phytochemicals. These phytochemicals induce antixenotic (antifeedant, repellent, anti-oviposition and adverse behavioral effects) and antibiotic (adverse effects on growth, development, survival) effects in insects. They constitute a variety of plant secondary metabolites like unusual aminoacids, sugars, alkaloids, terpenoids, flavonoids, polyacetylenes etc. (Dhaliwal et al. 2006). These allelochemicals may be of plant origin (botanicals, phytoalexins, allomones etc.) and animal origin. The allelochemicals produced by natural enemies like predators, parasitoids, pathogens have also significant importance in pest management programs. For example, delta-endotoxin produced by *Bacillus thuringiensis* possesses lethal toxicity against many lepidopterous and coleopterous insects (Dhaliwal and Arora 2003).

Allomones

Allomone originates from two Greek words “*Allos*” and “*Horman*” which refer to “other” and “to excite”, respectively. Allomones include those interspecific message-bearing chemicals (semiochemicals) which mediate chemical communication between emitter and receiver specifically providing adaptive advantages and recompenses to the emitter. Repellents, antifeedants, oviposition deterrents etc. are considered Allomones. For examples, Chemical emitted from Caterpillars of *Lycaena arion* act as an allomone because this chemical invites ants and triggers caring-giving behavior in them. The ants carry the caterpillar among their broods inside nest where caterpillar starts feeding on the larvae of ants (Pierce and Elgar 1985).

Kairomones

Kairomone is derived from two Greek words “*Kairos*” and “*Horman*” which mean “opportunistic” and “to excite”, respectively. Kairomones include those interspecific semiochemicals which stimulate chemical communication between emitter and receiver specifically providing adaptive benefits to the receiver. Attractants emitted from host plants for phytophagous insect pests, attractants emitted from host/prey or their products for entomophagous insects, aggregation stimulants etc. are referred to kairomones. For examples, the odor emitted from its host is a kairomone which benefits its parasitoid *Euclytia flavahe* (a parasitic fly) (Aldrich and Zhang 2002).

Synomones

Synomone is a derivative of two Greek words “*Syn*” and “*Horman*” which mean “with” and “to excite”, respectively. Synomones include those interspecific semiochemicals which trigger chemical communication between emitter and receiver specifically providing adaptive benefits to both the emitter and receiver.

Attractants emitted from plants parts, especially reproductive parts for pollinators as well as from pest-infested plants for entomophagous insects (predators and parasitoids) are referred to synomones. Defensive allelochemicals emitted from plants due to feeding of caterpillars act as synomones because these compounds attract the parasitoids which parasitize these caterpillars and save the host plants from herbivory (Dhaliwal and Arora 2003; Dhaliwal et al. 2006).

On the basis of chemical nature of biomolecules possessing semiochemical properties, semiochemicals are classified into twenty four categories. These categories include esters (carboxylic (430 esters), acetate (340 esters) and cyclic esters (75 esters), hydrocarbons (580 types), ketones (400 types), alcohols (primary (210 alcohols), secondary (150 alcohols) and tertiary alcohols (30 alcohols)), amines (300 types), aldehydes (260 types), carboxylic acids (210 types), epoxide (100 types), phenols (55 types), spiroacetals (50 types), diols (40 types), quinones (40 types), dioxy (30 types), sulfur compounds (30 types), ethers (20 types), furans (20 types), polyhydroxy (20 types), pyrans (15 types), triols (5 types) and oximes (5 types) (El-Sayed 2016).

Semiochemicals based biorational bioagents or biomolecules disrupt the feeding, mating or oviposition behavior of insects and have strong edge on the conventional insecticides in crop pest management program. Depending on the type and nature of semiochemicals, detection and monitoring of pest population, mating disruption, attract-trap-kill by annihilation or confusing strategy and push-and-pull, attraction of biocontrol agents (predators and parasites) are the practical roles of semiochemicals which can be utilized for effective, ecofriendly and economical IPM program of insect pests of various crops (Brown 2008; Heuskin 2009; Verheggen et al. 2010). The utilization of semiochemicals is preferred over synthetic insecticides because former have adverse effects on pests but no toxic effects on non-target organisms, possess least mammalian toxicity, are nonpersistent and environment-friendly, required in less quantity (low dose rate) and demonstrate slow rate of resistance developments in insects.

8.3.2. Insect pheromones: Implementation and potentials in IPM

Insect pheromones are those semiochemicals which are produced inside their body by special glands, then are released from their body, pass through air or water and are detected by the receiver (other insects of same species) with the help of different sensilla (Raina et al. 2003). Insect's pheromones elicit different types of behavioral or physiological changes in the receivers depending on the type of the pheromone. Chemical signals emitted from insect's pheromones may be short-term (e.g., pheromones used for cautioning danger or stimulating mating/reporducion) or long-lasting term (e.g., pheromones used for specifying territorial boundaries and marking food sources). These pheromones consist of a range of hydrophobic to hydrophilic peptides including long-chain saturated esters, aldehydes and alcohols. More than 1600 insect's pheromones have been isolated and identified from more than 1500 insect species (Arn et al. 1992; Islam 2012). Most commonly used pheromones in insect pest management program are sex pheromones which are most commonly released by females with some exceptions in insects where males release sex

pheromones (e.g. cotton boll weevil, *Anthonomus grandis*; cabbage looper, *Trichoplusia ni* and Mediterranean fruit fly, *Ceratitis capitata*). But the sex pheromones released by females attract opposite sex at longer distance, more strongly excite opposite sex to copulate and are more important in IPM than sex pheromones released by males in insects. The major insect's orders producing sex pheromones include Dictyoptera, Orthoptera, Hemiptera, Mecoptera, Coleoptera, Neuroptera, Lepidoptera, Diptera and Hymenoptera. Sex pheromones are synthesized from fatty acids (alcohols, aldehydes and acetates based pheromones are produced) or from linoleic acid or linolenic acid (straight-chain carbohydrates based pheromones are produced) obtained from plants during feeding (Landolt 1997; Chapman 2003).

Pheromones as behavior modifiers play a pivotal role in insect pest management program. The discovery of bombykol (sex pheromone of *Bombyx mori*) in 1959 by Adolf Butenandt motivated the scientists to explore and exploit the pheromones in IPM program of various insect pests of economic importance. Thousands of pheromones, parapheromones or pheromone mimics have been investigated, formulated and used against insect pest of economical crops (Table 8.3). They are used for detecting, monitoring, forecasting and control of insect pests' population using different techniques like mating-disruption or confusing/decoy technique, Monitoring technique, Mass-trapping technique and Attract-and-Kill technique (Horowitz and Ishaaya 2004; Witzgall et al. 2010).

8.3.2.1. Mating-disruption or confusing/decoy technique

In this technique, lures which are developed from synthetically produced pheromones are used. These lures are blend of major along with some minor chemical components that mimic the excitatory effects of the pheromone naturally produced by insects. This technique involves the introduction of multi-sources of sex pheromone in an ecosystem for making the male population confused and restraining their capability to trace calling-females. The lures or synthetically produced pheromones mask the natural pheromone plume released by female population; limit the ability of males to retort the calling-females in the ecosystem and divert the males to follow pseudo-pheromone-trails to trace the mates (Fig. 8.3). These phenomena either delay or prevent the mating process. Delay in mating imposes consequent negative impact on fertility and results in depositing fewer numbers of fertilized eggs by females during her life time; whereas, complete inhibition in mating devoid the females from depositing fertilized eggs, as the eggs get reabsorbed inside their reproductive system. In both cases, the population of the target insect pest is consequently reduced and losses are avoided (Murray and Alston 2010).

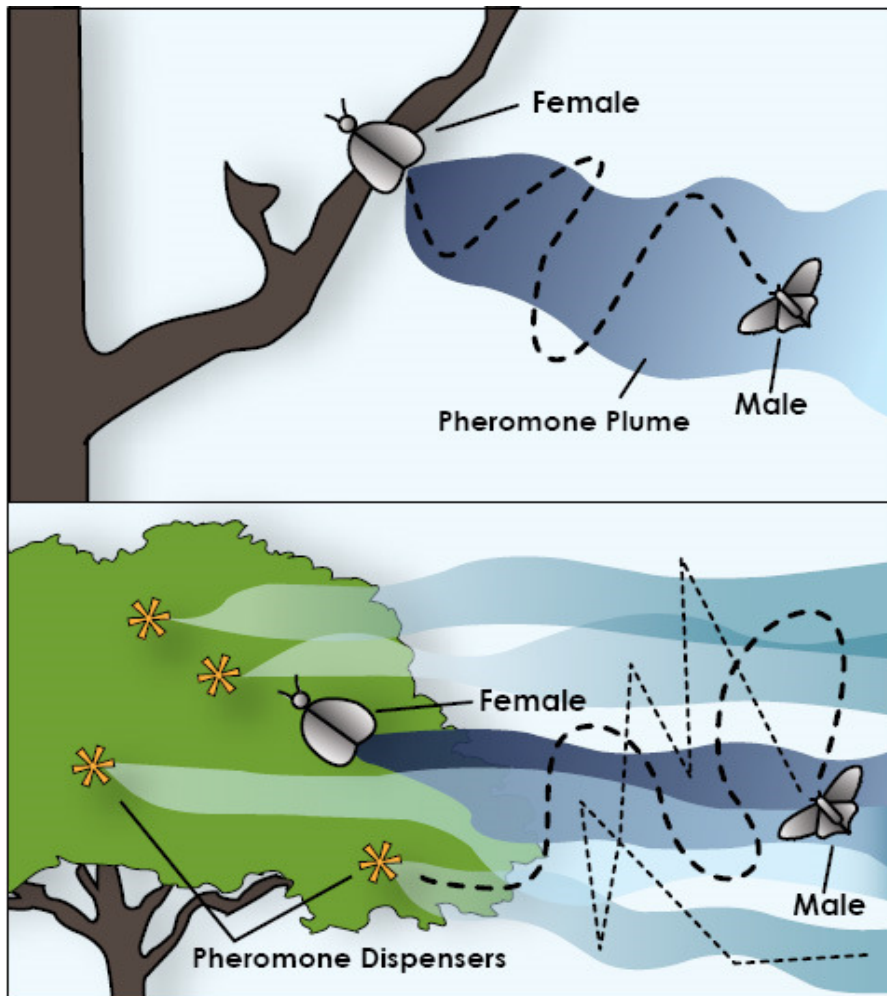


Fig. 8.3 A) Ecosystem without lure indicating normal male following the true trail and locating female for mating. B) Ecosystem with lure dispensers releasing synthetic pheromone volatiles which are masking the natural pheromone released by female, confusing the normal male to locate and respond the calling-female and diverting the male to follow pseudo-pheromone-trails. The confused male, if fly less randomly (following the thick dotted line), may settle on pheromone trap/dispenser or may fly down near female but mating will be delayed. The confused male, if fly arbitrarily (following the thin dotted line), will remain betrayed, never locate the female and mating will be prevented. (Reproduced with permission by: Utah State University, <http://utahpests.usu.edu/IPM/images/uploads/factsheet/codling-moth-md/fig-1-mating-disruption.jpg>).

The success of this technique depends on following considerations and factors (Cocco et al. 2013):

- 1) Determine the suitability of the field, crop or orchard for the implementation of mating-disruption technique. Square and rectangle field are the most suitable blocks whereas, long, narrow sites, few furrows and small backyard planting are inappropriate sites for this technique.
- 2) Planning area-wide and season-long/year-long monitoring programs
- 3) Implementation of mating-disruption technique on large area
- 4) Ecosystem harboring very high population of insect pests is absolutely wrong site whereas; ecosystem having low to moderate insect pest population is an appropriate site for the implementation mating-disruption technique. Very high insect pest population does not reduce rather sustains the chances of mating despite the implantation of sex pheromone.
- 5) This technique should be used in integration with other IPM components

8.3.2.2. Monitoring and pest-scouting technique

Monitoring and pest-scouting are the crucial components of any successful IPM program and make the foundation of pest management decisions. The application of pheromones is concerned with the detection pest incidence and monitoring population fluctuation during cropping season. After implementing pheromone traps, this technique helps in detecting both the occurrence and density of insect pest species in an agroecosystem. Monitoring the traps on regular basis also helps to estimate insect pest population, determine new hotspot at very early stage of the crop, define threshold, forecast the chance of outbreak of key pest species and track the incidence of any invasive insect species. Monitoring using pheromones is an important method for detecting quarantine insect pests like fruit flies (Dhaliwal et al. 2006).

8.3.2.3. Mass-trapping technique

In this technique, pheromones are employed in/on the traps having sticky surfaces or filled with any liquid (water, kerosene oil, alcohol etc.) to trap or catch the attracted insects. The shape, size, color, density, height and position of pheromone traps are the key factors which determine the successful results of the traps. Shape, size, color, height and position of pheromone traps vary depending upon the target insect species and crop and its stage; whereas density of traps per unit area depends on the area and economic importance of crop, geographical area and density of pest population. This technique is highly restricted to an ecosystem where chemical control with insecticides is either ineffective or intolerable due to environmental degradation (Pedigo 2003; Dhaliwal et al. 2006).

8.3.2.4. Attract-and-Kill technique

This technique is modified form of mass-trapping. In this technique, pheromone is coadministrated with any killing agent more specifically any odorless insecticides. The pheromone attracts the insect species while insecticide kills the attracted insect

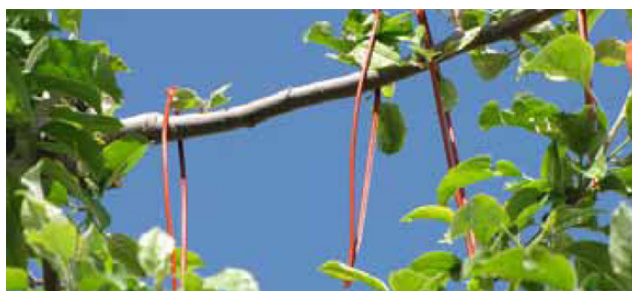
species by contact action. The mixed in insecticide enhance the attract-and-killing potency of the pheromone trap and overcome the issue of low trapping efficiency of pheromone traps. This technique is also termed as Male-Annihilation-Technique (MAT) when male attracting pheromone is used in trap. This technique is widely used to control fruit flies (Pedigo 2003; Dhaliwal et al. 2006).

8.3.2.5. Pheromone Nanogel Technique

With advent of nanotechnology, pheromone application technique has also been modified and improved. Low molecular mass gelator has been used to prepare a nanogel from methyl euginol (sex pheromone for fruit flies). This pheromone nanogel (nano-gelled pheromone) is highly stable at open conditions, slows down the volatilization of the pheromone evocatively and significantly, facilitates the handling and carriage of pheromone without preservation by refrigerator chilling and reduces the intensity of refreshing or recharging the pheromone in the field. This technique has transformed the conventional pheromone application technique (pheromone traps) into a simple, practical and low-cost approach having satisfactory safety profile, long-lasting residual activity, extraordinary efficacy and significant potential for crop protection (Bhagat et al. 2013)

8.3.2.6. Phromone dispensing technology

In this technique different kind of dispensers made up of materials which slow down the release of pheromone and enhance the shelf-life of the molecules. Different kind of pheromone dispensing techniques have been developed and used for the control of various insect pests especially fruit flies. For example SPLAT (Specialized Pheromone and Lure Application Technology) has been developed by ISCA Technologies, Inc., Chicago Ave, Suite C2 Riverside for the management of fruit flies. This technique has multiple application methods, is easy to apply on large and small area, ensure application of same quantity of pheromone, is rain-resistant, ensure the efficacy upto six months and can be mixed with kairomones or feeding stimulant. Isomate-CM/OFM TT dispenser (a "twin tube" assembly of two "ties" containing 423.6 mg of a multicomponent pheromone blend) implemented at a rate of 500 ties per ha (200 per acre); Checkmate dispensers (CM-OFM Duel membranes, a double packet of pheromone-loaded pads behind controlled-release membranes) installed at a rate of 500 ties per ha (200 per acre) and Checkmate Puffer pheromone dispensers (a plastic cabinet enclosing an aerosol canister containing the pheromone blends) deployed at a rate of 1 per acre all three in the upper one-third of the tree canopies suppressed adult catches of oriental fruit moth (OFM), *Grapholita molesta*, codling moth (CM), *Cydia pomonella* and lesser appleworm, *Grapholita prunivora* to near-zero levels for the entire season (Agnello and Reissig 2007; Murray and Alston 2010) (Fig. 8.4).



Isomate-CM/OFM TT (twin tube) dispenser



Checkmate CM-OFM Duel-membrane dispenser



Suterra CM/OFM Puffer

Fig. 8.4 Display of different pheromone dispensing technologies (Reproduced with permission by Utah State University Extension IPM Program, and uploaded of website: <https://www.google.com.pk/search?biw=1366&bih=624&noj=1&tbm=isch&oq>)

8.3.2.7. Microencapsulated pheromone technology

Microencapsulation is an advanced technology and is used to develop microencapsulated formulations of pheromones by interfacial polymerization. Small droplets of the pheromones are enclosed inside the polymer capsules which are small enough to be applied as suspension and regulate the pheromone release rate. Microencapsulated formulations of pheromones are easy to apply on large scale with conventional spray equipment, cause high levels of communication disruption of insects, are compatible with other chemical products (insecticides and fertilizers) in most of the tank spray system, ensure best coverage of the crop/tree with pheromone, have prolonged residual activity (days to weeks depending on climatic condition, capsule size as well as chemistry and properties of pheromone) and are convenient for integration with insecticide-based IPM program to reduce pest pressure. Microencapsulated pheromone technique has been reported to suppress oriental fruit moth (Il'ichev et al. 2006) and codling moth (Stelinski et al. 2005) effectively by disrupting mating response. CheckMate® Flowable is a product developed by Suterra® that consists of micro-encapsulated pheromone formulated for mating disruption in oriental fruit moths (CheckMate® OFM-F) and codling moth (CheckMate® CM-F) (Agnello and Reissig 2007; Murray and Alston 2010). Bohnenblust et al. (2011) evaluated three sex pheromone MD technologies (CM and OFM Disrupt Micro-Flakes, Isomate CM/OFM TT, and both a CideTrak OFM and a CideTrak CM dispenser containing both codlemone and pear ester), and four dispenser densities (250, 375, 425, and 500 dispensers ha⁻¹) for the management of the codling moth (CM), *Cydia pomonella* (L.), and the oriental fruit moth (OFM), *Grapholita molesta* (Busck) (both Lepidoptera: Tortricidae), in Pennsylvania apple orchards. They reported that CideTrak CM/pear ester combination and Isomate CM/OFM TT treatments both significantly minimized CM captures in traps in 2007 and 2008. Meanwhile, OFM trap shutdown was highest in the CheckMate Duel densities of 375 (99.9 ± 0.08%) and 500 dispensers ha⁻¹ (98.9 ± 0.07%) and the Isomate CM/OFM TT treatment (98.0 ± 1.13%), and lowest in the 250 dispensers ha⁻¹ density treatment (94.3 ± 3.23%).

8.3.2.8. Potential of pheromones in IPM

Use of pheromone based management system has an edge over conventional insect control program which comprises of insecticide spray. The former is safe for non-target organisms, highly species specific, selective, specifically targets the reproductive stages of insect life and prevents the production of most voracious and damaging stages. However, the later targets the damaging stages of insect life, is nonselective and toxic for non-target organisms. Pheromones in form of different techniques and technologies have important position in IPM program as they are highly target specific, ecofriendly and economical, require very low doses, are safe for natural enemies and compatible with other components of IPM program. However, ever, parapheromones or synthetic pheromones are available in the markets only for few insect species. A regular and routinely recharging or replacement of pheromone lures required for good and reasonable trapping of insects otherwise efficacy of the lures deteriorate with the passage of time and insect catching is reduced. An agroecosystem harboring insect pest complex cannot be

protected from damage by pheromone management system because pheromone is species specific and captures as well suppresses on one insect species not all.

Pheromone based management system, technologies or devices playing their vital role in controlling variety of insect pests of economic crops, fruits, vegetables, ornamentals, vineyards fiber and fodder crops and pastures. The most important and historical success stories involving exploitation of pheromone based management system include the significant suppression of codling moth (> 80% reduction in moth-catches/trap) and reduction in fruit losses (0.1-1% fruit damage) as well as in insecticide application (> 75% reduction) in pear, apple, pomegranate and walnut in California, Pacific Northwest, Sacramento valley, Lake County and Randal Island region. The capturing and suppressing of codling moth population in fruit orchards in many countries of the world is accomplished by using different types of pheromone dispensers (Hand-applied dispenser, Hollow-fiber dispensers, High-emission dispensers etc.), microencapsulated pheromones, pheromone traps, nanogelled pheromones and MAT-devices (Ahmed 2014). Hollow-fiber pheromone dispensers were used for mating disruption in IPM program of tomato pinworm (*Keiferia lycopersicella*) in 1970s and 1980s in Mexico successfully causing 30-35% reduction in fruit damage (Trumble 1997). A successful mating disruption program was deployed during 1980s in Coachella Valley, USA and many European countries against pink bollworm (*Pectinophora gossypiella*) on cotton using hollow-fiber, twisted-tie-rope, laminate-flake, microencapsulated-pheromone or laminated-membrane dispensers that caused 80-100% reduction in pesticide application against pink bollworm (Ahmed 2014). Mating disruption program using membrane, laminate and rope dispensers (hand-applied dispenserks), puff-type dispensers and microencapsulated formulations has been carried out successfully for oriental fruit moth in many countries (Pickel et al. 2002). For example, 0-3% damage was reported in peach orchards in California when hand-applied pheromone dispensers were deployed for mating disruption of oriental fruit moth. Manipulation of different types of pheromone traps (delta, funnel or water trapes) in IPM program (integrated with insecticides) of *Tuta absoluta* (tomato leafminer) demonstrated losses much below ETL (1-5%) in Egypt (Taha et al. 2013) and significant results against this notorious pest in Spain and Argentina (Botto 1999).

8.3.3. Plant-produced allelochemicals: Perspectives and potentials in IPM

In plants, two types of metabolites are produced as a result of metabolic processes. Primary metabolic processes in plant system produce primary metabolites (enzymes, hormones, carbohydrates, lipids, proteins and phosphorous compounds) from inorganic compounds for the growth and reproduction of plants. Some of these plant's primary metabolites act as nutrients, feeding stimulants and toxicants. As a result of secondary metabolites in plant system, secondary metabolites are produced that are considered to play important role in plant defense against herbivore feeding. Such types of plant metabolites illicit a chemical based communication between plants and insects and are called allelochemicals. These allelochemicals have antixenotic and antibiotic effects and play vital role in triggering resistance in plants against herbivores (Dhadialla and Bhathal 1994; Pedigo 2003). Plant produced

allelochemicals (Table 8.2) illicit intrinsic as well as extrinsic defense against herbivores. They may act as kairomones, allomones, synomones or alternatively (Price et al. 1980; Ahmad et al. 2004) depending on the nature of their effects on responding organism. An allelochemical, at the same time, may act as all aforementioned categories. For examples, terpenoids produced by pine tree as secondary metabolites not only act as allomones for phytophagous insects (herbivores) but also act as chemical cue for bark beetles eliciting kairomonic effects and help in searching their food source (bark of pine). Same terpenoids of pine trees also act as synomone when they attract predators of bark beetles (Nordlund 1981; Pasteel 1982). Different food bodies like nectors, pollens etc., plant volatiles and scents emitted from floral parts or glands act as synomones for predators, parasites and pollinators (Leius 1967; Smiley 1978; Read et al. 1970; Vinson 1984; Pellmyr and Thien 1986). The pine needles attacked by aphids volatilized a chemical odor which attract and help coccinellid predators to search their prey (aphids) (Kesten 1969). Flint (1979) has reported that cotton leaves damaged by insect pests especially by Lepidopterous pests produce a terpenoid (caryophyllene) that attract *Chrysoperla carnea* towards plants. The pants damaged by herbivores emit mixture of behavior-modifying volatile organic compounds which are called as herbivore-induced plant volatiles (HIPVs) (Mumm and Dicke 2010). Such HIPVs mainly consists of terpenes (monoterpenes, sesquiterpenes, homoterpenes), aromatic compound and green-leaf volatiles (C6 aldehydes, alcohols, and acetates) (Pichersky et al. 2006) which act as chemical cues to indicate the presence of potential host/prey and help their natural enemies to trace their prey/host (Verkerk 2004). A mixture of volatiles emitted from *Phaseolus lunatus* L. (lima bean plants) due to feeding of *Tetranychus urticae* Koch (two spotted spider mite) appeals the *Phytoseiulus persimilis* Athias-Henriot (predatory mite) (Dicke and Sabelis 1988; Du et al. 1998). As a result of pea aphid (*Acyrtosiphon pisum* (Harris) infestation on beans (*Vicia faba* L.), beans plant emit HIPVs which attract aphid parasitoids (*Aphidius ervi* Haliday). Stimulation of volatiles emission from the host plant *Ulmus minor* Mill. is triggered by the oviposition initiation of elm leaf beetle (*Xanthogaleruca luteola*) on its host plant. Then the emitted volatiles attract the egg parasitoid (*Oomyzus gallerucae* Fonscolombe) of elm leaf beetle (Meiners and Hilker 1997, 2000). The plant produced allelochemicals ingested by the phytophagous insects are cycled inside their bodies and then the biomolecules produced as byproducts act as kairomones for chemical communication between insects and its natural enemies (Vinson 1984). For examples, corn attacked by *Heliothis zea* (corn earworm) produces trichosane which is ingested by *H. zea* and then derived unchanged to its eggs where this chemical act as kairomone for *Trichogramma evanescens* (egg parasitoid) and help the parasitoid in locating the eggs of its host (*H. zea*) (Lewis et al. 1972). Allyl-isothiocyanate released from cruciferous plants helps the aphid parasitoid (*Diaeretiella rapae*) in searching its host (aphid) (Dhaliwal and Arora 2003). A large quantity of terpenoids is volatilized from the corn seedling attacked by armyworm (*Spodoptera exigua*) which attract females of *Apanteles marginiventris* (larval parasitoid wasp) and enhance parasitism (Dhaliwal and Arora 2003).

Monteith (1960) concluded that sometimes, secondary metabolites (allelochemicals) produced by one plant species retard the host/prey searching ability of natural enemies by masking chemical attractants produced either by other plant species or

emitted from the body of host/prey after cycling the plant metabolite in its body. For example, odorous chemical emitted from larch and larch sawfly (*Pristiphora erichsonii*) as secondary metabolite (allelochemical) demonstrates 80-90% parasitism of larch sawfly by its tachnid parasitoid in pure larch cultivation but attributes only 10-12% parasitism in mix cultivation because of masking effects of other allelochemicals emitted by other accompanying larch sawfly host-trees in mix cultivation. The allomones based plant defense system against herbivory also repel the natural enemies. For example, Methy Ketone, 2- tridecanon emitted from tomato not only repels herbivores but also deters the natural enemies (Williams et al. 1980; Dimock and Kennedy 1983). Similarly, volatiles released from glandular trichomes of plants deter coccinellids and chrysopid larvae (Belcher and Thurston 1982). Hydroxamic acid produced in graminaceous plant species like wheat maize etc. exhibits antixenotic and antibiotic effects against *Ostrinia nubilalis*, *Schizaphis graminum*, *Sitobion avenae* and other insect pests. The rice plant produces pentadecanal which demonstrates allelochemicals effects on various insect pests of rice including *Nilaparvata lugens*, *Sogatella furcifera*, *Chilo suppressalis* etc. Tomato foliage divulges antixenotic and antibiotic resistance for *Leptinotarsa decemlineata* and *Heliothes zea* due to presence of ruten and chlorogenic acid (catecholic amines), α -tomatine (glycoalkaloids), and 2-tridecanone as well as 2-undecanone (methyl-ketones) in tomato leaves (Dhaliwal and Bhathal 1994; Dhaliwal et al. 2006). E- β -farnesene (alarming pheromone) is released by potato plant (*Solanum berthaultii*) as allomonic chemical defense against the attack of *Myzus persicae* (aphid). Gossypol (excreted by gossypol glands) emitted from cotton leaves imposes antixenotic and antibiotic effects on various Lepidopterous pests like pink bollworm (*Pectinophora gossypiella*), american bollworm (*Helicoverpa* spp.), armyworm (*Spodoptera* spp.) and (*Trichoplusia ni*) (Dhaliwal and Arora 2003; Dhaliwal et al. 2006).

These plant produced allelochemicals either have allomonic, kairomonic or synomonic effects (Table 8.2). The allelochemicals having allomonic effects can be exploited for repelling or deterring the pest species from feeding, oviposition or sheltering on the crops and ultimately for minimizing the crop losses in an ecofriendly way. The allochemicals having kairomonic effects can be utilized for attracting pest species on trap crops or food baits; thus giving relief to the actual crop. While allelochemicals exhibiting synomonic effects can be exploited in the manipulation of biocontrol agents especially parasitoids facilitating the entomophagous insect in searching its host/prey. Likewise, gene-pole involved in synthesis of allomones and synomones in wild plants, if identified and characterized, can be engineered by modern biotechnological approaches in the cultivated crops and exploited in form of genetically modified crops for ecofriendly pest management program.

Table 8.2 List of plant produced allelochemicals with their target insect and effects

Allelochemicals	Source	Target insects	Effects	References
Allyl-isothiocyanate	cruciferous plants	aphid parasitoid (<i>Diaeretiella rapae</i>)	Synomonic effect	(Dhaliwal and Arora 2003)
Gossypol	Cotton plants	Lepidopterous pests of cotton	antixenotic and antibiotic effects	
E- β -farnesene	potato plant	Myzus; persicae (aphid)	Allomonic effects	
methyl-ketones	Tomato foliage	Leptinotarsa decemlineata and <i>Heliothes zea</i>	Antixenotic and antibiotic resistance	(Dhaliwal and Bhathal 1994; Dhaliwal and Arora 2003)
Catecholic amines	Tomato foliage	Leptinotarsa decemlineata and <i>Heliothes zea</i>	Antixenotic and antibiotic resistance	
Glycoalkaloids	Tomato foliage	Leptinotarsa decemlineata and <i>Heliothes zea</i>	Antixenotic and antibiotic resistance	
Pentadecanal	Rice plant	Various insects pests of rice including <i>Nilaparvata lugens</i> , <i>Sogatella furcifera</i> , <i>Chilo suppressalis</i> etc.	Allelochemicals effects	
Hydroxamic acid	graminaceous plant species	<i>Ostrinia nubilalis</i> , <i>Schizaphis graminum</i> , <i>Sitobion avenae</i> and other insect pests	antixenotic and antibiotic, antifeedant effects	Argandona et al. 1980. 1983; Givovich and Niemeyer 1994; Dhaliwal and Arora 2003
Methy Ketone, 2-tridecanon	emitted from tomato	Herbivores and natural enemies		Williams et al. 1980; Dimock and Kennedy 1983
Caryophyllene (terpenoid)	released by damaged cotton leaves	<i>Chrysopa carnea</i> (predator of soft bodied insects and eggs)		Flint et al. 1979
Sinigrin	released by mustard leaves infested with mustard aphids (<i>Brevicoryne brassicae</i>)	Attract both mustard aphids (<i>B. brassicae</i>) and its parasitoid (<i>Diaeretiella rapae</i>)		Read et al. 1970
Trichosane	produced by corn (<i>Zea mays</i>)	<i>Trichogramma evanescens</i> (egg parasitoid)		Lewis et al. 1972

8.3.4. Herbivore-produced allelochemicals: Perspectives and potentials in IPM

Phytophagous insects are the component of tritrophic interaction that manages the defense system of plants on one side while tackle the attack of their natural enemies on the other hand. The herbivores cope with the defensive system of plants and defend themselves from attack of natural enemies by producing different kinds of semiochemicals which either suppress or mitigate the plant's defense system or deter the natural enemies directly or indirectly (Dhadialla and Bhathal 1994; Ahmad et al. 2004). The sugar rich honeydew produced by aphids or lycaenid butterfly larvae attracts ants which get food from honeydew and in response protect aphids and lycaenid larvae from predators (Pierce and Mead 1981). The herbivore-produced allelochemicals may act as kairomones detected by their natural enemies. These herbivore's kairomones may be in form of their sex pheromones, (Kennedy 1984), body odor (Noldus and van Lentern 1985), aggregation pheromones (Wood 1982), odor of excretory products (Nordlund and Lewis 1985), odor of eggs (Jones et al. 1973) and body scales (Loke and Ashley 1984). According to Tinbergen (1972), the predatory wasp (*Philanthus triangulum*) of bee locates its prey (bees) by following the chemical clue of odor emitted from the body of bees. The predators of termites search them by following the chemical signals of foraging pheromones emitted by termite's population during foraging (Howse 1984; Ruther et al. 2002). Chemical odor emitted from the body of aphids elicits both the oviposition stimulant and arrestant effects on its predator, syrphid fly (*Syrphus corolla*) while attractant effects on its cecidomyiid predator (*Aphidoletes aphidimyza*) (Dhaliwal and Arora 2003; Dhaliwal et al. 2006). Attraction, retaining and searching behavior of *Apanteles plutella* (endolarval parasitoid) is stimulated by the combination of chemical elicitors produced by its host, *Plutella xylostella* (L.) and emitted by the host plant of Diamond back moth (*P. xylostella*) (Loke et al. 1992; Dhaliwal and Arora 2003). Tricosane synthesized and emitted from the scale of *H. zea* attracts *Trichogramma* spp. and enhances the egg parasitism from 13-22% (Jones et al. 1973; Lewis et al. 1975a, b). Hare et al. (1997) reported that exposure of *Aphytis melinus* DeBach (reared in laboratory parasitoid of the California red scale) to O-caffeoyltyrosine (kairomone) before augmentation enhanced the parasitism of *Aonidiella aurantii* (Maskell) (California red scale) by *A. melinus*.

The kairomones emitted by the herbivores also affect plant physiology. Carter (1939) reported fruit abortion and enhanced growth rate; whereas, Bultman and Faeth (1986) documented shedding of buds, fruits, flowers and leaves by plants in response of allelochemicals emitted by herbivores. The allelochemicals having allomonic effects elicit deterrent effects on host plants and their natural enemies. The allelochemicals (allomones) released by gall insects elicit the plants to produce galls as conducive habitat for gall insect. Cardiac glucosides derived from milkweed plant by milkweed butterfly are cycled and then are used as allomones which illicite vomiting in predators of this pest and deter predators from predation (Brown 1969). Similarly, tomatine (alkaloid) derived by corn earworm (*H. zea*) from tomato plants, when cycled in its body, induces negative impacts on the survival, longevity and larval growth of *Hyposter exigua* (larval parasitoid of *H. zea*) inside the body of host (Campbell and Duffey 1981). Ethanol derived by the *Drosophila melanogaster*

imposes adverse effects on the survival of its parasitic wasp. Similarly, nicotine when derived by hornworm from *Nicotiana tabacum* in high concentration executes adverse effects on the survival of *Apanteles* spp. inside the body of its host (Gilmore 1938).

8.3.5. Natural enemy-produced allelochemicals: Perspectives and potentials in IPM

Like herbivores, intraspecific communication is triggered in natural enemies by emitted pheromones especially sex pheromones (Eller et al. 1984; Swedenborg and Jones 1992) which have been assessed for determining various activities and biological parameters of natural enemies including activity of natural enemies in field, assessment of their population density and prediction of parasitism rates in field (Lewis et al. 1971; Morse and Kulman 1985). Aggregation pheromones have potential in manipulation of biocontrol system in IPM. For example, 2-isopropyl-3-methoxypyrazine (aggregation pheromone) produced by conspecifics attracts both sexes of *Coccinella septempunctata* adults (Al-Abassi et al. 1998). Combination of pheromones and HIPVs enhances the attraction of natural enemies. A combination of MeSA (HIPVs) and iridodial (aggregation pheromone) proved a stronger attractant for lacewing species (Jones et al. 2011). The semiochemicals released by the natural enemies also play important role in tritrophic interaction because such semiochemicals bring about changing in the behavior and physiology of both the herbivores and plants (Ahmad et al. 2004). The reviewed literature indicates that predators have evolved such system. Allomones produced and emitted by predators not only attract their prey but also help them to mimic their identity (Ahmad et al. 2004). Predators derive some chemicals from the body of their prey and then exploit these chemicals for mimicking their body odor with that of their prey (Vander-Meer and Wojcik 1982; Ahmad et al. 2004). The synomones released by the predators or parasitoids elicit changes in plants. Predators also produce chemicals having kairomonic properties and when these kairomones are detected by the herbivores (preys), they disperse from the area to sidestep their predation by the invading predators (Dicke and Grostal 2001). Formicid kairomones released by predatory ants elicit behavioral changes in terestrial ants, bees and wasps (Chadab 1979). Synomones released by the *Pheidole bicoins* (ant species) is a chemical indication of their presence. When presence of these ants is detected through the synomonic cues by *Piper cenocladum* plants, they start to produce food bodies for the predator ants (Risich and Rickson 1981).

8.4. Recent scenario of biorational pest management in Pakistan

In Pakistan, the concept of biorational pest management is mostly theoretical while its practical concept is very limited. The practical use of biorational pest management components on the farmer field is inadequate. Although such approach has great potential in IPM program but they are getting insignificant portion of the pesticide

market in Pakistan. Most commonly used biorational products include IGRs and pheromones.

The commercially available, marketed and used IGRs in Pakistan belong to triazine chitin synthesis inhibitors (CSI), Benzoylphenylurea CSI, Juvenile hormone mimics and Moulting hormone agonists. Among triazine CSI, buprofezin [(Z)-2-[(1,1-dimethylethyl)imino]tetrahydro-3-(1-methylethyl)-5-phenyl-4H-1,3,5-thiadiazin-4-one] (formula: C₁₆H₂₃N₃OS) is marketed and being used against variety of insect pests. Buprofezin not only impedes moulting process and demonstrates mortality of nymphs and larvae but also suppresses oviposition by adults and induces sterility in treated insects. This biorational product is found very effective against homopterans, coleopterans and mites in rice, cotton, fruits, vegetables and many other field crops and ornamental plants (Sontakke et al., 2013). Among Benzoylphenylurea CSI group, lufenuron [(N-[[[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy) phenyl] amino] carbonyl]-2,6-difluorobenzamide)]; (C₁₇H₈Cl₂F₈N₂O₃), triflumuron [(2-chloro-N-[[4-(trifluoromethoxy) phenyl] carbamoyl] benzamide); (C₁₅H₁₀ClF₃N₂O₃), diflubenzuron [(N-[(4-chlorophenyl) carbamoyl]-2,6-difluorobenzamide); (C₁₄H₉ClF₂N₂O₂), chlorfluazuron [(N-[(3,5-dichloro-4-[[3-chloro-5-(trifluoromethyl) pyridin-2-yl]oxy] phenyl) carbamoyl]-2,6-difluorobenzamide); (C₂₀H₉Cl₃F₃N₃O₃)] and teflubenzuron [(N-[(3,5-dichloro-2,4-difluorophenyl)carbamoyl]-2,6-difluorobenzamide); (C₁₄H₆Cl₂F₄N₂O₂) are being used effectively against various insect pests of economic crops. Lufenuron has been found very effective against various lepidopterous, dipterous and coleopterous pest in various field crops (Gogi et al. 2006; Saeed et al. 2012), vegetables, orchards (Akhtar et al. 2007) and storage structures (Sagheer et al. 2012). Satisfactory suppression of hairy caterpillar, *Euproctis lunata* Walk (Lymantriidae: Lepidoptera) has been achieved by the application of triflumuron and diflubenzuron in nurseries and young plantation (Rahman and Chaudhary 1987). Diflubenzuron and buprofezin explained excellent mortality of the wigglers and pupae of the mosquito (*Aedes aegypti*) (Jahan et al. 2011). Lufenuron, and triflumuron have been reported as harmless IGRs (clas 1) for beneficial insects fauna especially parasitoids and can be recommended for integrated pest management programs potentially designed for their preservation (Carvalho et al. 2010; Hussain et al. 2010; Sattar et al. 2011). Among IGRs, chlorfluazuron was the most toxic compound (LC₅₀ = 0.0006 mg a.i./ml) against *P. xylostella* in Pakistan (Abro et al. 2013). Viper[®] (Buprofezin) and Match[®] (Lufenuron) alone and in combination with two insecticides used for seed treatment [Confidor[®] (Imidacloprid) and Contest[®] (Thiamethoxam)] at their field recommended dose rate exhibited 80-100% reduction infestation and 65.3-100% larval mortality of *Chilo partellus* Swinhoe (Pyralidae: Lepidoptera) and 80-100% reduction in infestation and 75-100% maggots' mortality of *Atherigona soccata* Rodani (Muscidae: Diptera) upto 15DAT (Arif et al. 2013). IGRs like, lufenuron, triflumuron and buprofezin, demonstrated 96.6, 89.9 and 69.5, mortality of canola aphids as compared to carbosulfan (78.2%), respectively. These IGRs exhibited toxicity against the non-target organisms but lower than synthetic insecticides (Arif et al. 2013).

The most commonly used Juvenile hormone mimics in agroecosystem of Pakistan for plant protection against insect pests include fenoxycarb and pyriproxyfen.

Table 8.3 List of pheromones categories with examples, chemical names and target insects

Categories	Examples	Chemical names	Insects	References
Sex Pheromones	Gyptol	d-10-acetoxy-cis-7-hexadecen-1.ol	Gypsy moth (<i>Perthetria dispar</i>)	(Jacobson et al. 1970)
	Gyplure	d-12-acetoxy-cis-7-hexadecen-1.ol	Gypsy moth (<i>Perthetria dispar</i>)	
	Cuelure	4-[p-(acetyloxy)phenyl]-2-butanone OR 4-(<i>p</i> -hydroxyphenyl)-2-butanone acetate	Melon fruit fly (<i>Bactrocera cucurbitae</i>)	(Beroza et al. 1960; Vergas et al. 2000)
	ECB-Lure	Z11- and E11-tetradecenyl acetate (Z11- and E11-14:OAc)	European corn borer (ECB), <i>Ostrinia nubilalis</i> (Hubner)	(Ishikawa et al. 1999; Linn et al. 2007; Miura et al. 2009)
	Gossyplure	(1:1 mixture of Cis, Cis and Cis, trans isomers of 7,11E-hexadeca-7,11-dien-1-yl acetate)	Pink bollworm, <i>Pectinophora gossypiella</i> (Saund.) (Lepidoptera: Gelechiidae)	(Hummel et al. 1973; Golub et al. 1983)
	Litlure	a mixture of cis-9,trans-11-tetradecadienyl acetate (component A) and cis-9,trans-12-tetradecadienyl acetate (component B)	Tobacco cutworm, <i>Spodoptera litura</i> (F.)	(Tamaki et al. 1973)
	Spodolure	Mixture of (Z, E), 9,11 Tetradecanyl Acetate and (Z, E) 9,12-Dienyl Acetate (19:1)	Armyworm, <i>Spodoptera litura</i>	(Martinez et al. 1990)
	Looplure	(Z)-7-dodecenyl acetate	Cabbage looper, <i>Trichoplusia ni</i> (Hb.)	(Shorey et al. 1972; Bjostad et al. 1980)
	Heli-lure	Mixture of (Z) 11 Hexadecanal & (Z) Hexadecanal (97:3)	Red gram pod borer, <i>Helicoverpa. Armigera</i>	
	Trimedlure	mixture of <i>tert</i> -butyl (1E,2E,4E)-4-chloro-2-methylcyclohexane-1-carboxylate and <i>tert</i> -butyl (1E,2E,5E)-5-chloro-2-methylcyclohexane-1-carboxylate	Meditarrnian fruifly, <i>Ceratitits capitapa</i>	(Valega and Beroza 1967)
Bombykol	(10E,12Z)-hexadeca-10,12-dien-1-ol	Silkworm, <i>Bombyx mori</i>	(Butenandt et al. 1959)	
Leucilure	Mixture of (E)-11 hexadecenyl Acetate &	Brinjal Shoot and Fruit Borer <i>Leucinodes orbonalis</i>	(Zhu et al. 1987)	

Categories	Examples	Chemical names	Insects	References
		(E)-11-Hexadecen-1-ol (100:1)		
	Nomate-DBM, Checkmate- DBM	(Z)- Heaxadecanal -11- enal & (Z)-hexzadec-11- enyl Acetate OR mixture of (Z)-11- hexadecenal (Z-11- 16:Ald) and (Z)-11 hexadecenyl acetate (Z- 11-16:Ac)	Diamondback moth (DBM), <i>Plutella</i> <i>xylostella</i> (L.) (Lepidoptera:Yponomeu tidae	(Tamaki et al. 1977)
	Methyl eugenol	(4-allyl-1,2- dimethoxybenzene- carboxylate)	Fruit flies, <i>Bactrocera</i> Spp.	(Steiner et al. 1970)
	Amlure	(R)-acetoin	Chaffer beetle, <i>Amphimallon</i> sp	(Tolasch <i>et al.</i> 2003)
	Ferrolure (Ferrugineol")	4-methyl-5-nonanol	<i>Rhynchophorus</i> <i>ferrugineus</i> Oliv. (Coleoptera: Curculionidae)	(Hallett et al. 1993)
	Plodilure	blend of four active components, (Z,E)-9,12- tetradecadienyl acetate (Z9,E12-14:OAc), (Z,E)-9,12- tetradecadienol (Z9,E12-14:OH), (Z)-9- tetradecenyl acetate (Z9- 14:OAc) and (Z,E)-9,12- tetradecadienal (Z9,E12- 14:Ald) (100:11:18:12)	Indian meal moth, <i>Plodia</i> <i>interpunctella</i> Hübner	(Kuwahara et al. 1971)
Aggregation pheromones	Grandlure	Compounds-I [racemic grandisol, (±)- <i>cis</i> -2- isopropenyl- methylcyclobutaneetanol] Compound-II) <i>cis</i> -3,3- dimethyl-A1.B- Cyclohexanoneetanol) Compound-III+IV (a 50:50 <i>cis: trans</i> mixture of 3,3-dimethyl-A 1 – Cyclohexanoacetaldehyde	Cotton boll weevil (<i>Anthonomus grandis</i> (Boheman)).	(Tumlinson et al. 1969)
	Sitonlure	4-methyl-3,5- heptanedione	Pea and bean weevil (<i>Sitonia lineatus</i> (L.))	(Blight et al. 1987)
	Sitoplure	(R*, S*)-1- ethyl propyl- 2-methyl-3- hydroxypentanoate	Stored product weevils (<i>Sitophilus zeamais</i> (L.), <i>Sitophilus granarius</i> (L.) and <i>Sitophilus oryzae</i> (L.))	(Faustini 1982; Phillips 1997)

Categories	Examples	Chemical names	Insects	References
	Lepidolure	Tetradecen-1-ol-acetates(Z9-14:Ac and Z11-14:Ac)	Lepidopterans	(Van-der-Kraan and Ebbers 1990)
	Cydlure	(E,E)-8,10-dodecadien-1-ol / dodecan-1-ol / tetradecan-1-ol	Codling moth, <i>Cydia pomonella</i> L. (Olethreutidae: Lepidoptera)	(McDonough et al. 1969)
	LBAM-Lure	E11,14:OAc / E9,E11-14:OAc / Z11-14:OAc	Light brown apple moth, <i>Epiphyas postvittana</i> (Walker) (Tortricidae: Lepidoptera)	(Bradley et al. 1995)
	Sawfly-Lure	Acetates of pentadecanol / (2S, 3S, 7S)-3,7-dimethyl-2-tridecanol / (2S, 3R, 7R)-3,7-dimethyl-2-tridecanol	Sawflies, Neodiprion serrifer Geoffr. & Diprion pini L. (Hymenoptera: Diprionidae)	(Johansson et al. 2001)
	Totalure	Mixture of (3E, 8Z, 11Z)-3,8,11-tetradecatrien-1-yl acetate or TDTA (90%) and (3E, 8Z)-3,8-tetradecadien-1-yl acetate or TDDA (10%)	Tomato leafminer or tomato moth, <i>Tuta absoluta</i> (Meyrick) (Lepidoptera: Gelechiidae)	(Attygalle et al. 1996)

Moulting hormone agonists marketed and used as biorational products in IPM program of various sucking insect pests in Pakistan include methoxyfenozide and tebufenozoid. Priority[®] (Pyriproxyfen) and methoxyfenozid, alone and in combination with two insecticides used for seed treatment [Confidor[®] (Imidacloprid) and Contest[®] (Thiamethoxam)] at its field recommended dose rate exhibited 90.6 and 83.4% mortality of canola aphids as compared to carbosulfan (78.2%), respectively with least toxic effects on non-target organisms (Arif et al. 2013). Buprofezin, pyriproxyfen and diafenthiuron attributed higher reduction in whitefly population that endosulfan, imidacloprid and Thiamethoxam; whereas pyriproxyfen was found safe for parasitoids and predators of whitefly (Naveed et al. 2008).

Semiochemicals especially pheromones are being utilized in IPM program of various crops like cotton, grams, fruits etc. in Pakistan. Use of pheromones for detection and monitoring of pink bollworm (*Pectinophora gossypiella*), American bollworm (*Helicoverpa armigera*) and fruit fly species (*Bactrocera zonata*, *B. dorsalis*, *B. cucurbitae*) have been successfully employed in the fields. Shah et al. (2011) reported four specific sex pheromones lures; (10E 12E) – 10, 12 Hexadecadienal for *Earias insulana*, Z11-Hexadecenal Z11 octodecenal (10:2:2) for *Earias vittella*, Z7 Z11 – 16AC (50), Z7 E11 – 16AC (50) Hexadecadienyle Acetate for *Pectinophora gossypiella* and D. Z11-16AL (97), Z9 -16 AL (3) Hexadecenal for *Helicoverpa armigera* for their monitoring in the field. Pheromones are species specific and cannot be used for all fruit flies. Butanone acetate was found very effective for melon fruit fly as BA-trap attracted maximum population of melon fruit flies; whereas methyl euginol (ME) attracted more specimens of other fruit flies like *Bactrocera zonata*, *B. dorsalis* and *B. correcta* but no melon fruit fly individual was captured in

ME-trap. Pheromones admixing with odorless insecticides enhance the attract-and-kill potency and periodicity of pheromones and can also be used for management of fruit flies (Gogi et al. 2007).

Table 8.4 List of IGRs categories with their examples, active ingredient, properties, mode of action and target insects

Categories	Major group	Active ingredient (Generic names)	Properties/mode of action/effects	Target insects	References	
1) IGRs						
Chitin Synthesis Inhibitor	benzoylurea s or benzoylphen ylurea (BPUs)	Diflubenzuron	Stomach toxicants, sterilants, ruptured and malformed cuticle, death by starvation.	Coleopterans, Dipterans, Lepidopterans e.g. cabbage looper (<i>Trichoplusia ni</i>), Spodoptera littoralis, eggs of Helicoverpa armigera and <i>S.</i> litura, <i>Cydia</i> pomonella	(Retnakaran and Wright 1987; Khater 2003, Dhaliwal et al. 2006)	
		Triflumuron	Ovicidal action, reduction in the egg laying rate or hampering the hatching process by impeding embryonic development, alteration in cuticle composition, inhibition of chitin, abnormal endocuticular deposition that affects cuticular elasticity and firmness, abortive molting, larval and pupal abnormalities (larvae with weak and transparent cuticle, splitting of cuticle, small, shrunken, macerated larvae, distorted puparia, pharate pupae and failure of adult eclosion)			
		Teflubenzuron				
		Hexaflumuron				
		Chlorfluazuron				
		Chlorbenzuron				
		Dichlorbenzuron				
		Flucycloxuron				
		Flufenoxuron				
		Bistrifluron				
		Lufenuron				
		Novaluron				
		Noviflumuron				
		Penfluron				
		Flucycloxuron				
	triazine derivatives	Cyromazine (Larvadex ®, Trigard®)	Growth inhibition, expansion of the body wall abnormal internal growth and development.	Dipterans, leafminors	(O'Brien and Fahey 1991)	
	pyrimidine derivatives	Dicyclanil (ZR ®, ComWin ®),		dipteran	(Bowen et al.1999)	
		Buprofezin (Sitara®)	Inhibition of biosynthesis of chitin and prostaglandin	Most of the sucking insects especially Hemipterans	(Dhaliwal and Arora 2003; Dhaliwal et al. 2006)	
		Plumbagin	Derived from roots of <i>Plumbago capensis</i> (medicinal shrub), Inhibits ecdysis, have ovicidal effects, inhibits ecdysteroid biosynthesis, disrupt mating and reproduction of insects	Lepidopterous pests, like <i>Pectinophora</i> <i>gossypiella</i> , <i>Helicoverpa Zea</i> , <i>H.</i> <i>virescens</i> etc., red cotton bugs,		

Categories	Major group	Active ingredient (Generic names)	Properties/mode of action/effects	Target insects	References
Sclerotization inhibitors or accelerators	Sclerotization inhibitors	Ditertiary butyl alcohol (MON-0585)	Reductions in the levels of covalently bound catechols, reduction in phenoloxidase activity, malformations in the exoskeleton	Mosquito and other dipterans	
	Sclerotization inhibitors	α -methyl DOPA	Inhibits DDC enzymes (3,4-dihydroxyphenyl alanine decarboxylase) and kills insect during molting	Dipterans	
	Sclerotization accelerators	Cryomazine	Produces necrotic lesions in cuticle, extra-hardens the cuticle by adding an extra cuticular layer between endo- and exo-cuticle, non-expansion of insect's cuticle	Dipterans like blowflies, housefly, etc.	
MH-agonists	Ecdysteroid agonist	chromafenozide (Virtu®)	Contact and stomach action; interaction with the ecdysteroid receptor proteins; creates hyperecdysonism; synthesis and apolysis of cuticle but no sclerotization; feeding inhibition; larvae become dilapidated, slip their head capsule, and extrude their hind gut; death due to incomplete molting, starvation, and desiccation due to hemorrhage.		(Retnakaran et al. 1997; Dhadialla et al. 1998)
		Tebufenozide (Mimic®, Confirm®)	disrupt insect hormonal systems, and bind to the ecdysteroid receptors, thereby accelerating the molting process	Lepidoptera insects, especially, Spodoptera sp., Helicoverpa zea and Manduca sexta in cotton, cereal, maize, rice and vegetables.	(Smagghe and Degheele 1992; Palli et al. 1996)
		Halofenozide	Act as MACs (Molt Accelerating Compounds); Mimicking action of ecdysone, premature molting cessation of feeding and ultimately death of insects	Lepidoptera, Coleoptera and some Homoptera	(Potter 1998)
		Methoxyfenozide	Disruption of hormonal system; accelerating the molting process, hormonal imbalance, abnormal growth and development	Lepidoptera insects but more effective against budworm/bollworm and diamondback moth	(Wing 1988; Smagghe and Degheele 1998)

Categories	Major group	Active ingredient (Generic names)	Properties/mode of action/effects	Target insects	References
		Furan Tebufenozide	Inhibition of the activities various insecticides detoxifying enzymes like phenoloxidase, catalase, chitinase, superoxide dismutase, peroxidase acid phosphatase, carboxylesterase, glutathione S-transferase, MFO-O-demethylase; very high cytotoxicity.	Lepidoptera pests on crops and high security against the environment and non-target organisms	
MH-antagonists	Ecdysone antagonist	Diofenolan	Delay in larval–larval and larval–pupal ecdysis, ecdysial failure, mortality, severe reduction in pupation, deformed pupae, complete inhibition of adult emergence, and severely hamper the normal growth, development and metamorphosis	Lepidopteran pests and scale insects in fruit, field crops	(Streibert et al. 1994; Singh and Kumar 2011)
		Azadiractin (composed of 20 different compounds)	Inhibition of PTTH production; deformities after molts; reduced thriftiness; antifeeding and antioviposition effects; inhibit the development of egg, larvae and pupae; Block the molting of larvae and nymphs; disturb the mating and sexual communication; induce sterility in adults	Whiteflies, aphids, thrips, fungus gnats, caterpillar, beetles, mushroom flies, mealybugs, leafminers, moths and others on foods, greenhouse, crops, ornamental plants etc.	(Thomson 1992)
JHAs	Juvenile hormone agonists	Kinoprene	Juvenile hormone mimics; Juvenile hormone analogues	<i>Culex pipiens</i> Larvae; whiteflies, gnats, aphids, meal ybugs, and scales	(Hamaidia and Soltani 2014)
		Hydroprene	Juvenile hormone mimics; Juvenile hormone analogues; contact insecticides; abnormal or detrimental growth, development, and reproduction	stored-product insects, cockroaches	(Arthur et al. 2008)

Categories	Major group	Active ingredient (Generic names)	Properties/mode of action/effects	Target insects	References
		Methoprene	Juvenile hormone mimics; Juvenile hormone analogues; contact insecticides; abnormal or detrimental growth, development, and reproduction; prevent normal molting, egg-laying, egg-hatching, and development from the immature phase (i.e. caterpillar) to the adult phase	stored-product insects; beetles, flies, mosquitoes, ants, moths, mites, ticks, spiders	
		Fenoxycarb	non-neurotoxic carbamate insect growth regulator; ecdysis inhibition; suppresses reproduction; inhibits hatchability; mimics the action of the juvenile hormones on molting and reproduction; larvicide, ovicide	public health insects, including cockroaches, fleas, stored product pests, ants, mosquito larvae, moths, scale insects, and insects attacking vines, olives, cotton and fruit	(Edwards et al. 1991; Grenier and Grenier 1993)
		Pyriproxyfen	Juvenile hormone mimics; contact insecticides; abnormal or detrimental growth, development, and reproduction	stored-product insects; field crop pests, mosquitoes, ants, cockroaches	(Richardson and Lagos 2007; Kabashima et al. 2007)
		Juvabione and Dehydrojuvabion	Stifling of insect reproduction and growth; inhibits embryogenesis and eclosion from the egg, induce insect sterility	Stored grains insects, whitefly, aphids and other sucking insects,	(Metwally and Landa 1972)
AJHAs	Juvenile hormone antagonists	Precocene-I, Precocene-II, Precocene-III	cytotoxic action on the corpora allata ; Inhibits juvenile hormone biosynthesis and ovarian activation; alters sterility; disrupt the vitellogenesis in eggs inside the ovary; delays moulting; inhibits melanation, sclerotization, sexual maturity; causes a decrease in dry weight and protein content of the cuticle; causes decoloration	Majority of insects belonging to homopterans, hemipterans, orthopteran, dictyopterans, coleopterans; Lepidopterans; isopteran, hymenopterans, etc.	(Eid et al. 1988)

8.5. Conclusions

Biorational products denote biomolecules of natural origin that are active against pest populations, but relatively innocuous to nontarget organisms due to their low or no direct toxicity. Conventional insecticides are imposing severe health hazard effects and serving as a major source for ecological backlashes because they mostly target those systems of insect which have physiology exactly like that of higher animals and human being. Biorational products/approaches are based on the growth and development as well as communication system of insects which is quite different from that of higher animals and human being. Plant based secondary metabolites or phytoalexins involved in plant defense show insecticidal activities and can be employed in pest management program of various insect pest either by incorporating such molecules in insect diets (food traps) or cloning in transgenic plants. Semiochemicals are safe and eco-friendly substances without leaving any residues in the environment that's why they should be exploited for insect-pest management. Generally, biorational products are slow acting as compared to conventional nerve poisons. But the end users want that insects should die within no time and crop should be free of pests after insecticides application. This attitude and thinking of the end-user is a big hurdle in the acceptance of biorationals as pest management tool. This necessitates that distributors and users should be educated about the mode of action and safety of the biorational products. These products have great potential for replacing the persistent conventional insecticides, confirming effective cost-benefit-ratio, tackling ecological backlashes and ensuring food security with safe environment and enhanced exports. Unlike broad spectrum conventional insecticides, biorational products are highly target specific and commanding no or little mammalian toxicity or toxic effects on non-target organism. Such products have short residual activity that's why they should be employed when pest-insects are in their most susceptible life stages. The molecules used as biorational products are very active at very low concentration, safe for natural enemies of insect pests, do not accumulate in the environment and are degraded to simple nontoxic molecules. However, the large scale utilization of the biorational products undergoes some limitations. A huge amount of investment is involved in the development and marketing of biorational products. Their specificity to one species or closely related species limits their marketing potential. Similarly, most of the biorational molecules are photodegradable and face rapid reduction in their efficacy. Some biorational products like semiochemicals require area-wide application for getting effective and economical results.

The issues associated with biorational insecticides are not overwhelming; rather are addressable. Both the fundamental and applied aspects of such biomolecules need a very comprehensive research. There is need to investigate analogues of such molecules to enhance their stability in the system. A comprehensive research is required to explore the genomic and proteomics of such molecules for their insertion in plants through biotechnological approaches and developing genetically modified resistant plant species of economical crops. In the new era of biotechnology, most of the issues associated with these biorational products have been solved and these products are not only winning the reliability of the market and end user but also

demonstrating their worth and potential in sustainable IPM program of economic crops against insect pests.

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