INTER AND INTRASPECIFICITY OF CHEMICAL COMMUNICATION

A. Guerrero
Department of Biological Organic Chemistry, Jordi Girona Barcelona, Spain

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1. Introduction

Chemical ecology comprises the study of the interactions of organisms with their environment that are mediated by the chemicals they produce. An important part of these interactions relates to chemical communication in animals, the primary mode of information transfer in most groups of organisms. Even in the non-social animals, such as protozoans, annelids, molluscs, nematodes and many arthropods, chemical communication is used for a variety of purposes such as location of prey, avoidance of predators, sending signals to the same or different species for mating or aggregation, etc. The sophistication of this communication system is particularly high in those social insects and mammals that live as interacting groups of individuals in colonies or societies. In fact, the diversity of behavioral and physiological responses induced in many insects upon reception of chemical messages emitted by other insects of the same species may have been in large part the main factor for the evolution of high levels of sociality. In this chapter I will be dealing with the chemical interactions among invertebrate organisms either of the same (intraspecific communication) or different species (interspecific communication), paying particular attention to insects due to the prospective appreciation that a wise manipulation of their chemical communication system may be a valuable tool in new, ecologically-friendly, pest control strategies. Moreover, some of the advances in knowledge of insect interactions have provided guidelines and stimulation for research workers interested in exploring the chemical communication systems of other higher organisms, even mammals.

2. Terms used in chemical communication

A number of terms have been created to designate the various kinds of chemical interactions between individuals. In general, chemicals that mediate interactions between organisms are called *semiochemicals*, from the greek word *semeon*=signal or mark. The semiochemicals are divided into two major groups depending on whether the interactions are interspecific (*allelochemics*) or intraspecific (*pheromones*). However, these terms should not be considered as mutually exclusive since one particular product may be defined to act in one or more specific manners.

2.1 Allelochemics

This term, proposed by Whittaker in 1970, is used to describe semiochemicals which mediate interactions between organisms of different species, and have been classified in four categories: *allomones, kairomones, synomones* and *apneumones*.

Allomones (from the Greek *allos* + *hormon* = excite others) are chemicals released by one organism that induce a response to an individual of another species, the response being adaptively favorable to the emitter. Examples of allomones are the defensive secretions released by many insects which are poisonous or deterrent to predators. Thus, larvae of the family *Papilionidae* possess a cervical gland or osmeterium that produces a defensive secretion. When the larvae are disturbed they protrude the gland and try to apply part of the secretion to the source of perturbation. Allomones also serve plants as defense mechanisms against herbivores and reduce competition with other plants. The neotropical social wasp *Mischocyttarus drewseni* applies a secretion to the stem of its nest that repels foraging ants. Some tropical flowers which are pollinated by bats emit odours which attract bat to the flowers. The "secondary products" of plants are also allomones. These substances, which have no apparent role in the physiology of the plant, have presumably evolved as defense mechanisms against herbivores and other animals.

Kairomones (from the Greek *kairos* =opportunistic or exploitative) are chemicals released by one organism that induce a response to an individual of another species, the response being adaptively favorable to the recipient. The exudates from warm-blooded animals including humans that attract blood-sucking insects serve also as kairomones to these insects, for example the mosquito *Aedes aegypti* is attracted by (+)-lactic acid, an important constituent of the human sweat. The "secondary products" of plants, cited above as allomones, have been taken by certain herbivores, that have evolved the ability to tolerate or detoxify the chemicals, to use them as kairomonal stimulants for aggregation or feeding on the emitting plant. There have been discussions among zoologists about the value of this terminology and it has been suggested that kairomones may often be allomones or pheromones depending on the circumstances. Thus, for instance, American bolas spiders attract male moths as prey by emitting attractant allomones which act also as a sex pheromone produced by female moths.

Synomones are chemicals produced or acquired by an organism that evokes in another organism a behavioral or physiological response that is favorable to both the emitter and the receiver. This term has been regarded as allomones, as kairomones or as allomone-kairomones. Synomones may play important roles in maintaining the specificity of response of certain species to specific pheromones. Thus, the beetle *Ips paraconfusus* males produce cis-verbenol, ipsenol and ipsdienol as pheromones to attract other males to colonize trees while *Ips pini* produce linalool, cis-verbenol and ipsdienol. In laboratory and field tests ipsenol inhibited the response of *Ips pini* to its own pheromone extracts, and linalool also partially inhibited the response of *Ips paraconfusus* to its own extracts. Thus, ipsenol and linalool each act as synomones by allowing these species to avoid competitive circumstances.

Apneumones are chemicals emitted by a non-living source that induces a behavioral or physiological reaction that is favorable to a receiving organism but detrimental to an organism of another species that may be found on the nonliving material. This term was proposed by Nordlund and Lewis in 1976 but very few cases of this type of allelochemics have been found later in the literature.

2.2 Pheromones

This term refers to a substance secreted to the environment by an individual organism which elicits a specific reaction in a receiving organism of the same species. Pheromones are classified according to the response they elicit. Chemical stimuli that trigger an immediate and reversible change in the behavior of the recipient are called *releaser pheromones*, while those inducing delayed, lasting responses are referred to as *primer pheromones*. Pheromones may be further classified on the basis of the mediated interaction they induce, such as sex pheromones, aggregation pheromones, alarm pheromones, etc. The existence of pheromones has been known for many years. Ch. Butler in 1609 described how lone bees can be attracted and enraged to sting by the presence of a single bee sting. However, the first characterization was not reported until 1959 by Butenandt and coworkers on the silkworm moth. Since then, hundreds of pheromones have been identified because researchers were rapidly stimulated by the possibility of using pheromones for pest control. Consequently, far more is known about insect pheromones today than about any other group of animals. Because of the large body of knowledge of pheromones in comparison to other semiochemicals, in this chapter I will mainly concentrate on the intraspecific chemical communication in a variety of organisms.

3. Interspecific chemical communication

3.1 Allomones

Plants produce a wide variety of allomones to protect themselves from phytophagous insects and other herbivores. It is likely that the vast majority of secondary plant metabolites are biosynthesized to deter predation. Most toxic alkaloids, cyanogenic glycosides, cardiac glycosides and other toxic plant products are allomones. Some plants make herbicides to keep other plants from utilizing available water and nutrients. The classic example of this type of interaction is the alleleopathy of the walnut tree *Juglans spp*. This effect has long been recognized: the Roman scholar Pliny reported that the canopy of the walnut tree poisons the plants which it covers. The toxin responsible is called juglone and is stored in the leaves as a non-toxic glycoside derivative. The toxic substance is produced by hydrolysis of the glycoside and subsequent oxidation after the leaves have fallen on the ground. Some plants contain compounds that are not necessarily toxic but have antifeedant activity. We can broadly define insect *antifeedants* as substances which when tasted can result in cessation of feeding either temporarily or permanently depending upon potency. Well known antifeedants with important activity are:

1) Azadirachtin. This chemical has been identified from leaves and berries of *Azadirachta indica* (Indian neem tree) and *Melia azedarach*, trees commonly occurring in India and East and West Africa. These parts of the trees are widely used for chewing sticks for cleaning teeth and as a remedy against malaria. The compound is known for its very strong antifeedant activity against the desert locus *Schistocerca gregaria* (100% inihibition of feeding at concentrations of 40 μg/L or when impregnated on filter paper at concentrations of 1 ng/cm^2). The chemical is also one of the most potent antifeedants against *Spodoptera exempta*, a major graminaceous crop in East and South Africa. The chemical structure of azadirachtin is too complex to be synthesized on a practical level but since the yield is quite high (up to 800 mg from 300 g of seeds) and the tree is easy to cultivate, practical usage of the neem tree is a real possibility (Figure 1).

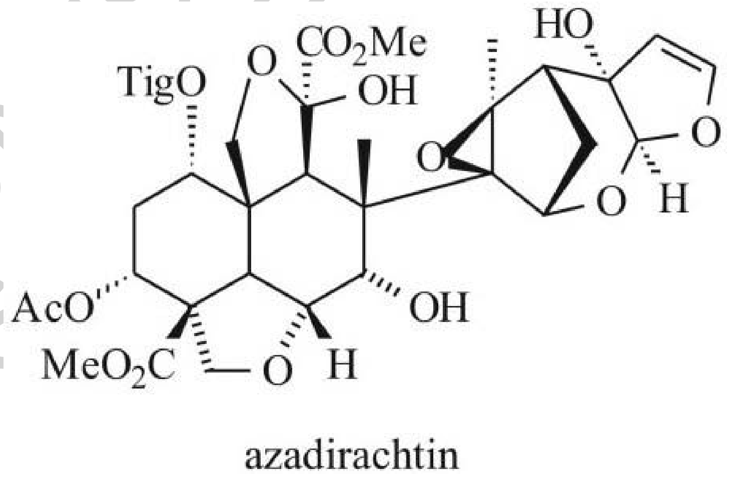

Figure 1: Structure of Azadirachtin

2) Harrisonin. This compound was isolated from leaves of *Harrisonia abyssinica*, a shrub widely used in East African folk for treatment of bubonic plague, hemorrhoids, snake bite, etc. The antifeedant activity against *Spodoptera exempta* is 20 ppm but it

also exhibits antibiotic activity against *Bacillus subtilis* at concentration of 5 μg/mL as well as cytotoxicity.

3) Polygodial, ugandensidial, warburganal and muzigadial. These chemicals have been found in the bark of the East African plants *Warburgia stuhlmanii* and *Warburgia ugandensis* and have shown highly potent antifeedant activity against *Spodoptera exempta* and *Spodoptera littoralis.* In addition, the latter two chemicals exhibit a broad antibiotic spectrum, as well as helicocidal activity against the schistosome-transmitting snails *Biomphalaria glabratus*, *Biomphalaria pfeifferi* (LD_{50} = 5 ppm within 24 h) and *Lymnaca natalensis* (LD_{50} = 5 ppm within 24 h). These compounds contain a dialdehyde moiety as a common feature that is essential for activity as demonstrated by structure-activity studies with the simplest compound, polygodial. These studies indicated that the activity was lost when one or both aldehydes were reduced to hydroxyl groups or oxidized to carboxyl groups. The yields of the four compounds from natural sources are not only low but also difficult to purify, so further studies on their potential applications must be relied on synthetic materials. These antifeedants taste spicy to the human tongue (Figure 2).

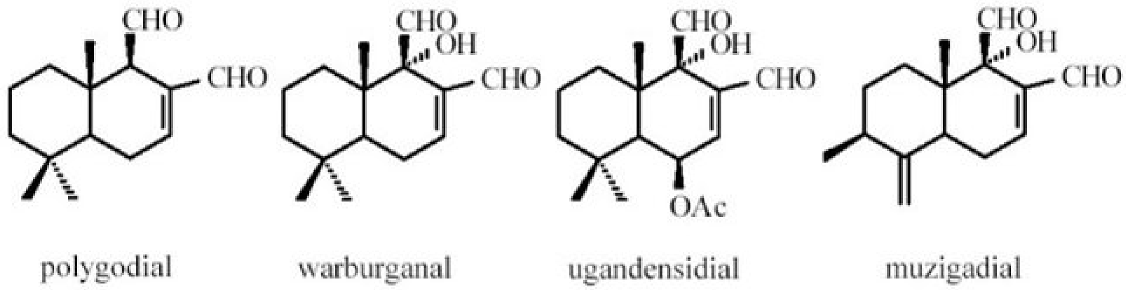

Figure 2: Structures of polygodial, warburganal, ugandensidial and muzigadial

4) Crotepoxide. This compound was isolated from leaves of *Croton macrostachys*, and exhibits tumor-inhibitory, antileukemic and antibiotic activity. The cytotoxicity and antifeedant activity are both dependent on the reaction between the nucleophilic receptor and electrophilic moiety of the active molecule (Figure 3).

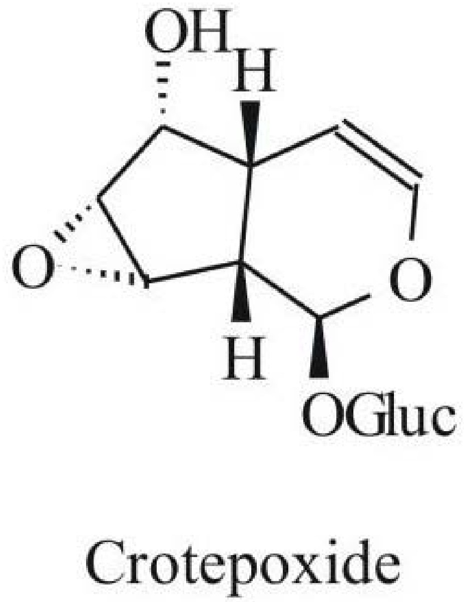

Figure 3: Structure of crotepoxide

The antifeedant compounds have been known for a number of years but are now finding a renewed interest. Electrophysiological studies with the sugar receptors of insects by Kubo and Nakanishi at Columbia University (N.Y.) show that the antifeedants act by irreversible blocking the sense of taste. The antifeedants tested to date are specific for certain insects, active at very low concentrations against a few insects, but generally inactive against the Southern armyworm *Spodoptera eridania*. These variable activities may serve as the basis for structure-activity relationships and mechanistic studies as well. The use of antifeedants has an important additional feature: the insect consumes little if any of the plant which implies a limit of damage. In this sense, pest control materials which are specific to insects and which affect metabolic pathways or cellular structures which are unique for insects are likely to be less toxic to mammals and thus may be superior as pesticides.

Antibiotics are also allomones because they are produced by microorganisms to inhibit the growth of other species of microorganisms. The chemical structures of antibiotics are quite varied and range from complex structures, like streptomycin, to simple structures like chloramphenicol.

Many arthropods (insects, spiders, millipedes, etc) make wide use of chemical defenses to deter predation. Quinones are one of the common types of defensive chemicals used by many different types of arthropods. Typical millipede quinones are 2-methoxy-3-methyl-*p*-benzoquinone, 2,3-dimethoxy-*p*-benzoquinone and 2,3-dimethoxy-*p*-benzoquinone. The African termites *Odontermes badius* and *Odontermes stercorivorus* secrete *p*-benzoquinone and the South American spider *Heteropachyloidellus robustus* uses 2,3-dimethyl-*p*-benzoquinone and 2,3,5-trimethyl-*p*-benzoquinone for defensive purposes. Other chemicals commonly used for defense are short chain aliphatic acids, aldehydes and ketones. As an example the defensive spray of the whipscorpion *Mastigoproctus giganteous* contains acetic acid and octanoic acid.

A number of studies have been done also on allomones of other animals. The sea hare *Aplysia brasiliana* is a large, slow gastropod molusk that has been shown to be distasteful to fish. This vulnerable animal owes its impalitability to a number of antifeedants found in its body tissue. Pacific sea whips (gorgonian corals) of the genus *Lophogorgonia* contain a neuromuscular toxin which possesses a remarkable cytotoxic, ichthyotoxic and antibacterial activity.

Not all allomones are used for defensive purposes. The floral scents of flowers that are used to attract insects for pollination are also allomones. The flowers of alfalfa contain simple terpenes (myrcene, limonene, linalool, ocimene) which are used by honeybees to locate the flowers. In this case, the allomones for the flowers serve as kairomones for the bees since they help the pollinator to find a source of nectar. A rather interesting allomonal interaction takes place between orchids of the genus *Ophrys* and certain solitary bees of the genus *Andrena*. The shape and color of the orchid's flower closely resembles the female bee whereas the flower's scent mimics the sex pheomone of the bees. Male bees trying to copulate with these flowers serve as their pollinators. The chemical that mimics the sex pheromone has been identified as (-)-δ-cadinene and it presumably smells similar to *trans*-farnesyl hexanoate and geranyl hexanoate, the two compounds produced by the female bee.

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Biographical Sketch

Angel Guerrero was born in Benaoján (Málaga, Spain) in 1947, received his BS degree from the University of Barcelona in 1968 and his PhD degree in Chemistry from the same University in 1973. He was appointed as Colaborador Cientifico of the Spanish National Research Council in 1974, and later promoted to Investigador Científico in 1987 and Profesor de Investigación in 2000. Currently he is the Director of the Department of Biological Organic Chemistry of the Institute of Chemical and Environmental Research in Barcelona. He is Fellow of the Royal Society of Chemistry and member of the International Society of Chemical Ecology and the Spanish Royal Society of Chemistry. He was visiting scientist at Cornell University in the period 1976-79, and later on at Stony Brook University, University of Chile, University of La Habana and Laboratoire des Médiateurs Chimiques at Versailles (France), among others. He is author or coauthor of more than 120 publications in renowned journals and has given 17 invited conferences and plenary lectures in domestic and foreign universities and congresses. His major research interest is focused on the chemistry and biological activity of insect pheromones, attractants and inhibitors for pest control.