Chemical Ecology

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Chemical ecology is the study of [naturally-occurring] chemicals involved in the interactions of living organisms. It focuses on the production of and response to signaling molecules (i.e. semiochemicals) and toxins. Chemical ecology is of particular importance among ants and other social insects – including bees, wasps, and termites – as a means of communication essential to social organization. In addition, this area of ecology deals with studies involving defensive chemicals which are utilized to deter potential predators, which may attack a wide variety of species. [Chemical ecology is interdisciplinary within the field of science where it combines research in chemistry, genetics, ecology, and environmental biology.]

This ecology related article is a stub.

Constitutive plant chemical defenses/Phytoanticipins

Plants produce primary and secondary metabolites. Unlike primary metabolites, which are used for growth or reproduction, the production of secondary metabolites is used for plant defense [1]. Secondary metabolites are continuously produced in the plant, independent of the presence of a threat, and therefore are constitutive chemical defenses. Three major groups are nitrogen compounds, phenolics, and terpenoids [1].

Nitrogen compounds

Alkaloids

Alkaloids are often used as a chemical defense in plants. Pyrrolizidine alkaloids (PAs) are mainly found in the following plant families: Echiteae, Asteraceae, Boraginaceae, Convolvulaceae, Orchidaceae and Leguminosae [2]. PAs are produced from putrescine in the N-oxide form in plant roots or shoots, or sometimes both [2]. PAs are toxic when ingested by generalist herbivores, but many specialist herbivores can digest this toxin by detoxifying and incorporating PAs in their tissues [2].

Caffeine is another alkaloid that is toxic to insects and fungi [1]. High levels of caffeine in coffee seedlings can result in allelopathy defense mechanisms against other plants that are competing for space and nutrients [1]. In coffee seedlings, allelopathy is seen through germination inhibition of other seeds in close vicinity [1].

Cyanogenic glucosides

Cyanogenic glucosides (CGs) are another nitrogen chemical defense used in plants. CGs are used against herbivores because of their bitter taste and their ability to release toxic hydrogen cyanide. They also induce the release of ketones or aldehydes. These chemicals are stored in vacuoles and when the cellular structure is disrupted, CGs react with degrading enzymes that release toxic hydrogen cyanide [3]. The release is stimulated by tissue disruption, such as an animal feeding on a plant [3]. Similar to pyrrolizidine alkaloids, specialist herbivores have evolved a mechanism to ingest CGs without harming themselves. Specialist herbivores have the ability to metabolize CGs and sequester them to use as their own defense mechanism against predators [3].

Phenolics

Phenolics

Phenolics are produced by the shikimic acid and malonic acid pathways in plants. Anthocyanins are water-soluble flavanoids. Flavanoids are one of the largest classes of phenolics [1]. They protect foliage against ultraviolet radiation and are also responsible for vibrant colours in many plants [1].

Tannins

Tannins are also water-soluble flavanoids and are stored in vacuoles of plant cells. Once a herbivore ingests a plant containing tannins, these toxic compounds bind to its salivary proteins and digestive enzymes (e.g. trypsin and chymotrypsin) resulting in protein inactivation [1]. Inhibition of digestive enzymes can cause failure of weight gain, eventually leading to herbivore death [1].

Lignin

Lignin, composed of hundreds or thousands of phenolic monomers, is found in the cell wall of plant cells and is a primary component of wood [1]. Lignin is insoluble, rigid and practically indigestible, therefore acting as an excellent physical barrier against herbivore and pathogen attacks [1].

Terpenoids

Terpenoids are found in all plants and are the largest class of secondary metabolites. The number of isoprene units used to synthesize them classifies terpenoids: two isoprene units in monoterpenoids, sesquiterpenoids with three units, and six units in triterpenoids.

Monoterpenoids and *sesquiterpenoids*

Monoterpenoids and sesquiterpenoids are the main components of essential oils, volatile compounds that contribute to the scent plants produce [1]. Essential oils are often toxic and help protect the plant against fungal or bacterial attacks [1]. Pyrethins are one example of monoterpenoid esters synthesized in chrysanthemum plants. Pyrethins act as insect neurotoxins and have been commercialized into insecticides through the analogue, pyrethroids [1].

Triterpenoids

Triterpenoids (e.g. cardiac glycosides) are not only toxic to insect herbivores, but also vertebrate herbivores, including humans. Cardiac glycosides can cause heart attacks if ingested in high doses. Contrastingly, some herbivores have learned to use triterpenoids for their benefit [1]. For example, Monarch butterfly caterpillars feed on milkweed containing high levels of triterpenoids. The caterpillars sequester cardenoloids, a type of triterpenoids, and then become highly poisonous to their predators once they morph into butterflies [1].

Saponins

Saponins are glycosylated triterpenoids found in cell membranes of many plants and give detergent properties, part hydrophobic and part hydrophilic [1]. These triterpenoids disrupt the cell membrane of the invading fungal pathogens [1].

Induced plant chemical defenses/Phytoalexins

Phytoalexins

Phytoalexins are isoflavonoids with antibiotic and antifungal characteristics produced in response to a pathogen attack [1]. An example is rishitin produced by tomatoes and potatoes against fungi such as *Phytophthora spp.,* known as infectious water moulds [1].

Furanocoumarins

Furanocoumarins are phenolic compounds produced as a result of herbivore or pathogen attack [1]. They are activated by UV light and integrate themselves into DNA, resulting in cell death of the herbivore [1].

Animal Chemical Defense

Animals, similarly to plants, use chemicals and toxins to defend themselves from predators. They can either synthesize the chemicals, or they can accumulate the toxins from food that they eat.

Synthesized

Puffer fish produce a very deadly toxin called Tetrodotoxin (TTX). These fish are slow swimmers and therefore adapted a behavior to protect themselves against predators. They engulf water and blow themselves up into a round ball, making it difficult to be eaten. The sharp spines make it an even less appealing meal, along with the fact that most produce the toxin TTX. TTX blocks voltage-gated sodium channels in the plasma membrane of cells. The TTX-producing bacteria, *Bacillus horkoshii*, live in the liver of puffer fish, making it possible for the toxin to thrive in their body whilst not destroying the fish [4].

Although many animals produce defense chemicals, not all of them are lethal or toxic. For example, an octopus squirts out ink that visually impairs its predators so that the octopus can make a quick escape. The ink is also thought to reduce the olfactory abilities of their predators, such as sharks, again, giving them time to escape [5]. Skunks also produce chemicals that are not actually toxic to their victims, but a malodorous secretion that is sprayed from the anal sac [6].

Most toxin-producing animals are brightly coloured or have obvious visual characteristics to deter predators. Puffer fish have their sharp spines, skunks have a white stripe down their back and some toxic octopi have bright blue rings. These adaptive visual characteristics that link a warning signal to a chemical defense towards predators is known as aposematism [7]. The evolution of aposematism is still under study. Bright colours attract predators to prey, so how these organisms evolved their warning signals from cryptic populations is puzzling [8].

Accumulated

Animals that accumulate toxins in their system are also aposematic. Earlier it was discussed how Monarch butterfly caterpillars accumulate toxins from plants and then when they evolve into a butterfly, they become poisonous to their predators. Their bright orange colours keep predators at bay, a trait sometimes mimicked by other organisms as a defense mechanism [1].

A well-known amphibian that accumulates toxins is the strawberry poison frog. Most aposematic poison frogs are ant specialists, from which they accumulate defensive alkaloids [7]. The strawberry poisonous frog, *Oophaga pumilio*, has 2 populations: cryptic and aposematic [9]. The brightly coloured aposematic frog becomes toxic by sequestering alkaloid compounds from ants and mites and is a more active and wider-foraging species. The cryptic frog is a non-toxic species and defends itself by hiding from its predator. The different behaviours of the two populations demonstrate avoidance learning among predators for cryptic frogs [9].

Pheromones

Sex Pheromones

Organisms often use chemicals in mate selection and attraction. These chemicals are invisible odours referred to as pheromones [10]. Pheromones are released into the environment by an organism, which then elicits a response from the receiving organism. Pheromones can be detected over great distances and are commonly studied in insects. Although this detection is significant, variation in the chemical composition and chemical release rates produce variation in mate response [11].

Research in the field of chemical ecology and pheromones blossomed in 1959 with the discovery of the pheromone Bombykol in domesticated silkworm *Bombyx mori*. The most common sex attractants are composed of mevalogenins and acetogenins [10]. In many moth and cockroach species, the most potent pheromones are known as E, E-dodecenyl acetate isomers [10]. Production of these pheromones relies greatly on hormones, such as juvenile hormone and ecdysteroids.

Sex Pheromone Detection

Laboratory tools used to identify pheromones have rapidly progressed since the 1960's and one of the most specific tools used is the electroantennogram (EAG). The EAG uses the male antennae as a very precise detector of active materials, such as pheromones, and the response is measured using an oscilloscope [10]. The oscilloscope measures the amplitude of response from the receiving organism, a male insect, via correlation with the insect's nerve impulses [10]. Pheromones have been effectively identified using EAG and continue to be identified using other developing technologies.

Trail Pheromones

Social insects use pheromones to maintain a high level of organization within their colony [12]. Many insects that are essentially wingless use terrestrial odour trails to locate a food source or a nesting site [12]. Ants (*Formicidae*) have been most commonly studied by researchers with regards to the chemical trail system. When an ant finds a food source, it feeds and then upon its return to the colony, the ant deposits chemical cues along a fairly narrow and accurate trail. The other worker ants become excited when the ant returns to the colony and they make their way to the food source, also depositing more chemical cues upon returning. Once the food source is exhausted, the ants no longer leave chemical cues. Thus, the old chemicals slowly become dissipated [12]. Ant pheromones are released from glandular organs such as the hindgut or the rectal gland. The first ant trail chemical discovered was methyl 4-methylpyrrole-2-carboxylate from the poison gland by Sonnet (1972) using a bioassay.

Territorial Pheromones

Territoriality is the act of defending a territory with a valuable source such as food or mates if the benefits outweigh the fitness costs. Territoriality is seen in most red-backed salamanders, which live under rocks and logs on eastern North American forest floors [13]. Male salamanders show aggressive behaviour towards other unfamiliar males. This aggression is signaled through pheromones that are found in the fecal pellets of invading males. The pheromones of intruders are detected through the vomeronasal organ of the male salamander, as they are known to have a very keen olfactory system [13]. The male salamander is not as aggressive towards females, which indicates strong territoriality for acquisition and protection of mates [13].

Alarm Pheromones

Alarm pheromones are important especially to soil organisms that live in a microorganism- and fungi-enriched environment. The orbatid mite, whose habitat is in the soil, releases alarm chemicals from the exocrine oil gland, the aromatic, 2-hydroxy-6-methyl-benzaldehyde (2,6-HMBD), along with terpenes and hydrocarbons. The pheromone is released to provide warning of conspecifics and as allomonal defense against predator species such as the scydmaenid beetle [14]. In an experiment where the oil glands were removed, predators quickly approached and attacked the mites. When the oil glands were present, predators kept their distance from the control mites. The pheromone was extracted from the mites and proven to act as an “alarm” cue towards predators, fending them off and in turn increasing the fitness of the mites [15]. Mite pheromone secretion also serves as a protecting agent against fungi.

Kin Recognition

Many organisms also use chemical cues to discriminate between kin and non-kin. Kin recognition is used to identify kin, remove potential intruders and use chemical cues to locate their colony. Kin recognition is also used to prevent inbreeding within colonies.

The pheromone of kin recognition has been extensively studied in social insects. In ant colonies, cuticular hydrocarbons (CHCs) are used as recognition cues to recognize members of their own colony and avoid members containing CHCs belonging to other colonies [16]. However, ant parasitic species have developed strategies to parasitize ant nests by enveloping themselves in a colony's CHCs. A parasite can initially enter a colony nest odourless and then slowly begin to mimic and integrate the colony scent that allows it to co-exist with the ant colony. Once familiar within the colony, the parasite begins to kill the colony by consuming the ants.

Colony recognition depends on genetics, as well as the environment. For example, honey bee colonies can differentiate between full and half siblings. Honey bees attack half-siblings as opposed to feeding and grooming full-siblings [17]. This type of recognition allows for a more efficient colony by maximizing altruism.

Lemurs use olfactory cues to discriminate between conspecifics and heterospecifics. Based on swab samples from scrotal and labial glands of lemurs, lemurs are able to discriminate between relatives and avoid genetically similar relatives to prevent inbreeding, increasing offspring fitness [18].

Humans

Chemical ecology is ever-present in human biology, whether it is defensive, for homeostasis or the selection of mates.

Defense

Scents on the human skin that are odourless to humans are often volatile to other organisms such as mosquitoes. Different composition of skin microbiota has differing attractiveness to mosquitoes and therefore leads to variation in probability of being bitten [19]. Higher levels of specific volatile compounds decrease the attractiveness of humans to mosquitoes and therefore may act as a defense mechanism. Future studies plan to inhibit microbial production of human odour or manipulate the composition of skin microbiota, which can reduce a person's attractiveness and in turn reduce their chance of contracting a disease, such as malaria [19].

Homeostasis

Humans are a very complex species made up of various biological systems that must coordinate with one another in order to maintain homeostasis. Homeostasis is defined as the regulation and maintenance of internal balance, often regulated by chemicals. For example, glycerophospholipids (found in the cell membrane) homeostasis in a mammalian cell is maintained through the coordination of synthesis, remodeling, degradation and intracellular transport [20]. Chemicals also play a large homeostatic role in the human digestive system. For example, leptin secreted by adipocytes suppresses hunger and helps control the size of the meal. People that cannot produce or recognize leptin do not feel satiation, which often leads to obesity [21].

Mate selection

Chemical ecology plays a major role in mate selection among humans. Dissimilar Major Histocompatibility Complex (MHC) genes are preferred in a mate because it results in heterogeneous MHC loci in offspring, which create a stronger immune response to pathogens [22]. Females naturally prefer the scent (chemical odour) of mates with dissimilar MHC loci, whereas females that are on a contraceptive pill (birth control) do not show a MHC-dissimilar male preference [22]. Furthermore, a study showed that African populations do not show significant preference to MHC-dissimilar mates, but it is hypothesized that pathogen-resistant MHC alleles have stronger selection than MHC-dissimilar alleles since these populations have higher pathogen pressure [22].

Chemical Ecology and Economics

The moth Lobesia botrana feeds on grapes, especially in large parts of Europe where it has caused devastating effects to vineyards [23]. Many insecticides have been used in the past, but are gradually being replaced by treatments that are more selective and less hazardous to human health. *L. botrana* females have a main pheromone compound known as (E, Z)-7,9-dodecadienyl acetate which has shown to elicit a strong attraction from the male counterpart. Advanced studies of this pheromone and mating strategies of *L. botrana* have led scientists to create a pheromone-mediated technique used to control the moth population. This technique is called mating disruption (MD). In mating disruption, artificial sex pheromones that are precise imitations of the real sex pheromones, are created by scientists and used in crop fields such as vineyards. The artificial pheromones mask the naturally produced pheromones, confusing the males and disrupting their ability to locate the females, and thus failing to reproduce. This eventually kills off the infesting population in a way that does not harm the surrounding environment [23].

The use of pheromones in pest management is currently a growing field of research worldwide.

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