8.04
Pheromones

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8.04.1 INTRODUCTION

Apart from optical, acoustic, and tactile stimuli, living organisms use chemical cues for the transmission of information. To transfer a message, all these channels may be used simultaneously or in distinct sequences, according to a specific hierarchy. Chemotaxis is a general archaic principle, and a wide range of living beings, from microorganisms to primates are capable of releasing chemical signals ("semiochemicals") which are used in intra- and interspecific communication.

The importance of the "chemical channel" and its role in communication depend on the development and use of alternative mechanisms. Humans appear to base communication primarily on sound and vision. In contrast, odor communication seems to be particularly important in insects; these relatively small living beings, who have to take their bearings in a spacious environment, have developed a multitude of glands for the production and release of chemical signals.[1]

Chemical signaling obviously evolved several times and for different reasons. The development of cell-aggregating compounds and the establishment of recognition substances appear instrumental to the formation of multicellular organisms; compounds used for communication within such cell aggregations may be regarded as antecedents of hormones and neurotransmitters, etc.

Inter- and intraspecific chemical defense in host–parasite interactions or in the struggle for living space among animals, plants, and microorganisms includes a broad spectrum of compounds which range from behavior-mediating deterrents or irritants to physiologically active compounds such as growth inhibitors, toxins, and antibiotics. Defense compounds are mostly used against several species and are often produced in large amounts.

Coevolution of plants and herbivores may form a special basis for the origin of systems of chemical communication.[2–4] Food constituents which attract both sexes will cause the discovery of sexual partners at places where food is found. Mimicking such signals through the storage and release of compounds by animals with the aim of attracting or deterring others will lead to the experience that metabolites of food and/or host compounds (or appropriate imitations thereof) may be advantageously used to specify a chemical message and thus facilitate its decoding by the receiver. In fact, striking similarities between volatiles from animals and plants point to coevolutionary processes in the relation between herbivores and their host plants.[5]

While the secretion of compounds which were simply sequestered from the environment or which represent products of primary transformations provides information about the quality of a food source or a potential habitat, endogenously produced semiochemicals merely describe the physiological state of the emitter.

According to their mode of action, semiochemicals which are biosynthesized by the emitter have been classified as intraspecifically active "pheromones"[6]—sub-groups "releaser" (causing a change of behavior in the receiver) and "primer" (causing a physiological impact on the receiver)—and as interspecifically active "allelochemicals"—sub-groups "kairomone" (beneficial for the receiver), "allomone" (beneficial for the emitter), and "synomone" (beneficial for the emitter and receiver)—see Figure 1. A review of this terminology was given by Nordlund.[7]

"Sex pheromones" of moths, produced by the females to attract males, are typical releasers. The "aggregation pheromones" of bark beetles represent another type of releaser: they are produced by one sex but attract both sexes and thus induce mass attack to overcome the host tree's resistance during colonization. "Trail pheromones" of ants, marking compounds, and alarm substances are further examples. Typical primers are compounds which are transmitted to suppress the development of ovaries in the receiver, to accelerate puberty, block pregnancy, or synchronize estrus. Whereas kairomones are predominantly used in host selection and prey location by interspecifics, allomones represent the whole spectrum of compounds which are used for camouflage and for defense in its widest sense, while synomones play a major role in symbiosis.

Although the above terminology basically represents a useful system, the fact that the classification of semiochemicals is predominantly carried out according to their biological function may sometimes cause confusion. Predators of several bark beetle species locate their hosts by orienting towards their prey's pheromones:[8] concerning the above definitions, in this example the same compound is produced as an intraspecifically acting pheromone, and it is interspecifically "illegitimately" used as a kairomone. An intraspecific attractant (pheromone) may interspecifically act as a repellent

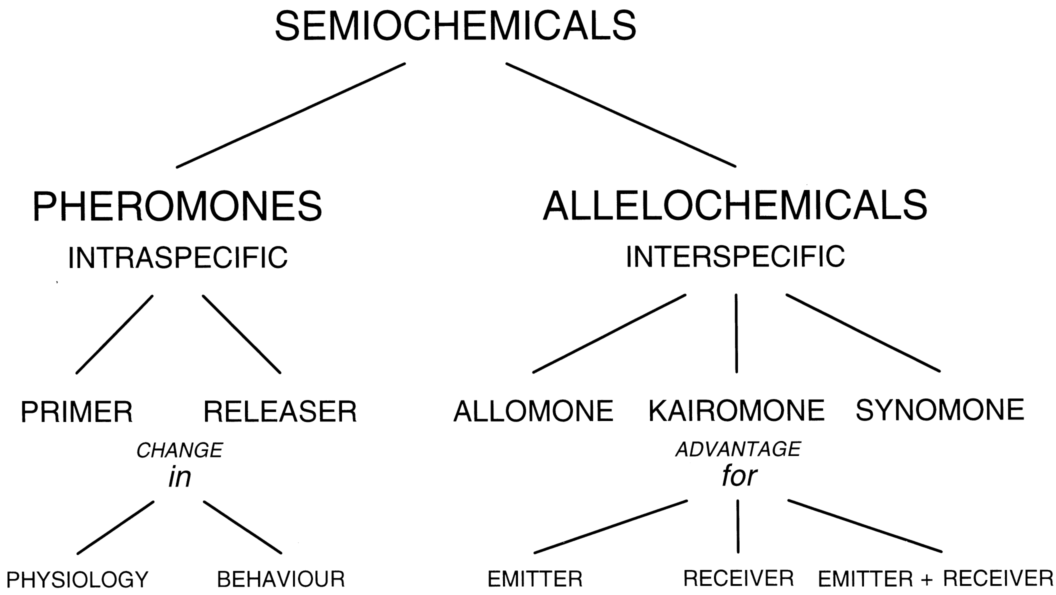

Figure 1 Nomenclature of semiochemicals.

(allomone) for a closely related species. A pheromone of a certain prey species may also be produced by a predator who deceitfully uses it as an allomone:[9] bolas spiders, *Mastophora cornigera*, attract their prey, male moths, by the release of (*Z*)-9-tetradecenyl acetate,[10] which is one of the most widespread sex pheromone components of female moths.[11] Moreover, a behavior-mediating releaser may at the same time act at a physiological level as a primer: 9-oxo-(*E*)-2-decenoic acid, which is secreted by the honey bee queen,[12] is a component of her pheromone blend, which forms the chemical basis of retinue response and suppresses the development of ovaries in the workers. The terminology for those semiochemicals which are simply sequestered from the environment or which are produced by associated microorganisms and thus not synthesized by the emitter is not well defined; the term "infochemicals" has been used.

Chemical communication over long distances requires specific signals which can be clearly distinguished as true "chemical messages," which are different from the "background noise" caused by odor compounds of the environment (see Figure 2). Generally, this is achieved on the basis of unique multicomponent mixtures of less specific compounds which are preferred over the use of species-specific substances, the production of which would require the (costly) development of species-specific enzymes. In many cases, several constituents of the bouquet act synergistically. The aggregation pheromone of the bark beetle, *Pityogenes chalcographus*, is represented by a mixture of 2-ethyl-1,6-dioxaspiro[4.4]nonane[13] and methyl (2*E*,4*Z*)-2,4-decadienoate.[14] The pure spiroacetal is only slightly active whereas the pure ester is not attractive at all, but a 95:5 mixture is highly attractive to both sexes. The spiroacetal is not species-specific as a bark beetle pheromone since it has also been identified as a plant volatile.[15] The above methyl ester is also a component of the secretion of the stink bug, *Euschistus*,[16] and, together with the corresponding ethyl ester, accounts for the aroma of Bartlett pears.[17] Whether the biosynthesis of spiroacetal and the ester proceeds via a common precursor remains to be investigated.

Enantiomeric composition of chiral compounds plays an important role in semiochemistry. Bark beetles which use chiral oxygenated monoterpenes in chemical communication may produce species-specific enantiomeric compositions and react with great sensitivity to non-natural proportions.[18] The female sex attractant of the Japanese beetle, *Popillia japonica*, is a chiral γ-lactone, and male response in these scarab beetles is significantly reduced by the presence of only 1% of the antipode.[19] In contrast, the bouquet which honey bee queens release to induce retinue response contains both enantiomers of 9-hydroxy-(*E*)-2-decenoic acid, and among other essential compounds the racemate is necessary to elicit this specific behavior.[20] Relations between enantiomeric composition and biological activity have been extensively discussed by Mori.[21–23]

Closely related species may produce bouquets which are chemically very similar. In such cases, species specificity of a signal may be based on quantitative differences (including enantiomeric proportions) in the secreted bouquet.