CHEMICAL SIGNALS IN THE SEA:
MARINE ALLELOCHEMICS AND EVOLUTION[1]

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ABSTRACT

Observations in chemical ecology suggest the coevolution of "natural products" of plants and the chemoreceptors of herbivorous insects. We have reviewed evidence which suggests that this coevolution extends back to the primordial protistans. Thus, the evolutionary pressure for the development of a chemosensory capability probably derived from the presence of metabolic products in the milieu. These products are considered to have been both cues to the location of prey and "membrane irritants" evolved in the initial phase of chemical protection. Sometime later this chemosensory capability provided several functions in the evolution of metazoans, i.e. the precursors of developmental signals, hormone function, and synaptic transmission.

We consider that most of the extant "natural products" of plants and marine invertebrates are protective allomones. A feature of allomone function that has been termed "antifeedant" or "feeding inhibitor" may represent the "cryptic odors" of Haldane. We provide evidence that the naphthoquinones with a juglone or naphthazarin structure have this activity. Octopus ink has a "cryptic odor" effect on moray eels. Marine Crustacea have, however, evolved an ability to perceive the orthoquinone precursors of the ink, a warning signal.

Evidence for an array of sex pheromones in a crab and a cycloid swimming pattern in a copepod that may enable it to follow a chemical gradient indicate the complexity of behavioral responses to chemical cues.

The earliest form of interaction between organisms was probably by means of chemical agents. This interaction involved both conflict and cooperation and its existence implies detection of these agents. Haldane (1955) first suggested that chemical communication is the most primitive form of communication, orginating with primordial unicellular organisms. He reasons that this primordial protistan communication was a necessary prelude to the evolution of metazoans and thus is a lineal predecessor of synaptic transmission and hormone reception. This early chemical communication may have evolved as an accessory to the active transport mechanism of the cell membrane or as a "membrane sensitivity" to metabolic by-products (Wynne-Edwards, 1962). That a

more detailed understanding of transducer physiology is central to further advances in neurobiology has been emphasized by Delbrück (1970). He considers the stimulus-response system represented by chemoreception or synaptic transmission to be homologous.

We wish to examine some of the recent concepts of chemical ecology and to present examples from the marine environment. Studies of chemoreception are providing evidence for the pervasive function of chemical signals in the environment. The "membrane sensitivity" concept of Wynne-Edwards may provide a clue to both the initial evolution of a transducer function and the continuing evolution of receptor sites of greater diversity and specificity. It is evident that this diversity has resulted from a continual interplay of chemical countermeasures and the development of neurosensory and behavioral adaptations to these agents.

ALLELOCHEMICS

At all levels of life we are finding examples of attack, defense, and behavioral response

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based on chemical agents. These interactions and the characterization of the chemical agents involved are the subject of the newly developing field of chemical ecology (Sondheimer and Simeone, 1970). Chemicals that are syntheized and released by one individual of a species to alter the behavior of other members of the species are termed pheromones. These signals range in their function from trail markers and territorial markers through alarm and defense signals to those which control caste structure in social insects and the sex pheromones that are calling signals and aphrodisiacs. Chemicals also have a wide range of interspecific interactions. A substance produced by one organism may influence the behavior of members of other species. A flower scent that enhances pollination is a well-known example. This field of chemical ecology has been termed allelochemics, and the chemical agents have been subdivided on the basis of function into allomones, which give adaptive advantage to the producing organism, and kairomones, which give adaptive advantage to the receiving organism (Whittaker and Feeny, 1971). The allomones include the repellents produced by many plants and animals, suppressants which inhibit competitors (e.g., fungal antibiotics), venoms, inductants (e.g., gall producing agents), and attractants (e.g., chemical lures). The kairomones include attractants (e.g., the scent of a prey), inductants (e.g., the factor that stimulates hyphal loop development in nematode-trapping fungi), danger signals (e.g., predator scents, secondary plant substances indicating toxicity), and stimulants (e.g., hormones that induce growth in the receiving organism).

The diverse natural products, coumarins, quinones, flavonoids, acetylenes, terpenoids, saponins, cardiac glycosides, alkaloids, thiols, and cyanogenic glycosides, which were long considered metabolic waste products, are now recognized to be allelochemic agents. Examination of the function of these natural products provides some insight into their evolution. Some of these compounds are toxic, some are chemical lures, others inhibit the growth of competitive plant species, but the bulk of these compounds probably function as "feeding inhibitors" of herbivores (Gilbert, Baker, and Norris, 1967; Munakata, 1970). The coevolution of butterflies and plants is considered by Ehrlich and Raven (1964). They emphasize the role of reciprocal selective responses during this evolution and conclude that "the plant-herbivore interface may be the major zone of interaction responsible for generating terrestrial organic diversity." The "accidental" evolution of a metabolic sequence resulting in the production of a noxious substance by a plant provided a selective survival advantage in the clone carrying this capability. Decreased predation by herbivores on those individuals containing the highest concentrations of the new substance resulted in genetic selection for increased synthesis and storage of the noxious substance. Such "protected" species experience an explosive increase because of their protection from contemporary phytophagous organisms. The first evolutionary response of the herbivores must have been the development of the capability to detect the compound, i.e. sensitive external chemoreceptors. Later evolutionary events led to the development in some individuals of a tolerance for the noxious substance. The herbivores which developed this tolerance then had access to a large food supply for which there was no competition. The ability to detect the substance then had an altered function, the feeding inhibitor was now a feeding stimulant. The present evidence of the repeated occurrence of this cycle is the existence of tightly coupled herbivorous insects and their host plants, presumably arising through coadaptation.

In 1955 Haldane, in a consideration of chemical communication and visual signals, wondered if cryptic odors had ever evolved. While most of the feeding inhibitors that have evolved are probably irritants, many may be cryptic odors. It is likely that the two activities may only differ in the membrane affected. The term irritant implies membranic sensitivity and, of those membranes of an organism in immediate contact with the environment, the chemosensory membranes are likely the most sensitive to chemical irritation. In an environment in which a major fraction of the information flow is chemical, any agent capable of disrupting the chemosensory organs of a predator would provide an ideal mechanism for "hiding" from that predator. Cryptic odors may be either "negative odors" altering, for protracted periods, the membrane potential of the dendrites and blocking their normal generator potential, or they may be the chemical equivalent of a

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"white noise," producing an "uncoded" array of spikes in the chemosensory neurons.

The best description of behavior suggesting a "cryptic odor" in the marine environment is that given by MacGinitie and MacGinitie (1968). The ink of an octopus is considered a "smoke screen"; however, it can also affect the olfactory sense. The MacGinities observed that after a moray eel swam through the ink cloud of an octopus it could no longer "recognize" an octopus. The moray eel apparently requires both visual and olfactory input for this recognition. They state, "We were surprised to find that the real effect of the ink of an octopus is to paralyze the olfactory sense of its enemies." The melanin of the ink is a polymer of oxidized L-DOPA. The polymerization proceeds through three orthoquinones, dopaquinone (6, Figure 1), dopachrome (7), and indole-5, 6-quinone (8). In the biosynthesis of melanin, this oxidation is catalyzed by polyphenyl oxidases; however, heavy metal ions can also catalyze the oxidation, and it can be readily demonstrated that the trace of heavy metal ions in seawater will rapidly convert L-DOPA to melanin. The octopus ink loses its potency with time, a factor that would indicate that the biological activity of the ink is due to the presence of the unstable monomer orthoquinones in the fresh ink (Kittredge, Takahashi, and Lindsey, unpublished data).

The observation of Gilbert et al. (1967) that juglone (5-hydroxy-1,4-naphthoquinone) (1, Figure 1) is a deterrent to feeding by the bark beetle, *Scolytus multistriatus*, suggested a similar function for the polyhydroxynaphthoquinones occurring in the echinoderms. These spinochromes are all derivatives of juglone (1) or naphthazarin (2). They occur as soluble salts in the tissues and may be present in considerable amounts in the larvae. They also occur as insoluble calcium salts in the spines and tests (Thompson, 1971). The echinoids have received the closest attention, but P. J. Scheuer and his group have demonstrated the presence of these compounds in the other four classes of this phylum—the holothurians, asteroids, ophiuroids, and crinoids (Singh, Moore, and Scheuer, 1967). They also demonstrated the presence of a substituted 2,5-benzoquinone (3) in the genus *Echinothrix* (Moore, Singh, and Scheuer, 1966). The crinoids are interesting in that they contain primarily a series of poly-hydroxyanthroquinones (e.g., rhodocomatulin,
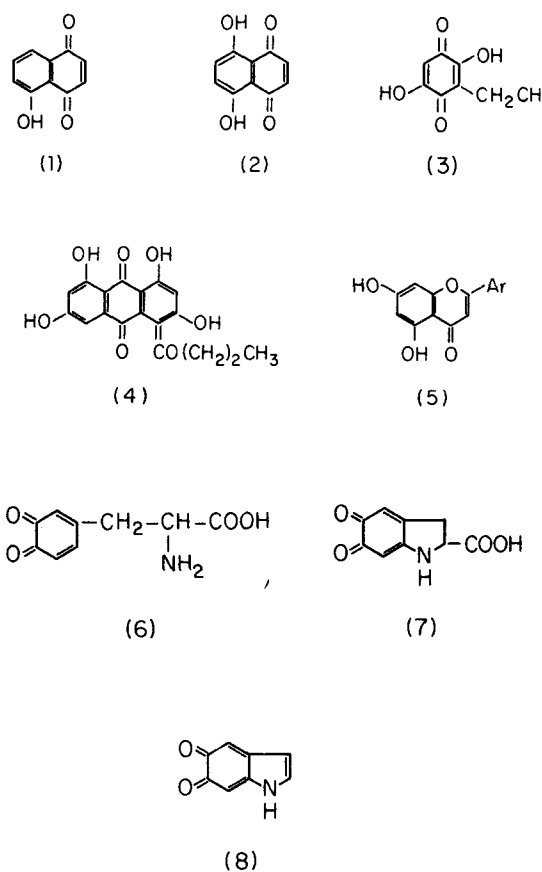

FIGURE 1.—Structures of compounds typical of those which may function as "cryptic odors." (1) juglone, (2) naphthazarin, (3) 2, 5-dihydroxy-3- ethylbenzoquinone, (4) rhodocomatulin, (5) flavone, (6) dopaquinone, (7) dopachrome, (8) indole-5,6-quinone.

4) (Sutherland and Wells, 1967; Powell, Sutherland, and Wells, 1967; Powell and Sutherland, 1967; Matsuno et al., 1972; Erdman and Thomson, 1972).

Utilizing the "feeding response" of the lined shore crab, *Pachygrapsus crassipes*, which consists of a rapid lateral movement of the mouthparts when presented with a feeding stimulus, we have bioassayed the "feeding inhibitor" activity of juglone and eight representative spinochromes. The "feeding stimulus" was a 20-μl aliquot of a 3-mM solution of taurine in seawater administered from a repeating syringe close to one of the antennules of the crab. Initially the crabs were immersed in a 1-μM solution of the naphthoquinone and tested for a feeding response. Five experimental and

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one control crab were utilized for each compound. No feeding responses were observed in any of the test crabs while all of the controls were positive. A second series of bioassays was designed to determine the onset of inhibition. The crabs were placed in seawater and stimulated with 20 μl aliquots of a solution of 3 mM taurine and 1 μM quinone. The stimulus was administered at 2 sec intervals to alternate antennules. Inhibition of the "feeding response" was observed at approximately 10 sec. The naphthazarin derivatives were apparently more potent than the juglone derivatives. We interpret these results as indicative of a "cryptic odor" function; the crabs cannot detect the feeding stimulant after a brief exposure to the quinone.

Many higher plants contain juglone or other hydroxynaphthoquinones or benzoquinones. These compounds also occur in fungi, lichens, pholangids, millipedes, and insects. 1,4-benzoquinones are the most common ingredient of insect defensive secretions and the 2,5-substituted 1,4-benzoquinones are characteristic of fungi. A similar "cryptic odor" function may be predicted for these compounds.

Norris (1969) compared the feeding deterrent activity of a number of substituted naphthoquinones. Juglone (1) and naphthazarin (2) were the most potent inhibitors. The apparent effectiveness of the hydroxy groups in the 5- or 5,8-positions in these naphthoquinones suggests an examination of the function of the major group of secondary plant metabolites, the flavones (5) (Harborne, 1972) which have a marked structural similarity.

Whittaker and Feeny (1971) predict "that research into the relations of multicellular marine algae and their consumers will reveal chemical defenses and responses paralleling those of higher plants and animals on land." The most likely candidates to fulfill this prediction are the highly halogenated hydrocarbons that are synthesized by algae and stored in the tissues of the herbivorous gastropod, *Aplysia californica* (Faulkner and Stallard, 1973; Faulkner et al., 1973). We would add to the prediction of Whittaker and Feeny that research into the relations of many marine invertebrates and their predators may reveal allomones. Some of the "natural products" of marine invertebrates that have been recently characterized and that may have this function are the halogenated antibiotics that have been isolated

from sponges (Sharma, Vig, and Burkholder, 1970; Fattorusso, Minale, and Sodano, 1972; Moody et al., 1972; Anderson and Faulkner, 1973). Steroid saponins that are toxicants or irritants have been characterized from holothuroids and starfish (Yasumoto, Nakamura, and Hashimoto, 1967; Tursch et al., 1967; Roller et al., 1969; Tursch, Cloetens, and Djerassi, 1970; Turner, Smith, and Mackie, 1971).

We recall a simple demonstration by the late C. F. A. Pantin of the sensitive chemosensory capability of sea anemones for saponin. The nematocysts of sea anemones require both a mechanical and a chemical stimulus for discharge. One can brush the surface of a sea anemone's tentacles with a clean glass rod without effecting any discharges. If, however the glass rod is first dipped into a dilute saponin solution, a massive discharge is effected.

An observation by Clark (1921) suggests the existence of allomones in crinoids. He discusses the avoidance of comatulid crinoids by fish and suggests the activity of glands at the base of the tentacles. The comatulids are unique in containing both polyhydroxyanthroquinones and aromatic polyketides (Kent, Smith, and Sutherland, 1970; Smith and Sutherland, 1971).

MARINE KAIROMONES

As in the terrestrial environment, invertebrates utilize chemical cues to locate hosts or to warn of predators. Davenport (1966) demonstrated the response of commensal polynoid polychaetes to a "host factor" in the water draining from tanks containing the host species of starfish. In an electrophysiological analysis of the antennular chemoreceptors of two commensal shrimps, Ache and Case (1969) demonstrated the specificity of the response to "host water" from the specific hosts, *Haliotis* spp. and *Strongylocentrotus* spp.

Predatory starfish induce an escape response in a variety of molluscs (Feder, 1967), and these behavioral responses probably effectively reduce the predation on these species that can detect the predator (Feder, 1963). The active materials in extracts of the starfish *Marthasteria glacialis* and *Asterias rubens* which induce the escape response have been shown to be steroid saponins (Mackie, Lasker, and Grant, 1968).

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The threshold for response by the snail, *Buccinum undatum* is $0.2 - 0.4 \times 10^{-9}$ M (Mackie, 1970), and the structure of these steroid glycosides has been determined (Turner et al., 1971).

A behavioral bioassay of one of the ortho-quinones derived from L-DOPA, dopachrome, utilizing the feeding response of the lined shore crab *Pachygrapsus crassipes* indicated that this quinone might also be a "cryptic odor." Electrophysiological studies, however, demonstrated that these results were misleading. Utilizing a preparation of the dactyl chemoreceptors of the spiny lobster *Panulirus interruptus*, we detected chemoreceptors for this quinone that were about a hundred times as sensitive as the general amino acid receptors in this preparation (Figure 2). While we have not explored the

range of specificity of these receptors, the results suggest that these crustaceans, the natural prey of the octopus, have evolved a mechanism for detecting the presence of the predator. Our results with the bioassay likely reflect a priority of responses to the two chemical stimuli (Kittredge, Takahashi, and Lindsey, unpublished data).

PHEROMONES

Unicellular chemical communication, analogous to Haldane's primordial protistan communication, is evident in the conjugation of ciliates. The microconjugant of a peritrichous ciliate, which is free swimming, can identify the macroconjugant, which is sessile, by chemicals released by the latter. Although evidence for
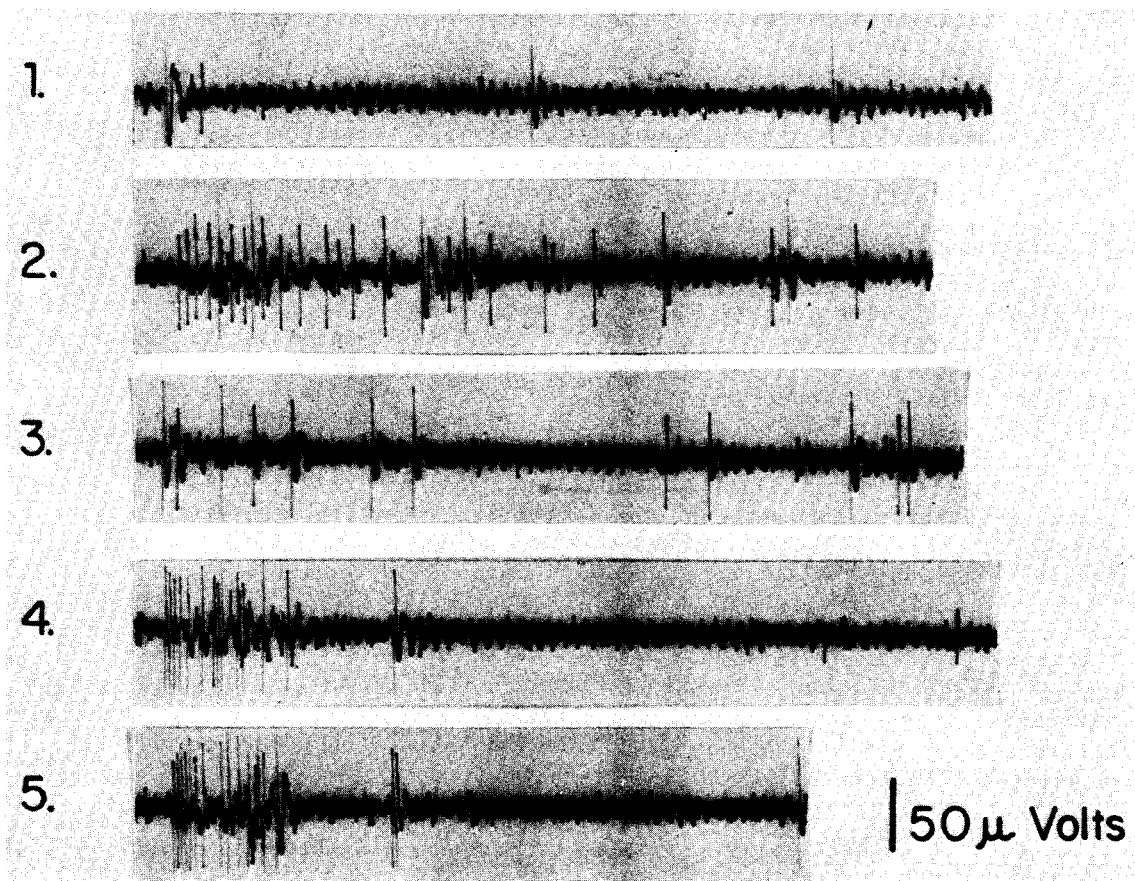

FIGURE 2.—Electrophysiological recordings from the dactyl chemoreceptors of a spiny lobster, *Panulirus interruptus*. (1) Seawater blank, (2) 10^{-5} M dopachrome in seawater, (3) Persisting spikes in dopachrome receptors (continuation of 2), (4) 10^{-3} M taurine in seawater, (5) 10^{-3} M taurine after dopachrome and a seawater wash.

the presence of a large number of agents chemo-
tropic for male gametes exists (Machlis and
Rawitscher-Kunkel, 1963), only two have
been chemically characterized. Sirenin, the
active compound produced by the female
gametes of the water mold *Allomyces*, has been
isolated and characterized as an oxygenated
sesquiterpene (Machlis et al., 1966), and its
structure has been uniquely established
(Machlis, Nutting, and Rapoport, 1968). It is
active in attracting male gametes at 10^{-10}M.
The corresponding work from the marine field
resulted in the characterization of the active
substance released by the female gametes of
the brown alga *Ectocarpus siliculosus* as allo-
cis-1-(cycloheptadien -2', 5'-yl)-butene-1 (Müller
et al., 1971). The receptor sites on the male
algal gametes evidence a low level of specificity.
Many lower hydrocarbons, esters, alcohols,
and aldehydes, at higher concentrations, will
mimic the natural compounds in attracting
male gametes (Cook, Elvidge, and Bentley,
1951; Müller, 1968; Hlubucek et al., 1970).

Though many efforts to demonstrate a chemo-
tactic response by mammalian sperm to sub-
stances from eggs have yielded negative results,
such attraction does occur in marine forms.
Sperm of the thecate hydroids *Campanularia
flexuosa* and *C. calceolifera* respond to a sub-
stance issuing from the aperture of the female
gonangium. The response is species specific
(Miller, 1966). Observations by Dan (1950)
suggest the activity of a similar substance from
the eggs of the medusa *Spirocodan saltatrix*
on the sperm of this species. The first examples
of sperm chemotaxis in vertebrates are described
in papers on fertilization in the herring *Clupea*
by Yanagimachi (1957) and in the bitterling
Acheilognathus by Suzuki (1961).

The attraction of the amoeboid form of the
slime mold *Dictyostelium discoideum* during
the aggregation phase which results in the
formation of a multicellular "slug" represents
the best studied protistan communication. The
attractant is cyclic adenosine monophosphate
(Konijn et al., 1968; Barkley, 1969). Pulses of
cyclic AMP radiate out through the soil
moisture at 5 min intervals from the center of a
growing aggregation. The gradient and the
pulse nature of the signal are maintained by
each inward streaming amoeba. Each amoeba
secretes a phosphodiesterase to break down the
cyclic AMP and, on sensing a pulse of cyclic

AMP, emits its own pulse of cyclic AMP about
15 sec after receiving a signal (Cohen and
Robertson, 1971; Robertson, Drage, and Cohen,
1972). Bonner (1969) has indicated the likely
course of the evolution of this communication
in the social slime molds. Soil bacteria, the food
of the solitary predecessors of the slime mold
amoeba, secrete cyclic AMP. It is reasonable
to assume that a mechanism which initially
increased the feeding success of these amoebas
developed, due to selective pressure, the requi-
site high sensitivity of response to a chemical
signal necessary for aggregation. This capacity
then facilitated the evolution of the social
species. This is very close to Haldane's premise
of the evolution of chemical communication
prior to the evolution of metazoans. In further
support of Haldane's premise of the lineage of
hormones, after aggregation is complete
the "metazoan" slug phase migrates to the soil
surface and then certain cells differentiate into
stalk cells which will eventually support the
spore head. Cyclic AMP is apparently the
chemical signal for the developmental differ-
entiation of some cells into stalk cells (Bonner,
1970).

The recent rapid growth of our understanding
of pheromone communication in insects was
founded on half a century of acute biological
observations which implicated the existence of
chemical messengers. The isolation and
chemical characterizations of a growing number
of pheromones, and the concomitant behavioral
studies, have provided the basis for our
appreciation of the role of chemical communica-
tion in the life cycle of many species. Among the
many recent reviews are those of Beroza (1970)
and Jacobson (1972). Electrophysiological
investigations of chemoreception in insects
have demonstrated that the receptor cells may
be divided into two groups, either "specialists"
or "generalists" (Yamada, 1970). Among the
"specialists" are the pheromone receptors and
the receptors for specific secondary plant sub-
stances that act as phagostimulants (Schoon-
noven, 1968). While remarkable success has
been achieved in recording the response of
single receptor cells as well as the summed
receptor potential of all the antennal chemore-
ceptors (electroantennogram) these workers
have had to contend with a technical problem
inherent in studies with this material. Evalua-
tion of the response of a chemosensory organ

or a single cell is difficult when the stimulant must be presented in the gas phase. Each species of stimulant molecule must partition between the gas phase and an aqueous film. The active concentration at the receptor membrane is unknown. A study of the physiology of pheromone reception by aquatic organisms would avoid this limitation.

A survey of the literature reveals that, as in the field of entomology, there exists a broad basis of behavioral observations suggesting the role of chemical communication in the aquatic environment. These studies suggest that marine invertebrates are primarily dependent on chemoreception for information from their environment. The input is composed of a broad spectrum of chemical messages ranging from species specific pheromones eliciting stereospecific responses, e.g., mating behavior, epidemic spawning, aggregation, or alarm behavior, through those kairomones triggering metamorphosis or migration to the cues indicating the proximity of predators or prey.

The closest parallel to insect pheromone communication observed in marine organisms are the sex pheromones of marine crustacea. The first experimental demonstration of "chemical recognition" by marine crustacea is the description of the behavior of male copepods *(Labidocera aestiva)* by Parker (1902). In a series of elegantly simple experiments he demonstrated that "they [the females] probably give rise to some substance that serves as a scent for the males; in other words, the males are probably positively chemotropic toward the females." Moreover Parker noted that "they [the males] seldom pass near the tube without some characteristic reaction. Usually they made one or two quick circles as they swam by, or even a somersault-like motion; these were observed fifteen times when the females were in the tube, never when they were not." Lillelund and Lasker (1971) observed similar swimming behavior in male *Labidocera jollae.* Although *L. jollae* females swim in a seemingly random pattern with only occasionally looped excursions, the males frequently vary their random course of a few seconds duration by swimming in circles, covering a small area intensively. Of greater interest was the observation that rather than circles, the path of the males often resembled a curtate cycloid. The males occasionally progressed for several centimeters in this curtate

cycloid path (Figure 3). These observations, although obtained during feeding studies, suggest an important aspect of the physiology of pheromone response in small crustacea—the mechanism of sensing a chemical gradient. Crisp and Meadows (1962) have stated that, because of the small distance between the chemosensory organs of barnacle cyprid larvae, these larvae cannot detect a chemical gradient and thus
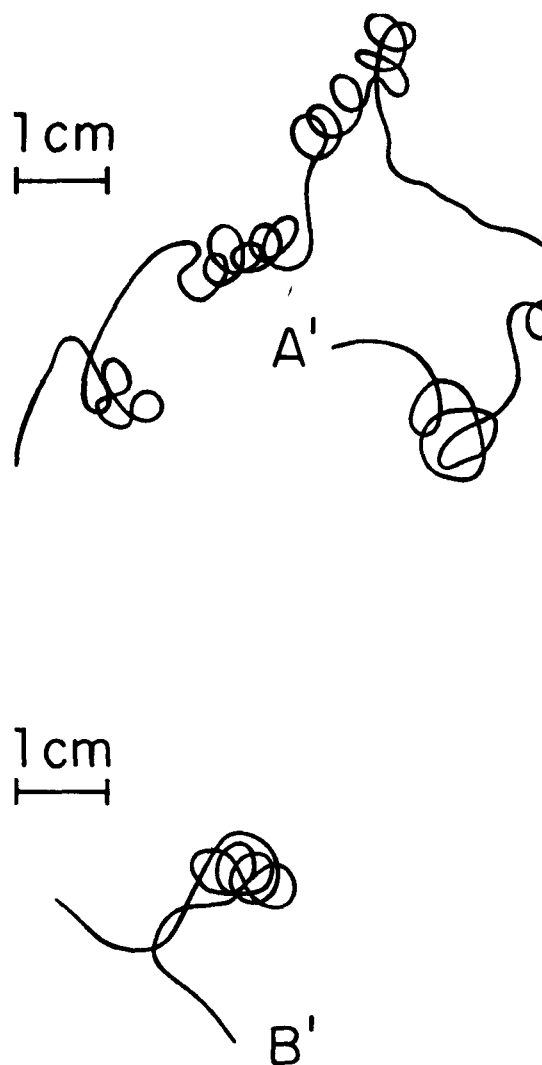

FIGURE 3.—Swimming behavior of a male copepod *Labidocera jollae.* A' and B' mark the termini of the tracings. The upper trace shows both an occasional circular swimming course, progression in a curtate cycloid course and "doubling back." The lower trace is an extreme example of the "doubling back" behavior.

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cannot exhibit chemotactic behavior. This reasoning has been applied to all small marine crustacea including copepods. From the above observations it is apparent that the reasoning of Crisp and Meadows is invalid for *Labidocera* and probably for other small crustacea. The critical dimension is the diameter of the circular course, not the dimensions of the organism. A circular swimming pattern in a concentration gradient of a stimulant would result in a sinusoidal variation in the signal intensity. Alteration of the radius of curvature of the swimming course in response to this sinusoidal input would result in cycloidal progression in the gradient. It appears from the observations of the behavior of male *L. jollae* in the feeding experiment that a threshold level of stimulant will trigger a circular swimming pattern, if this circular course results in the detection of a gradient, the circular course will become a curtate cycloid with the ratio of the major to the minor radius being a function of the intensity of the gradient. A frequent observation is a doubling back. If several progressions of the cycloid result in loss of the gradient signal (as must frequently occur in a medium in which the dimensions of the turbulent flow are of the same scale as the swimming pattern), the swimming plots indicate that the male *Labidocera* can effectively loop back through the area where the signal was initially detected (Figure 3). These observations indicate some power of spatial orientation and short term memory in *Labidocera*.

In crabs the male is attracted to the premolt female. During this attraction phase he may display a stance characterized by standing on the tips of his dactyls and elevating his body. He will seize the premolt female and place her below his body. He will protect her during the vulnerable molting period and they copulate immediately after molting. Ryan (1966) demonstrated pheromone communication in this interaction. Water from a tank containing a premolt female *Portunus sanguinolentus*, when added to a tank containing a male of this species, elicited the premolt stance. Evidence that the pheromone is released from the antennule glands was provided by sealing these glands and noting the absence of the stimulating factor.

We have examined this pheromone communication in the lined shore crab, *Pachygrapsus crassipes*. We isolated an active substance and found that it behaved chromatographically like the molting hormone, crustecdysone. Pure crustecdysone is active in stimulating all of the precopulatory behavior of male lined shore crabs from an early search behavior through the display stance to seizing the female. The threshold for stimulating the stance is 10^{-13} M (Kittredge, Terry, and Takahashi, 1971). Confirmation of the identification has been obtained by injecting tritiated crustecdysone into intermolt female Dungeness crabs *(Cancer magister)* and detecting its release as the females entered premolt. Recently we have detected the presence of two additional pheromones released by the female lined shore crabs. Compound A is released in addition to crustecdysone prior to molt. After molting compound A is no longer released into the water, but, if the female is held in isolation from male crabs, a second compound, B, is released. It is likely that the postmolt female has a different message to transmit.

Evolutionary biologists concerned with the inception of pheromone communication have long been puzzled by a dilemma. This chemical communication implies two new capabilities, that to synthesize a messenger compound and the ability to receive the message and translate it into a behavioral response. The improbability of the simultaneous occurrence of these two *de novo* events suggests a stepwise sequence. The observation that the molting hormone of crustacea can function as a sex pheromone indicates that the primordial Arthropoda, through an evolutionary sequence that resulted in structuring the receptor site for the hormones on chemosensory membranes, were able to initiate pheromonal communication (Kittredge and Takahashi, 1972).

SUMMARY

Evidence from the literature supports Haldane's premise that chemical communication is the most primitive form of communication and thus the lineal predecessor of synaptic transmission and hormone function. Transducers of environmental chemical information have likely evolved in response to the metabolic products released by their prey and by competitive organisms. This coevolution of "natural products" and the respective transducers has existed from the earliest metabolic product that happened to be a membrane irritant to the

present. We thus consider it likely that most of the "natural products," not only of terrestrial plants, but also of marine plants and invertebrates, function as allomones, kairomones, or pheromones. Faulkner and Anderson (In press) have provided a review of the chemistry of the "natural products" of marine organisms.

Conceptually, in such a "chemical environment" the most effective protection from a predator would be a "cryptic odor," an irritant that disrupts chemoreception. These cryptic odors may be released into the environment, as is the active component of octopus ink, they may exist in the epidermal tissues or glands where they would function at the inception of attack, or they may be contained in the eggs or larvae. Most sessile marine invertebrates reproduce by epidemic spawning, the simultaneous release of the gonadal products of an entire local population of a species. Most sessile marine invertebrates are also filter feeders. The prime advantage of epidemic spawning is the enhancement of fertilization. However, in the densely populated benthic environment, a heavy loss of eggs or larvae to filter feeders may occur. The presence of a "feeding inhibitor" in the eggs or larvae would reduce such losses. Reiswig (1970) reported that they observed epidemic spawning of the sponge *Neofibularia nolitangere* on a Jamaican reef. At the time they were measuring the water pumping rate of other sponges. When the epidemic spawning of *N. nolitangere* started, the pumping rate of the species under study, *Verongia* sp, abruptly decreased and remained negligible for 2 days. *N. nolitangere* is known to contain toxic substances.

The evidence for chemical cooperation, from gamones to sex pheromones, suggests a pattern of increasing complexity in the function of chemical cues. The behavioral response of even a "simple" crustacean to a chemical gradient appears to involve at least some short term "memory" or a type of "chemical-spatial" sense that we have not observed in such clear-cut form in any other organism.

The study of the chemical ecology of the marine environment is scarcely in its infancy. The chemical characterization of some of the intraspecific and interspecific messages in the sea and the physiology of their perception are challenges. Solutions to these paired problems will provide insights into the evolution of chemical transduction and perhaps expose a hierarchy of perception from membrane irritation to synaptic transmission.

ACKNOWLEDGMENTS

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