CHEMICAL DEFENSES OF ARTHROPODS

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To Ann

Preface

The motto of many arthropods may well be "I'll survive through natural products chemistry." The dawning has been slow, but it is now evident to both biologists and chemists that these invertebrates have a remarkable biosynthetic virtuosity when it comes to producing defensive compounds for utilization against their omnipresent enemies. In particular, research conducted in the last three decades has demonstrated that a wide variety of arthropods synthesize an incredible diversity of natural products in their exocrine glands. Many of these compounds are unique natural products that are often limited in their known arthropod distribution to a few species. In short, arthropods have already proved to be full of chemical surprises in spite of the fact that the defensive products of relatively few of these animals have been subjected to analytical scrutiny. It seems likely that the best is yet to come. While vigorous collaborative undertakings between chemists and biologists have made this insect chemical revolution possible, they have also exposed our lack of comprehension of the *modi operandi* of these defensive secretions. Furthermore, although we now know a considerable amount about the natural products chemistry of species in several arthropod taxa, for the most part we are at a loss to explain why particular species generate such idiosyncratic products in their defensive glands. We hope that this flagrant lacuna in our knowledge of arthropod chemical ecology will be filled by biologists who will pursue these invertebrates in the field, where their chemical defenses are utilized.

This volume was written in order to analyze the significant progress that has characterized the fairly recent and numerous developments in the study of arthropod chemical defenses. In addition, an attempt has been made to indicate major topics that can be fruitfully investigated in probing a multitude of questions that now characterize this rapidly expanding area of chemical ecology. In analyzing the subject of arthropod chemical defenses, I became convinced that these invertebrates are wondrous animals, a view that I hope I am at least moderately successful in imparting to both biologists and chemists.

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Murray S. Blum

Contents

Chapter **1**

The Many Faces of Defensive Secretions

Things are seldom what they seem. The defensive exudates of arthropods are no exception to this generalization. These secretions sometimes originate from unlikely sources and their known modes of action are often as multifarious as their compositions. Furthermore, the possessors of these highly adaptive discharges must often tolerate the presence of toxic compounds in these exudates which often cover a large area of the producer's body. Even at this early juncture in our comprehension of the *raison d'être* of arthropod defensive secretions, it is obvious that these animals have evolved an incredible variety of mechanisms for optimizing the effectiveness of their chemical defensive systems. It appears that many arthropods have admirably exploited their potential as natural product chemists as a means of deterring the ubiquitous and omnipresent predators with which they share their world.

I. VARIED SOURCES OF DEFENSIVE EXUDATES

Although the deterrent secretions of arthropods generally originate in exocrine glands which are readily classified as defensive organs (e.g., the poison glands of hymenopterans), other glandular and nonglandular discharges, which are normally identified with other functions, have also frequently been adapted to serve the role of highly effective defensive exudates. Furthermore, in some cases the products of exocrine glands are in admixture with small quantities of products which are obviously of nonexocrine origin. Enteric discharges are frequently produced by some insects and in addition to ingested food, these regurgitations may be fortified with blood (Cuénot, 1896b). Indeed, blood in itself is often discharged reflexively as a defensive vehicle, and in some cases it contains highly toxic compounds which have been synthesized *de novo* by the arthropod. Therefore, it seems imprudent at this time to generalize about the composition of these defensive secretions except to note that compounds of both intrinsic and extrinsic origin have been utilized by arthropods for chemical defense.

A. Salivary Secretions

The labial (salivary) glands of many arthropods have been converted into important defensive organs. In some cases the compounds synthesized in these glands possess no obvious digestive roles and it appears that these salivary products have been evolved to function primarily as allomonal or pheromonal agents.

1. Salivary Venoms ("Spitting")

Many groups of predatory arthropods (e.g., Reduviidae, Asilidae) utilize salivary venoms to immobilize their prey as one of the special functions of external digestion. These salivary secretions, which appear to be rich in digestive enzymes, can obviously function defensively against both invertebrate and vertebrate aggressors. In at least one case, the salivary venom can be forcibly spat for a considerable distance and this protein-rich secretion, aimed with great accuracy, may function admirably to deter vertebrate predators if it strikes sensitive tissues on the head.

The assassin bug *Platymeris rhadamanthus* reacts to disturbances with a stereotyped series of behavioral reactions which usually result in the forcible discharge of copious quantities of salivary venom (Edwards, 1962). Spitting does not require physical contact since sudden movements in the vicinity of the bug resulting in changes in incident light may trigger expectoration. An adult of *P. rhadamanthus* can eject its saliva up to a distance of 30 cm and a stimulated bug may spit once or twice or if highly excited, 15 successive times at a rate of 3–5 spits/second. A single series of salivary ejaculations may contain up to 2 mg of saliva containing from 9 to 20% solids. Rostral deflection enables the bug to achieve a "firing arc" of about 65° as the penultimate segment of the rostrum is deflected over and to one side of the body. Deflection of the terminal segment of the rostrum while each jet of saliva is ejaculated insures great accuracy in aiming the discharges toward the source of the disturbance (Edwards, 1962).

The saliva of *P. rhadamanthus* is enriched with a trypsin-like protease, hyaluronidase, and phospholipase (Edwards, 1961). Contact of this enzyme-rich solution with the eye or nose membranes of vertebrates results in intense local pain, vasodilation, and edema; these physiological reactions serve admirably to deter vertebrate predators such as reptiles, birds, and monkeys. The aposematic coloration of *P. rhadamanthus*, two blood red patches on the wings contrasting to jet black coloration elsewhere, should make this reduviid conspicuous to even the most hyperopic vertebrate predators. However, this spitting reduviid has a vertebrate parallel in *Naja nigricollis*, the spitting cobra, which can similarly eject a salivary venom at potential predators with great accuracy. The parallel evolution in insects and reptiles of the same defensive mechanism of spitting clearly emphasizes the probability that the same novel and effective systems to deter predators may be evolved in disparate taxa.

2. *Entspannungsschwimmen*

The aquatic bug *Velia capraii* has adapted its presumably proteinaceous saliva to effect a remarkable escape reaction. In response to a variety of stimuli, this hemipteran will discharge its saliva onto the water, a reaction that effectively lowers the surface tension of the water behind the bug. This enables *V. capraii* to rapidly propel itself across the water surface and thus puts considerable distance between itself and the source of the disturbance (Linsenmair and Jander, 1963). This escape reaction occurs after saliva is discharged posteriorly from the rostrum and the bug may be propelled 10–25 cm by the contracting water surface on which it is riding. *Entspannungsschwimmen* has been independently evolved by the staphylinids *Stenus bipunctatus* and *S. comma* but in this case the surface tension of the water is lowered by pygidial gland products rather than a salivary gland secretion. The exudate of the beetles arises from two pairs of pygidial glands and is primarily composed of three monoterpenes—isopipertenol, 1,8-cineole, and 6-methyl-5-hepten-2-one (Schildknecht, 1970) and a piperidine (Schildknecht *et al.*, 1975b, 1976). The monoterpenes are surface active and have been demonstrated to propel a surrogate "beetle" through the water in the same manner as *S. bipunctatus*. However, the main spreading agent is stenusine, *N*-ethyl-3-(2-methylbutyl)piperidine, a product from the larger pair of pygidial glands.

3. *Entangling Saliva*

Many syrphid larvae feed on aphids, a predatory habit that frequently produces confrontations with aggressive ants. The formicids guard their aphid wards assiduously, receiving in exchange droplets of honeydew which the latter provide upon appropriate tactile stimulation. Syrphid larvae, however, have evolved an effective defense against the ants that attempt to interfere with their daily aphid repast. When attacked by an ant, a syrphid larva (*Syrphus* sp.) arches its body in order to position its mouthparts on the body of the assailant. The larva then discharges a drop of viscous fluid onto the ant and the latter immediately releases its mandibular grip on the syrphid and attempts to remove the exudate which now entangles it (Eisner, 1972). The oral discharge originates in the salivary glands and almost certainly represents a proteinaceous "glue."

Although syrphid larvae have probably adapted the products of a digestive organ to function as a physical deterrent to predators, it remains to be seen whether this salivary secretion may be diluted enterically in order to provide digestive enzymes. It is possible that in the Arthropoda viscous salivary secretions may be utilized with some frequency as entangling agents *per se*. The salivary glands of many insect species are composed of paired lobes which often contain viscous proteinaceous constituents which, if secreted externally, could easily entangle small predators. Edwards (1962) reported that the salivary venom of the reduviid *Platymeris rhadamanthus* consisted of a viscid protein mixture which was diluted by the watery accessory gland secretion of the salivary apparatus during the discharge process. The external secretion of salivary proteins *in the absence of an aqueous diluent* may have provided arthropods with a readily available glue to be utilized against small predators.

4. *Salivary Gland Natural Products*

When restrained, adults of the earwig *Labidura riparia* discharge a pungent secretion from the mouth which is strongly repellent to ants (M. S. Blum, unpublished data, 1978). We have determined that this defensive material originates in the capacious salivary glands extending through the thorax and into the abdomen. These glands are usually turgid with a clear yellow secretion that contains several volatile compounds. The salivary secretion of *L. riparia* does not appear to be composed of a typical proteinaceous mixture and it is not unlikely that one of the primary functions of the gland is to serve as the source of a repellent exudate. Other examples of the salivary glands synthesizing volatile exocrine products indicate that these organs may not be an uncommon source of defensive natural products in the Arthropoda.

Many species of termites appear to utilize proteins and *p*-benzoquinones derived from the salivary glands as part of their defensive exudate. These protein–quinone mixtures react to form rubbery products which will be discussed in the next section.

Male bumblebees scent mark many territorial sites with cephalic secretions which are strongly odoriferous. These secretions consist of acyclic mono-, sesqui-, and diterpene alcohols and acetates, as well as straight chain alcohols, esters, aldehydes, and hydrocarbons (Calam, 1969; Kullenberg *et al.*, 1970; Svensson and Bergström, 1977). Some of these compounds are identical to well-known arthropod defensive compounds and it would be surprising if these aposematically colored insects did not secrete these cephalic products when molested. Recently, the source of these natural products has been established as the cephalic lobes of the salivary glands (Kullenberg *et al.*, 1973). These results further document the salivary glands of insects as a potentially rich source of natural products and emphasize the importance of establishing with certainty the morphological sources of defensive compounds identified in the cephalic secretions of arthropods.

B. Physical Deterrents of Exocrine Origin

The exudates from arthropod exocrine glands often become very viscous after being discharged and these secretions may immediately deter the would-be attacker especially if the discharge fouls its mouthparts. These arthropod "glues" appear to be derived from a variety of compounds which, in some cases, may react with the primary resinous constituent(s) in the exudate. In some cases adhesive secretions are normally present on parts of an arthropod's body and these viscid products appear to retain their properties for a considerable length of time. In addition to the viscous components, these exudates may also be enriched with low molecular-weight compounds that may increase the deterrency of the secretion or for that matter may possess other functions as well. Obviously, viscid exocrine secretions constitute a potpourri that, however, share at least one property that enables them to be grouped together, they are all of proved effectiveness as defensive secretions. Resinous secretions which are derived primarily from nonexocrine sources (e.g., blood) will be discussed separately.

1. *Spiders*

The scytodid *Scytodes thoracica* captures its prey by ejecting a viscid secretion and it has been suggested that this glue can also function as a defensive secretion (Monterosso, 1928). This suggestion has been confirmed by McAlister (1960) who examined the defensive behavior of the spider *S. intricata* in the presence of the scorpion *Centruroides vittatus*. After the scorpion had grasped the spider with a palp, the latter ejected a copious amount of secretion from its chelicerae toward the source of tactile disturbance. The scorpion's chelicerae, palps, and cephalathorax were bathed by the viscid secretion and the palp which had originally restrained the spider was glued to the substrate. Usually the sprayed scorpion displayed an immediate but awkward escape reaction, primarily because its legs were often glued together. Attempts by the irritated scorpions to sting the offending glue resulted in their telsons becoming entangled in the viscous secretion. The scytodids were none the worse for their brief encounters with the aggressive scorpions.

2. *Centipedes*

Viscous threads are discharged from the posterior legs of lithobiid centipedes; these sticky exudates effectively entangle predatory spiders and ants (Verhoeff, 1925). The viscid and proteinaceous secretions originating from ventral segmental glands of geophilid centipedes effectively deters small predators such as ants (Jones *et al.*, 1976a). In addition to entangling these insects, these secretions are highly repellent because of the presence of cyanogenic compounds.

3. *Millipedes*

Viscous secretions are discharged from the ozopores of millipedes in two unrelated families but in both cases volatile exocrine products play a major role in augmenting the deterrent efficacy of the exudates. When disturbed, the glomerid millipede *Glomeris marginata* coils itself into a ball of cuticular-plated armor in much the same manner as an armadillo. If prodded, the coiled diplopod discharges from middorsal glandular pores a viscous proteinaceous secretion which can both entangle and repel small arthropods. This exudate is fortified with two quinazolinone alkaloids (Y. C. Meinwald *et al.*, 1966; Schildknecht *et al.*, 1966c, 1967c) which are both toxic and distasteful. In combination with the proteinaceous glue, this secretion presents a formidable obstacle to predators.

The sticky whitish secretion of the polyzoniid millipede *Polyzonium*