LEPIDOPTERA AND PYRROLIZIDINE ALKALOIDS
Exemplification of Complexity in Chemical Ecology[1]

MICHAEL BOPPRÉ

Forstzoologisches Institut der Universität Freiburg
Fohrenbühl 27, D-7801 Stegen-Wittental
Federal Republic of Germany

Abstract—Pyrrolizidine alkaloids (PAs) are defensive secondary metabolites found in numerous plant groups. Various insects belonging to different orders have special requirements for these compounds and sequester them from such plants for their own defense and often as pheromone precursors. The fitness of these insects depends on PAs and, in some cases, PAs even act as regulators of androconial organ development. This article discusses selected behavioral, chemical, physiological, and phylogenetic aspects of insect–PA relationships, and raises questions about the complex interactions of the variety of PA-related adaptations as they occur among a diverse array of species. Although many superficial similarities are recognized, few generalizations can yet be drawn. However, insect–PA relationships not only exemplify basic features of chemical ecology but illustrate a multiplicity of aspects and adaptations, which we should expect to find in any thorough study of insect–plant relationship.

Key Words—Pyrrolizidine alkaloids, pharmacophagy, male pheromones, chemical defense, Lepidoptera, Danainae, Arctiidae, *Heliotropium, Senecio, Crotalaria*

INTRODUCTION

The large array of physiological, behavioral, chemical, and ecological phenomena involved in sequestration of secondary plant metabolites can, in practice, only be investigated in relatively few cases. Nonetheless, from this sample

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[1] Paper presented at the Symposium "Sequestration of Natural Products by Insects" during the 5th Annual Meeting of the International Society of Chemical Ecology, Athens, Georgia, June 24–27, 1988.

we hope to discover basic mechanisms—or even rules—governing chemically mediated interactions among organisms. The producers and consumers of pyrrolizidine alkaloids (PAs) appear to be well suited for such studies because they exhibit many features similar to those found in other systems of insect–plant relationships: on the one hand, PAs occur in a great variety of plant species and PAs are chemically distinct but quite diverse; on the other hand, various unrelated insects exhibit relationships to PA plants, and these are phenomenologically similar but nevertheless of different kinds. The polyphyletic development of both PA plants and the insect groups that exploit them enables us to undertake a comparative approach, leading to insights into evolutionary developments and processes. Furthermore, the associations of insects with PAs raise challenging questions for research into sensory physiology, sociobiology, biochemistry, and other fields peripheral to chemical ecology.

A significant and increasing amount of data on relationships between insects and plants containing pyrrolizidine alkaloids is now available. For example, we have learned that insects gather PAs not only from their primary host plants but also independently from nutrient uptake; insects store PAs for their protection against predators; and much is now known about PAs as precursors for male pheromones. Two examples suffice to illustrate the attraction of the subject: (1) Male milkweed butterflies (Danainae) visit withered PA-containing plants and extract PAs. These substances are required as precursors for biosynthesis of the quantitatively dominant pheromone component danaidone (Figure 1A) necessary for courtship success. In addition, males store PAs for their defense and also transfer significant amounts in the spermatophores, causing protection of
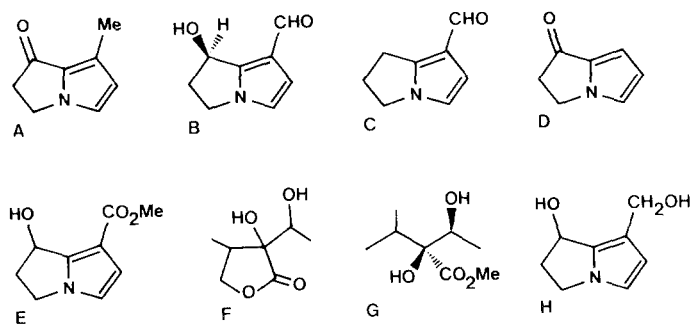

FIG. 1. Molecular structures of derivatives of pyrrolizidine alkaloids identified from androconial organs in Lepidoptera (see Table 4). A: danaidone, B: R-($-$)-hydroxydanaidal, C: danaidal, D: nordanaidone (S. Schulz, personal communication), E: methylhydroxydanaidoate, F: ithomiine lactone [2-hydroxy-2-(1-hydroxyethyl)-3-methyl-γ-butyrolactone]; methylviridiflorate (G) and the necine pyrrole (H) are probably intermediates. G shows relative configuration.

females and eggs. (2) Larvae of *Creatonotos* (Arctiidae) are polyphagous but PAs alone can elicit feeding behavior. Those individuals that have PAs are protected from predators, and males with PAs also use them as precursors for biosynthesis of hydroxydanaidal (Figure 1B), which is emitted by coremata and appears to bring about the formation of mating assemblages. Thus there is an individual variation in the pheromonal strength of the males that is directly related to the amount of PAs gathered (as in the danaines, but here the amount per adult male is fixed for life); furthermore, in *Creatonotos* the development in size of the pheromone disseminating apparatus is also controlled by the amount of PA, i.e., PAs serve as organ-specific morphogens.

Neat as these brief summaries may sound, and although there is considerably more knowledge available than I have mentioned, our understanding of these phenomena is nonetheless superficial. Many aspects have yet to be investigated and, although many of the details involved might seem rather subtle, they are basic to our understanding not only of the two examples mentioned above, but also with respect to other organisms that sequester PAs.

This article addresses the multiplicity of phenomena involved in insect–PA relationships from a chemoecological perspective, and draws attention to some of the gaps in our knowledge that are rarely emphasized. Thus in the following sections, selected aspects are highlighted without comprehensive treatment of the subject and the respective literature. [For details and references on insects and PAs see reviews by Boppré (1986), Schneider (1987), Eisner and Meinwald (1987).]

PYRROLIZIDINE ALKALOIDS

PAs are chemically defined as ester alkaloids composed of an amino alcohol (necine; originating from 1-hydroxymethyl-pyrrolizidine) and mono- or dicarboxylic acids (necic acids; often C_7–C_{10} oxygenated and highly branched acids (Figure 2). Thus, saturated and unsaturated PAs are known that are mono- or diesters or macrocyclic diesters. PAs often occur as *N*-oxides; free-base alkaloids and their water-soluble *N*-oxides readily interconvert. To date, about 200 structures have been characterized, but many more have yet to be identified. [For details and references on PA chemistry see reviews by Bull et al. (1968), Robins (1982), Wróbel (1985), Mattocks (1986).]

PLANTS CONTAINING PAs

Plant species belonging to more than 60 genera in a dozen or so families have been recognized to produce PAs as secondary compounds. PAs have been found most widely in species of *Senecio* (Asteraceae), *Heliotropium* (Boragi-
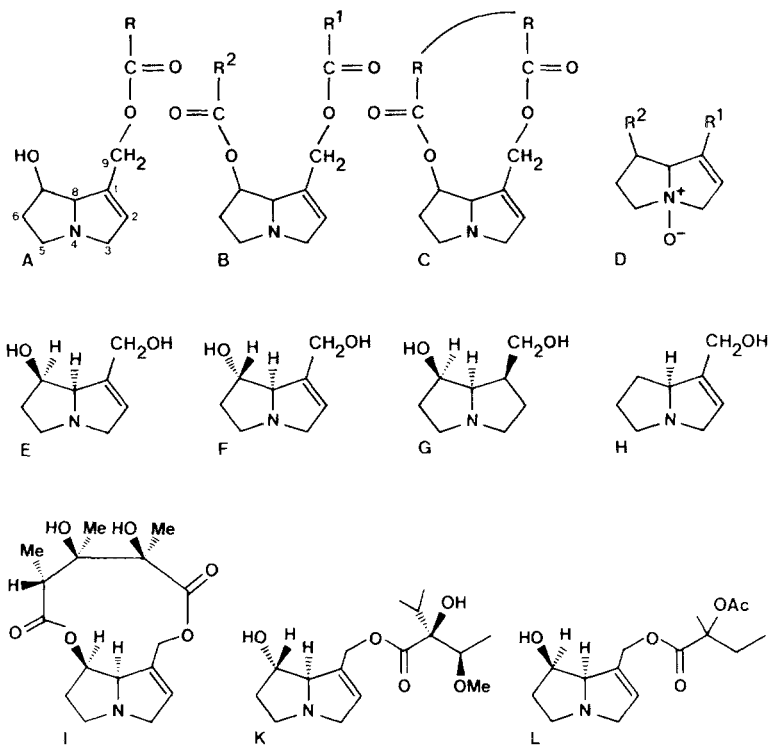
FIG. 2. General structure of pyrrolizidine alkaloids (A–C) and PA N-oxides (D) and molecular structures for examples of necine alcohols (E: retronecine; F: heliotridine; G: platynecine; H: supinidine) and of free bases (I: monocrotaline; K: heliotrine); L: the insect metabolite callimorphine. E–L show absolute configurations.

naceae), and *Crotalaria* (Fabaceae) (Smith and Culvenor, 1980), but these genera have been investigated much more thoroughly than others because of their importance for domestic animals and man. Their PAs usually consist of the necines retronecine and heliotridine (Figure 2E,F); retronecine appears as the most common amino alcohol in PAs.

Generally, a given plant species contains several PAs; such a set consists of PAs of similar structure, and these PAs tend to be characteristic of plant genera or even some higher groupings. Reported amounts of PAs are >5% (maximum: 17.99% dry weight in *Senecio riddellii*; Molyneux and Johnson, 1984) or as low as 0.001% of dry weight; a common figure is 0.1% or so. Considerable intraspecific variation also occurs (e.g., Johnson and Molyneux, 1985), involving both qualitative and quantitative composition as well as spatial

and temporal distribution of PAs, a result of the physiological state of the individual plant as well as of its environmental conditions.

Although we talk often about PA plants, from a chemoecological point of view they are anything but uniform. The (chemical) definition of PAs is quite broad, and our biological knowledge should forbid us to group all the different structures under one term; for convenience only, the general term is still employed. Provoked by the pathogenicity of (certain) PAs, an impressive amount of knowledge on PA chemistry and toxicology has been gathered, but ecological aspects have been relatively neglected. Most studies have focused solely on the identification of the molecular structures; thus for extraction and isolation of PAs standard techniques have been employed, which, on the one hand, usually involve dried plant material only and, on the other hand, carry the risk of chemical degradation (e.g., reduction of N-oxides; cf. Hartmann and Toppel, 1987) during the procedures.

Some valuable information is available on ecophysiological matters, but it is presently incomplete and too limited to permit an understanding of PA plants in a wide sense. Evidence from *Senecio* and *Crotalaria* favors the idea that N-oxides are the form by which PAs are synthesized, translocated, and accumulated, while seeds seem to contain free-base alkaloids exclusively (cf. Hartmann et al., 1988). Is this situation common to the entire spectrum of PA plants? Studies involving examples from a range of unrelated species and considering different physiological states are urgently required, since the physicochemical properties of free bases and N-oxides are quite different and must have different biological effects on insects in the context of perception, toxicity, degradation, solubility, and transportation. Further basic tasks include details on the occurrence of PAs in nectar, the changes in PAs when a plant is withering or drying, and the stability of PAs as well as their derivatives (see below).

PAs IN PLANTS—WHAT FOR?

The majority of known PAs cause serious diseases in domestic animals and man—the leading motive for most studies on PAs. In contrast to many other secondary plant metabolites, the noxious actions of PAs are not instantaneous but appear only after weeks or months of incubation and in an indirect way. In the vertebrate metabolism, unsaturated ester alkaloids (those with 1,2-dehydro-1-hydroxymethyl-pyrrolizidines) are converted into pyrroles (Figure 1H), which are responsible for hepatotoxic, mutagenic, oncogenic, and other deleterious effects. [For review and references on toxicological aspects see Bull et al. (1968), Mattocks (1986).] If PAs with other structures are harmless, what are their biological roles?

Although some domestic herbivores consume PA plants (particularly if there is shortage of other food), PAs actually protect their producers significantly from herbivory. Grazing animals usually avoid PA plants, apparently because of their deterrent taste; for humans, PAs taste bitter. One can speculate that it has to be a kind of gustatory "aversion receptor" that protects herbivores from uptake of PAs, i.e., from being poisoned. This receptor probably has low specificity, otherwise the great number of different PAs would not be explicable since one would have to expect selective pressure on the plants to synthesize PAs with less diverse structures. Is it a general "bitter receptor," with a wide reaction spectrum, i.e., does it sense other types of noxious compounds, too? If so, it might not have evolved as a response to the "invention" of PAs by plants but antedate this incident(s). Could we then propose that the (PA) plants have merely taken advantage of a sensory system generally present in animals? (See below on aversion in nonherbivorous vertebrates and insects.) Unfortunately, so far, this matter represents nothing but speculation.

To a great extent, PAs appear to protect plants from damage not only by vertebrates but also by insects. Comparatively few species are known to utilize PA plants as hosts, and the aversion receptor postulated above might be present in insects also: PA-contaminated but otherwise adequate food is rejected by locusts, many lepidopteran larvae, cockroaches, ants (Bernays and Chapman, 1977; Bentley et al., 1984; Boppré et al., in preparation)—even by species that naturally do not encounter PAs (e.g., *Periplaneta, Blatta*). PA-containing nectar is avoided by many nectar-foraging species, and insects storing PAs are protected from predators including invertebrates (see below). It must be emphasized, however, that we have no idea what would happen to an unadapted insect if it lacked the taste barrier and took up PAs. One cannot predict the physiological reactions of invertebrates from knowledge of the toxicology in vertebrate metabolism.

The undoubted protective role that PAs have for plants cannot explain the entire phenomenology of such compounds within the plant kingdom. Why do we find amounts of PAs that are much higher than required for deterring herbivores? For example, seeds of *Crotalaria* may contain as much as 5% PAs by dry weight. Of course, the reproductive organs may require the best protection possible, but the plant should not invest more energy in PA synthesis than needed. Toppel et al. (1988) have recently shown for *Crotalaria* that in the course of germination PAs are metabolized as a nitrogen source; the seedlings do not contain PAs at all. Thus, the secondary compounds are also relevant for primary metabolism, a fact that also can be inferred from the great variations observed in PA content of the plants (see below) but which by no means contradicts the role of PAs as defensive chemicals.

PA-ADAPTED INSECTS

Insects have selectively adapted to most of the defensive mechanisms of plants; a variety of species utilize PA plants as hosts, and yet others depend on PAs and gather them from plants independently of feeding. Not very many species have been investigated in detail. The following accounts focus on Lepidoptera and are further restricted to examples dealing with the Asteraceae, Boraginaceae, and Fabaceae, simply because other systems have hardly been looked at.

Considering the disjunct phylogeny of taxa making use of PA plants and the different types of PA insects, adaptations to utilize PAs must be polyphyletic in origin. As with PA chemistry, few other generalizations can be drawn, although the phenomena obviously exhibit similarities. In any case, one has to differentiate between three types of associations (Table 1): insects taking advantage of (1) the nutritional value only, (2) both the primary and the secondary metabolites, and (3) PAs alone.

Insects utilizing PA plants solely as food sources demonstrate, perhaps, the most original adaptation, apparently enabling them to exploit a food resource with limited competition. We know too little of the few species belonging to this category, but it seems that they are mostly polyphagous and handle PAs unspecifically by converting and/or excreting them.

Lepidoptera restricted to PA-containing host plants (e.g., *Tyria, Utetheisa, Nyctemera*) seem to take advantage of PAs themselves in one way or another. They have probably adapted to avoid harm and, apparently, they have means of recognizing PA plants. Since a PA plant is not only characterized by the possession of PAs, one can imagine a variety of cues that are capable of guiding an insect to its host, but critical investigations regarding this point are entirely lacking. Host records of insects using PA plants indicate, however, that different Lepidoptera do use different stimulus patterns for egg-laying and/or phagostimulation, because various species exhibit different host ranges (Table 2), indicating that PAs cannot be the only cues (but see discussion of pharmacophagy below).

Straightforward detection and recognition of PAs is a basic feature of pharmacophagous species. By definition, species of this category search for the allelochemics directly, take them up, and utilize them for a specific purpose other than primary metabolism or (merely) host recognition (Boppré, 1984b), i.e., they often gather secondary plant compounds independently of foraging for nutrients. Pharmacophagy with respect to PAs has been demonstrated for *Creatonotos* larvae (Table 2) but is most easily recognized in all those Lepidoptera (and other insects) that, in their adult stage, visit withered or decaying PA plants

TABLE 1. EXAMPLES OF LEPIDOPTERA AND OTHER INSECTS SHOWING DIFFERENT KINDS OF PA SEQUESTRATION

ORDER, Family, Genus	Larval host(s) contain PAs	Adults visit dry PA plants		Adults store PA	PA-derived pheromone[b]
LEPIDOPTERA					
Noctuidae					
Spodoptera[1]	− / +		−	−	−
Arctiidae					
Spilosoma[1]	− / +		−	− / +	−
Arctia[1]	− / +		−	− / +	−
Creatonotos[1]	− / +[c]		−	− / +	− / +
Phragmatobia[3]	− / +		−		+
Pyrrharctia[3]	− / +		−		+
Tyria[1,4]	+		−	+	−
Amphicallia[1]	+[c]		−	+	−
Utetheisa[5]	+[c]		−	+	+
Nyctemera[6,7]	+[c]	males	females	+	− / ?
Rhodogastria[7]	−	males	females	+	−
Halysidota[8–10]	−	males	females		
Cisseps[8–10]	−	males	(females)		+
Ctenuchiidae					
Euchromia[7]	−	males	females	+	−
Ctenucha[10]	−	(males)	females		
Lymire[8,9]	−	males	(females)		
Euceron[8,9]	−	males	(females)		
Danainae[11]					
Danaus	−	males		+	+
Amauris	−	males		+	+
Euploea	−	males		+	+
Ithomiinae[8,12]					
Several genera	−	males		+	+
COLEOPTERA					
Chrysomelidae					
Longitarsus[13]	+		−		
Gabonia[14]		males			
Nzerekorena[14]		males	females		
DIPTERA					
Melanochaeta[15]		males	females		
Eutropha[15]		males	females		
Chlorops[15]		males	females		

TABLE 1. Continued

ORDER, Family, Genus	Larval host(s) contain PAs	Adults visit dry PA plants		Adults store PA	PA-derived pheromone[b]
ORTHOPTERA					
Pyrgomorphidae					
Melanoplus[16]	− / +	−		−	−
Zonocerus[17]	− / +	males	females	+ / −	

[a] Note that the list is not comprehensive and, in part, generalized; for simplification it is based on genera, which does not necessarily imply that the information indicated is valid for all species (e.g., of Halysidota longa 99% males are attracted to PA baits, of H. tessellaris 90.9% females; Goss, 1979); the levels of investigation are also quite different. The references given provide a basis to the partly extensive literature. [1]Rothschild et al. (1979); [2]Boppré and Schneider (1989); [3]Krasnoff et al. (1987); [4]Ehmke et al. (personal communication); [5]Culvenor and Edgar (1972), Conner et al. (1981); [6]Benn et al. (1979); [7]Boppré (1981); [8]Pliske (1975); [9]Goss (1979); [10]Krasnoff and Dussourd (1989); [11]refs in Ackery & Vane-Wright (1984); [12]Brown (1984, 1987); [13]Boppré (1983); [14]Scherer and Boppré (1990); [15]Boppré and Pitkin (1988); [16]Ehmke et al. (1989); [17]Bernays et al. (1977), Boppré et al. (1984).
[b] See Table 4.
[c] See Table 2.

(Table 1) and extract PAs from the dry material by using a liquid released through their proboscides. In most of these species the larvae feed on PA-free hosts, but this need not necessarily be the case (see Nyctemera, Table 1). In experimental situations, they will also go for certain pure PAs, i.e., orientation to PA sources has to be mediated olfactorily and also be solely related to PAs and not to any other plant product.

We do not know much about preferred species of PA plants, but plants with structurally different PAs are attractive (Table 3). Because of their high molecular weight, intact esters are unlikely to have sufficient volatility to mediate attraction. But we must ask precisely what cue(s) enable PA pharmacophagous insects to recognize PA sources. Recently, two independent approaches to this question revealed that hydroxydanaidal (Figure 1B), previously well known as male pheromone (see below), is the airborne signal from a variety of PA sources (Krasnoff and Dussourd, 1989; Bogner and Boppré, 1989; compare Pliske et al., 1976). Discrepancies exist, however, since Krasnoff and Dussourd (1989) found S-$(+)$-hydroxydanaidal more attractive than the respective R-$(-)$-enantiomer, while Bogner and Boppré (1989) found the opposite. The latter authors put forward evidence that hydroxydanaidal is a spontaneous degradation product that emanates in minute quantities from all those PAs that have either retro-

TABLE 2. EXAMPLES OF ARCTIID MOTHS ASSOCIATED WITH PA PLANTS DEMONSTRATING HOST RECOGNITION/SELECTION IS NOT ONLY DUE TO PAs[a]

	Amphicallia	Nyctemera	Utetheisa	Creatonotos
Heliotropium	–	–	+	+
Crotalaria	+	–	+	+
Gynura	–	+	–	+
Non-PA plants	–	–	–	+
Purified PAs	?	?	–	+

[a]Boppré, unpublished field records from Kenya and laboratory tests.

necine or heliotridine as the necine and are present as free bases. This finding explains the given but not very high specificity of attraction and suggests why plants must be withered (or damaged) to be attractive and lure best if remoistened. The study also demonstrated receptor cells for the perception of secondary plant metabolites that have similar specificity and sensitivity as receptors for sensing female pheromones in moths (e.g., Mustaparta, 1984). (At close range to the source, gustation also seems to be involved: Lepidoptera probe with their proboscides before eventually applying liquid to extract and imbibe PAs.)

Field observations on the biology of Lepidoptera that gather PAs as adults have revealed that nectar can be a potential source of PAs. Chemically, PAs have been recognized in honey of *Senecio* and *Echium* (up to 3.9 ppm; Deinzer et al., 1977; Culvenor et al., 1981), and flowers of the Eupatoriae (Compositae) are considered to be a major source of PAs for Lepidoptera (e.g., Brown, 1984). The flowers of the PA plant *Gynura scandens* are exclusively visited by PA insects, and these exhibit the same sex bias as at withered plants or artificial baits; other Lepidoptera completely ignore these flowers (Boppré, unpublished). Some novel PAs were first found in *Euchromia* moths that had visited *Gynura* flowers (Boppré and Edgar, unpublished; compare Wiedenfeld, 1982). In contrast, flowers of other PA plants (e.g., *Heliotropium*) are utilized by a wide spectrum of nectar foraging insects. This suggests that the nectar of PA

TABLE 3. PLANT GENERA MOST FREQUENTLY USED AS PA SOURCES BY ADULT LEPIDOPTERA

Asteraceae	*Ageratum, Eupatorium, Senecio, Gynura*
Boraginaceae	*Heliotropium, Tournefortia*
Fabaceae	*Crotalaria*

plants does not necessarily contain these secondary products—an aspect requiring further investigation. Furthermore, some orchids (*Epidendrum* sp.) are pollinated exclusively by adult Lepidoptera that are pharmacophagous with respect to PAs; apparently, these plants do not provide PAs but cheat PA insects to take advantage of specialists for pollination (Goss and Adams, 1976; DeVries and Stiles, 1989).

How elaborate the gathering of PAs can be is shown by danaine butterflies that vigorously scratch plant tissue with their legs to get access to PAs (which they then suck up with their proboscides). They need, however, a starting point such as a hole made by beetles (Boppré, 1983); undamaged tissue is ignored, apparently lacking the volatile cue for attraction.

Foraging PAs can thus be of great cost with respect both to phylogenetic adaptations and to the time and effort invested by individuals. One may therefore expect that PAs play significant roles in the lives of PA insects.

PAs AND THEIR ROLES FOR INSECTS

PAs for Defense. The great majority of insects that utilize PA plants in one or another way are aposematically colored and behave conspicuously. This suggests, in combination with the information above on the protective role of PAs for plants, that insects do store PAs and use them for their own protection. Storage of PAs by Lepidoptera was first demonstrated by Aplin and Rothschild (1968, 1972), and numerous similar studies have been undertaken since; the analyses reported by Brown (1984a,b, 1987) are outstanding for their detail.

Most species related to PA plants that have been analyzed chemically have been found to store PAs in their bodies (Table 1); the amounts can be as high as 20% of the insect's dry weight (e.g., Brown, 1987). Detailed analyses on the qualitative and quantitative composition of PAs in insects reveal, however, many intra- and interspecific differences. PAs found in insects do not necessarily represent fingerprints of the PAs found in their host(s); rather, there are great differences in the patterns, both qualitative and quantitative (e.g., Culvenor and Edgar, 1972; Aplin and Rothschild, 1972); even sex differences occur in PA storage by larvae that had fed on the very same individual plant. Are we dealing with selective uptake, selective metabolism, or perhaps selective conversion due to selective use? What is the role of "callimorphine" (Figure 2L), a PA not known from plant sources but found in several arctiids jointly with host plant PAs (Aplin et al., 1968; Edgar et al., 1980; Wink et al., 1988; L'Empereur et al., 1989). Unfortunately, studies considering both plants and insects at the same time are rare. We also need many more qualitative and quantitative PA profiles of several insect species to learn about individual (and sex-specific) variation, selectivity of uptake and utilization in sympatric species, and differences among populations. Further questions of general importance include: do

adult Lepidoptera extracting PAs from withered material of a given plant obtain the same amounts and types of PAs as obtained by larvae feeding on the living tissues? Extracts of insects usually reveal a high percentage of PAs in their *N*-oxide forms; did the insects take up *N*-oxides or did they oxidize free bases? If the latter (as demonstrated for *Rhodogastria*; Wiedenfeld and Boppré, unpublished) is the case, is *N*-oxidation caused by an adapted mechanism or is it simply an obligatory metabolic process? Are the polar *N*-oxides more or less or equally defensive (and/or repellent) compared to free bases or are they better suited for transport within the body? Thus, merely recognizing that an insect is associated with a PA plant is insufficient to predict if and how it sequesters the plant chemicals.

Although storage of PAs does not inevitably imply a protective function, we know from the meticulous studies of Eisner (1980, 1982) and Brown (1984a,b, 1987) that Lepidoptera (*Utethesia* and Ithomiinae) can be protected from predation (by *Nephila* spiders) by stored PAs they had gathered, respectively, as larvae or adults. Both these workers also demonstrated that, in their examples, PAs alone were responsible for protection.

With several other species the situation is more complex since they possess self-manufactured, toxic secretions in addition to PAs (see Blum, 1981; Rothschild, 1985; for general accounts and references) and/or they store other chemicals sequestered from plants. For example, *Danaus plexippus* can store cardenolides from larval hosts and the adult butterflies gather PAs in a pharmacophagous way (e.g., Brower, 1969; Kelley et al., 1987);[2] however, Ithomiinae and *Euploea core*, for example, do not store the defensive compounds present in their host plants (Brown, 1984a,b, 1987; Malcolm and Rothschild, 1983) and seem to rely only on PAs obtained as adults. Are different (sets of) compounds effective against different predators, do they act synergistically, and/or are several chemicals utilized to ensure protection if one or the other type is not available at a given habitat or time? Last, but not least, the considerable intraspecific variation in PA storage, particularly in pharmacophagous species, and the resulting "palatability spectrum" is of great relevance and deserves detailed study—also in the context of (auto-)mimicry.

At this point we should consider the potential predators for PA insects. Since PA insects are diverse with respect to, among other factors, size, activity pattern, and habitat, the range of potential predators is great and includes organisms with quite different physiology and life-styles (vertebrates as well as invertebrates). As with plants (see above) the question of unpalatability vs. toxicity arises (see also discussion by Brower, 1984). Is the knowledge of the

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[2] Interestingly, often (always?) the ability to utilize PAs is associated with the ability to utilize cardenolides, but no common denominator of PAs and these glycosides is recognized (e.g., Rothschild et al., 1970).

toxicology, indicated above and largely derived from studies of domestic animals, really applicable to insectivores such as birds, bats, lizards, and toads? Would, for example, amounts of PAs accumulated through insectivory fall below the poisoning threshold? Likewise, in this context it must be asked again: why do insects usually avoid PAs and what kind of harm do they risk with ingestion of these compounds?

Taste rejection of PA-storing insects by predators suggests that PAs are located on the prey's outer surface. Indeed, biological observations verify this: *Nephila* spiders release Ithomiinae and *Utetheisa* unharmed from their webs (Eisner, 1982; Brown, 1984a), and *Creatonotos* and *Rhodogastria* survive attacks by toads and lizards, which spit them out (Boppré, unpublished). From Brown's studies we know about the quantitative distribution of PAs/PA N-oxides in the various body parts of ithomiine butterflies (accumulation in exoskeleton and reproductive tissues), but we lack information as to how PAs are transported. If PAs are ingested by larvae, the problem of how PAs reach the cuticular surface is less intriguing than in those Lepidoptera that gather PAs as adults, i.e., after the cuticle has been formed. In many arctiid adults, malodorous froth exuded from prothoratic glands immediately after an attack seems to support instant taste recognition. If adults have access to PAs, the froth of *Rhodogastria* is loaded with PA N-oxides (Wiedenfeld and Boppré, unpublished).

The transport of PAs in insect bodies must relate to how PAs pass the gut membranes. Because PAs are large molecules, some kind of carrier molecules should be expected (Hartmann, 1985; Wink and Schneider, 1988). Surprisingly, experiments with *Creatonotos*, the larvae of which happily consume glass-fiber disks impregnated with PAs (Boppré, unpublished), indicate that if the insects had ingested pure PAs in this way the effect of these chemicals on morphogenesis (see below) is 10–100 times weaker than if PAs had been provided naturally, i.e., unextracted via plant tissue (Boppré, unpublished). This may suggest attachment of PAs in plants to other molecules, resulting in more efficient metabolism (translocation, storage, conversion?) in insects. Perhaps, we even should ask whether poisoning of vertebrates is greater if PAs are ingested with plant tissue then in pure form, implying that LD_{50} tests with pure chemicals might be misleading. Based on available evidence, storage for defense seems to be the primary function in most, if not all, insect–PA relationships, but in many it is not the only one.

PA-Derived Male Pheromones. In Lepidoptera, utilization of PAs as precursors for male pheromones is widespread although not general (Table 1). Figure 1 shows the structures of PA-derived compounds identified from androconial organs in Lepidoptera, and Table 4 links them to the respective genera. It shows that unrelated species end up with similar or even identical pheromone components, regardless of the stage in which PAs are consumed. Nevertheless, in chemoecological terms this is not a basis for establishing a rule. As the infor-

TABLE 4. LEPIDOPTERA USING PA-DERIVED MALE PHEROMONES[a]

Family genus	A	B	C	D	F	Amount (μg/male)	Release
Danainae[1,2b]							
Danaus	x					0–500	I
Lycorea	x						I
Amauris	x	(x)					I
Euploea		x	(x)				I, II
Ithomiinae[3–5b]							III
Prittwitzia				x	x	0.01–0.2	
Mechanitis					x		
Tithorea					x		
Arctiidae[c]							
Utetheisa[6]		x	x			0–30	I
Phragmatobia[7]		(x)	x			0–24	I
Pyrrharctia[7]		x	(x)			0–10	I
Cisseps[8]		x				0–0.12	I
Creatonotos[9]		x				0–400	III

[a] A: danaidone, B: hydroxydanaidal, C: danaidal, D: methyl-hydroxydanaidoate, F: ithomiine lactone, (Figure 1), the amounts found, and the behavioral situation for release [I: briefly, close to the female; II: patrolling with expanded hairpencils; III: for long, stationary (luring males and females?]. [1]Refs. in Ackery and Vane-Wright (1984); [2]Schulz (1987); [3]Edgar et al. (1976); [4]Haber (1978); [5]Schulz et al. (1988); [6]Culvenor and Edgar (1972), Conner et al. (1981, 1989); [7]Krasnoff et al. (1987), Krasnoff and Roelofs (1989); [8]Krasnoff and Dussourd (1989); [9]Schneider et al. (1982); Wunderer et al. (1986); Boppré and Schneider (1989).
[b] PA uptake by adults.
[c] PA-uptake by larvae.

mation provided in Table 4 also indicates, the respective species differ strikingly in the quantities of PA-derived compounds, they have quite different courtship strategies, and their pheromones come into play in different behavioral contexts, suggesting different roles, i.e., broadcasting different messages to the female (Boppré, 1984a).

In *Danaus chrysippus* (and probably many other danaine butterflies), mechanical contacts between abdominal hairpencils and alar glands are required for synthesis of danaidone (Boppré et al., 1978). Thus, in addition to the costs of foraging for PAs (plus producing appropriate enzymes), the males employ two sets of glandular organs and perform a peculiar precourtship activity. Must danaidone synthesis occur outside the body in order to avoid poisoning by PA metabolites? Perhaps so, but other species (e.g., *Lycorea*) manage without alar organs. It is also puzzling why so many species utilize hydroxydanaidal as a male pheromone (component). The idea that this molecule might be less costly to synthesize than other PA derivatives (e.g., danaidone) receives some support

by finding that hydroxydanaidal appears as a spontaneous degradation product (see above).

There are two enantiomeric forms of hydroxydanaidal but the androconia of *Creatonotos* and (all?) other Lepidoptera that use PAs as precursors emit *R*-(−)-hydroxydanaidal only (Figure 1B, Table 4). This detail is by no means trivial in an ecological context because insect olfactory receptors usually discriminate between enantiomers and, according to textbook knowledge, the enantiomeric configuration should not be changed in the course of biosynthesis of hydroxydanaidal from PAs. It was completely unexpected to find, from feeding experiments, that *Creatonotos* can utilize PAs with retronecine or heliotridine, in the latter case converting the configuration at C-7 (Bell et al., 1984; Bell and Meinwald, 1986; compare Wink et al., 1988). This mechanism, in consequence, enables *Creatonotos* to take advantage of a wider spectrum of species of PA plants than it could otherwise do. What happens in such insects as *Euploea*, which gather PAs as adults?

Because hydroxydanaidal is not only a pheromone but also the volatile principle responsible for attraction of insects to PAs (see above), certain insects might get confused—PA sources smell like male androconia and, in turn, androconia smell like PA sources. In fact, coremata of *Pyrrharctia* and *Creatonotos* attract PA insects (Krasnoff and Dussourd, 1989; Boppré, unpublished).

Referring to the androconial secretions as male pheromones is not very meaningful because the messages male pheromones carry are generally little understood and certainly not uniform (Boppré, 1984a). In any case, it is very surprising that a diversity of Lepidoptera use derivatives of (defensive) plant metabolites as male pheromone precursors. Utilization of plant products for pheromone biosynthesis is not restricted to PAs; the bark beetles (Scolytidae) provide a well-known example (e.g., Borden, 1985). However, in certain PA insects the question has a special dimension because of the linkage between chemical defense and chemical communication.

Based on the fact that hydroxydanaidal-deficient males of *Utetheisa* are unsuccessful in courtship, Conner and Eisner suggested the females might sexually select for males with a high ability to sequester PAs, a trait that might be inheritable (Eisner, 1980; Conner et al., 1981). Finding that males also donate substantial amounts of PAs with their spermatophores (Brown, 1984, 1987) resulted in an even more plausible hypothesis: since the male pheromone is derived from the nuptial gift, it might indicate to the female the amount of protective chemicals she can expect to gain during copulation (Eisner and Meinwald, 1987; Dussourd et al., 1988). Although several of the assumptions lack confirmation as yet, for *Utetheisa* there is some good evidence in favor of the hypothesis (see also Conner et al., 1989). The hypothesis is also of great value for studies on other species utilizing PAs for both defense and chemical communication. However, considering the differences in courtship behavior, the

fact that some species have to make do with a fixed amount of PAs gathered as larvae while others can increase their drug budgets as adults, and considering the existence of additional chemicals (e.g., extracts of male danaine hairpencils revealed bouquets comprised of up to 50 volatiles found only in the androconia; Schulz, 1987), without modification the hypothesis is unlikely to be equally valid for the entire variety of species.

More thorough studies focusing on how male butterflies handle ingested PAs are required for our understanding of the chemoecological aspects. What is the order of priority and what are the budgets if PAs are used for pheromone biosynthesis, for protection, and for incorporation into spermatophores? This question is of particular importance if PA resources are limited, and the answer must be expected to differ among species of PA insects. Furthermore, are the various PAs obtained by an insect from different plant species used equally or are there differences such that, for example, only certain PAs are stored for defense while others are converted into pheromones? Is there a difference between utilization of N-oxides and free bases, and/or are pure PAs less efficiently used (see above)?

Further questions arise from sex-specific sequestration of PAs. Among those species gathering PAs as adults, there is often a male bias, but others have female and yet others no sexual bias (Table 1). In *Creatonotos*, there is a significant sexual difference in the amount of PAs taken by larvae in ad libidum experiments (Boppré, unpublished). Particularly informative might be comparative studies with closely related species that behave differently. For example, *Amauris ochlea* and *A. niavius* are sympatric congeners. In the former, males exclusively are found at PA baits or plants, but in the latter species, a high proportion of females also visit such PA sources (Boppré, unpublished). Again a sensory physiological aspect appears, which seems promising for a study on the evolution of receptor specificity.

PAs as Morphogens. A unique effect of PAs has been recognized in arctiid moths of the genus *Creatonotos*. The amount of PAs consumed by larvae not only determines the amount of male pheromone [R-($-$)-hydroxydanaidal] but also the size of the coremata (Schneider et al., 1982; Boppré and Schneider, 1985, 1989). Morphogenesis of these androconial organs (and of these alone) is quantitatively dependent upon the amount of PAs ingested by a larva; there is no previous knowledge of a similar morphogenic effect generated by a secondary plant metabolite. Recently, however, we found considerable variation in the size of coremata in a field population of *Teracotona* (Boppré, unpublished), and we are curious to study if PAs (or other secondary plant substances) act as morphogens.

Other Functions? There are many further facets in insect–PA relationships, making the complex situation discussed above even more involved, but the subject cannot be treated comprehensively here. One could add that Pliske

(1975a,b) and Goss (1979) speculate on a nutritive function for PAs, but there is no evidence for such an idea. In the case of Danainae and Ithomiinae there is debate on the evolutionary origins of their relation to PA plants. However, the most significant increase in the complexity of the subject occurs when non-lepidopteran insects associated with PA plants are considered in addition; Table 1 lists just a few examples.

EPILOGUE

PAs belong to the best investigated natural products and many aspects of sequestration of these allelochemics by insects (mainly Lepidoptera) have been studied. Despite our present knowledge, many questions naturally arise that demonstrate we have seen only "the tip of the iceberg" so far. The many aspects described here are of unequal importance and cannot be considered at once; they are neither meant to cause confusion nor to discourage specific studies; rather, they are intended to stress the research challenge provided by insects and PAs. However, we have to consider the complexity which is, I think, the fascination of chemical ecology. We should increase detailed studies and stress comparative approaches but refrain from generalizing conclusions; as shown above, to date we know quite a few examples but there is no model representative for insect–PA relationships.

Raising open questions on insect–PA relationships should also illuminate the many tasks for biological disciplines not directly involved in chemical ecology. These include studying such different subjects as receptors, morphology, ethology, orientation, phylogenetics, and even developmental processes.

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