



The chemical defenses of millipedes (diplopoda): Biochemistry, physiology and ecology



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ABSTRACT

Millipedes are some of the earliest examples of terrestrial animals, and fossils from the early Carboniferous Period indicate they were also some of the earliest prey. These fossils record ozopores, the openings of chemical defense glands, occurring along the length of the body. The secretions of these glands may consist of topical irritants, repellents, anti-feedants, or, in the case of the large and widespread Order Polydesmida, hydrogen cyanide (HCN) gas that can be fatal to other arthropods or even small vertebrates in a confined environment. Müllerian mimicry rings may develop in which unrelated species of millipedes that co-occur closely resemble one another, while participating in a completely differently patterned ring in another part of their geographic range. Chemistry is not the only defense of millipedes. Polyxenids carry tufts of entangling setae, many species rely on crypsis and the ability to roll into a smooth, resistant sphere or coil, and still others have spikey projections that may deter soft-mouthed predators. Nevertheless, chemical defense has been of significance in helminthomorph millipedes at least since the Lower Carboniferous. The distribution of classes of chemical defense compounds follows major phylogenetic groupings. Evidence suggests that the defensive glands of Glomerida arose independently of those of the Helminthomorpha.

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1. Introduction

The earliest evidence of chemical defense by an arthropod consists of ozopores on the segments of fossil millipedes from the Devonian and Viséan (Lower Carboniferous) of Scotland (Shear, 1994; Shear and Edgecombe, 2010; Wilson, 2006). The earliest review of millipede chemical defenses, a remarkably prescient one, was written by O. F. Cook in 1900. In this essay, Cook (1900) mentioned the stickiness of polyzoniid secretions, discussed the use of millipedes by primates for self-anointing, and postulated that there were at least four different classes of compounds involved. That same year, Béhal and Phisalix (1900) found quinones in the secretion of "Julus terrestris". The facts about millipede chemical defenses were last effectively reviewed in English by Blum (1981), and by Eisner et al. (1978). Popular accounts of several species were provided by Eisner et al. (2005), and Demange (1993) produced a summary in French. Since the early 1980s, the defensive substances of many additional species have been characterized—more than 140 species have now been studied, in contrast to the 56 listed by Eisner et al. (1978). Improved analytical methods have allowed the discovery of components present in extremely small amounts and the estimation of the percent composition of secretions. We also know more about the various chemoecological roles played by millipedes, so the time seemed ripe for another comprehensive review of the subject, and that is the purpose of this article (for a review of millipede systematics and evolution in general, see Sierwald and Bond, 2007).

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2. Classes of secretions

The defensive substances produced by millipedes cannot be characterized as a whole, because entirely different classes of molecules are produced by different taxa. Table 1 lists as completely as possible the species that have been studied so far, their chemical products, and literature citations for the identification. Eight classes of compounds, sometimes widespread, or restricted to one taxon or a few related ones, can be recognized. In each case only a few, usually more recent, references are given in the listing below; more complete, older references may be found in Eisner et al. (1978) and Table 1. Structural formulas for some of these compounds are shown in Figs. 1 and 2.

Quinazolinone alkaloids, glomerin and homoglomerin (Fig. 1K, L), are produced by the two species of glomeridans that have been studied up to this time (Schildknecht et al., 1966a, 1966b; Meinwald et al., 1966; Shear et al., 2011).

Heterocyclic nitrogen-containing compounds have been detected from members of the Order Polyzooniida. These include polyzonimines (Fig. 1M), nitropolyzonamines (Fig. 1N), buzonamine and spiropyrrrolizidine oximes (Meinwald et al., 1975; Kuwahara et al., 2007).

Terpenes such as pinenes and limonene have also been found in polyzooniidans as well as in the siphonophoridans examined, where they are not accompanied by polyzonimines and others listed just above (Shear & Jones, unpublished data; see Table 1).

Benzoquinones and hydroquinones (Fig. 1J, Fig. 2) with numerous substitutions (largely methyl and/or methoxy groups) have been recorded from many species in the orders Spirobolida, Julida, and Spirostreptida. 2-methyl-3-methoxy-1,4-benzoquinone occurs almost universally in these species and is generally the greatest component where a mixture is found (Attygalle et al., 1993; Buden et al., 2004; Sekulic et al., 2014).

Fatty acid esters and a few other aliphatic compounds occur in conjunction with quinones, and may serve as solvents or themselves be aversive (Shimizu et al., 2012).

Aliphatic compounds (i.e., Fig. 1B) including [E]-2-octenal have recently been reported from one species of julidan in conjunction with benzoquinones (Bodner and Raspotnig, 2012). 1-octen-2-ol was found in the secretion of the polydesmidan *Niponia nodulosa* (Omura et al., 2002a).

Phenols (including *o*-cresol [Fig. 1G], *p*-cresol [Fig. 1H], and guaiacol [Fig. 1I]), are produced by callipodidans (i.e., Curcic et al., 2009; Shear et al., 2010; Makarov et al., 2010), by stemmiulidans (Shear and Jones, unpublished data), by one parajulid julidan (accompanied by benzoquinones), and by some polydesmidans, where, except in a few cases, they are secreted in addition to cyanogenics (Taira and Arakaki, 2002; Shear et al., 2007).

Cyanogenics such as mandelonitrile (Fig. 1D) and benzoyl cyanide (Fig. 1E) make up the main defenses of all but a few polydesmidans. When secreted, the cyanogenics are mixed with an enzyme that degrades them to HCN and benzaldehyde (Fig. 1C) or benzoic acid (many authors; see Eisner et al., 1978, also Omura et al., 2002b).

A number of compounds have been found as “one-off” in a variety of species; the status of these compounds is at present uncertain since the results have not been duplicated by other investigators, or were obtained by methods less reliable than those now in use. These compounds are in bold type in Table 1. Of particular interest is the detection of (1E)-2-nitroethylbenzene and (1Z)-2-nitroethylbenzene in the doratodesmid polydesmidan *Eucondylodesmus elegans* by Kuwahara et al. (2002). This species evidently lacks the usual cyanogenic system of the Polydesmida. We have found similar compounds in two New Zealand dalodesmids, but one of them also had the cyanogenic system (Shear & Jones, unpublished data). Clearly more investigations of dalodesmids and doratodesmids are warranted.

2.1. Unpublished results

Research in collaboration with T. H. Jones and others has preliminarily characterized the secretions of members of the orders Platydesmida, Siphonocryptida, Siphonophorida and Stemmiulida, which up to this time have remained unknown. They are included in Table 1 and in the discussions below pending publication of the details. Species in the orders Polyxenida, Sphaerotheriida and Chordeumatida, are, to the extent of present knowledge, devoid of at least exocrine chemical defenses. Some doubt has been expressed regarding the absence or presence of chemical defenses in Glomeridesmida, but Shear et al. (2007) examined a species of *Glomeridesmus* using scanning electron microscopy and found no evidence of ozopores, and there are no primary reports of chemical defenses in this order.

3. Repugnatorial glands

Eisner et al. (1978) recognized three types of glands in millipedes: the median, two-armed glands in Glomeridae, the bilateral, bipartite glands of the Polydesmida, and bilateral single-chambered glands, differing in shape, from the other orders with chemical defenses. The orders Polyxenida, Glomeridesmida, Sphaerotheriida and Chordeumatida lack glands.

3.1. Type 1

Shown in Fig. 3, and found only in Glomerida (Eisner et al., 1978, and references therein; Shear et al., 2011). The gland openings are mid-dorsal, transverse slits in the inter-ring cuticle just anterior to rings 4–11 (though the glands themselves are located in the preceding ring); the pores do not open within the ring as shown by Eisner et al. (1978, Fig. 2A), but at least in

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