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A Review of the Chemical Ecology of Antarctic Marine Invertebrates[1]

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SYNOPSIS. **The interdisciplinary field of marine invertebrate chemical ecology is relatively young, and particularly so in polar marine environments. In this review we present evidence that the incidence of chemical defense in antarctic benthic marine invertebrate phyla is widespread. Mechanisms of chemical defense have been detected in antarctic representatives of the Porifera, Cnidaria, Brachiopoda, Tunicata, Nemertea, Mollusca and Echinodermata. This argues against earlier biogeographic theories that predicted a low incidence of chemical defense in polar waters where levels of fish predation are low. Selection for chemical defense in benthic sessile and sluggish marine invertebrates is likely a response to an environmentally stable community shown to be structured primarily by biotic factors such as predation and competition. Holoplankton and the eggs, embryos and larvae of both benthic and planktonic antarctic macroinvertebrates may also employ chemical defense to offset mortality during characteristically slow development and long life span where susceptibility to predation is seemingly high. While most research to date has focused on the role of secondary metabolites in mediating predation, it is likely that bioactive compounds in antarctic marine invertebrates also serve roles as antifoulants and allelochemics. The diversity of bioactive metabolites detected to date in antarctic marine invertebrates sets the stage both for continuing and for broadening efforts to evaluate their functional and ecological significance.**

INTRODUCTION

The role of chemical defense in mediating marine invertebrate predator-prey interactions has received considerable attention (reviewed by: Bakus *et al.*, 1986; Paul, 1992; Pawlik, 1993; Hay, 1996). As is true of marine plants (Hay and Fenical, 1988; Hay, 1992; Hay and Steinberg, 1992), sessile and sluggish marine invertebrates are extremely vulnerable to mobile predators. Moreover, marine invertebrates are subject to having their tissues fouled by settling larvae, diatoms and other algal cells, and in the case of sponges, soft corals, bryozoans and other sessile marine invertebrates, to overgrowth by species competing for space. Ultimately, the ability of these organisms to chemically defend themselves can play a significant role in regulating predator-prey interactions and structuring marine communities (Bakus *et al.*, 1986; Paul, 1992; Pawlik, 1993; Hay, 1996).

Most of the research on marine invertebrate chemical ecology has focused on tropical environments (Bakus *et al.*, 1986). The coral reefs of the tropics are well known for their high species diversity and communities comprised of individuals and colonies competing intensely for space and food. Under such conditions, it is not surprising that many sessile or sluggish marine invertebrates have evolved chemical means of defense (Bakus *et al.*, 1986; Paul, 1992, Pawlik 1993; Faulkner, 1996 and references within). Early studies examining geographic patterns of chemical defense (as measured by ichthyotoxicity) in marine invertebrates noted a decrease in chemically defended species as one moved from tropical to temperate marine habitats (Bakus and

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[1] Invited mini-review.

Green, 1974; Green, 1977; Bakus, 1981). Based on these comparisons, and the observation that fish predation on benthic marine invertebrates decreased with increasing latitude (Vermeij, 1978), an inverse correlation between chemical defense and latitude in marine invertebrates was proposed (Bakus and Green, 1974).

Although the antarctic benthic marine environment has been classically considered to be harsh environmentally, studies have shown that with the exception of organisms living in the most shallow water (less than 33 m depth) where anchor ice and ice scour are important structuring forces (Dayton *et al.*, 1969, 1970), the benthic community is remarkably rich and stable (Dell, 1972; Dayton *et al.*, 1974; Richardson and Hedgpeth, 1977; Dayton 1989, 1990; White, 1984). The assemblage of marine organisms comprising this community has evolved during the events preceding the cretaceous breakup of Gondwanaland and the movement of the antarctic continent southward. The establishment of a circumpolar current effectively isolated the continent, and its climate remained temperate to sub-tropical until 22 million years ago (Dayton *et al.*, 1994). The marine biota, therefore, has its origins in warmer climates and is relatively old (Dell, 1972). According to Dayton *et al.* (1994) the shallow-water antarctic marine fauna is derived from 1) relict autochthonous fauna, 2) eurybathic fauna from deeper water, and 3) cool-temperate species, mostly from South America.

The factors responsible for structuring this complex sponge-dominated community appear to be primarily biological in nature. For example, competition for space is intense between certain species of sponges, several of which are capable of dominating space if released from predation pressure (Dayton *et al.*, 1974; Dayton, 1989). Moreover, although fish predators that browse on sessile marine invertebrates such as sponges are indeed rare in high latitudes (Eastman, 1993), there is a very high incidence of predation in Antarctica by mobile macroinvertebrates, particularly echinoderms such as sea stars (Dearborn, 1977; McClintock, 1994). In the water column, there are a variety of abundant planktivorous fish that are known to ingest zooplankton (*e.g.*, Foster *et al.*, 1987; Eastman, 1991) as well as extremely dense swarms of predatory amphipods (*e.g.*, Rakusa-Suszczewski, 1972). While overall grazing or predation pressure (per unit time) is arguably higher in tropical marine systems (Vermeij, 1978), some antarctic macroinvertebrate grazers and predators occur in extremely high densities and consequently are capable of exerting considerable predation pressure (Fig. 1A). Moreover, antarctic organisms often have very long lifespans (Clarke, 1983), the effect of which may be that predation intensity averages out over lifespan to be similar to that in temperate or even tropical marine systems (Fig. 1B). As one of the oldest, most environmentally stable and intensely biologically structured marine systems, the antarctic benthos is well suited for the evolution of chemical defense mechanisms.

There has been a plethora of bioactive secondary metabolites (defined as those compounds with no definitive role in primary metabolic pathways) isolated from marine invertebrates (Scheuer, 1990; Attaway and Zaborsky, 1993; Faulkner, 1996). These compounds have been isolated primarily from sponges and cnidaria (predominantly soft corals), although smaller numbers of other members of marine invertebrate groups have also yielded bioactive secondary metabolites (Baker, 1996; Faulkner, 1996 and references within). Although the descriptive chemical studies published on novel secondary metabolites from marine invertebrates number in the thousands, there are comparatively few studies which provide ecological information about the functional significance of these compounds. In many instances, biological activity has been measured simply as the ability of a compound to cause cell lysis or inhibit growth of a non-marine microbe. While such information may have utility in pharmaceutical studies (Munro *et al.*, 1987; Scheuer, 1990; Hay and Fenical, 1996), much remains to be learned about the ecological significance of such bioactive compounds. This is particularly true in polar waters, where chemical ecological studies of marine invertebrates have only recently begun, with the vast majority of studies having been conducted in McMurdo Sound, Antarctica (77°S, 166°E).

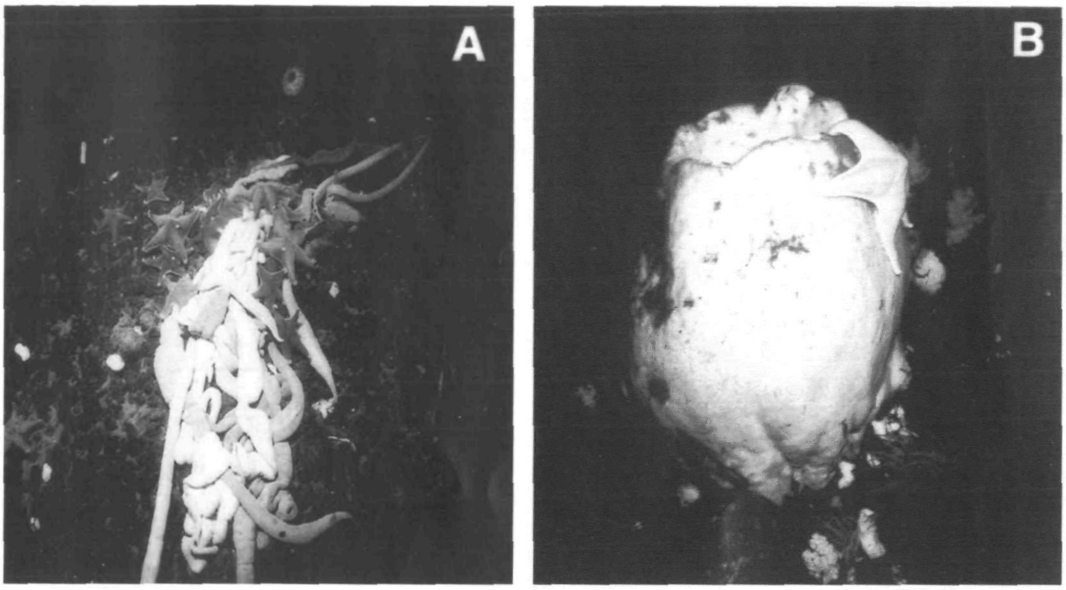


FIG. 1. *In situ* photographs of antarctic benthic predation events representative of different time scales. A. Mass feeding aggregation of the antarctic nemertean worm *Parborlasia corrugatus* and the antarctic sea star *Odontaster validus*. These common predation events may occur over a time scale of a few hours (McClintock, Baker, Heine pers. obs.; photo by J. Heine). B. The antarctic spongivorous sea star *Acodontaster conspicuus* preying on a large vase sponge. These predation events may last months to years (Dayton *et al.*, 1974; photo by J. Mastro).

While the data base for antarctic waters is consequently regional in its scope, it can be expected to have wide applicability as the shallow epi-macrofauna of McMurdo Sound is generally circumpolar in its distribution (Hedgpeth, 1969; Dell, 1972; Arnaud, 1974; White, 1984). The purpose of this paper is to provide an overview of what is currently known of the chemical ecology of antarctic marine invertebrates and suggest directions for further research. We include in this review both information on the broad bioactive nature of secondary metabolites and wherever possible information that is of ecological significance. To date, ecological studies in Antarctica have focused primarily on evaluations of how defensive chemistry may inhibit feeding by likely or known predators, similar to studies in temperate and tropical marine environments (Paul, 1992; Pawlik, 1993; Hay, 1996).

EMPIRICAL STUDIES

Sessile macroinvertebrates

Sponges.—The sponges of McMurdo Sound, Antarctica have been the focus of chemical studies to date (Table 1). On the eastern side of McMurdo Sound, Antarctica, approximately twenty-one species of conspicuous marine sponges occur in near-shore waters accounting for 55% of the benthic surface area below 33 m depth (Koltun, 1970; Dayton *et al.*, 1974). Dayton (*et al.*, 1974) was the first to suggest chemical defenses occurred in antarctic sponges, having observed no predation on the sponges *Leucetta leptorhapsis*, *Dendrilla membranosa* and *Isodictya erinacea*, all of which apparently lacked physical defenses against spongivorous sea stars. In the first quantitative studies of chemical bioactivity, McClintock (1987) and McClintock and Gauthier (1992) found a number of antarctic sponge extracts caused mortality in goldfish or inhibited growth in allopatric microorganisms. Moreover, Blunt *et al.* (1990) found the incidence of antiviral activity similar in marine sponges from temperate waters of New Zealand (37%) and polar antarctic waters (33%). In addition, Battershill (1990) conducted immunological assays with three antarctic sponges from McMurdo Sound (*Cinachyra antartica*, *Latrunculia* sp., *Polymastia* sp.) and found

TABLE 1. *Chemical and ecological bioactivity*[a] *of antarctic shallow-water marine invertebrate.*

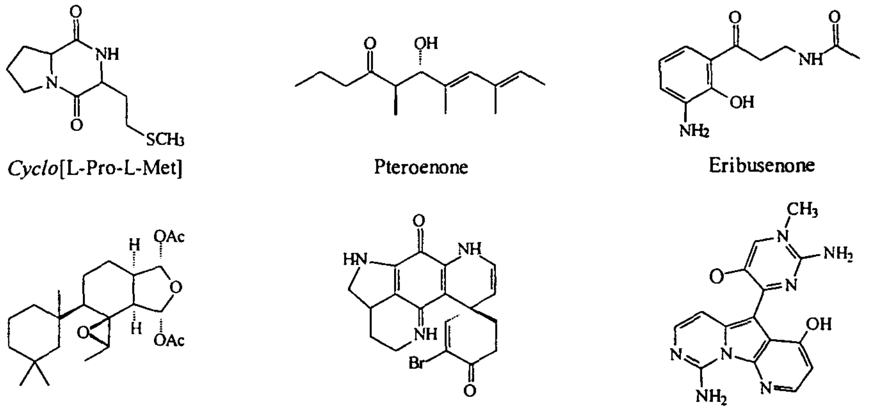
	Anti-microbial	Anti-foulant	Cyto-toxic	Tube-foot retraction	Feeding deterrence	Activity in:				
				Sea stars	Fish	Compound	Extract	Tissue	Whole animal	Reference[b]
PORIFERA										
Calyx acuarius	+			+			+			1
Cinachyra antarctica				+			+			1,2,3,4,5,6
Dendrilla membranosa	+			+		+	+			1,2
Gellius benedeni	+			+			+			1,2
Haliclona sp.				+			+			1
Haliclona dancoi	+			+			+			1,2
Homaxonella balfourensis	+			+			+			1,2
Inflatella belli				+			+			1
Isodictya erinacea	+			+		+	+		+[c]	1,2,3
Kirkpatrickia variolosa	+			+		+	+			1,2,3,7,8,9
Latrunculia apicalis	+			+		+	+			1,2,3,6,10
Leucetta leptorhapsis	+		+	+		+	+			1,2,3
Polymastia invaginata	+			+			+			1,2
Rosella nuda				+			+			1
Rosella racovitzae				+			+			1
Sphaerotylus antarcticus				+			+			1
Tetilla leptoderma				+			+			1
CNIDARIA										
Alcyonium paessleri	+	+	+	+	+		+	+		11,12,13
Clavularia frankliniana	−	−	−	+	+		−	+		11,12,13
Gersemia antarctica	+	+	+	+	+		+	+		11,12,13
BRACHIOPODA										
Liothyrella uva				+	+		+	+		14
ASCIDACEA										
Cnemidocarpa verrucosa			−		+		+	+		15
NEMERTEA										
Parborlasia corrugatus			+		+	+	+	+	+	16,17
MOLLUSCA										
Austrodoris kerguelensis				+	+	+		+		18,19,20
Clione antarctica	−				+	+	−		+	2,21,22,23
Marseniopsis mollis				+	+	+		+	+	18,19,24
Tritoniella belli				+	+	+			+	18,19,25
ECHINODERMATA										
Perknaster fuscus			+	+					+[c]	26
Diplasterias brucei				+			+		+[c]	27

[a] Data only presented for species tested against antarctic microbes, microalgae, macroinvertebrate gametes, macroinvertebrates or fish.

[b] References: McClintock *et al.*, 1993*a*[1]; Baker and McClintock unpublished[2]; Baker *et al.*, 1993[3], 1995[4]; Molinski and Faulkner, 1987[5]; Yang *et al.*, 1995[6]; Jayatilake *et al.*, 1995[7]; Perry *et al.*, 1994[8]; Trimurtulu *et al.*, 1994[9]; Blunt *et al.*, 1990[10]; Slattery and McClintock, 1995[11]; Slattery *et al.*, 1995[12]; Slattery, 1994[13]; McClintock *et al.*, 1993*b*[14]; McClintock *et al.*, 1991[15]; Heine *et al.*, 1991[16]; W. Kem unpublished[17]; McClintock *et al.*, 1992*a*[18]; McClintock *et al.*, 1994*d*[19]; Davies-Coleman and Faulkner, 1991[20]; McClintock and Janssen, 1990[21]; Bryan *et al.*, 1995[22]; Yoshida *et al.*, 1995[23]; McClintock *et al.*, 1994[24]; McClintock *et al.*, 1994*c*[25]; McClintock *et al.*, 1992*b*[26]; McClintock and Baker, 1997[27].

[c] Whole animal activity detected in developing embryos.

them all capable of rejecting tissues from congeners, concluding these sponges were capable of producing defensive chemicals that were toxic to genetically dissimilar tissues. The results of these studies suggested that a variety of antarctic sponges harbor toxic compounds. Nonetheless, while these bioassay approaches provide useful infor-



Cyclo[L-Pro-L-Met] Pteroenone Eribusenone

Dendrillin Discorhabdin G Variolin A

FIG. 2. Chemical structures of bioactive compounds isolated from antarctic organisms (clockwise from upper left): The bacterium *Pseudomonas aeruginosa* isolated from the surface of the sponge *Isodictya setifera*, the pteropod *Clione antarctica*, and the sponges *Isodictya erinacea*, *Dendrilla membranosa*, *Latrunculia apicalis* and *Kirkpatrickia variolosa*.

mation which may be of pharmacological or agrochemical importance, they provide little information of demonstrative ecological significance. Subsequent investigations by McClintock *et al.* (1994*a*) focused on examinations of the feeding deterrent characteristics of hexane, chloroform and methanol (non-polar to polar) extracts of antarctic sponges employing a tube-foot assay using an ecologically relevant predator, the common antarctic spongivorous sea star *Perknaster fuscus*. Significant tube-foot retraction activity was detected in the chloroform and methanol extracts of 75% of eighteen species tested. These levels of deterrence are similar to levels measured in reef fish presented feeding pellets containing extracts of Caribbean sponges in the laboratory (Pawlik *et al.*, 1995). The bioactive compounds likely responsible for feeding deterrence or additional biological activity have been elucidated in five of these antarctic species.

A variety of bioactive metabolites have been identified from antarctic sponges (Baker *et al.*, 1993, 1994; Fig. 2). Diterpene metabolites, including dendrillin, 9,11-dihydrogracilin A, membranolide and picolinic acid have been extracted from the tissues of *Dendrilla membranosa* (Molinski and Faulkner, 1987, 1988; Baker *et al.*, 1993, 1994, 1995). The latter compound causes sea star tube-foot retraction (McClintock *et al.*, 1994*b*). *Kirkpatrickia variolosa* has been found to produce variolins, a novel group of alkaloids, which have been demonstrated to have antitumor and antiviral activity (Perry *et al.*, 1994; Trimurtulu *et al.*, 1994). A purple pigment in *K. variolosa* causes tube-foot retraction in the antarctic sea star *Perknaster fuscus* (Baker and McClintock, unpublished). Moreover, a bioactive stilbene derivative has been isolated from *K. variolosa*, the first such observation of a stilbene from a marine invertebrate (Jayatilake *et al.*, 1995). The antarctic sponge *Latrunculia apicalis* has been found to contain a variety of discorhabdin pigments (Yang *et al.*, 1995; Baker *et al.*, 1993, 1994) which are cytotoxic (Blunt *et al.*, 1990) and cause tube-foot retraction in *P. fuscus* (Baker and McClintock, unpublished). Recent work with the sponge *Leucetta leptorhapsis* has indicated the presence of highly cytotoxic lipids (Baker *et al.*, 1993) that cause feeding deterrence in antarctic seastars (McClintock *et al.*, 1993*a*). The antarctic sponge *Isodictya erinacea* contains the secondary metabolites eribusenone, 7-methyladinine, and *p*-hydroxybenzoic acid (Baker *et al.*, 1994; Moon *et al.*, in preparation). Bioactive metabolites have also been isolated from microbes associated with antarctic sponges. Jayatilake *et al.* (1996) recently isolated a series of diketopiperazines and phenazine alkaloids from the bacterium *Pseudomonas aeruginosa* associated with the antarctic sponge *Isodictya setifera* (Fig 2.). Finally, the antarctic sponge *Artemisina apollinis* has been found to possess 28 steroidal derivatives including a new group of natural products (Seldes *et al.,* 1990). The ecological roles of bioactive compounds isolated from *L. leptorhapsis*, *I. erinacea*, and *I. setifera* are currently unknown.

Although it is possible that some of the bioactive metabolites in antarctic sponges are "evolutionary baggage" with no current adaptive significance, it is more likely that given the extreme age of the marine benthos, there has been ample time for defensive metabolites to have evolved in response to sympatric predators, fouling organisms, or competitors. In this respect, it is of interest to consider whether congeners from other latitudes have similar or different chemical defenses, or lack chemical defenses entirely. The answer appears to vary with species, as might be expected of sponges under different selective pressures. For example, the antarctic congeners of *Haliclona* and *Mycale* are devoid of the types of secondary metabolites found in their tropical counterparts (alkaloids in *Haliclona* (Schmitz *et al.*, 1978; Sakai *et al.*, 1986; Baker *et al.,* 1988; Crews *et al.*, 1994) and terpenes or mycalamides from *Mycale* (Perry *et al.*, 1988; Fusetani *et al.*, 1991; Tanaka *et al.*, 1993)). Alternately, antarctic *Latrunculia* and *Dendrilla* both produce derivatives (discorhabdin G and dendrillin, respectively [Yang *et al.*, 1995; Baker *et al.*, 1995]) of secondary metabolites found in temperate and tropical congeners (Karuso *et al.*, 1984; Mayol *et al.*, 1985; Molinski and Faulkner, 1987; Blunt *et al.*, 1990) and the tropical sponge *Leucetta microraphis* harbors leucettamols (Kong and Faulkner, 1993) that are similar in structure to cytotoxic lipids produced by the antarctic congener *Leucetta leptorhapsis* (Baker *et al.*, 1993). More information is needed to provide a more comprehensive evaluation of phylogenetic influences on patterns of chemical defense in antarctic sponges.

In many cases it is those antarctic sponges with color that have proven to be bioactive to date (Baker and McClintock, personal observation). At first examination these would appear to be examples of warning coloration or aposematism (Guilford and Cuthill, 1991; Rosenberg, 1991). However, Pawlik *et al.* (1995) found no evidence of aposematism in tropical marine sponges. Moreover, it is unlikely aposematism occurs in antarctic sponges, as the antarctic marine benthos is depauperate in visually oriented browsing predators such as fish which feed on sessile invertebrates (most antarctic benthic fish eat crustaceans; Eastman, 1991, 1993). In this regard, even if aposematism occurred in sponges (but see Pawlik *et al.*, 1995), there should be little evolutionary selection for warning coloration in antarctic sponges when their primary predators are sea stars (Dearborn, 1977; McClintock, 1994), which orient to prey chemically (Sloan, 1980). Nonetheless, it is intriguing that antarctic sponges employ their colored pigments as a chemical defense. For example, pigments from the colored sponges *Latrunculia apicalis* and *Kirkpatrickia variolosa* are bioactive and cause sea star tube-foot retraction (Baker and McClintock, unpublished).

Soft corals.—Chemical studies of antarctic soft corals have focused on three antarctic species that occur in McMurdo Sound (Table 1). Two of these species, *Alcyonium paessleri* and *Clavularia frankliniana* are extremely abundant along the east side of McMurdo Sound (Dayton *et al.*, 1974; Slattery, 1994). The third species, *Gersemia antarctica*, is much rarer, and within McMurdo Sound is confined to its western regions (Slattery and McClintock, 1995). All three of these soft corals are chemically defended. Organic extracts of *A. paessleri* and *G. antarctica* inhibit the attachment of marine antarctic bacteria (Slattery *et al.*, 1995). In addition, organic extracts exhibit antifoulant activity in field experiments causing inhibition of diatom settlement. This is important as diatoms are one of the primary fouling organisms in antarctic benthos (El-Sayed and Fryxell, 1993). Two potential soft coral predators, the antarctic sea stars *Odontaster validus* and *Perknaster fuscus*, show tube-foot retractions to organic and aqueous extracts of all three soft coral species (Slattery and McClintock, 1995).

Aqueous homogenates of two of the soft corals, *A. paessleri* and *G. antarctica*, are toxic to antarctic sea urchin larvae, suggesting that similar to tropical marine invertebrates toxicity and feeding deterrence are not predictably related (Pawlik *et al.*, 1995). Distinct secondary metabolites responsible for toxicity or feeding deterrence may be present in these soft corals (Slattery *et al.*, 1995). Chimyl alcohol has been detected in the tissues of *C. frankliniana* and causes rejection of treated shrimp-discs in the omnivorous sea star *Odontaster validus* (McClintock *et al.*, 1994*c*).

Bryozoans.—While antarctic bryozoans can be dominant members of antarctic benthic communities (Foster, 1969), only one study has investigated their biological activity. Winston and Bernheimer (1986) investigated the extracts of five species of antarctic bryozoans collected from the Antarctic Peninsula and examined hemolytic activity against mammalian erythrocytes. Extracts of one species, *Carbasea curva*, caused significant lysis of mammalian cells, suggesting the presence of bioactive secondary metabolites. No investigations have yet been conducted to determine the nature of the secondary metabolite(s) nor to examine their ecological significance. Winston and Bernheimer (1986) indicate that *C. curva* is one of the most abundant bryozoans found in benthic samples from the Antarctic Peninsula or the Ross Sea, and that the toxic substance may be employed in chemical defense, explaining the success of a weakly calcified body plan.

Brachiopods.—One of the few Antarctic Peninsular organisms which has been studied for its chemical defense is the common antarctic brachiopod *Liothyrella uva*. This punctate terebratulid species is common at depths of 5–300 m (Voss, 1988). Ecological assays indicate that extracts of whole soft body tissues cause significant retraction of the sensory tube-feet of six species of antarctic sea stars (Table 1; McClintock *et al.*, 1993*b*), several of which are likely predators of brachiopods (McClintock, 1994). Ground body tissues embedded in agar pellets containing krill meal resulted in significant feeding deterrence in an allopatric fish, the Sheepshead Minnow *Cyprinidon variegatus* (McClintock *et al.*, 1993*b*). Studies are needed to determine if ecologically relevant fish are also deterred. The nature of the bioactive compound(s) responsible for feeding deterrence are unknown. The results of this study further support the hypothesis that unpalatability occurs in brachiopods in temperate, tropical, and polar environments (Thayer and Allmon, 1991). A chemical means of defense may be particularly important from an evolutionary perspective due to the slow growth and late reproduction which characterizes the life history of brachiopods (Thayer, 1985).

Ascidians.—Although there are many species of antarctic ascidians, only one species has been chemically investigated. The common solitary ascidian *Cnemidocarpa verrucosa* is a large conspicuous species which is found in McMurdo Sound, and has a circumpolar distribution (Kott, 1969; Dayton *et al.*, 1974). McClintock *et al.* (1991) conducted an analysis of the palatability and chemical defense of the tunic, ovitestes, branchial basket, body wall, endocarps and intestines. They found that the tunic was deterrent to sympatric pelagic and benthic fish, in addition to an allopatric fish model (Table 1). Nonetheless, homogenates of the tunic were not cytotoxic to sea urchin gametes, suggesting that the bioactive compound(s) are not toxic. The heavy fouling of the tunic surface by bryozoans and hydroids indicates that bioactive chemicals are not effective antifoulants. Mature ovitestes are rejected by antarctic fish and alginate krill pellets containing lipophilic extracts of ovitestes are rejected by the antarctic sea star *Odontaster validus*, a likely predator of settling larvae (Dayton *et al.*, 1974), indicating that the eggs and larvae may possess a chemical defense (McClintock *et al.*, 1991; McClintock and Baker, unpublished).

Mobile macroinvertebrates

Nemerteans.—One of the most conspicuous benthic invertebrates in shallow antarctic waters is the large (up to 1 m extended body length) nemertean worm *Parborlasia corrugatus* (Fig. 1A; Knox, 1970, Gibson, 1983). Despite their high abundance and rich energy content, and obvious lack of skeletal defenses, individuals are rarely if ever preyed upon (Dayton *et al.*, 1974; Heine *et al.*, 1991). Cytotoxicity assays indicate homogenates of the whole body tissues cause mortality in gametes of the antarctic sea urchin *Sterechinus neumayeri*. In addition, ecological bioassays indicate two common species of antarctic fish show significant rejection of body tissues (Table 1; Heine *et al.*, 1991). Both toxicity and feeding-deterrent characteristics of this species may result from the production of a copious acidic (pH = 3.5) mucus (Heine *et al.*, 1991). The defensive properties of this acidic mucus may be diminished through neutralization in seawater. Nonetheless, the mucus of *P. corrugatus* also harbors a potent toxic neuropeptide (William Kem, unpublished).

Molluscs.—Investigations of chemical defense in antarctic molluscs have been limited to species occurring in McMurdo Sound (Table 1). Nonetheless, many of these species have circumpolar distributions, and their defensive chemistry is likely similar across a wide geographic range. Ecological bioassays indicate the mantle tissues of the antarctic nudibranchs *Austrodoris kerguelensis* and *Tritoniella belli* are rejected by two species of sympatric antarctic fish, and cause significant tube-foot retractions in four species of sympatric antarctic sea stars (McClintock *et al.*, 1992*a*). *Austrodoris kerguelensis* produces a series of bioactive acid glycerides (Davies-Coleman and Faulkner, 1991) which remain to be evaluated for ecological function, while *T. belli* contains chimyl alcohol which causes feeding deterrence in the sea star *Odontaster validus* (McClintock *et al.*, 1994*b*). This proven feeding deterrent may be derived from its diet of the soft coral *Clavularia frankliniana* (McClintock *et al.*, 1994*b*). The prosobranch *Marseniopsis mollis*, which has an internalized vestigial shell, has mantle tissues which are rejected by antarctic fish and sea stars (McClintock *et al.*, 1992*a*) and the compound homarine has been isolated from the mantle, foot and viscera (McClintock *et al.*, 1994*c*). Homarine causes feeding deterrence in the omnivorous *O. validus* at levels spanning those detected in the body tissues of *M. mollis* (McClintock *et al.*, 1994*c*). Homarine was not found in the tunic of the antarctic ascidian *Cnemidocarpa verrucosa*, the presumed primary prey of this gastropod (McClintock *et al.*, 1994*c*). Nonetheless, homarine has been isolated from the dense assemblage of epizooites which foul the tunic of this ascidian (McClintock *et al.*, 1994*c*), suggesting that these fouling organisms (primarily bryozoans and hydroids) may be grazed by *M. mollis* and be the dietary source of this defensive compound.

The common pelagic pteropod *Clione antarctica* occurs in vast swarms seasonally in antarctic continental shelf waters (Foster, 1987). Intact live sea butterflies and whole body homogenates imbedded in pellets containing feeding stimulants are consistently rejected by the antarctic zooplanktivorous fish *Pagothenia borchgrevinki*, a significant pteropod predator (Foster *et al.*, 1987), indicating the presence of chemical defense (McClintock and Janssen, 1990). Interestingly, the abundant antarctic hyperiid amphipod *Hyperiella dilatata* abducts and carries a single live individual of *C. antarctica* (Fig. 3), providing itself with a means of chemical defense from fish predators (McClintock and Janssen, 1990). The nature of the compound responsible for chemical deterrence in *C. antarctica* has recently been elucidated to be a novel bioactive linear hydroxyketone, named pteroenone (Fig. 2; Bryan *et al.*, 1995; Yoshida *et al.*, 1995). This is one of the first defensive compounds isolated from a planktonic macroinvertebrate, and supports recent evidence that feeding deterrent properties of oceanic holoplankton may be widespread (McClintock *et al.*, 1996). As *C. antarctica* is extremely abundant, the trophic implications of chemical defense in modeling energy flow in the antarctic water column must be considered. Moreover, if additional organisms receive defensive characteristics through their association with chemically defended species (*e.g.*, McClintock and Jansson, 1990), this furthers the complexity of planktonic ecosystems (McClintock *et al.*, 1996).

Echinoderms.—Research conducted with temperate and tropical echinoderms has indicated that a large number of species may possess bioactive compounds, particularly those which are saponin-related (Verbist, 1993). Bioactivity appears to occur most fre-

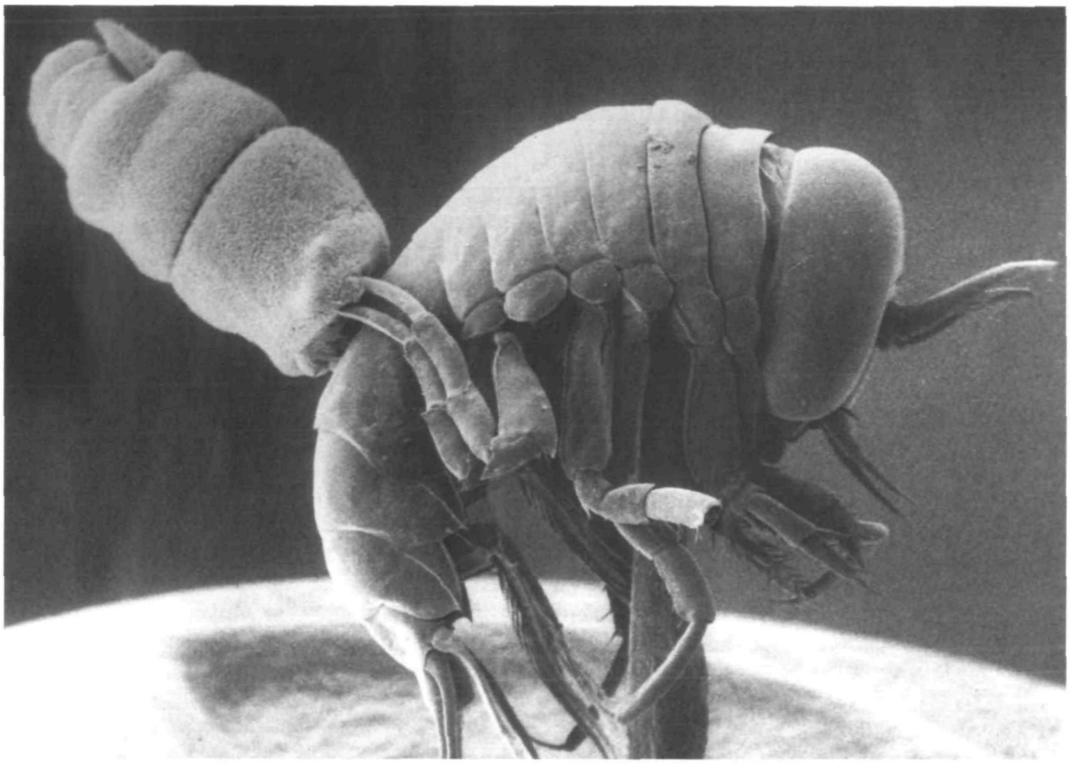


FIG. 3. The antarctic hyperiid amphipod *Hyperiella dilatata* shown grasping the chemically defended pteropod *Clione antarctica* (McClintock and Janssen, 1990). This unique association provides a mechanism for amphipods to defend themselves against their primary predators, antarctic fish. Magnification is approximately ×500.

quently in the body tissues of the holothurians and asteroids (Mackie *et al.*, 1977). McClintock (1989) examined the toxicity of the body wall of 23 species of antarctic echinoderms to the mosquitofish *Gambusia affinis*. Patterns of toxicity were class specific, and similar to patterns seen in temperate and tropical species, with the highest levels of toxicity occurring in the body tissues of holothuroids and asteroids. Two of three species of holothuroids tested were toxic, while seven of thirteen species of asteroids tested caused mortality in fish. Toxicity was not found to be related to the amount of skeletal material present in the echinoderm body wall, although the degree of skeletal armament was generally low among antarctic species (McClintock, 1989).

The common spongivorous sea star *Perknaster fuscus* possesses the bioactive tetrahydroisoquinoline alkaloid fuscusine (Kong *et al.*, 1992). This is only the second report of an alkaloid in the body wall tissues of a sea star, the first being imbricatine, a benzyltetrahydroisoquinoline alkaloid which occurs in the sea star *Dermasterias imbricata* on the west coast of North America. This compound is known to induce a flight response in a sea anemone (Patherina and Anderson, 1986). Crude homogenates of the body wall tissues of *P. fuscus* are toxic to the sperm of the antarctic sea urchin *Sterechinus neumayeri*, cause an inhibition of the righting response of the antarctic sea star *Odontaster validus*, and elicit significant tube-foot retractions in the sympatric antarctic sea stars *O. validus*, *O. meridionalis*, *Acodontaster conspicuus* and *Diplasterias brucei* (Table 1; McClintock *et al.*, 1992*b*). At least one of these sea stars, *Odontaster validus*, is an opportunistic echinovore (McClintock, 1994). It is of some significance that while a number of antarctic sea stars are included in the diets of echinoderms and sea anemones (Dearborn, 1977), *P. fuscus* has never been observed as a prey item (Dayton *et al.*, 1974). This may be attributable to its chemical defense. Possessing such an effective means of defense has important ramifications in maintaining populations of this spongivorous sea star, as it is responsible for keeping one of the primary space-dominating antarctic sponges (*Mycale acerata*) at levels which allow increased species diversity (Dayton *et al.*, 1974). Steroidal glycosides and polyhydroxylated steroids have recently been isolated from the antarctic sea star *Acodontaster conspicuus* and the ophiuroids *Ophiosparta gigas* and *Ophionotus victoriae* (D'Auria *et al.*, 1993, 1995; Iorizzi *et al.*, 1996; De Marino *et al.*, 1997). Bioassays indicate that steroidal glycosides and polyhydroxylated steroids isolated from *A. conspicuus* cause significant growth inhibition in three species of antarctic marine bacteria isolated from the surfaces of antarctic sponges and echinoderms (De Marino *et al.*, in press). This suggests one ecological role of these compounds may be in the prevention of microbial fouling.

In one of only two studies to focus on the chemical defense of early life stages of antarctic marine invertebrates, McClintock and Vernon (1990) examined the icthyonoxic characteristics of the eggs and embryos of fifteen species of antarctic echinoderms, primarily sea stars. Using the common killifish *Fundulus grandis* as a model predator, they offered pellets impregnated with echinoderm tissues and a feeding stimulant to fish. Chemical feeding deterrents occurred in the large yolky eggs of the pelagic lecithotrophic sea stars *Perknaster fuscus* and *Porania antarctica.* Brooded embryos of the sea stars *Notasterias armata* and *Diplasterias brucei* were also noxious. The chemical deterrents were effective at ecologically relevant concentrations. In a more recent study, McClintock and Baker (1997) demonstrated that the lecithotrophic eggs, embryos and larvae of five species of antarctic marine invertebrates (including three echinoderms) were unpalatable or chemically defended from ecologically relevant benthic and water column invertebrate predators (sea stars, sea anemones and amphipods). Two echinoderms with planktotrophic modes of reproduction (the sea urchin *Sterechinus neumayeri* and the sea star *Odontaster validus*) lacked chemical defense in their eggs or larvae. Therefore, similar to tropical marine invertebrates (Lindquist and Hay, 1996), large yolky lecithotrophic embryos and larvae are more likely to be chemically defended. This may be especially true in antarctic embryos or larvae where very slow development results in substantial periods of time spent in the plankton or on the benthos (Pearse *et al.*, 1991).

SUMMARY AND FUTURE DIRECTIONS

The unique environmental and biotic factors that characterize shallow antarctic shelf waters have resulted in communities structured by biotic factors such as predation and competition (Dayton *et al.*, 1974). The present review indicates that selection for ecologically relevant secondary metabolites has occurred in a wide variety of representative organisms (reviewed in Table 1). Nonetheless, while much of the research conducted to date on chemical defense has been conducted in the laboratory using ecologically relevant predators (as essentially has been the case for temperate and tropical marine invertebrates), there is a need to extend studies to the field, as has been done to a limited extent in tropical marine environments (Paul, 1992; Pawlik, 1993; Hay, 1996). Much also remains to be learned about additional novel bioactive compounds, and there is a need for further evaluation of the functional roles of known compounds. In addition to defense from predation, factors most likely to be mediated by defensive metabolites include fouling and allelochemical interactions. For example, sessile antarctic benthic organisms are subject to particularly intense fouling pressure by benthic diatoms. Allelochemistry could be important because in contrast to the generalized perception of reduced growth rates in polar species, there are species that grow rapidly and crowd out other species, eventually monopolizing space if released from predation (Dayton *et al.*, 1974, Dayton, 1989).

To date, few investigations have extended studies of defensive metabolites to antarctic macroalgae (Amsler *et al.*, submitted). Such studies will be of particular interest given current theories relating defensive chemistry in macroalgae to biogeographic patterns of herbivory (Estes and Steinberg, 1988; Steinberg and Paul, 1990; Hay, 1992). Initial investigation suggests that antarctic brown algae produce defensive polyphenolics, similar to their temperate and tropical counterparts, perhaps explaining their seemingly low levels of herbivory (Amsler, McClintock and Baker, unpublished).

As in all planktonic systems, there is a need to extend the evaluation of chemical defense to marine invertebrate holoplanktonic organisms in antarctic waters. Of particular interest will be those holoplanktonic organisms that comprise significant biomass in pelagic foodwebs, such as salps and pteropods. Chemically mediated predation may have profound effects on modeling energy flow in such systems (McClintock *et al.*, 1996). Moreover, more information on the role of secondary metabolites in mediating patterns of predation on the pelagic embryos and larvae of macroinvertebrates is needed, along with more quantitative information on abundances and diets of likely planktonic predators.

Finally, studies are needed to determine if antarctic microorganisms (*e.g.*, bacteria, microalgae) employ defensive chemistry (*e.g.*, Jayatilake *et al.*, 1996), if macroinvertebrates utilize microbial defensive metabolites, and if defensive chemistry in antarctic organisms is static or can be induced in response to a variety of ecological constraints.

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