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SYMPOSIUM

Overview of the Chemical Ecology of Benthic Marine Invertebrates along the Western Antarctic Peninsula

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Synopsis Thirteen years ago in a review that appeared in the American Zoologist, we presented the first survey of the chemical and ecological bioactivity of Antarctic shallow-water marine invertebrates. In essence, we reported that despite theoretical predictions to the contrary the incidence of chemical defenses among sessile and sluggish Antarctic marine invertebrates was widespread. Since that time we and others have significantly expanded upon the base of knowledge of Antarctic marine invertebrates' chemical ecology, both from the perspective of examining marine invertebrates in new, distinct geographic provinces, as well as broadening the evaluation of the ecological significance of secondary metabolites. Importantly, many of these studies have been framed within established theoretical constructs, particularly the Optimal Defense Theory. In the present article, we review the current knowledge of chemical ecology of benthic marine invertebrates comprising communities along the Western Antarctic Peninsula (WAP), a region of Antarctica that is both physically and biologically distinct from the rest of the continent. Our overview indicates that, similar to other regions of Antarctica, anti-predator chemical defenses are widespread among species occurring along the WAP. In some groups, such as the sponges, the incidence of chemical defenses against predation is comparable to, or even slightly higher than, that found in tropical marine systems. While there is substantial knowledge of the chemical defenses of benthic marine invertebrates against predators, much less is known about chemical anti-foulants. The sole survey conducted to date suggests that secondary metabolites in benthic sponges are likely to be important in the prevention of fouling by benthic diatoms, yet generally lack activity against marine bacteria. Our understanding of the sensory ecology of Antarctic benthic marine invertebrates, despite its great potential, remains in its infancy. For example, along the WAP, community-level non-consumptive effects occur when amphipods chemically sense fish predators and respond by seeking refuge in chemically-defended macroalgae. Such interactions may be important in releasing amphipods from predation pressure and facilitating their unusually high abundances along the WAP. Moreover, recent studies on the sensory biology of the Antarctic keystone sea star *Odontaster validus* indicate that chemotactile-mediated interactions between conspecifics and other sympatric predatory sea stars may have significant ramifications in structuring community dynamics. Finally, from a global environmental perspective, understanding how chemical ecology structures marine benthic communities along the WAP must increasingly be viewed in the context of the dramatic impacts of rapid climatic change now occurring in this biogeographic region.

General environmental and biotic characteristics of the Western Antarctic Peninsula

The Western Antarctic Peninsula (WAP) stretches over 1500 km from its base in the Bellingshausen Sea (75°S, 80′W) to the South Orkney Islands off the tip of the peninsula in the Southern Ocean (60°S, 43′W). South America is 1000 km to the northwest of the peninsula. The continental shelf of the WAP extends some 200 km offshore, averaging depths of 400 m before transitioning to a steep continental slope that descends several thousands of meters to the deep sea. The WAP supports a remarkably productive marine ecosystem (Clarke et al. 2007;

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Ducklow et al. 2007). This is due in part to its close proximity to the world's largest current, the Antarctic circumpolar current (ACC), which transports nutrients and ocean heat from circumpolar deep water (CDW). The nutrient-replete waters that are transported across the shelf by the ACC, coupled with the extended photoperiods and reduced duration and extent of annual sea ice that occurs at these comparatively high Antarctic latitudes, fuels very high levels of primary production. This production manifests itself not only in a seasonally abundant phytoplankton assemblage comprised mostly of diatoms and cryptomonads (Garibotti et al. 2003a, 2003b), but also in dense coastal underwater 'forests' of macroalgae that can extend to depths of 40–50 m (Amsler et al. 1995; Wiencke and Clayton 2002). Secondary production along the WAP is equally impressive, particularly in terms of production of krill and salps (Ross et al. 1996; Loeb et al. 1997). At depths below the extent of the macroalgal forests or on shallower vertical rock faces, there exists a rich suspension-feeding macroinvertebrate assemblage comprised of sponges, soft corals, bryozoans, hydroids, and ascidians (DeLaca and Lipps 1976). Higher trophic levels include remarkably high densities of crustacean mesograzers (Richardson 1977, Huang et al. 2007), as well as generalist macroinvertebrate predators that include nemerteans (DeLaca and Lipps 1976), sea stars, sea urchins, sea cucumbers and brittle stars (Dearborn et al. 1983, 1984), fish (Eastman 1993), and largely krill-dependent and fish-dependent sea birds, including penguins and a variety of marine mammals (Williams 1995; Costa and Crocker 1996).

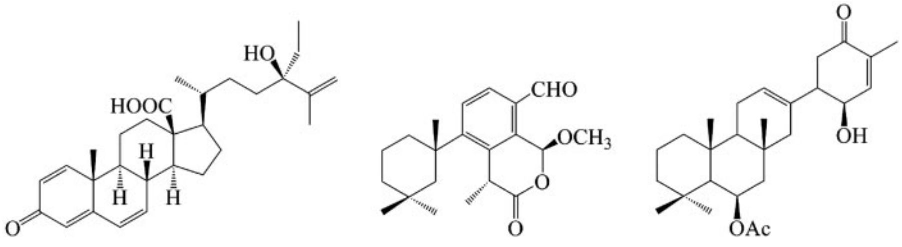
Much like the soft and hard bottom benthic marine communities of McMurdo Sound in the Ross Sea that were so elegantly described by Paul Dayton and his colleagues in the late 1960s and 1970s, and despite some coastal regions experiencing periodic disruption of the benthos by iceberg scour (anchor ice is essentially absent along the WAP) (Smale 2007), the benthos of the WAP appears to be relatively stable environmentally and 'biologically accommodated' (*sensu* Dayton et al. 1974). In other words, the benthos appears to be structured in large part by predatory and competitive interactions. Our own anecdotal *in situ* observations along the WAP indicate that open space on hard benthic substrates is at a premium and that sessile and sluggish marine invertebrates are subject to substantial predation pressure, especially through the foraging activities of abundant sea stars (C.D. Amsler and B.J. Baker, personal observation). As the Antarctic Peninsula separated from South America over 25 million years ago, despite some taxonomic connectivity that remains with South America, the current benthic marine invertebrate fauna of the WAP is largely an ancient, endemic one (Aronson et al. 2007). As such, the benthos has had ample opportunity to evolve the types of predatory and competitive relationships that select for chemical defenses (Amsler et al. 2000a).

Anti-predator chemical defenses

Chemical feeding deterrents have been investigated in selected marine invertebrate phyla along the WAP that are known from studies conducted elsewhere in Antarctica (Amsler et al. 2001a, 2001b; Lebar et al. 2007; Avila et al. 2009), as well as from temperate and tropical marine ecosystems (Paul and Puglisi 2004; Paul et al. 2006; Sotka et al. 2009), to harbor unpalatable secondary metabolites. Sponges top this list as they often possess bioactive secondary metabolites (McClintock and Baker 1997a; Paul and Puglisi 2004; Paul et al. 2006; Avila et al. 2009) and occur in abundance along the WAP (Peters et al. 2009). Moreover, they are dominant members of benthic marine communities in non-peninsular regions of Antarctica (Dayton et al. 1974; Dayton 1989; McClintock et al. 2005). Pioneering studies of the chemical anti-feedant ecology of Antarctic sponges were first conducted in sponges from McMurdo Sound, Ross Sea. These studies relied on an indirect measure of feeding deterrence that exploited the chemotactile retraction of sensory tube feet of the common spongivorous sea star *Perknaster fuscus* (McClintock 1987; McClintock et al. 1994, 2000). However, in the most comprehensive study to date of the chemical feeding deterrent properties of Antarctic sponges along the WAP, Peters et al. (2009) examined the chemical anti-feedant properties of 27 common sponges that occur near Palmer Station, Anvers Island. Importantly, feeding deterrence was evaluated directly, taking advantage of the propensity of the common omnivorous sea star *Odontaster validus* to position themselves in laboratory seawater tanks with several of their arms splayed back at the air–water interface exposing the ambulacral feeding grooves. As such, feeding deterrence could be directly evaluated by placing a piece of fresh sponge tissue or an alginate food pellet containing tissue-level concentrations of either hydrophilic or lipophilic sponge extract on to the tube feet in the ambulacral groove equidistant between the mouth and the tip of the arm. Acceptance or rejection could be clearly evaluated by following the movement of the tissue or food pellet to the mouth, or the discarding of the tissue or food pellet from the ambulacral groove.

Peters et al. (2009) framed their study of the chemical defenses of sponges along the WAP within the theoretical constructs of Optimal Defense Theory (ODT) (Rhoades 1979; Cronin 2001). The ODT evaluates variations in defenses within organisms, making the implicit assumption that defenses invoke some cost in fitness, and thus sets the stage for predictions of when and where defenses should be allocated in lieu of internal competition for resources invested in growth, reproduction and defense. In terms of chemical defenses, the synthesis of secondary metabolites is assumed a measurable cost. At the level of the individual, the ODT predicts that defenses should be allocated to the most valuable or vulnerable tissues. This, of course, will vary with the type of predator and prey. In the case of sponges along the WAP, Peters et al. (2009) assumed that sea stars were the most common predators of sponges, and that according to the ODT, coupled with the extraoral mode of feeding of sea stars, sponge chemical defenses should be primarily allocated to the outermost 'tissues' (we use the term 'tissue' loosely here) where they would be most effective against sea star predators that feed by extruding their cardiac stomach against the sponge's surface. While one might question whether sponges have the capacity to differentially allocate chemicals to their outer layers, there is evidence to support this capability (e.g., Furrow et al. 2003; Peters et al. 2009). To test this hypothesis, both the outer and inner tissues of sponges were examined. Feeding assays revealed that 78% of the 27 species of sponges had outer tissues that were deterrent to sea stars. Of these, 62% were found to have inner tissues that also deterred feeding by sea stars. In order to evaluate whether secondary metabolites were responsible for the observed deterrence, a subset of 12 sponge species that had deterrent tissues were extracted and re-assayed as extracts imbedded in food pellets. In every case, either the hydrophilic or lipophilic extract was deterrent. These findings indicate that sponges along the WAP exhibit an incidence of chemical defense against predators (sea stars rejected outer tissues of 78% of the sponges) that is slightly higher than that in a similar survey of tropical sponges where 69% of the species were found to be chemically defended against fish (Pawlik et al. 1995). This pattern lends support to earlier predictions that selection for chemical anti-feedant defenses are under strong selection in Antarctic sponges (Amsler et al. 2000b), and supports the conclusions of Amsler et al. (2000a) and Becerro et al. (2003) that marine sponges do not display a latitudinal gradient in chemical defenses. Peters et al. (2009), however, found only weak support for the predictions of the ODT. Only 8 of 21 (38%) of the sponge species examined had unpalatable outer tissues and palatable inner tissues. As the remaining 62% of the sponges had both unpalatable outer and inner tissues, this suggests that, in the context of their study, the ODT is either based on inappropriate assumptions or that the sponges along the WAP may also be subject to predation by biting predators capable of consuming both outer and inner tissues. Recently, the most likely group of biting predators, the amphipods, while found to occur in relatively high abundance and diversity in association with Antarctic sponges along the WAP, have been ruled out as a source of significant sponge predation (Amsler et al. 2009a). As such, the chemical defenses of inner tissues of sponges may either indicate the presence of a group of biting predators yet to be determined, or that deterrent secondary metabolites associate with the interstices of sponges may serve an alternate role (see below).

To date, seven sponge species from the WAP have been demonstrated to produce secondary metabolites. Four of the sponge species, *Suberites* sp., *Latrunculia apicalis*, *Leucetta leptorhapsis*, and *Kirkpatrickia variolosa*, had previously been studied from McMurdo Sound, Ross Sea, and the chemistry, suberitenones [e.g., suberitenones C (3, Fig. 1)] (Shin et al. 1995), discorhabdins (Yang et al. 1995), rhapsamine (Jayatilake et al. 1997), and variolins (Parry et al. 1994; Trimurtulu et al. 1994), respectively, were similarly documented in the WAP-collected specimens. One sponge species, *Isodictya erinacea*, from the WAP was found to be devoid of the eribusinone chemistry previously documented in specimens from McMurdo Sound (Moon et al. 2000). Another species, *Dendrilla membranosa*, was found to elaborate a different suite of membranolides along the WAP (Ankisetty et al. 2004) [e.g., membranolides B (2, Fig. 1)], as compared to specimens collected in McMurdo Sound. Collectively, these findings indicate that some Antarctic sponge species display intraspecific variation in their production of secondary metabolites, at least across biogeographic scales of thousands of kilometers. Whether this may be due to differences in types or levels of predation, fouling organisms, organisms competing for space, phenotypic induction, or genetic differences is unknown. Two sponge species, *Crella* sp. and *I. antarctica*, have not been reported from McMurdo Sound, but WAP-collected specimens have been found to



Norselic Acid A (**1**) Membranolide B (**2**) Suberitenone C (**3**)

Fig. 1 A representative of the norselic acids, the membranolides, and the suberitenones from the sponges *Crella* sp., *Dendrilla membranosa*, and *Isodyctya antarctica*, respectively (shown from left to right). These compounds were all isolated from sponges collected within 2 km of Palmer Station, Anvers Island, on the WAP.

elaborate norselic acids [e.g., norselic acid A (1, Fig. 1)] (Ma et al. 2009) and ceramides (Park et al. unpublished), respectively.

Lipophilic extracts from *D. membranosa* from the WAP cause feeding deterrence in the Antarctic amphipod *Gondogeneia antarctica* at tissue-level concentrations (Amsler et al. 2009a) and appear to elaborate multiple deterrent metabolites. The chemical nature of these metabolites is currently being studied (Amsler et al. 2009a, Baker unpublished results). The sponge, *Crella* sp., produces a suite of steroidal carboxylic acids, the norselic acids (1, Fig. 1). At tissue-level concentrations, norselic acid A impregnated in alginate food pellets is not a feeding deterrent to the sympatric amphipod *G. antarctica* (Ma et al. 2009). However, at three times this isolated concentration, an 18% decrease in consumption by amphipods relative to a control was statistically significant; considering that traditional protocols of chemical isolation are inefficient and other norselic acid forms were not present, the higher concentration is likely more representative of actual concentrations of the natural product in this sponge. The sea star *O. validus* was not deterred by either concentration of norselic acid A when presented in alginate food pellets in feeding assays but was slightly deterred at 10× natural concentration (Ma et al. 2009).

Anti-predatory chemical defenses occur in both colored and non-colored WAP sponges (McClintock, personal observation) and as such there does not appear to be strong aposematic selection. Sea stars, one of the primary consumers of Antarctic sponges, are not visual predators. McClintock and Baker (1998) hypothesized that colored pigments (e.g., discorhabdins and variolins) in present day Antarctic sponges may be 'relict pigments' that evolved under aposematic selection in ancient, warmer Antarctic seas when visual predators, including fish and turtles, presumably preyed upon sponges. Those pigment compounds with inherent anti-foulant or anti-feedant properties have remained under selective pressure and been retained. The alternate hypothesis that color in sponges reflects their phylogenetic history, that is, they are colored simply because their ancestral lineages were colorful, lacks support. For example, Antarctic species of the genera *Haliclona* and *Calyx* lack color while their temperate and tropical counterparts are brightly colored. Moreover, species of Antarctic genus *Leucetta* are colorless, while their tropical counterparts are colored.

While a number of soft-coral and hydroid species occur along the WAP, and some in relatively high abundance, there have been no studies to date on their chemical ecology (but see Slattery and McClintock 1995, 1997; Slattery et al. 1995, 1998 for chemical studies of soft corals conducted in the Ross Sea). In a study of the chemical bioactivity of five species of bryozoans collected during a cruise along the WAP, Winston and Bernheimer (1986) found that whole-tissue extracts of one of the most common brachiopods, *Carbasea curva,* caused high levels (50–60%) of hemolysis in human and canine erythroctyes. They suggested that the putative toxin might be an effective chemical deterrent to predators, and such defenses would be expected to be under strong selection due to unusually weak calcification. Future studies are needed using ecologically relevant methods to validate this hypothesis.

Brachiopods from temperate and tropical latitudes have been found to be unpalatable to potential predators (Thayer 1985; Thayer and Allmon 1991). The single brachiopod species that has been investigated in Antarctica for its chemical defenses, the punctate terebratulid *Liothyrella uva*, is particularly abundant along the WAP. Near Palmer Station on Anvers Island this species can comprise up to 6% of the wet biomass between depths of 20–30 m in localized regions (Zamorano 1983). McClintock et al. (1993)

conducted initial studies on its chemical defenses. Fresh whole-animal, soft-tissue homogenate was tested in sea star sensory tube-foot retraction bioassays and found to elicit significantly greater duration of tube-foot retraction in six species of sympatric predatory sea stars when compared to controls comprised of seawater alone or homogenate of the soft tissues of a sympatric limpet. Moreover, lyophilized brachiopod tissues finely ground into a powder and embedded in agar pellets containing krill powder as a feeding stimulant elicited significant feeding deterrence in an allopatric marine fish. While neither of these approaches provided an ecologically relevant measure of feeding-deterrent properties, they argued for expanded studies of chemical defenses in *L. uva* using direct feeding assays and sympatric predators. A decade later, Mahon et al. (2003) demonstrated that both live, whole *L. uva* or lyophilized tissues ground into a fine powder and imbedded in alginate food pellets were unpalatable to sympatric omnivorous macropredators, including the sea star *O. validus* and the fish *Notothenia coriiceps*. Subsequent investigations of the palatability of discrete components of the body (testes, ovaries, peduncle, intestine/stomach, and lophophore) revealed that the peduncle (the attachment stalk of punctate brachiopods) was unpalatable to both sea stars and fish. A chemical defense was invoked as there was no correlation between the energetic content of the discrete tissues and their palatability, and as such low nutrient value could not explain the lack of palatability. The investigators concluded that their findings supported the predictions of the ODT as the peduncle is the most vulnerable body component as it occurs outside the confines of the shell. Moreover, the peduncle secures the entire individual to the substrate and thus its defense serves to maximize fitness.

Ascidians comprise an ecologically dominant group of benthic sessile marine invertebrates in Antarctica. Their distribution and abundance are among the most well documented of any benthic marine invertebrate group along the WAP (Sahade et al. 1998; Tatián et al. 1998; Kowalke et al. 2001; Ramos-Esplá et al. 2005). Until very recently, with the exception of a single species, nothing was known about whether ascidians from this biogeographic region possess chemical defenses against predators. McClintock et al. (2004) examined the chemical anti-feedant properties of the tall (up to 7 m!) cylindrical colonial ascidian *Distaplia cylindrica* collected from soft sediments near Palmer Station, Anvers Island. Using the feeding-assay protocols described above for sponges, they found that the omnivorous sea star *O. validus* rejected pieces of whole-colony tissue while accepting similarly sized alginate control food pellets. Moreover, alginate pellets containing tissue-level concentrations of lipophilic and hydrophilic extracts of *D. cylindrica* were unpalatable to sea stars, thereby reflecting the presence of defensive secondary metabolites. As the outer tunic of this species was found to possess a pH of 1.5 (attributable to sulfuric acid), the investigators examined whether agar food pellets prepared at tunic-level pH were deterrent to *O. validus*. They found this to be the case. Thus, both organic and inorganic chemicals deter sea star predators. Interestingly, McClintock et al. (2009a) observed that colonies of *D. cylindrica* harbor the dexaminid amphipod *Polycheria antarctica* f. *acanthopoda*. The amphipods live in domiciles that they excavate in the tunic of the ascidian. This burrowing association could provide structural or chemical refuge from prospective fish predators. In support of this hypothesis, the sympatric omnivorous fish *N. coriiceps*, a common predator of amphipods, consistently spit out bite-sized pieces of fresh tunic from *D. cylindrica*.

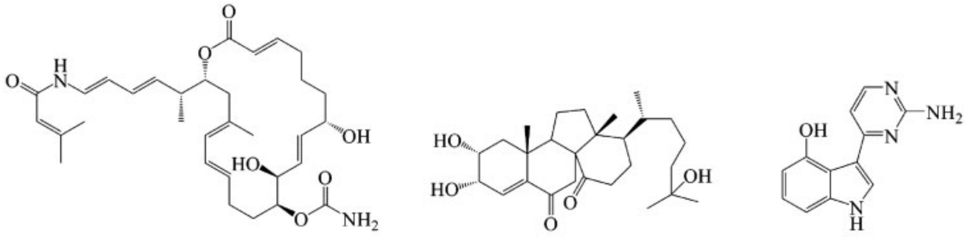
In the most comprehensive investigation to date of the palatability and chemical anti-predatory defenses of ecologically important ascidians of the WAP, Koplovitz et al. (2009) examined the palatability of 12 species of colonial and solitary ascidians to a sympatric omnivorous fish (*N. coriiceps*) and a predatory sea star (*O. validus*). One hundred percent of the fresh ascidian tissues were unpalatable to fish, while 57% were unpalatable to sea stars. Lipophilic and hydrophilic extracts of 11 of the ascidian species were embedded in alginate food pellets at tissue-level concentrations and tested in fish and sea star bioassays. Only one extract, the lipophilic extract of the colonial ascidian, *Distaplia colligans,* caused deterrence, and then only in fish. Curiously, extracts of its congener *D. cylindrica* were not deterrent to sea stars, as had been observed earlier by McClintock et al. (2004), perhaps indicating that there is intraspecific variation in chemical defense across even relatively small spatial scales, as in some soft corals (e.g., Slattery et al. 2001), or that there is interannual variation in the production of chemical defenses. Feeding-deterrent bioassays with ascidian extracts imbedded in alginate food pellets were also conducted using a model amphipod predator. Again, only one of the ascidians, *D. cylindrica*, had an extract that was deterrent to amphipods. Thus, overall, organic chemicals appear to play a relatively minor role in contributing to the unpalatable nature of ascidians along the WAP. Nonetheless, inorganic acids may play a more important role. Koplovitz et al.

(2009) measured low pH (2.0–2.5 pH) in the outer tunic of five (four colonial and one solitary) of the 12 ascidians examined. While fish readily consumed agar food pellets adjusted to pH levels as low as 2, sea stars were strongly deterred from feeding on agar food pellets when reduced to only five pH units. Thus, either organic or inorganic chemical defenses explained feeding deterrence in five of seven of the ascidian species found to be unpalatable to sea stars. In contrast, only one of the 12 species of ascidians investigated was chemically defended from predation by fish. This could reflect a higher degree of predation pressure on ascidians from sea stars along the WAP, or suggest that for some species the toughness of the tunic could contribute to unpalatability in weakly jawed Antarctic fish.

Secondary metabolites are more typically associated with colonial tunicates than with solitary ones (Blunt et al. 2009, and previous reviews in this series). Chemical analyses have been reported for only two species of WAP tunicates, both of which are colonial. The first such report (Diyabalanage et al. 2006) described the macrolide polyketide palmerolide A (4, Fig. 2) from *Synoicum adareanum*, collected in the vicinity of Palmer Station. Subsequently (Heimbegner et al. submitted), found four further members of the palmerolide family. The palmerolides display potent cytotoxicity toward certain mammalian cell lines but as yet have not been ascribed an ecological role. The same tunicate elaborates a series of ecdysteroids, the most unusual of which is abeohyousterone (5, Fig. 2). Ecdysteroids are employed by crustaceans as molting regulators, suggesting a likely ecological role for these compounds in the tunicate, particularly given the abundance of crustacean mesograzers found in the WAP benthos (Huang et al. 2007). A second, as yet undescribed, species of *Synoicum* collected from the same location yielded a series of indole alkaloids (Lebar et al. submitted), previously known as the meridianins (Franco et al. 1998). The meridianins (e.g., 6, Fig. 2) were first reported from the colonial tunicate *Aplidium meridianum* collected from South Georgia Island and, like the palmerolides, display potent cytotoxicity toward select mammalian cell lines; no ecological function, however, is currently known.

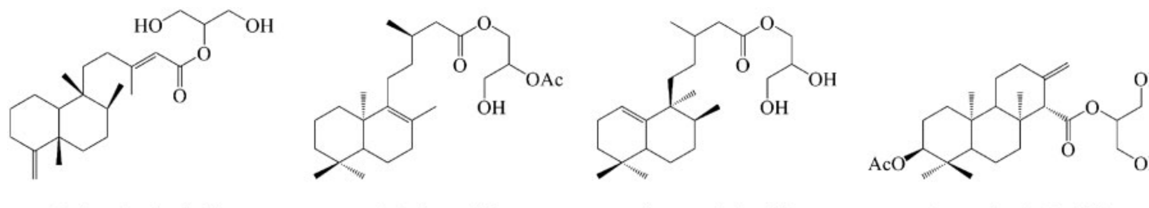
The sea slug *Austrodoris kerguelenensis* is widely distributed in the Antarctic and in southern South America (Wägele 1990) and it has been studied extensively as a source of natural products (see Lebar et al. 2007), one collection of which was evaluated in regard to feeding deterrence (Iken et al. 2002). Animals from the Ross Sea (Davies-Coleman and Faulkner 1991; Gavagnin et al. 1995, 2003a, 2003b), the Weddell Sea (Iken et al. 2002), and the WAP (Gavagnin et al., 1999, Diyabalanage et al., submitted) have been analyzed, resulting in a suite of clerodane, glycerides, e.g., palmadorin A (7, Fig. 3) (Gavagnin et al. 2003a, 2003b; Diyabalanage et al. submitted), labdane (e.g., 8, Fig. 3) (Davies-Coleman and Faulkner 1991; Gavagnin et al. 1995), halimane [e.g., austrodorin (9, Fig. 3)] (Gavagnin et al. 1995, 1999) and isocopalane diterpene [e.g., austrodorin-B (10, Fig. 3)] (Gavagnin et al. 1999), as well as two nor-terpenes (Gavagnin et al. 2003a, 2003b). Distinct collections, perhaps representing distinct populations, appear to give rise to unique suites of these compounds (Gavagnin et al. 1999), which is not inconsistent with the limited dispersal (because of direct development) and mobility options available to these slow-moving invertebrates (Wilson et al. 2009). While fractions of *A. kerguelenensis* rich in natural products and collected from the Weddell Sea, proved a deterrent to feeding by the sympatric sea star predator *O. validus* (Iken et al. 2002), it remains to be demonstrated that different suites of compounds, from different populations, are similarly effective.

While crustaceans are generally not considered likely candidates for chemical defenses due to their mobility and exoskeleton, McClintock et al. (2003) found that brooded juveniles of the Antarctic isopod *Glyptonotus antarcticus* collected near Palmer Station, Anvers Island, were unacceptable to sea stars



Palmerolide A (**4**) Abeohyousterone (**5**) Meridianin A (**6**)

Fig. 2 Representative natural products isolated from colonial tunicates collected within 2 km of Palmer Station, Anvers Island, Western Antarctic Peninsula.



Palmadorin A (**7**) Labdane (**8**) Austrodorin (**9**) Austrodorin-B (**10**)

Fig. 3 Representative natural products isolated from individuals of the Antarctic nudibranch, *Austrodoris kerguelenensis*, collected within 2 km of Palmer Station, Anvers Island, Western Antarctic Peninsula.

(*O. validus*) in feeding bioassays. While their deterrent properties may be attributable in part to the serration and spination of their exoskeleton, a lipophilic extract of the brooded juveniles was also deterrent in sea star assays, indicating that defensive chemicals may contribute to their defense. Chemical defenses against predators have been reported in the offspring of other crustaceans, including the larvae of the sub-tropical pea crab *Pinnotheres ostreum* (Luckenbach and Orth 1990).

Three classes of the Echinodermata, notably the Holothuria, Asteroidea, and Crinoidea, are known to include species that elaborate chemical defenses against predation (Slattery 2010). Despite this common knowledge, to date there are no studies of the chemical anti-feedant properties of adult echinoderms along the WAP. The one study that has been conducted examined the chemical anti-feedant defenses of brooded embryos and juveniles of the sea stars *Neosmilaster georgianus* and *Lysasterias perrieri* (McClintock et al. 2003). Whole embryos and juveniles of both species were rejected by the omnivorous sea star *O. validus*, as was a methanol extract (indicative perhaps of an asterosaponin) of embryos of *L. perrieri*. As the embryos of *N. georgianus* lack a structural defense, the basis for its lack of palatability is also likely to be chemical in nature, and could be attributable to noxious compounds that are not soluble in methanol. The presence of chemical defenses in the embryos of these two species of sea stars adds to a growing list of Antarctic marine invertebrates with either brooding or broadcasting lecithotrophic modes of reproduction that produce chemically defended offspring (McClintock and Baker 1997b). While these two sea-star species both brood their offspring, the provisioning of brooded embryos with chemical defenses may ensure that crawl-away juveniles are chemically defended when they lack a refuge in size. Remarkably, a number of Antarctic sea stars also broadcast their conspicuous lecithotrophic larvae into the plankton where they spend a very long time (several months) prior to settlement (Pearse et al. 1991). Under such circumstances, chemical defenses may be essential to their survival (McClintock and Baker 1997b; McClintock et al. 2001).

Potential antibacterial and anti-foulant chemical defenses

Unlike the substantial body of work that exists on the chemical feeding-deterrent properties of Antarctic benthic marine invertebrates from the WAP, there is very limited information about the prospective roles of secondary metabolites as anti-foulants. Peters et al. (2010) examined the bioactivity of organic extracts from 25 species of Antarctic demosponges against 20 bacterial isolates collected from the surfaces of sponges near Palmer Station, Anvers Island. Employing microbial growth inhibition protocols they found that the vast majority of both natural and 3× concentrations of both lipophilic and hydrophilic extracts of the sponges caused no inhibition of bacterial growth. Indeed, only a single sponge extract was found to consistently inhibit growth of bacterial isolates. Provided that the lack of activity is not attributable to the bacterial strains tested being isolated from the surfaces of sympatric sponges and thus possessing resistance to a common suite of defensive metabolites, it would appear that there is a general lack of antibacterial activity in WAP sponges.

In a similar survey of chemical antibacterial defenses of ascidians from the WAP, Koplovitz et al. (unpublished) tested lipophilic and hydrophilic extracts of 14 common ascidian species against the identical suite of bacterial isolates tested by Peters et al. (2010). The results were highly consistent with those of Peters et al. (2010); only one lipophilic extract from one of the 14 ascidians, the colonial species *Distaplia colligans*, demonstrated broad-spectrum activity against bacterial isolates. That ascidians also lacked broad antibacterial activity despite the bacterial strains being isolated from sympatric sponge surfaces, provides compelling evidence that there is indeed a general lack of antibacterial chemical defenses in Antarctic sponges and ascidians from the WAP. This may be because they are exposed to lower levels of pathogenic bacteria than are those that occur in warmer seas (e.g., Cervino et al. 2006). Nonetheless, some marine invertebrates along the WAP clearly exploit antimicrobial chemical defenses. For example, both lipophilic and hydrophilic extracts of the lophophore and gut of the Antarctic brachiopod *L. uva* posses potent activity against several strains of Antarctic bacteria (Mahon et al. 2003). This may be attributable to these two organs being more exposed to pathogens borne by the water-column.

Only a single study has been completed on potential anti-foulant properties of Antarctic benthic marine invertebrates along the WAP. Peters et al. (2010) examined the potential anti-foulant properties of 25 Antarctic sponges and found that in contrast to their conspicuous lack of anti-pathogenic activity, hydrophilic, and especially lipophilic, sponge extracts, caused high mortality in the sympatric chain-forming diatom *Syndroposis* sp. Indeed, 96% of the lipophilic extracts examined caused 100% mortality at tissue level concentrations. Further studies are needed using bioassay-guided fractionation to isolate and characterize these compounds and evaluate the concentration of compound necessary to inactivate diatoms. Ultimately, the concentration of any given compound on the surfaces of sponges needs to be measured to see whether they occur at ecologically relevant levels. Unlike water-borne bacteria, which may pass through, or be consumed by, sponges, diatoms represent a significant fouling threat to internal and external sponge tissues. This could be important in Antarctica where seasonal blooms of benthic diatoms occur just as in temperate and tropical seas (Amsler et al. 2000a, 2000b). While studies of the potential anti-foulant properties of Antarctic ascidians against benthic diatoms are underway (Koplovitz et al. unpublished), many colonial species are conspicuously devoid of fouling organisms. Given the high level of fouling pressure from benthic diatoms and the high incidence of anti-diatom activity observed in sponges, it is likely that many colonial ascidians will be found to rely on either inorganic (sulfuric acid) or organic (secondary metabolite) defenses to keep both the oral siphons and pharyngeal filter baskets of multitudinous individuals free of diatoms or other fouling organisms.

Sensory ecology

Despite a preponderance of Antarctic benthic marine invertebrates that belong to groups known to have relatively sophisticated chemosensory behaviors that influence detection of prey, conspecific and intraspecific interactions, and predator avoidance, only a few studies of sensory ecology have been conducted along the WAP or, for that matter, elsewhere in Antarctica. In laboratory studies, Zamzow et al. (2010) examined how the presence of an omnivorous benthic fish (*N. coriiceps*) that includes both macroalgae and amphipods in its diet influences habitat choice (macroalgal type) by two common sympatric amphipods (*Gondogeneia antarctica* and *Prostebbingia gracilis*) that occur along the WAP. In the presence of fish cues (fish-scented seawater), *G. antarctica* moved from a preferred alga that it consumes to one that was structurally complex and chemically defended. In contrast, *P. gracilis*, which eats neither macroalga, preferred to associate with the same structurally complex and chemically defended alga both in the presence and absence of fish cues. Thus, amphipods chemically detect fish predators and appear to exploit chemically defended and structurally complex algae as a likely refuge from predation by fish. These findings suggest that non-consumptive effects (NCE) (Peckarsky et al. 2008) may be important in shaping community-level trophic interactions that contribute to the remarkably high densities of amphipods along the WAP (Huang et al. 2007; Amsler et al. 2009a).

Mahon et al. (2002) observed that the limpet *Nacella concinna*, a species that occurs in great abundance along the WAP (Fig. 4), has the ability to escape predation from the common sympatric sea star *O. validus*. Individuals display a graded response that includes extension of the pallial tentacles, followed by mushrooming and rotation of the shell, and then flight. This escape response is chemotactic as it is mediated by a combination of both tactile and chemical stimuli. Kidawa (2001, 2005a, 2005b) examined a variety of aspects of the chemosensory biology of the ubiquitous keystone sea star *O. validus* at King George Island in the South Shetlands. Her studies demonstrated that *O. validus* can chemically detect differences between conspecifics that have been starved or fed, a chemosensory response that could be important in increasing foraging efficiency by stimulating searching behavior in individuals exposed to satiated conspecifics. This may facilitate conspecific group attacks known to occur in *O. validus* when preying on large sea stars (Dayton et al. 1974). Kidawa also documented sequential feeding behaviors that manifest themselves in a dose dependent manner to food stimuli (amino acids). Moreover, individuals may detect and initiate early stages of feeding behavior in response to single

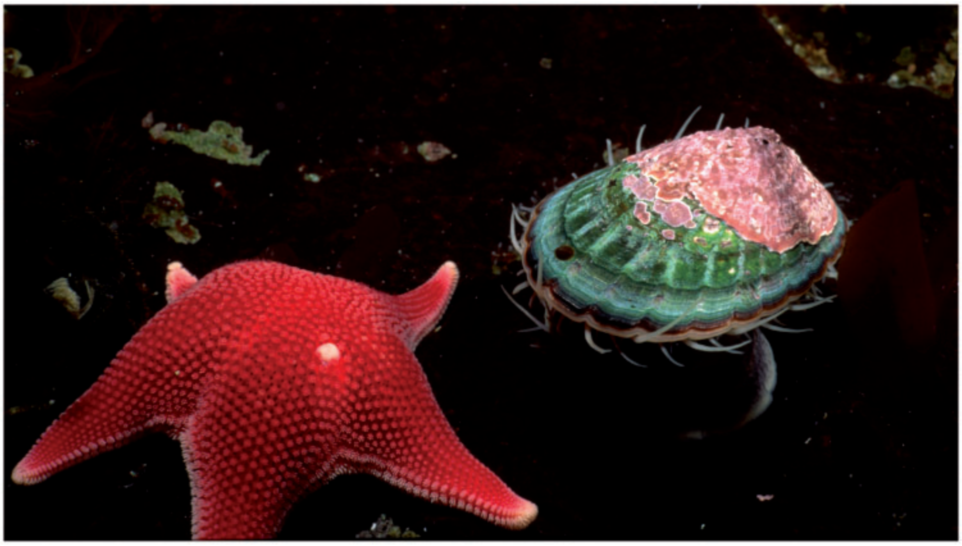


Fig. 4 The common sea star, *Odontaster validus,* and limpet, *Nacella concinna*, two ecologically important species that occur in marine benthic communities along the Western Antarctic Peninsula. Their chemosensory behaviors are important in determining conspecific and interspecific interactions that impact population and community ecology (Mahon et al. 2002, McClintock et al. 2008a, 2008b). Photo by Dan Martin.

amino acids, yet a complete sequence of feeding behaviors accompanies exposure to mixtures of amino acids. Finally, juvenile *O. validus* were found to be more sensitive to chemical stimuli than adults.

Using time lapse videography, McClintock et al. (2008a) conducted mesocosm-based studies to expand investigations of intraspecific interactions in the keystone *O. validus* at Palmer Station. They found that individuals located prey (wounded sea urchin) using short-distance chemoreception and then through chemotactile recognition, engaged in arm fencing bouts with a conspecfic in the near vicinity of the prey. Bouts between two individuals lasted about 20 min with the defeated sea star retreating from the prey. In most cases, the largest sea star prevailed. Such intraspecific behaviors are likely to influence patterns of dispersal of *O. validus* and as such have ramifications in terms of individuals' fitness, population structure, and community composition. In a related study, McClintock et al. (2008b) examined interspecific interactions between *O. validus* and three common species of sympatric sea stars. While *O. validus* did not respond behaviorally to contact with *Labidiaster annulatus* or *Diplasterias brandti*, their movement rates increased significantly (two- to six-fold) when they contacted *P. aurorae*. As movement was always in the opposite direction, this was deemed a 'flight response'. Moreover, fleeing individuals triggered an 'alarm response' in conspecifics encountered during flight, resulting in the encountered individual immediately changing course and moving away from *P. aurorae*. These interactions are clearly mediated by chemotactile perception as physical contact always occurred immediately prior to the initiation of flight behavior. Collectively, these studies and those of Kidawa (see above) indicate that chemosensory behaviors have an important role to play in the ecology of this keystone species.

Comparisons with other polar and temperate and tropical marine environments

The only location other than the WAP where the chemical ecology of nearshore sessile and sluggish benthic marine invertebrates has been systematically investigated is in McMurdo Sound on the Ross Sea [several studies have examined deep water species from the Weddell Sea (Avila et al. 2009)]. Given the circumpolar distributions of many of the ecologically dominant benthic marine invertebrates, coupled with the similarity of macroinvertebrate predators and fouling organisms, it is not surprising that there is little evidence of significant qualitative or quantitative differences in chemical defenses seen in the WAP and McMurdo Sound (McClintock and Baker 1997a; McClintock et al. 2005; Amsler et al. 2000a, 2001b; this review). Based on these similarities, there is ample justification (e.g., intraspecific differences in secondary metabolites production—see below) to extend the biogeographic analysis of the chemical ecology of marine benthic macroalgae and invertebrates to other regions of

Antarctica. For example, the coastlines of the Bellingshausen and Amundsen Seas, as well as coastal regions of eastern Antarctica are poorly studied. The Arctic has received considerably less attention with respect to the chemical ecology of benthic marine invertebrates. This is in part due to the difficulty of working in deep water under the ice cap, or the lack of types of invertebrates conducive to chemical defenses that occupy the soft sediments off northern Alaska and Russia. At least one study has examined the palatability of marine macroalgae to amphipods and sea urchins near Spitsbergen, Norway (Wessels et al. 2005).

With respect to comparisons with temperate and tropical marine communities, despite earlier predictions of an inverse correlation between latitude and the incidence of chemical defenses in benthic marine invertebrates (Bakus and Green 1974), this is clearly not a general pattern. For example, the incidence of chemical defenses in Antarctic sponges is as high, or even slightly higher, than that found in tropical species (Pawlik et al. 1995, Peters et al. 2009).

Becerro et al. (2003) found no geographic trend in their evaluation of the chemical defenses of temperate and tropical sponges. Instead, they postulate that recurrent selection for chemical defenses as a general life-history strategy may explain geographic patterns. Chemical defenses are also common in Antarctic soft corals, shell-less mollusks, brachiopods and echinoderms (Amsler et al. 2001b). In contrast, Antarctic ascidians are poorly defended chemically. Ascidians, despite largely lacking secondary metabolite defenses against predators, exploit an inorganic chemical (sulfuric acid) against sea star predators (especially colonial ascidians) and likely the protection afforded by their tough outer tunic (especially solitary ascidians). While not the purview of this review, it is noteworthy that a high incidence of chemical anti-feedants also occurs among ecologically dominant species of macroalgae of the WAP (Amsler et al. 2005, 2009b). The overall levels of unpalatability are comparable to those found among tropical macroalgae (Amsler et al. 2005).

Conclusions and future directions

The studies cited above that are framed in the ODT generally support predictions that chemical defenses are allocated to the most vulnerable or valuable tissues. However, the presence of chemical defenses within the tissues of some WAP sponges suggests that predators other than sea stars may also be important, or that the assumptions of the ODT are inappropriate. Future studies are needed to determine the selective pressures responsible for internal chemical defenses. There is evidence of heterogeneity in intraspecific secondary metabolite chemistry over both local (<2–3 km) and regional (>1000 km) spatial scales in select WAP benthic macroinvertebrates (nudibranchs and sponges, respectively). This indicates that chemical selection may operate across a broad spectrum of spatial scales, or that there is phenotypic plasticity in response to changes in grazing pressure or abiotic stress. The presence of ecdysteroid-like compounds in the WAP ascidian *Synoicum adareanum* suggests a potential to defend their tissues from arthropod predators (e.g., crustacean amphipods) by employing a strategy similar to that found in terrestrial plants which elaborate ecdysteroids that short-wire molting in herbivorous insects. Surveys of both sponges and ascidians indicate a general lack of antibacterial chemistry. However, potent potential anti-foulant chemical defenses with broad-spectrum activity against benthic diatoms are common among sponges, and future studies are needed to evaluate this topic in other divergent taxa and to determine the ecological relevance of the reported *in vitro* activity. One of the least studied and most fruitful areas for future research is in the realm of sensory ecology. Despite only barely cracking the lid, what has been gleaned from key invertebrate predators to date indicates that chemical sensing plays an important role in mediating both direct and indirect (NCE) predatory effects on populations and communities.

Sotka et al. (2009) summarized the need to better understand the mechanisms that mediate the fate and consequences of secondary metabolites produced by microbes, algae and invertebrates in freshwater and marine communities. They suggested that by exploiting techniques and approaches developed in pharmacology, much could be learned about the ecological interactions between metabolites and consumers at the molecular and biochemical level. This might include the biochemical fate of secondary metabolites within consumer's tissues (absorption, distribution, metabolism/detoxification, and excretion), chemical sensory factors such as taste, as well as nutrient–toxin and consumer–prey interactions with respect to generalist versus specialist predators. This approach offers considerable potential for framing questions about the chemical ecology of Antarctic marine invertebrates. Moreover, as Sotka et al. (2009) pointed out, this approach would facilitate predictions about how consumer–prey interactions will be altered by the impacts of climatic change such as rising seawater temperature and decreasing pH (ocean acidification). This is particularly poignant for marine invertebrates that occur along the WAP, as this is arguably the most rapidly warming region of our planet (Clarke et al. 2007; Ducklow et al. 2007). Moreover, due to a unique combination of abiotic and biotic factors it is also one of the most susceptible to the impacts of acidification of the oceans (McClintock et al. 2008c, 2009, McNeil and Matear 2008; Fabry et al. 2009).

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