

Marine Chemical Ecology: A Science Born of Scuba

*Joseph R. Pawlik, Charles D. Amsler, Raphael Ritson-Williams,
James B. McClintock, Bill J. Baker, and Valerie J. Paul*

ABSTRACT. For more than 50 years, organic chemists have been interested in the novel chemical structures and biological activities of marine natural products, which are organic compounds that can be used for chemical defense and chemical communication by diverse marine organisms. Chemical ecology, the study of the natural ecological functions of these compounds, is an interdisciplinary field involving chemistry, biology, and ecology. Examples of ecological functions of marine natural products include distastefulness that inhibits feeding by predators, settlement cues for larvae, allelopathic effects that prevent fouling by epiphytes and overgrowth by competitors, and pheromones for mate-searching behavior. Much of the research in marine natural products and marine chemical ecology has used scuba diving and related undersea technologies as necessary tools. The breadth of marine organisms studied and the types of experiments conducted under water have expanded with technological developments, especially scuba diving. In this paper, we highlight the importance of scuba and related technologies as tools for advancing marine chemical ecology by using examples from some of our own research and other selected studies. We trace the origins of marine chemical ecology on the heels of marine natural products chemistry in the 1970s and 1980s, followed by the development of increasingly sophisticated ecological studies of marine algae and invertebrates in Caribbean, tropical Pacific, and Antarctic waters.

Joseph R. Pawlik, Department of Biology and Marine Biology, UNCW Center for Marine Science, 5600 Marvin K Moss Lane, Wilmington, North Carolina 28409, USA. **Charles D. Amsler**, Department of Biology, Campbell Hall 464, 1300 University Blvd, University of Alabama at Birmingham, Birmingham, Alabama 35294-1170, USA. **Raphael Ritson-Williams**, Smithsonian Marine Station at Fort Pierce, 701 Seaway Drive, Fort Pierce, Florida 34949, USA. **James B. McClintock**, Department of Biology, Campbell Hall 464, 1300 University Blvd, University of Alabama at Birmingham, Birmingham, Alabama 35294-1170, USA. **Bill J. Baker**, Department of Chemistry, University of South Florida, 4202 E. Fowler Ave CHE 205, Tampa, Florida 33620, USA. **Valerie J. Paul**, Smithsonian Marine Station at Fort Pierce, 701 Seaway Drive, Fort Pierce, Florida 34949, USA. **Correspondence:** V. Paul, paul@si.edu.

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INTRODUCTION

Natural products are chemical compounds derived from natural sources, including plants, animals, fungi, and bacteria. Marine natural products research involves determining the structure, function, and biosynthesis of these compounds from marine microbes, phytoplankton, macroalgae, sponges, tunicates, and corals, among others. Natural products are also called secondary metabolites because they are small molecules with no known function in the primary metabolism of the organisms that produce them. As a scientific discipline, marine natural products research is an offshoot of the much older study of terrestrial secondary metabolites found primarily in vascular plants, insects, bacteria, and fungi. Many marine natural products possess novel functional groups and molecular structures compared to those from terrestrial sources. To date, 21,800 natural products have been described from marine organisms (MarinLit, 2011; Blunt et al., 2011).

Marine natural products include diverse classes of compounds, such as terpenes, phenols, polyphenolics, acetogenins, peptides, alkaloids, and others. Most research on marine natural products focuses on their potential biomedical uses. Metabolites from marine organisms have shown antitumor, antiviral, and anti-inflammatory activities, and several of these are currently in clinical trials to establish their effectiveness as new drugs, or are in clinical use (Newman and Cragg, 2004; Molinski et al., 2009; Villa and

Gerwick, 2010). In addition, some marine natural products may realize their biomedical potential by becoming useful molecular or biochemical probes (Mayer et al., 2010, 2011). Through detailed mechanistic studies, these biochemical probes may lead to the discovery of receptor proteins, enzymes, or other macromolecular targets. The improved understanding of biochemistry and cell and molecular biology that has resulted from these studies may ultimately lead to the discovery of new drugs (Mayer et al., 2010).

The study of the ecological functions of natural products is termed “chemical ecology.” While the roles of natural products in terrestrial plants and insects are relatively well studied, much less is known for marine natural products. Examples of ecological functions of natural products include distastefulness that inhibits feeding by predators, settlement cues for larvae, allelopathic effects that prevent fouling by epiphytes and overgrowth by competitors, and pheromones for mate searching behavior. Marine chemical ecology relies on chemical and ecological experimentation to determine the individual or suite of compounds responsible for driving the observed interactions. Determining the compounds responsible for ecological interactions can open a window into other interdisciplinary fields that contribute to ecology, including studies of animal behavior, neurobiology, sensory ecology, reproduction, predator–prey and plant–herbivore interactions, competition, symbiosis, and dispersal and recruitment.

Much of the research in marine natural products and marine chemical ecology has used scuba diving and related undersea technologies as necessary tools. Until the invention of scuba diving, most of the ocean depths were obscured from basic observation, and many marine organisms could not be readily collected. Sampling of the benthos at depths greater than a few meters was carried out using nets and dredges; this was often compared to collecting rainforest insects by pulling a butterfly net behind a low-flying plane. Beginning in the 1960s and 1970s, scuba diving became an essential tool for the collection of benthic marine organisms, particularly macroalgae and invertebrates, for studies of their natural products chemistry (Scheuer, 1990). Also, it was not until scientists could use scuba that they could begin to observe ecological and behavioral interactions in situ and also conduct manipulative experiments to better understand the mechanisms underlying marine behavioral and ecological interactions. Marine chemical ecology has now developed into a broad research area encompassing studies of the chemical mediation of a variety of ecological interactions among marine organisms. The field has been comprehensively reviewed on a regular basis (Paul, 1992; McClintock and Baker, 2001; Paul and Puglisi, 2004; Paul et al., 2006, 2007, 2011b; Amsler, 2008; Paul and Ritson-Williams, 2008; Hay, 2009; Pawlik, 2011), and it is not our intention to duplicate these reviews. Instead, we will highlight the importance of scuba and related technologies as tools for advancing marine chemical ecology by using examples from some of our own research and other selected studies.

HUMBLE BEGINNINGS: TOXICITY ASSAYS TO MORE RELEVANT TECHNIQUES

The field of marine natural products chemistry experienced a “gold rush” in the 1970s and 1980s, when organic chemists took advantage of two emerging technologies: scuba diving and rapidly advancing spectroscopic methods (mostly nuclear magnetic resonance, or NMR, spectroscopy). The result was a rapid increase in the number of publications describing novel metabolites from benthic marine invertebrates and algae (reviewed by Faulkner and Fenical, 1977; Scheuer, 1978–1983). Relying on the assumption that secondary metabolites must serve some function for the organism that produces them, many of these publications ascribed ecologically important properties to new compounds without empirical evidence; in fact, whole reviews of chemical ecology from this period were compiled of references with little or no experimental data to support an ecological function for secondary metabolites (Karuso, 1987).

At about the same time, ecologists were also taking advantage of the advent of scuba diving and describing the distributions and abundances of benthic animals and plants previously known only from much less effective sampling methods, such as dredging (see other contributions in this volume). The assumption of many of these researchers was that anything sessile and soft-bodied must be chemically defended to avoid consumption by abundant and ever-present predators (Randall and Hartman, 1968; Bakus and Green, 1974). In an effort to introduce empiricism to what was otherwise descriptive work on species abundances, some ecologists began extrapolating chemical defenses from toxicity assays in which fish (usually goldfish or mosquito fish) or invertebrates were exposed to aqueous suspensions of crude organic extracts of invertebrate tissues (Bakus and Green, 1974; Jackson and Buss, 1975). Subsequent studies that have compared data from these types of toxicity assays with more relevant feeding experiments have found no relationship between them (Schulte and Bakus, 1992; Pawlik et al., 1995; Tarjuelo et al., 2002).

Beginning in the mid to late 1980s, the first publications began to appear that employed more ecologically relevant techniques for addressing the biological functions of secondary metabolites from marine animals and plants. These were born of collaborations between students and young faculty primarily educated in marine biology and ecology and established natural products chemists who had developed an interest in the ecological functions of secondary metabolites. Some of this work began in the rocky intertidal of Southern California, with members of John Faulkner’s natural products group at Scripps Institution of Oceanography collaborating with graduate-student marine ecologists to produce some of the first studies of chemical defenses of sponges (Thompson, 1985; Walker et al., 1985) and intertidal snails (Albizati et al., 1985; Pawlik et al., 1986). However, it was scuba diving that allowed these and other researchers unprecedented access to marine organisms in the subtidal environment,

where the vast majority of marine biodiversity is found, permitting the collection of rare organisms and large quantities of patchily distributed organisms, comparative collections across broad geographic regions, and most importantly, manipulative experiments to test hypotheses about the functions of secondary metabolites in the field. The following provides a regional glimpse of a variety of important chemical ecological studies that elucidated the diverse role of secondary metabolites in population and community structure.

INTO THE FIELD

CHEMICAL ECOLOGY IN THE CARIBBEAN

The transition from toxicity screening to more ecologically relevant studies of secondary metabolites from marine organisms began with studies of the chemical defenses of macroalgae from Caribbean coral reefs (Paul and Fenical, 1983, 1986; Paul and Hay, 1986). At first, these studies relied on research scuba diving for collecting alone; not only were ample volumes of algae needed for the isolation of secondary metabolites, but these collections had to be separated by species, as in the case of the common calcareous algae in the genus *Halimeda* (Paul and Fenical, 1983). Algae of this genus yielded halimedatrial, a diterpenoid trialdehyde that was active in a series of antimicrobial, antimitotic, and toxicity assays, but was also tested in artificial foods as a feeding deterrent against damselfishes and herbivorous mollusks (Paul and Fenical, 1983, 1986). The geographically extensive collections of algae, gathered by diving from a research vessel as a mobile diving platform, combined with chemical analysis of the concentrations of the metabolites, allowed the authors to determine that higher levels of defensive metabolites were correlated with higher levels of herbivory (Paul and Fenical, 1986). Field assay methods were developed to survey interspecific differences in chemical and morphological defenses in Caribbean macroalgae (Paul and Hay, 1986). In what is perhaps the first use of saturation diving in the service of marine chemical ecology, researchers using the *Hydrolab*, then in St. Croix, U.S. Virgin Islands, monitored levels of secondary metabolites in *Halimeda* over the course of the night and day (Hay et al., 1988b). Saturation diving from the *Hydrolab*, and later the *Aquarius* habitat on Conch Reef, near Key Largo, Florida, has proven to be a particularly useful technology for time-intensive research. Saturation divers live for a week or more at 15 m depth in the habitat, essentially a stationary submarine, and can use standard scuba diving gear to perform research dives of 6 hours or longer per day at the same depth as the habitat. This allows research divers to carry out time-consuming observations or manipulations that could never be accomplished by diving from the surface. Night- and day-long studies of *Halimeda* living on the coral reef resulted in the discovery that these algae invest high concentrations of chemical defenses in the new, unpigmented,

soft, and nutritionally valuable tissues that grow rapidly at night, with a subsequent reduction in chemical defenses in these tissues as they turn green and become photosynthetic, age, and become protected from herbivores by calcification (Hay et al., 1988b).

Research on the chemical ecology of macroalgae in the Caribbean accelerated rapidly, with defensive roles assigned to metabolites from several species in different taxonomic groups (Hay et al., 1987, 1988a, 1990; Paul et al., 1987). Again, this research required geographically extensive collections using scuba, but also included field observations of species abundances and herbivory. Many of these studies introduced novel field and laboratory experiments to assess chemical defenses by using diverse consumers, including fishes, sea urchins, sea slugs, polychaete worms, and amphipod crustaceans (Hay et al., 1987, 1988a, 1988c; Hay and Fenical, 1988). These studies tested fundamental hypotheses about plant–herbivore interactions that had previously only been applied to terrestrial systems.

Scores of papers were published over the ensuing two decades that further refined our understanding of the chemical ecology of macroalgae on Caribbean reefs (reviews in Hay and Steinberg, 1992; Hay, 1997, 2009; Duffy and Hay, 2001; Paul et al., 2001, 2006, 2007, 2011a; Paul and Puglisi, 2004; Amsler, 2008). This knowledge came with new developments in laboratory and field assays designed to test algal chemical defenses against a variety of potential threats, including grazers, competitors, and fouling organisms (Hay et al., 1998). Diving technologies were fundamental to the collection of subject and assay organisms (Figure 1a), as well as to the field assays themselves (Figures 1b–d). Some recent studies have focused on the antimicrobial and allelopathic effects of Caribbean macroalgae, including the negative effects of macroalgal extracts on adult corals (Rasher and Hay, 2010) and settlement of coral larvae (Kuffner et al., 2006; Paul et al., 2011a), antimicrobial effects of macroalgal extracts and compounds (Kubanek et al., 2003; Engel et al., 2006), and both inhibitive and stimulative effects of algal extracts on bacteria cultured from the surfaces of Caribbean corals and macroalgae (Morrow et al., 2011). Recently, saturation diving has again been employed to study plant–herbivore interactions at the ecosystem level, with the *Aquarius* habitat off Key Largo, Florida, serving as a base for saturation dives to nearby Conch Reef (Burkepile and Hay, 2008, 2010). Large-scale caging studies that require long-term saturation dives have revealed that the abundance and diversity of herbivores dramatically affects macroalgal cover on reefs, with indirect effects on the survival of reef-building corals (Burkepile and Hay, 2010).

Investigations of the chemical ecology of Caribbean coral reef invertebrates tracked that of macroalgae, with studies focusing on gorgonian corals among the earliest (Gerhart, 1984; Pawlik et al., 1987; Harvell et al., 1988; Harvell and Fenical, 1989; Pawlik and Fenical, 1989; Van Alstyne and Paul, 1992; Slattery, 1999). The technical requirements for these studies were the same as for those focused on macroalgae, with scuba diving figuring prominently in the collection of both subject and assay



FIGURE 1. Photographs illustrating various field methods that use scuba diving for studies of marine chemical ecology in the Caribbean. (a) A diver examines and prepares to collect marine cyanobacteria, *Lyngbya* spp., that are overgrowing a gorgonian (photo by Karen Lane Schroeder); (b) A diver observes fishes feeding during an underwater feeding assay. Paired feeding assays are commonly used to test the palatability of algal extracts and natural products. Artificial food made with palatable algae is attached to polypropylene lines, with one line containing control food cubes and one containing food with extracts or pure compounds at their natural concentrations (photo by R. Ritson-Williams); (c) Gray angelfish, *Pomacanthus arcuatus*, feeds on the palatable sponge *Chondrosia collectrix* attached to a brick. Angelfishes are major consumers of some species of Caribbean sponges (photo by J. Pawlik); (d) Predator exclusion (“caging”) experiment set-up on Conch Reef, Florida. In this case, replicate sponge pieces are placed inside and outside of cages to observe net differences in growth after one year for species that are protected by chemical defenses and those that are not (photo by J. Pawlik).

organisms and in field experiments. Initial surveys of the chemical defenses of gorgonians against generalist predatory fishes suggested that there was some interspecific variation in the levels of defense (Pawlik et al., 1987), but subsequent experiments after assay techniques had been refined revealed that gorgonians were broadly defended by secondary metabolites, and that structural defenses in the form of small calcareous spicules were likely not effective defenses against coral reef consumers that are accustomed to eating limestone when grazing on calcified macroalgae and reef-building corals (O'Neal and Pawlik, 2002).

The chemical ecology of a variety of less sedentary Caribbean marine invertebrates, ranging from planktonic larvae (Lindquist and Hay, 1996; Bullard and Hay, 2002) to hydroids on floating mats of *Sargassum* seaweed (Stachowicz and Lindquist, 1997) to crustaceans that co-opt defended algae or invertebrates to protect themselves by association (Stachowicz and Hay, 2000; Stachowicz, 2001), has been studied. For the beautiful feather-duster worms (Sabellidae) that are common to some Caribbean reefs, the relative speed with which these tube-dwelling worms retract their feeding radioles correlated to chemical defense, with those that retracted more slowly having more potent defenses (Kicklighter and Hay, 2007), with the trade-off between defense and escape speed extending to spaghetti worms (Terebellidae) and others as well (Kicklighter et al., 2003; Kicklighter and Hay, 2006).

Caribbean sponges are perhaps the best-understood aquatic organisms in terms of their chemical ecology, from the level of molecule to ecosystem (Pawlik, 2011), again thanks to the various diving technologies that have contributed to their study. Sponges are now the dominant habitat-forming organisms on many Caribbean reefs, and their populations are increasing (Mallao et al., 2008; McMurray et al., 2010). The earliest studies of Caribbean sponge ecology suggested that fish predators had little impact on sponge distributions (Randall and Hartman, 1968), an idea that was subsequently overturned (Pawlik, 1997). A survey approach that considered secondary metabolites as well as structural and nutritional defenses was used to investigate defenses against fish predators (Chanas and Pawlik, 1995, 1996; Pawlik et al., 1995), with chemical defense clearly playing the dominant role (Jones et al., 2005). The secondary metabolites responsible for chemical defense were isolated and identified using laboratory and field experiments for most of the common sponge species on Caribbean reefs (Albrizio et al., 1995; Wilson et al., 1999; Kubanek et al., 2001; Pawlik et al., 2002); for the oroidin class of compounds of the genus *Agelas*, the molecular basis for chemical defense was explored using both natural and synthetic metabolites (Assmann et al., 2000; Lindel et al., 2000). At the same time, studies of chemical defenses of Caribbean sponges against other potential threats were proceeding, including defenses against invertebrate predators (Waddell and Pawlik, 2000a, 2000b), invertebrate and coral competitors (Engel and Pawlik, 2000; Pawlik et al., 2007), fouling (Kubanek et al., 2002), and microbial pathogenesis (Newbold et al., 1999; Kelly et al., 2005).

Technologies more advanced than simple scuba diving, including saturation and technical diving, have contributed to

research into the chemical ecology of Caribbean sponges, and these studies have advanced our understanding of how secondary metabolites influence the entire reef community (Pawlik, 2011). A novel use of the *Aquarius* habitat on Conch Reef, off Key Largo, Florida, was as a platform for long-term videography of fish and sea turtle behavior in response to an array of reef, seagrass bed, and mangrove sponges (Dunlap and Pawlik, 1996). It was discovered not only that angelfishes and turtles preferred to eat sponges that were chemically undefended in feeding experiments with generalist fish predators, such as bluehead wrasses (Pawlik et al., 1995) (Figure 1c), but also that parrotfishes, long thought of as grazers on only algae and corals, were voracious sponge predators (Dunlap and Pawlik, 1996, 1998). These studies led to the determination that sponges on Caribbean reefs could be placed into three categories: (1) chemically defended species that are left alone by predators, (2) palatable species that are consumed by sponge-eating fishes, and (3) preferred species that are removed from the reef and persist only in refuge habitats, such as the interstices of the reef or seagrass or mangrove habitats where predators do not forage (Pawlik, 1997). Resource trade-offs between investment in chemical defenses and reproduction or growth are responsible for the presence of both defended and palatable sponge species on Caribbean reefs, a concept that was tested by observing the healing rates of defended and palatable sponges (Walters and Pawlik, 2005) by conducting long-term growth experiments with sponges inside and outside of cages (Leong and Pawlik, 2010) (Figures 1c–d), and by using diving to survey patterns of sponge recruitment to a shipwreck adjacent to a reef off Key Largo, Florida (Pawlik et al., 2008). These studies provide strong evidence that fish predation is the dominant force structuring sponge communities in the Caribbean, and that the secondary metabolites produced by chemically defended sponges come at a cost to reproduction, growth, or both of these life functions (Pawlik, 2011).

CHEMICAL ECOLOGY IN THE TROPICAL PACIFIC

The earliest investigations of chemical ecology in the tropical Pacific were studies of the comparative toxicities of extracts of sponges, sea cucumbers, and soft corals (Bakus and Green, 1974; Bakus, 1981; Coll et al., 1982). Natural products chemist John Coll and ecologist Paul Sammarco developed a collaboration that led to some of the earliest field studies of allelopathy and antifouling in marine chemical ecology. Focusing on the taxonomically diverse and chemically rich alcyonarians (soft corals) of the Great Barrier Reef, this research team discovered that some species of soft corals were competitively dominant over both soft and hard corals (Labarre et al., 1986; Alino et al., 1992). Subsequent work demonstrated that the allelopathic effects of soft corals against each other extended to the inhibition of settlement of hard corals (Maida et al., 1995), and evidence of toxic effects of specific metabolites from soft corals on hard corals (Aceret et al., 1995). More recently, this group has developed more effective methods of assessing antifouling activity in the field (Maida et al., 2006).

Studies of the chemical ecology of macroalgae in the tropical Pacific followed those done in the Caribbean by Valerie Paul and coworkers. Observations of macroalgal blooms and the persistence of macroalgae in the presence of herbivorous fishes were made by scuba divers in the field (Figure 2a), suggesting that these algae were defended from grazers. Experiments were conducted to determine palatability of the natural compounds with and without confounding factors of food quality or structural defenses (Paul et al., 1990; Van Alstyne and Paul, 1990; Duffy and Paul, 1992; Schupp and Paul, 1994). Often potential herbivores had species-specific preferences that allowed them to specialize on otherwise chemically defended algae (Hay and Steinberg, 1992; Paul et al., 2001). As experiments progressed, researchers found that the concept of algal chemical defense was more complex. Some algae had variable concentrations or different compounds across space and time (Steinberg and Paul, 1990; Meyer and Paul, 1992; Paul and Van Alstyne, 1992; Puglisi and Paul, 1997; Van Alstyne et al., 2001). Other compounds found in marine algae inhibited the growth of pathogens, suggesting that some natural products are important for other functions that contribute to survival, such as reducing disease (Puglisi et al., 2007; Lane et al., 2009). Extensive research has shown that natural products from algae inhibit biofouling on their surfaces (reviewed in Fusetani, 2004, 2011; Lane and Kubanek, 2008). Halogenated furanones produced by the red alga *Delisea pulchra* in Australia inhibited herbivory and also the growth of algae on its surface (Wright et al., 2004; Dworjanyn et al., 2006). Chemically rich macroalgae can negatively affect corals through allelopathic interactions when they are in contact (Rasher and Hay, 2010; Rasher et al., 2011). These types of studies continue today and are important for defining how algae can persist in herbivore-rich habitats and compete with other benthic organisms.

Although benthic blue-green algae (Cyanobacteria) are not related to eukaryotic macroalgae, they fill a similar ecological role. Extensive work on the Pacific island of Guam was conducted to study the chemical ecology of marine benthic cyanobacteria, and also to determine which factors might affect their growth and persistence in coral reef habitats (Figure 2b). Cyanobacteria are prolific producers of natural products (Tan, 2010), some of which have been tested for their feeding deterrent properties (Paul and Pennings, 1991; Pennings et al., 1996, 1997; Thacker et al., 1997; Nagle and Paul, 1998, 1999). In situ manipulations, including caging experiments, showed that the exclusion of herbivores can sometimes contribute to macroalgal and cyanobacterial bloom formation and growth (Thacker et al., 2001). Benthic surveys using scuba showed that some blooms of cyanobacteria were regulated by large storms that produced heavy wave action that dislodged the cyanobacteria (Becerro et al., 2006). Research on benthic cyanobacteria is ongoing around the world, as these organisms can form large-scale blooms that kill many benthic organisms (Paul et al., 2005, 2007; Watkinson et al., 2005).

Studies of specialist consumers, especially herbivores that specialize on chemically defended algae or cyanobacteria, are

revealing much about how natural products can influence trophic interactions. Saccoglossans, a group of opisthobranch mollusks, often specialize on green algae, and they can sequester algal secondary metabolites, which are then used for their own defense against predators (Paul and Van Alstyne, 1988; Hay et al., 1990; Becerro et al., 2001). By stealing defensive compounds from their food sources, these soft-bodied slugs avoid the costs of making chemical defenses. Possibly the best-studied specialists are sea hares, which sequester dietary-derived natural products primarily in the digestive gland (Pennings and Paul, 1993; de Nys et al., 1996; Ginsburg and Paul, 2001). Some sea hares, such as species of *Dolabella* and *Stylocheilus*, bioaccumulate natural products from cyanobacteria (Pennings and Paul, 1993; Pennings et al., 1996, 1999, 2001). Demonstrating the potential for studies of chemical ecology to generate possible new drugs, the sea hare *Dolabella auricularia* was discovered to contain natural products with anticancer properties (Flahive and Srirangam, 2005; Sato et al., 2007). Subsequent collection and isolation required huge numbers of sea hares, until it was discovered that the animals were sequestering the compounds from their cyanobacterial food (Luesch et al., 2002), illustrating the importance of in situ observations of species interactions for discovering the dietary source of a natural product.

A variety of sessile benthic invertebrates from the tropical Pacific have been the focus of chemical ecology research. Chemical defenses of Pacific soft corals and gorgonians were studied on the reefs of Guam for many years (Wylie and Paul, 1989; Van Alstyne et al., 1994; Puglisi et al., 2000, 2002). Slattery and coworkers characterized changes in steroids and secondary metabolites over the reproductive period of *Simularia polydactyla*, and determined that chemical defenses of this soft coral were transferred to its eggs and larvae (Slattery et al., 1999). Considerable variation was observed in concentrations of defensive terpenes in *S. polydactyla* and *S. maxima* at different reefs on Guam. Scuba was used to conduct transplant studies and video transects that linked higher levels of defensive compounds in soft corals that lived on reefs with higher levels of predation by butterflyfishes, suggesting that predation induced greater production of the defensive compound pukalide in the corals (Slattery et al., 2001). The soft coral *S. maxima* was further studied to determine how bleaching might influence its production of defensive compounds. During a natural bleaching event of soft coral colonies in the field, concentrations of a defensive compound decreased but recovered again after several months. Predation rates increased on bleached colonies, and extracts of bleached colonies did not deter predation (Slattery and Paul, 2008). Most recently, studies of hybridization within the genus *Simularia* have revealed that hybrid soft corals exhibited greater fitness than the parental species, including stronger allelopathic effects against one parental species and stronger antipredatory defenses than either parental species (Slattery et al., 2008).

Sponge chemical defenses have also been investigated in the Pacific. One sponge, *Dysidea* sp., overgrew and killed another

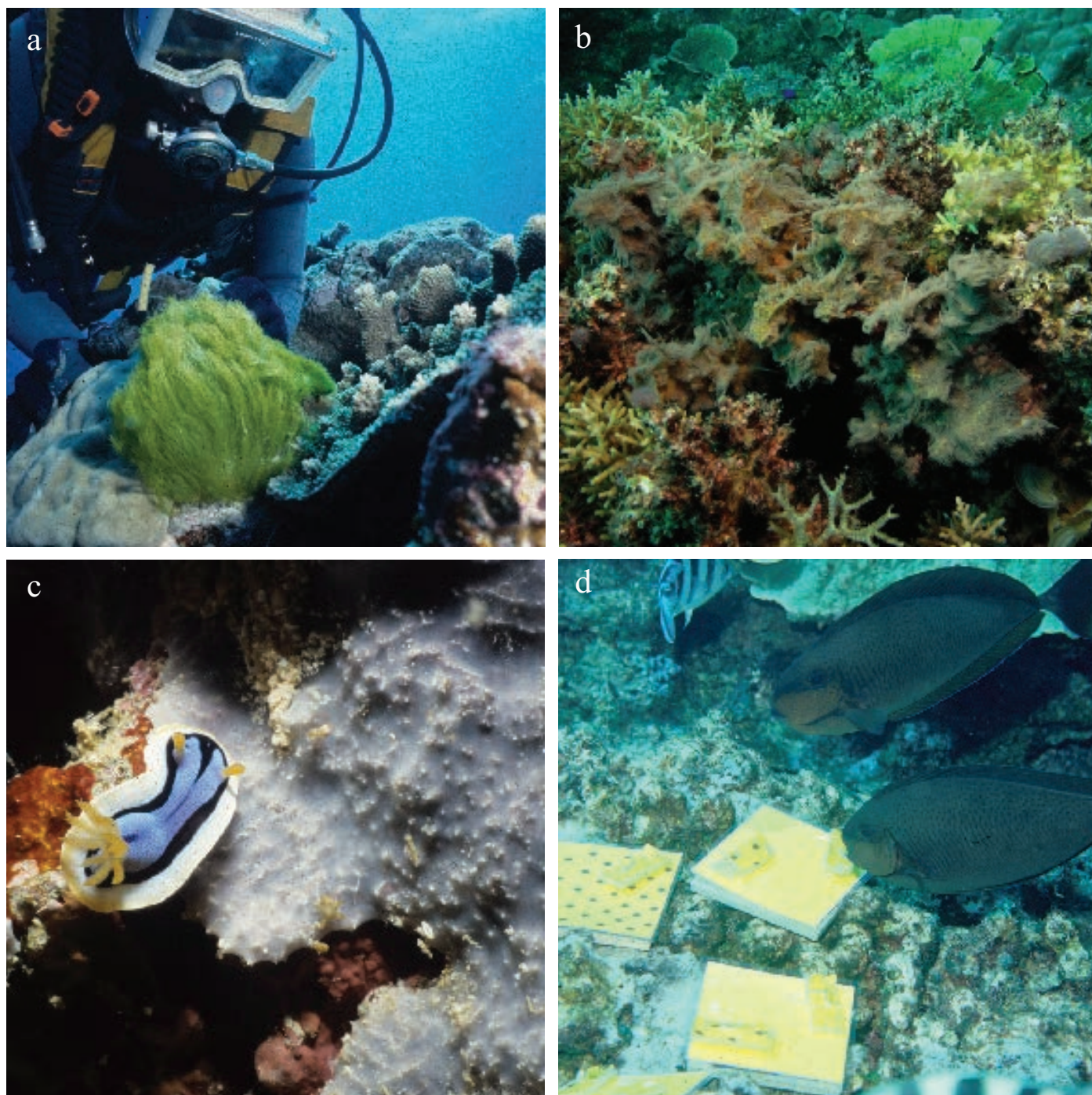


FIGURE 2. Photographs illustrating various field methods that use scuba diving for studies of marine chemical ecology in the tropical Pacific. (a) A diver examines the chemically rich green alga *Chlorodesmis fastigiata* before collection (photo by V. Paul); (b) Mixed assemblages of cyanobacteria overgrow corals (photo by R. Ritson-Williams); (c) The dorid nudibranch *Chromodoris lochi* eats an unidentified sponge (photo by V. Paul); (d) A feeding assay examines chemical defenses and the role of aposematic coloration in phyllid nudibranchs (photo by R. Ritson-Williams).

sponge, *Cacospongia* sp., on Guam. The sponge *Dysidea* sp. contained the compound 7-deacetoxyolepupane, which deterred fish predators in situ (Thacker et al., 1998). Using scuba, these researchers also tested for allelopathic effects of this compound by attaching agar strips containing natural concentrations of 7-deacetoxyolepupane onto the co-occurring sponge *Cacospongia* sp. After seven days, the presence of this compound alone caused sponge tissue necrosis similar to that observed in the sponge–sponge interactions. This chemically mediated competition was first observed by divers in the field, and through extensive field-based ecology using scuba it was shown that the isolated sponge compound had multiple ecological functions in competition and predator defense (Thacker et al., 1998).

As in the Caribbean, sponge consumers have also been studied in the tropical Pacific, and again, underwater observations were critical to understanding predator–prey interactions. Dorid nudibranchs are specialized predators on sponges (Figure 2c), but in the tropical Pacific sponge diversity is so large that it would be impossible to test every possible combination of nudibranch and prey. Perhaps the earliest investigation linking a nudibranch to its prey did so by demonstrating the presence of structurally complex natural products called macrolides in the dorsal tissues of the large Spanish Dancer nudibranch, *Hexabranchus sanguineus*, and in the sponge *Halichondria* sp., collected by night diving on Kwajalein atoll in the Marshall Islands (Pawlik et al., 1988). This study went on to demonstrate that the macrolides were “stolen” by the nudibranch from its sponge diet and passed on to the egg masses of the slug, and that these metabolites were highly effective chemical defenses against co-occurring fish and crab species (Pawlik et al., 1988). Observations of another dorid nudibranch, *Glossidoris palida*, determined that the nudibranch was eating the sponge *Cacospongia* sp., from which it would sequester compounds for defense (Avila and Paul, 1997; Becerro et al., 1998). Many brightly colored nudibranchs can be observed by divers during the day, which appears to be a strategy to advertise their chemical defense. The phyllidiid nudibranch *Phyllidiella granulatus* was frequently seen in Guam, and when the nudibranchs were offered alive to fish they were never eaten (Ritson-Williams and Paul, 2007). Underwater observations showed that *P. granulatus* was eating the sponge *Acanthella cavernosa*, and laboratory analyses found that these two organisms had many of the same natural products. In situ feeding assays with the sponge compounds showed that they inhibited fish predation at levels below natural concentrations (Figure 2d). Using an underwater video camera, fish predators were found to avoid these sponge compounds without tasting them, demonstrating modification of fish behavior by chemical defenses in the field (Ritson-Williams and Paul, 2007). This study illustrates not only the potency of marine chemical defenses but also the complexity of ecological interactions that can only be observed by conducting research under water.

Often, marine natural products from soft bodied invertebrates are assumed to be defensive compounds. While this is

certainly the best-studied ecological role of natural products, it is not their only function. Tetrodotoxin and its analogs are potent neurotoxins that have been found in a wide variety of marine and terrestrial organisms (Zimmer and Ferrer, 2007), and these compounds are typically assumed to have a defensive function. Tetrodotoxin and several analogs were found in a planoceric flatworm species that eats mobile snails. In situ experiments were conducted to see if a natural assemblage of reef fish would eat whole live flatworms (Ritson-Williams et al., 2006). Reef fish ate almost all of the flatworms offered, suggesting that tetrodotoxin is either not defensive or not detected by these predators and providing further evidence that toxicity is not the same as antipredatory defense. Further investigation showed that tetrodotoxin was actually used by the flatworm to kill prey items, which are mostly gastropod mollusks (Ritson-Williams et al., 2006). These experiments show the importance of field experiments using scuba to elucidate the function of a secondary metabolite.

CHEMICAL ECOLOGY IN ANTARCTIC WATERS

The history of chemical ecology in Antarctica is more recent than at lower latitudes. The first scientist to use scuba diving as a research tool in Antarctica was Michael Neushul in 1958 (Neushul, 1959, 1961). Neushul described the benthic marine communities along the western Antarctic Peninsula currently being studied by chemical ecologists, particularly the macroalgal flora (Neushul, 1965, 1968). Since Neushul's time, it has become known that chemical defenses against predation are widespread in the Antarctic marine flora and fauna (reviewed by Amsler et al., 2001a, 2001b, 2008, 2009a; Avila et al., 2008; McClintock et al., 2005, 2010; McClintock and Baker, 1997, 1998), which is in contrast to predictions made before field studies were initiated in Antarctica that included scuba diving (cf. Amsler et al., 2000). Diving collections have also facilitated the elucidation of many of the secondary metabolites that mediate these ecological interactions (Figures 3a–d; Amsler et al., 2001a, 2001b; Lebar et al., 2007).

A majority of the diving-based studies of Antarctic marine chemical ecology have been conducted from the United States Antarctic Program (USAP) facilities at Palmer Station (64°46'S, 64°03'W) off the western Antarctic Peninsula and at McMurdo Station (77°51'S, 164°40'E) in McMurdo Sound, the southernmost extension of the Ross Sea that abuts land. The communities in these two areas differ markedly. Like at other sites along the northern half of the western Antarctic Peninsula, at Palmer Station qualitative and quantitative diving observations reveal that the communities are dominated by forests of large brown macroalgae to depths of 30–40 m or greater (Amsler et al., 1995; DeLaca and Lipps, 1976). The algal biomass in these communities rivals that in temperate kelp forests, particularly in the upper 20–30 m (Amsler et al., 1995). At greater depths or, beginning at approximately 30 m on vertical rock walls, sessile invertebrates dominate the benthos, including sponges, tunicates,

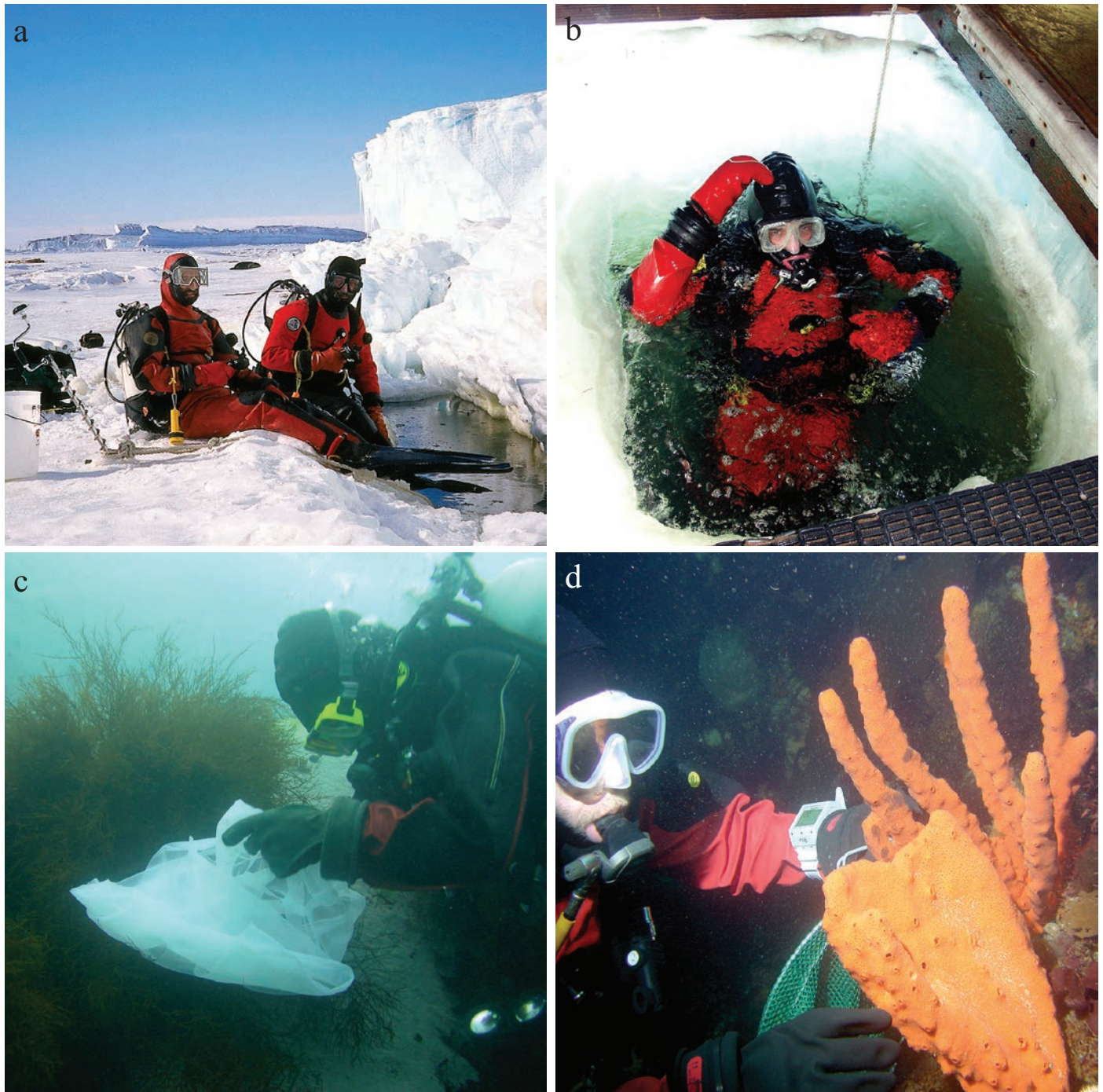


FIGURE 3. Marine chemical ecology research in Antarctic waters. (a) Diving through a natural crack next to a small, grounded iceberg in McMurdo Sound (photo by C. Amsler); (b) A diver returning to the surface in a melted dive hole within a McMurdo Sound dive hut (photo by C. Amsler); (c) A diver collecting amphipods from macroalgae near Palmer Station (photo by B. Baker); (d) A diver collecting the sponge *Halicionissa verucossa* near Palmer Station (photo by B. Baker).

soft corals, and bryozoans (Figure 3d; C. Amsler and B. Baker, personal observations). At McMurdo Station, smaller red macroalgae are present at some but not most dive sites in the 2–20 m depth range (Miller and Pearse, 1991). Otherwise, sessile, benthic organisms are sparse down to approximately 33 m depth due to the formation of anchor ice, which disrupts communities by ripping objects, including benthic organisms, from the bottom (Dayton et al., 1969, 1970). However, below 33 m qualitative and quantitative diving observations have revealed rich benthic invertebrate communities dominated by sponges (Dayton, 1979; Dayton et al., 1974).

Most current benthic marine research, including chemical ecology, at Palmer Station and other sites along the western Antarctic Peninsula is carried out in open water without solid overhead ice cover, and the equipment and techniques are very much like those used in colder temperate waters. Scientific diving in McMurdo Sound is primarily carried out through land-fast sea ice. Divers gain access by drilling, melting, or blasting holes through the ice or by diving through naturally occurring cracks (Figures 3a–b; Lang and Robbins, 2009). Because water visibility is commonly in the 100–200 m range in McMurdo Sound, USAP regulations do not require divers to be tethered to the surface in this overhead diving environment so long as the bottom is within the depth limits for the dive, a down-line with strobe lights and flags extends from the dive hole all the way to the bottom, and water currents are negligible (Lang and Robbins, 2009). In both regions, variable volume drysuits with thick undergarments are used for thermal protection. Water temperatures along the western Antarctic Peninsula range from approximately -1.5°C to $+2.0^{\circ}\text{C}$ and the water temperature in McMurdo Sound is typically -1.8°C during the diving season, so regulator freeze-up is a concern, particularly when temperatures are below 0°C . “Sling-shot” (“Y”) or “H” valves can be used to allow a diver to mount two completely independent regulators on a single tank so that the primary regulator can be turned off if it freezes-up and free-flows, thereby allowing the diver to make a controlled ascent with the remaining gas. United States Antarctic Program regulations require such a valve system in overhead environments such as that in McMurdo Sound (Lang and Robbins, 2009), and these are also commonly used along the Antarctic Peninsula as an extra safety precaution.

At Palmer Station, a majority of the macroalgal flora is unpalatable to common sympatric animals that include algae in their diet (Amsler et al., 2005; Aumack et al., 2010; Huang et al., 2006). Overall, nearly half of the macroalgal species have been shown to be unpalatable because they produce chemical defenses, including all of the large brown macroalgae that dominate the community in terms of biomass, as well as most of the more common red macroalgae (Amsler et al., 2005; Aumack et al., 2010). Hence, on a biomass basis, well over 90% of the macroalgal flora resists herbivory using chemical defenses. A number of the specific secondary metabolites responsible for this bioactivity have been identified (Ankisetty et al., 2004).

Early in these studies of macroalgal chemical ecology at Palmer Station, divers recognized that the dominant macroalgae were supporting very dense assemblages of amphipods. Subsequent quantitative diving collections of the amphipods along with their host algae revealed densities of 2–20 amphipods g^{-1} algal wet weight (Figure 3c; Huang et al., 2007), which when combined with algal biomass data from this community (Amsler et al., 1995) resulted in estimated amphipod densities ranging from approximately 30,000 to 300,000 amphipods m^2 of the benthos in solid stands of the dominant macroalgae (Amsler et al., 2008). These amphipods appear to benefit the macroalgae by keeping them relatively clean of epiphytic microalgae and filamentous algae, which otherwise would heavily foul them (Aumack et al., 2011). The amphipods also benefit from the association by gaining a refuge from omnivorous fish predators (Zamzow et al., 2010). Consequently, these two numerically dominant components of the benthic flora and fauna appear to exist in a community-wide, mutualistic relationship with its basis in the widespread occurrence of chemical defenses in the dominant macroalgae.

On a species-by-species basis, an even higher percentage of the sponge species (Figure 3d) at Palmer Station are unpalatable to the dominant sea star predator in the community, *Odontaster validus*. Peters et al. (2009) found that 78% of the 27 species examined were unpalatable to the sea star, and in all cases tested the unpalatability could be explained by the production of defensive metabolites. This prevalence of chemical defense against macro-predators is comparable to that observed in Caribbean sponges (Pawlik et al., 1995). However, amphipods were deterred from feeding by extracts of only 2 of 12 randomly chosen demosponge species (Amsler et al., 2009b). With tunicates from this community, even though 100% of 12 species were unpalatable to omnivorous fish and 58% were unpalatable to sea stars, chemical defenses explained the unpalatability to fish in only one tunicate species (Koplovitz et al., 2009). Either secondary metabolites or low tunic pH could explain the unpalatability in five of the seven tunicate species unpalatable to sea stars (Koplovitz et al., 2009). Similar to sponges, only one of ten tunicate species' extracts deterred amphipods from feeding (Koplovitz et al., 2009).

In McMurdo Sound, only two species of fleshy macroalgae occur throughout most of the year and both are unpalatable to sympatric sea urchins because they produce defensive secondary metabolites (Amsler et al., 1998). Divers commonly observe the sea urchins covered with these chemically defended red algae (Amsler et al., 1999; Miller and Pearse, 1991). Laboratory studies motivated by these diving observations demonstrated that although the urchins do not eat the chemically defended algae, they preferentially chose these algae to cover themselves with over other available objects. The algae provide urchins with a physical defensive barrier against their main predators, two large species of sea anemones (Amsler et al., 1999). Moreover, the chemically defended algae benefit because the urchins hold large amounts of drift algae in the photic zone where they can still photosynthesize (Schwarz et al., 2003) and produce spores

for the next algal generation (Amsler et al., 1999). Consequently, this is a second mutualistic relationship between Antarctic macroalgae and potential herbivores that is based on the common occurrence of chemical defenses in Antarctic macroalgae.

Although no comprehensive or randomized-sampling survey of the palatability of sponge species has been completed in McMurdo Sound, divers have observed that only relatively few sponge species are commonly preyed on by sea stars (Dayton et al., 1974; Amsler, Baker, and J. McClintock, pers. obs.). All such species for which chemical defenses have been examined were undefended (McClintock et al., 1994, 2000) while most other sponge species in the community have been shown to elaborate defensive metabolites (reviewed by Amsler et al., 2001b). Unlike at Palmer Station, divers do not observe high densities of amphipods associated with benthic organisms in this community (Amsler, Baker, McClintock, pers. obs.). Sea stars are clearly the dominant predators of sponges, although some nudibranchs also specialize on sponges (Dayton et al., 1974; Dearborn, 1977; McClintock, 1994). Unlike lower-latitude communities, there are no vertebrate or other important visual predators of sponges and they have likely been absent for millions of years (Aronson et al., 2007). Because the sponges do not occur shallower than approximately 30 m depth, sponges are unlikely to be subjected to damaging levels of ultraviolet radiation (Karentz and Lutze, 1990). At lower latitudes, sponge pigmentation has been hypothesized to be involved in aposematism (warning coloration) (Harrison and Cowden, 1976; but see Pawlik et al., 1995) and photoprotection against ultraviolet radiation (Bergquist, 1978; Harrison and Cowden, 1976). Neither of these roles would appear to be of selective advantage in Antarctica, at least at locations other than the western Antarctic Peninsula, particularly if one assumes some metabolic cost to production of the pigments (McClintock and Baker, 1998). However, all pigments so far identified from Antarctic sponges have been found to have chemical defensive properties against potential predators, pathogens, or biofoulers (McClintock et al., 2005). It has been hypothesized that these pigments may originally have been of selective value because of other roles but have been maintained in Antarctic sponges because they secondarily took on defensive functions that remain advantageous in the modern Antarctic environment (McClintock et al., 2005).

Diving observations in McMurdo Sound also revealed a unique symbiotic relationship in the plankton that is mediated by chemical defenses. Divers ascending from the benthos noticed a pteropod (pelagic mollusk), *Clione antarctica*, being carried on the backs of the amphipod *Hyperietta dilatata* (McClintock and Janssen, 1990). The pteropods are chemically defended from fish predation by the polyketide pteroenone (Bryan et al., 1995; Yoshida et al., 1995), whereas the amphipods are readily consumed. However, when the amphipods are carrying a captured pteropod, they too are rejected as food by the fish (McClintock and Janssen, 1990). This is likely detrimental for the pteropods, which apparently are unable to feed while being carried by the

amphipods, and this relationship has been referred to as an “antagonistic symbiosis” by McClintock and Baker (1997). Dead pteropods were never detected being carried in situ by amphipods, suggesting that they are periodically released and replaced with a fresh individual (McClintock, pers. obs.).

CONCLUSIONS

Scuba diving and other undersea exploration technologies have played a fundamental role in the birth and development of both marine natural products research and marine chemical ecology. Again, the purpose of this contribution has not been to exhaustively review marine chemical ecology, but rather to provide insight into the development of this scientific subdiscipline in response to the rise of undersea technologies. Research boundaries continue to be expanded, with increasing reliance on scuba diving using nitrox mixtures for safer dives and longer bottom times, and mixed-gas technical diving to reach even greater depths (Lesser et al., 2009). Moreover, researchers interested in marine chemical ecology are now using scuba for field studies around the world, including in the North Sea (Toth and Pavia, 2002), Mediterranean (Tarjuelo et al., 2002; Becerro et al., 2003; Haber et al., 2011; Noyer et al., 2011), Red Sea (Ilan, 1995; Kelman et al., 2000; Burns et al., 2003), mid-Atlantic (Ruzicka and Gleason, 2009), and temperate South Pacific (Wright et al., 2000; Duckworth and Battershill, 2001). This discipline is only a few decades old, and vast undersea habitats remain poorly studied in terms of the chemical defenses and signals involved in their ecology, particularly the open-water plankton, the meiofauna and infauna of sandy and muddy benthic habitats, and the deep-sea benthos, including hydrothermal vent and seep communities. Perhaps new undersea technologies will expand ecological and chemical studies to these habitats as well.

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We dedicate this chapter to the memory of two pioneers in marine natural products chemistry, Paul J. Scheuer and D. John Faulkner, who collaborated with and inspired marine biologists and ecologists to investigate the ecological roles of marine natural products.

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