Chemical Ecology in the Marine Environment

Many plants and animals, both terrestrial and marine, produce compounds that help them survive by, for example, deterring potential predators, warding off pathogens, keeping their living space free from competitors, and even reducing the impact of exposure to environmental stresses, such as high levels of solar UV radiation. Thus, these chemicals have an enormous impact on the outcome of interactions between species and the structure and function of communities and ecosystems like coral reefs.

The following slides provide examples of the diverse roles that secondary metabolites play for marine organisms and illustrate some of experimental methods used by marine ecologists and chemists to determine natural functions of these compounds.

Presentation Prepared by Dr. Niels Lindquist, University of North Carolina at Chapel Hill
The mouths of fishes and other consumers in the oceans have a tremendous impact on the evolution of defensive adaptations of sessile marine invertebrates and seaweeds, including the production of noxious tasting and highly toxic chemicals.
Animals that are mobile or that have hard shells or spines are typically not defended by noxious or toxic chemicals.
Nudibranches, also called sea slugs, are a commonly cited example of how organisms with potent chemical defenses have little need for a physical defense, such as a hard shell, to protect against potential predators. Nudibranches typically get their defensive chemistry from the sponges, bryozoans, and sea squirts that they eat. Nudibranches also put defensive compounds in their soft egg ribbons.
Preference assays, like the one shown to the right, offer a range of potential prey species to common predators. Those species avoided by predators are frequently chemically defended.

Caging experiments help to further illustrate the role of predators in eliminating poorly defended prey from habitats, like coral reefs, where predators are abundant.
After identifying low preference prey species, ecologists determine if they are chemically defended by incorporating their chemical extracts into a food that predators, such as the fish shown here, readily eat. This simple feeding assay offers each fish (typically 10-15 individuals) a food pellet containing the extract and an identical food pellet lacking the extract. The numbers of control and treatment pellets eaten are tabulated, graphed and statistically compared to determine if the extract is distasteful to the fish.
More ecologically realistic feeding assays are then conducted by placing control and extract-treated foods on the reef where many different species of fish can feed on them.
Examples of Chemically Defended Marine Organisms

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Sponges are an abundant group of coral-reef invertebrates that are very chemically rich. Recent studies have shown that many sponge chemicals effectively deter potential predators, and many of the distasteful compounds, such as formoside, have now been isolated and structurally characterized.
Gorgonians, a type of soft coral, are closely related to hard corals but lack the hard calcium carbonate skeleton. Their soft texture would seem to make them susceptible to diverse reef predators, but the many novel compounds they produce effectively protect them from predators.
Hydroids are benthic cnidarians related to corals and anemones.

Stinging organelles called nematocysts (shown above) protect hydroids that lack a chemical defense.

Chemicals, like tridentatol A, defend some hydroids from predators.
Bryostatins are isolated from the bryozoan, *Bugula neritina*, but are produced by a symbiotic bacterium. The bryostatins are concentrated in the bryozoan’s larvae and protect the larvae from predation by fishes. Bryozoans are filter feeding invertebrates.
Tunicates, also called sea squirts, are a rich source of bioactive chemicals, several of which have been shown to deter feeding by fish, crabs and snails. One group of tunicates commonly found on coral reefs host symbiotic microalgae that have been proposed to be the source of some of the compounds isolated from the animal.
This unique marine isopod, a type of crustacean, has a thick carpet of blue-green alga growing on it. The alga produces a noxious compound that deters fish from eating the isopod. Because the isopod isn’t eaten by fish, instead of hiding from fish, the isopods live on sun exposed substrates where their symbiont gets plenty of light for photosynthesis. The isopod also eats its symbiont.
File clams are the bivalve equivalent of nudibranchs. Getting virtually no protection from their shells, they instead have very sticky and distasteful tentacles that deter many predators.
Even some fish have chemical defenses, like the venomous fins of the lionfish. Beware – lionfish have now been seen off the east coast of the U.S.

Trunkfish secrete chemicals that deter predators, but don’t put one in your saltwater aquarium – its chemicals will kill all the fish in your tank!

See more examples at www.geocities.com/mtoxins
Like larvae of *Bugula neritina*, larvae of other benthic marine invertebrates are chemically defended too. When larvae are chemically defended, mom typically produces a few large larvae that are brightly colored, and released during daylight hours despite the risk of being easily seen by fishes.

Larvae and eggs that aren’t chemically defended tend to be small, produced in large numbers, and released by mom under the cover of darkness when it is difficult for fish to see them.
Chemical defenses of juvenile stages of marine plants and invertebrates have rarely been examined, primarily because they tend to be small and difficult to study.

A newly settled and metamorphosed sponge larvae – the earliest juvenile stage.
Do marine consumers avoid chemically defended prey because the compounds taste bad or because they’re toxic?

Think about the Australian delight called Vegemite - a combination of yeast, malt, and vegetable extracts with lots of added salt. Australian love it but most Americans don’t. So bad taste seems to defend Vegemite against predation by Americans. Australians, however, aren’t dropping dead in the streets, so it isn’t toxic. But, would starving Americans eat it? - probably.

Food can be a severely limiting resource for many marine organisms, so bad taste alone is unlikely to be an effective defensive strategy. To be an effective defense, deterrent compounds should harm consumers. This hypothesis, however, has rarely been tested.
Fish are difficult test subjects for long-term feeding studies because they quickly learn to avoid foods containing compounds that make them sick. This was the case when pinfish (pictured above) were offered a small food pellet containing didemnin cyclic peptides produced by a Caribbean sea squirt. The compounds made the fish vomit about 1 hour after ingesting the pellet. By the third day of the study, the fish refused to eat the treatment pellet, even if it did not contain didemnins. The fish did not reject the food because of the taste of the didemnins, but instead by the flavor of the food. Control pellets, which were identical to the treatment pellets except they did not contain didemnins, were always eaten by control pinfish.
Unlike fish, sea anemones are stupid consumers that have trouble learning to avoid new foods that are toxic. Although the didemnins also caused anemones to vomit, they ate a small food pellet containing didemnins each day it was offered. After 32 days, anemones ingesting the didemnin-treated pellet grew 80% slower and produced 45% fewer babies than did control anemones. These results indicates that consumers can be harmed by some compounds produced by marine plants and invertebrates.

didemnin B
Bioactive chemicals also aid many sessile organisms, such as sponges and sea squirts, in their battles for living space on crowded coral reefs. Siphonodictyal is a compound found in the mucus exuded by a sponge. This mucus, which is toxic, covers neighboring organisms such as corals.
Many sessile marine organisms are surprising clean given the abundance of algal spores and invertebrate larvae that could settle and grow on them. One way some seaweeds and invertebrates keep clean is to produce compounds that deter or kill settling larvae and spores. Zosteric acid, isolated from the young shoots of a seagrass, is an example of a potent antifouling compound.
mycosporin-like amino acids  
(a.k.a. MAAs)

These compounds are produced by marine plants, including the zooxanthellae of corals and sea whips. MAAs absorb solar UV radiation and act as a sunscreen that protect the alga and their host from sunburn.
This presentation has provided a number of examples of chemically defended marine organisms and highlighted some of the ecological roles for these compounds.

The study of marine natural products and marine chemical ecology benefits more than just the biologists and the chemists. Our society benefits too because many important practical applications have been discovered for the unique compounds produced by marine plants and animals. More information on this topic can be viewed on the “practical applications of marine natural products” presentation.

Parting Punch – Talk about examples from your own experiences with noxious foods, perhaps even some that made you feel like vomiting!