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The biogeography of polyphenolic compounds in marine macroalgae: temperate brown algal defenses deter feeding by tropical herbivorous fishes

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Summary. Many tropical brown algae have low levels of polyphenolic compounds and are readily consumed by herbivorous fish. In contrast, temperate brown algae often produce large quantities of phenolic compounds causing them to be distasteful to herbivorous gastropods and sea urchins. We hypothesized that tropical brown algae do not use phenolic compounds as antiherbivore defenses because these compounds are not effective deterrents against tropical fish. To test our hypothesis, we assessed the ability of extracts from 8 tropical and 13 temperate algae with a broad range of phenolic levels to deter feeding by herbivorous fishes on Guam. Extracts of the high-phenolic ($>2\%$ d.w.) temperate brown algae consistently deterred feeding by herbivorous fishes, whereas extracts from low phenolic ($<2\%$ d.w.) temperate and 6 of 8 low-phenolic tropical brown algae did not. Thus, phenolic compounds could be effective feeding deterrents towards herbivorous fishes on Guam, but for unknown reasons they are not used by Guamanian brown algae.

Key words: Brown algae – Biogeography – Chemical defenses – Herbivory – Polyphenolic compounds

Many plants and animals produce toxic or deterrent compounds that enable them to persist in habitats where they would otherwise be consumed by predators or overgrown by competitors (Harborne 1977; Rosenthal and Janzen 1979). Evolutionary theory suggests that the production of defensive chemicals should be greatest in habitats in which selective pressures for their use are highest, i.e. where predatory or competitive pressures are most intense (Rhoades 1979). Therefore, biogeographic trends in defensive strategies should reflect trends in the intensity of predation or competition.

The intensity of predation in marine benthic communities is thought to increase with decreasing latitude (Bakus 1969; Vermeij 1978; Bertness et al. 1981); however, between-habitat levels of predation within the tropics can be as different as those between biogeographical regions (Ortega 1986). On tropical reefs, fishes and sea urchins play a major role in structuring algal communities (Randall 1961; Ogden et al. 1973; Sammarco et al. 1974; Ogden and Lobel 1978; Hay 1981a, b, 1984a, b; Hay et al. 1983; Sammarco 1982; Carpenter 1986; Lewis 1986). Herbivorous fishes have probably been one of the primary selective forces on marine macrophytes on tropical reefs; however, their ability to determine community structure in some areas may have declined in the Caribbean in recent years because of overfishing (Hay 1984a). In contrast, the major herbivores in temperate subtidal and intertidal communities are gastropod molluscs and urchins (Paine and Vadas 1969; Foreman 1977; Mann 1977; Duggins 1980; Lubchenco 1980; Dethier 1982; Hawkins and Hartnoll 1983; Witman 1987; Horn 1989).

Because the intensity of predation is higher in tropical than temperate latitudes, one would expect that the production of chemical defenses should be greater in tropical marine organisms, including the macroalgae. This appears to be true in green algae (Chlorophyta), red algae (Rhodophyta), and brown algae (Phaeophyta) of the order Dictyotales. Tropical species in these taxa produce a wide variety of deterrent or toxic compounds including terpenoids, aromatics, and acetogenins (Fenical 1975; Norris and Fenical 1982; Faulkner 1984; Paul 1985; Paul and Fenical 1987; Hay and Fenical 1988; Van Alstyne and Paul 1988a). In contrast, relatively few species of temperate red and green algae are known to produce secondary metabolites; however, a few temperate red algae of the families Bonnemaisoniaceae, Plocamiaceae, and Rhodomelaceae produce terpenoid and aromatic secondary metabolites (Fenical 1975; Faulkner 1984). In contrast, many temperate brown algae of the order Fucales (rockweeds) produce large quantities of polyphenolic compounds (Ragan and Glombitza 1986,

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Steinberg 1989). Although polyphenolic compounds may have evolved for purposes other than feeding inhibition, they are effective feeding deterrents against several species of herbivorous gastropods and one herbivorous urchin (Geiselman and McConnell 1981; Steinberg 1988). Polyphenolic compounds appear to be absent or in very low concentration in all species of tropical brown algae that have been tested, even in tropical fucoids which have well-defended temperate congeners (Steinberg 1986, 1989; Steinberg and Paul in press). Why then, do tropical brown algae lack these defenses that are common in temperate species?

We hypothesized that tropical brown algae lack polyphenolic compounds becasue these compounds are ineffective against tropical herbivorous fishes. We experimentally tested this hypothesis on Guam by examining the ability of extracts from 21 species of temperate and tropical brown algae to deter feeding by fishes in the field.

Methods

Collection and study sites

Algae were collected from several sites in Guam, Washington, and California. About 10 to 20 individuals were collected of each species. Five individuals were used for measurement of polyphenolic compounds. The temperate brown algae *Alaria marginata, Costaria costata, Egregia menziesii, Fucus distichus, Hedophyllum sessile, Laminaria dentigera, Pelvetiopsis limitata* and *Postelsia palmaeformis* were obtained from Tatoosh Island, WA, USA (48°23′ N, 124°44′ W) in November, 1986. *Agarum fimbriatum* was collected from San Juan Island, WA, USA (48°33′ N, 123°00′ W) and *Cystoseira osmundacea, Halidrys dioica* and *Sargassum muticum* were collected from Santa Catalina Island, CA, USA (33°26′ N, 118°30′ W) in November, 1986. The tropical brown algae *Dictyota bartayresii, Dictyota cervicornis,* and *Hydroclathrus clathratus* were collected in Cocos Lagoon, Guam (13°15′ N, 144°40′ E) in December 1986. *Sargassum polycystum, Padina tenuis* and *Turbinaria ornata* were collected from Agat Bay, Guam (13°24′ N, 144°39′ E) in November, 1986. *Sargassum cristaefolium* and another morph of *Turbinaria ornata* were collected from behind the University of Guam Marine Laboratory in Pago Bay, Guam (13°25′ N, 144°47′ E) in December 1986. *Turbinaria ornata* from Agat Bay was smaller, tougher and had larger spines than the Pago Bay form.

The feeding experiments took place on a small patch reef (2–5 m depth) in Cocos Lagoon at the southern tip of Guam. This reef was primarily made up of the coral *Acropora formosa*. Many species of herbivorous fishes were seen grazing at the site during our experiments including parrotfish (*Scarus sordidus* and *Scarus schlegeli*), surgeonfish (*Acanthurus nigrofuscus, Acanthurus nigricans, Naso literatus, Zebrasoma scopus* and *Zebrasoma flavescens*) and rabbitfish (*Siganus spinus* and *Siganus argentus*).

Analysis of phenolic compounds

A Folin-Denis analysis for total phenolics was used to quantify the differences in concentrations of phenolic compounds among algal species. Replicate measurements were made on five individuals from each of the species from which polyphenolics were measured. In order to confirm the presence of polyphenolic compounds in these extracts, we also used staining with Lindt's reagent, a stain specific to phloroglucinol derivatives (Ragan and Craigie 1978), to assay the presence or absence of polyphenolics. Because the Folin-Denis analysis quantifies hydroxylated aromatic groups it will also measure other non-phenolic metabolites such as ascorbic acid. Non-phenolic compounds included in Folin-Denis measurements are assumed to be relatively low in concentration (D. Rhoades, pers. comm.).

About 5 g (fresh weight) of algae from each plant was weighed and extracted in 70% methanol by grinding in a Waring blender for 1 to 2 min. The remaining solid material was filtered and the filtrate was assayed for total phenolics by a Folin-Denis analysis as described by Swain and Goldstein (1964). Five additional 5 g pieces were weighed and dried in a drying oven at 60° C for at least 24 h. The dried algae were then weighed to obtain a dry:wet weight ratio that was used to convert phenolic concentrations to a dry weight measurement. Brown algal extracts used in feeding experiments were run on Silica Gel 60 F254 Thin Layer Chromatography plates in 6:2:1 dichloromethane:methanol:water. These plates were later stained with Lindt's reagent and the presence or absence of spots containing phloroglucinol derivatives was noted.

Grazing assays

Algal extracts were prepared for use in field deterrence assays by grinding 500 to 1000 g of fresh plant material (about 5 to 15 individual plants) in methanol using a Waring blender for 1 to 2 min. The extracts were filtered through a Whatman #1 filter. A Buchi rotary evaporator was used to evaporate excess methanol and the remaining water and methanol were removed by heating the extract at low heat under a fume hood. The dried extract was weighed and stored in a freezer prior to being used in feeding experiments. Extracts from algae collected in California and Guam were prepared in Guam. Extracts from algae that were collected in Washington were prepared at the Friday Harbor Laboratories and were shipped to Guam as dried extracts without solvents. Shipping times varied from 5 to 10 days. Qualitative assays with Lindt's reagent (see above) demonstrated that polyphenolic compounds were still present in the high-phenolic extracts after being transported to Guam. Extracts were generally prepared several weeks before they were used and were kept in a freezer at −80° C to minimize the breakdown of secondary metabolites.

The abilities of algal extracts to deter feeding by fishes were tested as described by Paul and Van Alstyne (1988a, b). Similar feeding experiments have also been described by Paul (1987), Paul et al. (1985), and Wylie and Paul (1988). Fish were offered 9 to 23 paired sets of four pieces of *Enteromorpha clathrata* that had been woven into 0.5 m pieces of 3 strand, 7 mm thick polypropylene rope. In each set of feeding experiments a total of 15 g (wet weight) of *E. clathrata* was used for controls and 15 g (wet weight) of *E. clathrata* was coated with algal extracts as experimental treatments. *E. clathrata* is a highly palatable alga for herbivorous fishes on Guam (Van Alstyne and Paul, pers. observ.). Thus, these assays allow us to determine whether the compounds present in the brown algal extracts are sufficiently deterrent to mask the palatable features of this preferred food. We had been conducting feeding experiments at the patch reef in Cocos Lagoon for over a year prior to conducting these experiments. The fishes inhabiting the reef appear to recognize *E. clathrata* visually and initially will consume it readily.

In each pair of ropes in the feeding experiments, one set of *E. clathrata* was coated with extract and one set with solvent (aqueous acetone) only, which served as a control. *E. clathrata* that was coated with algal extracts was slightly darker than the control pieces; however, as demonstrated by the differences in responses to the 21 algal extracts tested, differences in the color of control and extract-treated pieces cannot explain the differences in feeding patterns among these two food types. During the feeding experiments the fish were offered only *E. clathrata* with or without brown algal extracts; they were never offered whole brown algal pieces.

The concentrations of extract used (2% of the wet weight of *E. clathrata*) approximated the concentrations of extracts that we obtained in extracting the whole algae. The pairs of ropes were placed on the reef and removed when at least half of the *E. clathrata* pieces had been consumed. The remaining pieces of *Enteromorpha* were scored as the number of pieces that were consumed out of the original four pieces on that rope.

Statistical analyses were performed by first subtracting the number of extract-coated pieces that were consumed from the number of control pieces consumed for each pair of ropes. These results were then analyzed with a Sign test for paired comparisons (Sokal and Rohlf 1981) to determine whether significantly ($\alpha = 0.05$) more control pieces were consumed than extract-treated pieces.

Because of the short duration of these experiments (5 to 15 min), little of the extract dissolved before the ropes were removed. Algal extracts were still visible on the *E. clathrata* at the end of the experiments. Even if some of the compounds were lost, the assay would still be a conservative one for the effects of phenolic compounds on feeding by fish.

Results

Analysis of phenolic compounds

The concentrations of polyphenolic compounds measured with a Folin-Denis analysis for total phenolics gave similar results to those previously reported for tropical and temperate brown algae (Steinberg 1985, 1986, 1989). Brown algae from Guam had consistently low ($<2\%$ by dry weight) levels of polyphenolics (Table 1), whereas temperate brown algae from Washington and California had both high-phenolic ($>2\%$ by dry weight) and low-phenolic species (Table 2). Phenolic concentrations were high in both temperate members of the order Fucales. However, fucoid brown algae from tropical habitats had low levels. All temperate algae in the order Laminariales except *Agarum* had low concentrations of polyphenolic compounds. Thus, although phylogenetic trends at the ordinal level existed within habitats, they did not hold up between biogeographic zones.

Table 1. Concentrations of polyphenolic compounds (as % of dry weight ±1 SD for N individual plants) in tropical brown algae as measured using a Folin-Denis analysis for total phenols and results of staining TLC plates with Lindt's reagent, a stain specific for phloroglucinol derivatives

Species	*N*	[phenols]	Stain reaction
Order Dictyotales			
Dictyota bartayresii	5	0.19±0.03	–
Dictyota cervicornis	5	0.53±0.21	–
Padina tenuis	4	0.74±0.35	+
Order Scytosiphonales			
Hydroclathrus clathratus	5	0.50±0.16	–
Order Fucales			
Sargassum polycystum	5	0.84±0.23	–
Sargassum cristaefolium	5	1.24±0.14	–
Turbinaria ornata (Agat)	4	1.44±0.24	+
Turbinaria ornata (Pago)	5	1.62±0.22	–

Table 2. Concentrations of polyphenolic compounds (as % of dry weight ±1 SD for N individual plants) in temperate brown algae as measured using a Folin-Denis analysis for total phenols and results of staining TLC plates with Lindt's reagent, a stain specific for phloroglucinol derivatives. High-phenolic species are those whose mean phenolic concentration is greater than 2% of the alga's dry weight. The values reported parenthetically are mean phenolic concentrations for these species from Steinberg (1985)

Species	*N*	[phenols]	Stain reaction
High-phenolic species			
Order Fucales			
Cystoseira osmundacea	5	– (4.42)	+
Fucus distichus	5	5.36±1.48 (4.35)	+
Halidrys dioica	5	– (12.54)	+
Pelvetiopsis limitata	5	11.12±1.93 (4.93)	+
Sargassum muticum	5	– (3.77)	
Order Laminariales			
Agarum fimbriatum	5	– (4.08)	+
Low-phenolic species			
Order Laminariales			
Alaria marginata	5	1.35±0.19 (0.43)	–
Costaria costata	5	0.71±0.19 (0.31)	–
Egregia menziesii	5	0.25±0.03 (0.96)	
Hedophyllum sessile	5	1.96±0.55	+
Laminaria dentigera	5	0.72±0.50 (0.49)	–
Nereocystis luetkeana	5	0.59±0.07 (0.44)	–
Postelsia palmaeformis	5	0.49±0.15 (1.65)	–

Staining with Lindt's reagent showed that all of the high-phenolic temperate species contained phloroglucinol derivatives. Only 2 of the tropical species and one of the low-phenolic temperate species tested contained sufficient amounts of these compounds to be detectable with TLC and staining with Lindt's reagent. Therefore, the substances being detected by the Folin-Denis analyses in low-phenolic species are primarily non-phenolic compounds that contain hydroxylated aromatic groups or other reducing compounds that react with the Folin-Denis reagents. Data from nuclear magnetic resonance (NMR) spectroscopy has shown that some polyphenolic compounds are present in many low-phenolic temperate brown algal species (Ragan and Glombitza 1986; Steinberg, pers. comm.).

Grazing assays

All six of the extracts from high-phenolic species deterred feeding whereas only two of the 15 extracts from the low-phenolic species were significantly ($P<0.05$) avoided (Fig. 1). There was a significant tendency ($P<0.001$ using a Fisher's Exact Test) for fish to be deterred by high-phenolic extracts but not low-phenolic ones, regardless of the origin of the plants from which the extracts were made. Only extracts of two of the tropical algal species, *Dictyota bartayresii* and *D. cervicornis*, significantly deterred feeding (Fig. 1). None of the low-phenolic temperate species appeared to inhibit feeding (Fig. 1); however, all of the extracts from high-phenolic

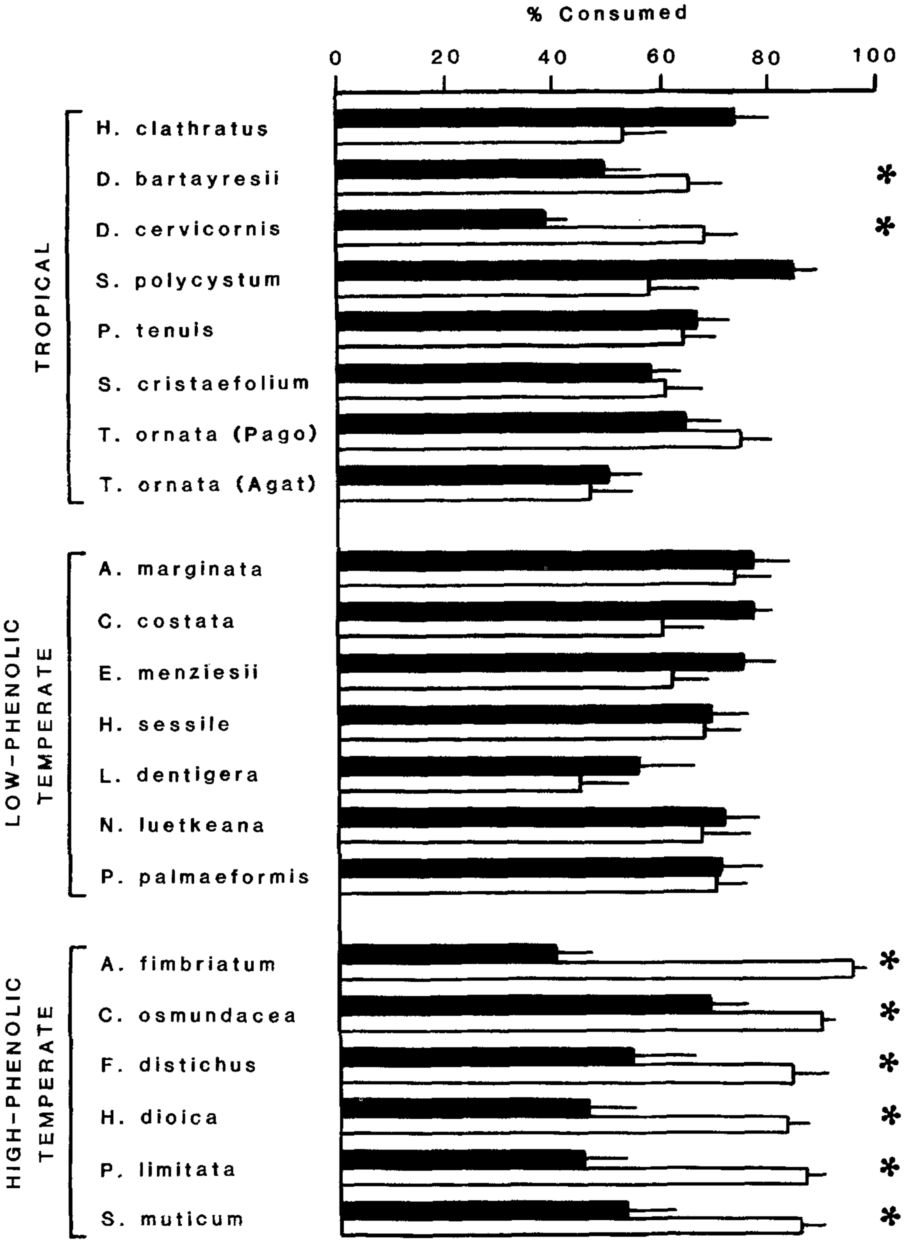

Fig. 1. Ability of tropical, low-phenolic temperate, and high-phenolic temperate brown algal extracts to deter fish feeding. Values given are the mean percentages of extract-coated (solid bars) and control (open bars) *Enteromorpha* pieces consumed during a feeding experiment. Horizontal lines represent 1 SE. Asterisks demark significantly different ($P < 0.05$) consumption rates of treated and control *Enteromorpha* as determined by a Sign test ($n = 9$ to 23)

temperate species were significantly deterrent (Fig. 1). Thus, temperate polyphenolic compounds do deter feeding by tropical herbivorous fishes on Guam.

Discussion

Polyphenolic compounds are absent or occur in low amounts in brown algae from several sites in the tropical Indo-West Pacific. Previously published values of total phenolic concentrations in *Sargassum* spp. and *Turbinaria* spp. from Tahiti and the Great Barrier Reef range from 0.26% to 1.77% by dry weight (Steinberg 1986). Phenolic concentrations in brown algae from Guam were similar, ranging from 0.19% to 1.62%. Values of phenolic concentrations in algae from other tropical locations have not been published. Thus, it is not known if a lack of high concentrations of phenolic compounds is a ubiquitous feature of all tropical phaeophytes. Ragan and Glombitza (1986) list phenolic concentrations for all brown algal species in which phenolic concentrations have been measured; all are from temperate locations. In general, temperate species within the orders Chordariales, Desmarestiales, Dictyosiphonales, Scytosiphonales, and Sphacelariales contain low levels (range: <0.1 to 1.6% d.w.) of phenolic compounds and members of the orders Ectocarpales, Dictyotales, and Laminariales contain both high- and low-phenolic species (range: <0.1 to 15% d.w.). Temperate species within the order Fucales are primarily high-phenolic plants (range: <0.1 to 15% d.w.); however, tropical members of this group contain low levels of phenolic compounds. Temperate brown algae from Australia and New Zealand likewise have representatives in both the high-phenolic and low-phenolic categories (Steinberg 1989).

In general, tropical marine organisms appear to be better defended against attacks from predators then do their temperate counterparts. Many tropical macroalgae combine chemical and morphological defenses to persist in reef habitats where herbivores are numerous and diverse (Hay 1984b; Paul and Hay 1986; Paul and Van Alstyne 1988a). The ability of gastropod and bivalve shells to resist crushing appears to increase with decreasing latitude (Vermeij 1978). Both sponges and holothurians have higher proportions of toxic species in lower than higher latitudes (Bakus 1974; Bakus and Green 1974). The only circumstance in which this trend is known to be reversed is in the production of phenolic compounds by brown algae (Steinberg 1986).

Brown algal phenolic compounds have been shown to be effective feeding deterrents towards several grazers, including gastropods and urchins (Geiselman and McConnell 1981; Steinberg 1989). However, these compounds may be present in algae for reasons other than defense against herbivores. Brown algal polyphenols have been suggested to have a number of physiological or ecological functions (Ragan and Glombitza 1986). These include the uptake of metal ions, inhibition of bacterial, fungal, or viral growth, inhibition of the growth of potential competitors or fouling organisms, or aiding in recovery from wounding. Herbivore deterrence may simply be a pleiotropic effect of polyphenolic compounds, which evolved in these algae for other reasons. Nonetheless, polyphenolic compounds appear to provide an effective means of deterring at least some tropical herbivorous fishes. Although many marine algae produce compounds that function as herbivore deterrents, there have been no studies that conclusively demonstrate that herbivores impose selective pressures on the production of secondary metabolites. Directional selection for traits that confer resistance to herbivory has been demonstrated in the morning glory *Ipomoea purpurea* (Rausher and Simms 1989).

Tropical brown algae use several other methods in order to avoid being consumed; these include escapes in time and space as well as the production of morphological and non-phenolic chemical defenses. Several tropical browns produce non-polyphenolic secondary metabolites, including some that have been shown to be deterrent towards herbivores. These include hydroquinones (Fenical et al. 1973), diterpenoids (Gerwick 1981; Rao et al. 1986), and phenolic lipids (Gerwick and Fenical 1982). Of the seven species of brown algae commonly found on reefs around Guam only *Dictyota* spp. produce secondary metabolites (Paul 1987). Crude extracts of both *Dictyota* species deterred feeding by fish. Many *Dictyota* spp. produce diterpenoid alcohols that have been shown to be deterrent towards herbivorous fishes and sea urchins (Hay et al. 1987a, b, 1988). These compounds are produced by both tropical and temperate species in several genera.

Since phenolic compounds appear to be effective feeding deterrents towards tropical herbivorous fish, why are they not used by tropical brown algae? We suspect that the answer to this question may lie in the physiological mechanisms involved in producing and storing phenolic compounds that could be affected by tropical-temperate differences in temperature and nutrient regimes. However, at present there is little data available to either support or refute these hypotheses. Further studies examining the effects of high temperatures and low nutrient concentrations on the production of polyphenolic compounds will be necessary to test these hypotheses.

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References

Bakus GJ (1969) Energetics and feeding in shallow marine waters. Intern Rev Gen Exp Zool 4:275–369

Bakus GJ (1974) Toxicity in holothurians: a geographic pattern. Biotropica 6:229–236

Bakus GJ, Green G (1974) Toxicity in sponges and holothurians: a geographic pattern. Science 185:951–953

Bertness MD, Garrity SD, Levings SC (1981) Predation pressure and gastropod foraging: a tropical-temperate comparison. Evolution 35:995–1007

Carpenter RC (1986) Partitioning herbivory and its effects on coral reef algal communities. Ecol Monogr 56:345–363

Dethier MN (1982) Pattern and process in tidepool algae: factors influencing seasonality and distribution. Bot Mar 48:343–348

Duggins DO (1980) Kelp beds and sea otters: an experimental approach. Ecology 61:447–453

Faulkner DJ (1984) Marine natural products: metabolites of marine algae and herbivorous marine mollusks. Nat Prod Rep 1:251–280

Fenical W (1975) Halogenation in the Rhodophyta: a review. J Phycol 11:245–259

Fenical W, Sims JJ, Squatrito D, Wing RM, Radlick P (1973) Zonarol and isozonarol, fungitoxic hydroquinones from the brown seaweed *Dictyopteris zonaroides*. J Org Chem 38:2383–2386

Foreman RE (1977) Benthic community modification and recovery following intensive grazing by *Strongylocentrotus droebachiensis*. Helgol Wiss Meeresunters 30:468–484

Geiselman JA, McConnell OJ (1981) Polyphenols in brown algae *Fucus vesiculosus* and *Ascophyllum nodosum*: chemical defenses against the marine herbivorous snail, *Littorina littorea*. J Chem Ecol 7:1115–1133

Gerwick WH (1981) The natural products chemistry of the Dictyotaceae. Dissertation, University of California, San Diego, CA, USA

Gerwick WH, Fenical W (1982) Phenolic lipids from related marine algae of the order Dictyotales. Phytochem 21:633–637

Harborne JD (1977) Introduction to Ecological Biochemistry. Academic Press, New York, New York, USA

Hawkins SJ, Hartnoll RG (1983) Grazing of intertidal algae by marine invertebrates. Oceanogr Mar Biol Ann Rev 21:195–282

Hay ME (1981a) The functional morphology of turf-forming seaweeds: persistance in stressful marine habitats. Ecology 62:739–750

Hay ME (1981b) Herbivory, algal distribution, and the maintenance of between habitat diversity on a tropical fringing reef. Am Nat 118:520–540

Hay ME (1984a) Patterns of fish and urchin grazing on Caribbean coral reefs: are previous results typical? Ecology 65:446–454

Hay ME (1984b) Predictable spatial escapes from herbivory: how do these affect the evolution of herbivore resistance in tropical marine communities? Oecologia 64:396–407

Hay ME, Fenical W (1988) Marine plant-herbivore interactions: the ecology of chemical defense. Ann Rev Ecol Syst 19:111–145

Hay ME, Colburn T, Downing D (1983) Spatial and temporal patterns in herbivory on a Caribbean fringing reef: the effects on plant distribution. Oecologia 58:299–308

Hay ME, Duffy JE, Pfister CA, Fenical W (1987a) Chemical defense against different marine herbivores: are amphipods insect equivalents? Ecology 68:1567–1580

Hay ME, Fenical W, Gustafson K (1987b) Chemical defense against diverse coral-reef herbivores. Ecology 68:1581–1591

Hay ME, Renaud PE, Fenical W (1988) Large mobile versus small sedentary herbivores and their resistance to seaweed chemical defenses. Oecologia 75:246–252

Horn MH (1989) Biology of marine herbivorous fishes. Oceanogr Mar Biol Ann Rev 27:167–272

Lewis SM (1986) The role of herbivorous fishes in the organization of a Caribbean reef community. Ecol Monogr 56:183–200

Lubchenco J (1980) Algal zonation in a marine rocky intertidal community: an experimental analysis. Ecology 61:333–344

Mann KH (1977) Destruction of kelp beds by sea urchins: a cyclical phenomenon or irreversible degradation? Helgol Wiss Meeresunters 30:455–467

Norris JN, Fenical W (1982) Chemical defense in tropical marine algae. In: Rutzler K, Macintyre IG (eds) The Atlantic Barrier Reef Ecosystem at Carrie Bow Cay, Belize. In: Structure and Communities. Smithsonian Contributions in Marine Science 12:417–431

Ogden JC, Lobel PS (1978) The role of herbivorous fish and urchins in coral reef communities. Environ Biol Fish 3:49–63

Ogden JC, Brown RA, Salesky N (1973) Grazing by the echinoid *Diadema antillarum* Philippi: formation of halos around West Indian patch reefs. Science 182:715–717

Ortega S (1986) Fish predation on gastropods on the Pacific Coast of Costa Rica. J Exp Mar Biol Ecol 97:181–192

Paine RT, Vadas RL (1969) The effects of grazing by sea urchins, *Strongylocentrotus* spp., on benthic algal populations. Limnol Ocean 14:710–719

Paul VJ (1985) The natural products chemistry and chemical ecology of tropical green algae of the order Caulerpales. Dissertation, University of California, San Diego, California, USA

Paul VJ (1987) Feeding deterrent effects of algal natural products. Bull Mar Sci 41:514–522

Paul VJ, Fenical W (1987) Natural products chemistry and chemical defense in tropical marine algae of the phylum Chlorophyta. In: Scheuer PJ (ed) Marine Bioorganic Chemistry. Springer, Berlin Heidelberg New York, pp 1–29

Paul VJ, Hay ME (1986) Seaweed susceptibility to herbivory: chemical and morphological correlates. Mar Ecol Prog Ser 33:255–264

Paul VJ, Van Alstyne KL (1988a) Chemical defense and chemical variation in some tropical Pacific species of *Halimeda* (Halimedaceae; Chlorophyta). Coral Reefs 6:263–269

Paul VJ, Van Alstyne KL (1988b) The use of ingested algal diterpenoids by *Elysia halimedae* MacNae (Opisthobranchia: Ascoglossa) as antipredator defenses. J Exp Mar Biol Ecol 119:15–29

Paul VJ, Hay ME, Duffy JE, Fenical W, Gustafson K (1987) Chemical defense in the seaweed *Ochtodes secundiramea* (Montagne) Howe (Rhodophyta): effects of its monoterpenoid components upon diverse coral-reef herbivores. J Exp Mar Biol Ecol 114:249–260

Ragan MA, Craigie JS (1978) Phenolic compounds in brown and red algae. In: Hellebust JA, Craigie JS (eds) Handbook of Phycological Methods, Vol II. Cambridge Univ Press, Cambridge, UK, pp 157–179

Ragan MA, Glombitza K (1986) Phlorotannins, brown algal polyphenols. In: Round FE, Chapman DJ (eds) Progress in Phycological Research, Vol 4. Biopress Limited, Bristol, pp 129–241

Randall JE (1961) Overgrazing of algae by herbivorous marine fishes. Ecology 42:812

Rao CB, Pullaiah KC, Surapaneni RK, Sullivan BW, Albizati KF, Faulkner DJ (1986) The diterpenes of *Dictyota dichotoma* from the Indian Ocean. J Org Chem 51:2736–2742

Rausher MD, Simms EL (1989) The evolution of resistance to herbivory in *Ipomoea purpurea*. I. Attempts to detect selection. Evolution 43:563–572

Rhoades DF (1979) Evolution of plant chemical defense against herbivores. In: Rosenthal GA, Janzen DH (eds) Herbivores: Their Interaction with Secondary Plant Metabolites. Academic Press, New York, New York, USA, pp 1–55

Rosenthal GA, Janzen DH (1979) Herbivores: Their Interactions with Secondary Plant Metabolites. Academic Press, New York, New York, USA

Sammarco PW (1982) Effects of grazing by *Diadema antillarum* Philippi (Echinodermata: Echinoidea) on algal diversity and community structure. J Exp Mar Biol Ecol 65:83–105

Sammarco PW, Levinton JS, Ogden JC (1974) Grazing and control of coral reef community structure by *Diadema antillarum* Philippi (Echinodermata: Echinoidea): a preliminary study. J Mar Res 32:47–53

Sokal RR, Rohlf FJ (1981) Biometry. W.H. Freeman and Company, New York, New York, USA

Steinberg PD (1985) Feeding preferences of *Tegula funebralis* and chemical defenses of marine brown algae. Ecol Monogr 55:333–349

Steinberg PD (1986) Chemical defenses and the susceptibility of tropical brown algae to herbivores. Oecologia 69:628–630

Steinberg PD (1988) The effects of quantitative and qualitative variation in phenolic compounds on feeding in three species of marine invertebrate herbivores. J Exp Mar Biol Ecol 120:221–237

Steinberg PD (1989) Biogeographic variation in brown algal polyphenolics and other secondary metabolites: comparison between temperate Australasia and North America. Oecologia 78:373–382

Steinberg PD, Paul VJ (1990) Fish feeding and chemical defense of tropical brown algae in Western Australia. Mar Ecol Prog Ser (in press)

Swain TS, Goldstein JL (1964) The quantitative analysis of phenolic compounds. In: Pridham JB (ed) Methods in Polyphenol Chemistry. MacMillan, New York, New York, USA, pp 131–146

Van Alstyne KL, Paul VJ (1988) The role of secondary metabolites in marine ecological interactions. Proc 6th Internat Coral Reefs Symp 1:175–186

Vermeij GJ (1978) Biogeography and Adaptation: Patterns of Marine Life. Harvard Univ. Press, Cambridge

Witman JD (1987) Subtidal coexistence: storms, grazing, mutualism, and the zonation of kelps and mussels. Ecol Monogr 57:167–187

Wylie C, Paul VJ (1988) Feeding preferences of the surgeonfish *Zebrasoma flavescens* in relation to chemical defenses of the tropical algae. Mar Ecol Prog Ser 45:23–32