Chemical Defense in Tropical Marine Algae

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ABSTRACT

Chemical and taxonomic studies of the benthic algae of Carrie Bow Cay, Belize, have revealed that species of certain families of the Rhodophyta, Phaeophyta, and Chlorophyta produce unique or unusual secondary compounds. Analysis of the structural organic chemistries of these natural products shows that the substances produced consist largely of halogenated and non-halogenated terpenoids including monoterpenoids (C_{10} compounds), sesquiterpenoids (C_{15} compounds), and diterpenoids (C_{20} compounds), and larger compounds of mixed acetate-mevalonate origin. These secondary compounds, hypothesized to be feeding deterrents developed as defenses against herbivores, were examined for antibiotic activity and toxicity. Fish toxicity experiments using *Eupomacentrus leucostictus* and these compounds revealed sublethal to lethal effects. One compound, elatol, from *Laurencia obtusa* was found to inhibit sea urchin egg development totally. Field observations indicate that marine algae having these secondary metabolites are not eaten by many herbivores, and biological activity testing suggests that certain of these compounds may be responsible. In some cases, specialized grazers have apparently co-evolved to tolerate these potential chemical "deterrents," and may in turn use them in their own defense against predation.

Introduction

Land plants have evolved elaborate morphological and chemical defense mechanisms against

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herbivores (Fraenkel, 1959; Whittaker and Feeney, 1971). Since Janzen (1973) put forth the working hypothesis that the primary role of secondary compounds in higher plant vegetation and seeds is defense against herbivores and microorganisms, it has been generally recognized that these natural products may either serve as feeding deterrents or attractants in terrestrial plant-animal interactions (see, for example, Harbourne, 1977), or function as allelopathic chemicals (Müller, 1970) or antibiotics. The same evolutionary pressures responsible for the many biologically active compounds found in terrestrial vegetation have been predicted to have parallels in marine vegetation (Whittaker and Feeney, 1971; Kittredge, 1976). Predaceous fishes and invertebrate animals have been important forces acting as agents of natural selection in the evolution of protective mechanisms (Bakus, 1964; 1966; 1969).

The world-wide distribution of herbivorous marine fishes shows a concentration, both in species diversity and biomass, on tropical reefs (Hiatt and Strasburg, 1960). Herbivorous fishes generally dominate fish communities on tropical reefs (Bardach, 1959; Hiatt and Strasburg, 1960); and the number and biomass of both vertebrate and invertebrate herbivores are two of the striking features of Caribbean coral reefs (Ogden, 1976).

Marine algae have developed several defenses in response to herbivory (see for example, Paine and Vadas, 1969; Vadas, 1977; 1979). Algal species may deter herbivores in one or more of the following ways: (1) by having a resistant or unpalatable physical structure (for example, the calcareous nature of some Rhodophyta, Chloro-

phyta, and Phaeophyta, or the tough texture of certain Phaeophyta), or a morphology that makes it difficult for the herbivore to attach to feed (see Hay, 1981); (2) by residing in habitats that are cryptic or unfavorable for herbivore feeding (Ogden et al., 1973; Adey and Vassar, 1975), such as in crevices where they are inaccessible, in areas of high surf or strong surge where herbivores cannot attach themselves for feeding, or in areas where herbivores are subject to increased predation; (3) by having heteromorphic life histories, with a fast growing stage and a resistant stage (Lubchenco and Cubit, 1980); (4) by living in association with toxic or unpalatable algae (see plant defense guilds of Atsatt and O'Dowd, 1976); (5) by being unpredictable in occurrence in time or space (for example, ephemeral species, or species having rare or patchy distribution) (Littler and Littler, 1980); and/or (6) by producing secondary metabolites (Fenical, 1975), ranging from unpalatable to toxic, as chemical defense against herbivores.

Since the pioneering work of Pratt et al. (1951) reporting antibacterial activity of various seaweed extracts, several investigators have demonstrated the antibiotic activity of extracts from some tropical algae (for example, Burkholder et al., 1960; Olesen et al., 1964; Sieburth, 1964; Burkholder, 1973; Bhakuni and Silva, 1974; Núñez and Serpa Sanabria, 1975). Studies of Boyd et al. (1966) on the effects of selected tropical algae on human erythrocytes found that the extracts from six brown algae agglutinated blood groups O and A. More recently, Targett and Mitsui (1979) studied the effects of aqueous extracts from tropical algae on fish erythrocyte hemolysis and fish mortality, and Targett (1979) developed a behavioral bioassay (gastropod tentacle withdrawal) to test extracts from marine algae for biological activity. In another study, both seasonal variability and locality differences of the tropical algal extract's antibiotic activity against selected pathogenic bacteria was observed (Almodóvar, 1964). Hornsey and Hide (1974) found similar seasonal variation in their screening experiments for antimicrobial activity of British marine algae. Sieburth (1968) offered some ecological interpretation of the role of algal antibiot-

ics in marine algal-algal and algal-animal interactions. Unfortunately, there have been few quantitative studies on the diets of marine herbivores, and our knowledge of feeding behavior and food preferences of tropical herbivores is still too inadequate to be conclusive. What is known on tropical fish diets can be found in Randall (1967), while sea urchin diets have been summarized by Lawrence (1975).

In this paper we provide an overview of interactions between tropical reef algae and herbivores in the Caribbean, with reference to our identification of specific compounds from Belize reef algae. On the basis of the antimicrobial activity and fish toxicity of these compounds we present hypotheses of their ecological role in reef algal-animal interactions.

Over the past four years at Carrie Bow Cay, off the coast of Belize, we have investigated the systematics of the benthic algae as well as the chemical nature of their secondary compounds. Some of the Chlorophyta, Phaeophyta, and Rhodophyta synthesized unusual secondary products which in the laboratory showed biological activity against selected micro-organisms and a reef fish. Many of the relatively abundant algae that were accessible to potential herbivores were found to contain these biologically active substances. We hypothesize that these compounds have been selected for by the intense grazing pressure on tropical marine algae and that they function to minimize population losses by inhibiting or repelling herbivores. Our present analysis indicates that tropical reef algae are chemically defended from many generalist herbivores, while some specialist herbivores have evolved a physiological tolerance to these natural products.

Materials and Methods

Field trips were made to Carrie Bow Cay on the barrier reef of Belize (16°48′N; 88°05′W), during the spring (March–May) of 1976, 1977, and 1978 (for a review of the biological and geological features of Carrie Bow Cay, see Rützler and Macintyre, herein: 9). During each expedition, benthic macro-algae were collected for subsequent studies on their systematics and chemistry. Homogeneous collections were identified and separated into specimens for chemical analysis and vouchers for taxonomic verfication; the former were preserved in isopropanol, the latter in 4% Formalin-seawater.

Voucher specimens have been deposited in the U.S. National Herbarium, Smithsonian Institution. The following algal species were chemically investigated in this study. Chlorophyta: *Caulerpa cupressoides* (Vahl) C. Agardh, *C. mexicana* (Sonder) Kützing, *C. racemosa* (Forsskål) J. Agardh, *C. serrulata* (Forsskål) J. Agardh emend Børgesen, *C. sertularioides* (Gmelin) Howe, *C. verticillata* J. Agardh, *Rhipocephalus phoenix* (Ellis and Solander) Kützing, and *Udotea flabellum* (Ellis and Solander) Howe. Phaeophyta: *Dictyota bartayresii* Lamouroux, *Stypopodium zonale* (Lamouroux) Papenfuss, *Sargassum polyceratim* var. *ovatum* (Collins) Taylor, and *Turbinaria turbinata* (Linnaeus) Kuntze. Rhodophyta: *Liagora farinosa* Lamouroux, *Asparagopsis taxiformis* (Delile) Trevisan; *Ochtodes secundiramea* (Montagne) Howe, *Laurencia caraibica* Silva, and *L. obtusa* (Hudson) Lamouroux.

The biological activity of the secondary compounds produced by the marine algae was investigated by nutrient agar plate disc assay methods in the laboratory of W. Fenical, and by fish toxicity experiments. Antibacterial activity was examined on the basis of inhibition of *Staphylococcus aureus* Rosenbach, *Bacillus subtilis* (Ehrenberg) Cohn, and *Escherichia coli* (Migula) Castellani and Chalmers, and antifungal activity was assessed against the human pathogen *Candida albicans* (Robin) Berkhout. Toxicity to fish was tested using *Eupomacentrus leucostictus* (Müller and Troschel) with serial dilutions of the alga's natural compounds in seawater (as outlined by Sun and Fenical, 1979), and the crude extract. In each treatment (three replicates), either the extract or the pure compound was added directly to the seawater with the aid of an ethanol dispersant; controls were untreated seawater and seawater containing only the ethanol. Fish mortality within one hour was considered to indicate a toxic compound, and sublethal effects, such as loss of equilibrium and respiratory stress were noted as "strong" or "mild." Results of the antimicrobial and ichthyotoxic experiments are summarized in Table 32.

Results and Discussion

CHLOROPHYTA.—Of the benthic algae in the vicinity of Carrie Bow Cay (Norris and Bucher, herein: 167), the green algae are perhaps the most abundant in biomass, having representatives throughout the diverse intertidal and subtidal habitats. Three families predominate, the Codiaceae with species of *Avrainvillea* and *Codium*, Udoteaceae with *Halimeda*, *Penicillus*, *Rhipocephalus*, and *Udotea*, and the Caulerpaceae with species of its monotypic genus, *Caulerpa*.

The species we investigated from these families produced unusual secondary metabolites. Of six species of *Caulerpa* from Carrie Bow Cay, *C. cupressoides*, *C. mexicana*, *C. racemosa*, *C. serrulata*, *C. sertularioides*, and *C. verticillata*, all but *C. mexicana* contained the known compound caulerpin (Figure 181a, compound I). This substance was originally isolated from *C. racemosa*, *C. serrulata*, and *C. sertularioides* by Aguilar-Santos and Doty (1968). In recent studies of *C. taxifolia* (Vahl) C. Agardh, Maiti and Thomson (1977) re-examined the structure of caulerpin (Aguilar-Santos, 1970) and found it to be a derivatized indole dimer.

We found that species of *Caulerpa*, *Halimeda*, *Penicillus*, *Rhipocephalus*, and *Udotea* also produce terpenoids of rather complex structure. Although it is difficult to analyze many of these compounds thoroughly because of their instability, we have isolated from *Rhipocephalus phoenix* two sesquiterpenoids, rhipocephenal and rhipocephalin, designated as compounds II and III respectively (Figure 181b). These compounds typify the struc-

TABLE 32.—Compounds identified from tropical benthic algae of Carrie Bow Cay, and results of biological activity tests (compound designations identified in Figures 181, 182; 0 = no response, + = positive response, NT = not tested)

Species	Compound	Antimicrobial activity	Toxicity to fish
CHLOROPHYTA			
Caulerpa cupressoides	I	0	NT
C. racemosa	I	0	+[1]
C. serrulata	I	0	NT
C. sertularioides	I	0	NT
C. verticillata	I	0	NT
Rhipocephalus phoenix	II	+	+[2]
R. phoenix	III	+	+
PHAEOPHYTA			
Sargassum polyceratinum var. ovatum	IV	+[3]	NT
Turbinaria turbinata	IV	+	NT
Dictyota bartayresii	V	+	0
Stypopodium zonale	VI	+	+
RHODOPHYTA			
Asparagopsis taxiformis	VII	+	NT
Ochtodes secundiramea	VIII	+	NT
O. secundiramea	IX	+	NT
Liagora farinosa	X	+	+
Laurencia caraibica	XI	+[4]	NT
L. obtusa	XII	+	NT

[1] Lewin, 1970 [2] Sun and Fenical, 1979 [3] Glombitza, 1977 [4] Izac, 1979

tural types we have detected in the Caulerpaceae and in some species of the Codiaceae and Udotaceae. Compounds II and III were ichthyotoxic at the 2 and 10 μg/ml levels, respectively, against *Eupomacentrus leucostictus*; when these compounds were placed in food offered to this fish it was not eaten (Sun and Fenical, 1979). We are continuing studies with *Halimeda* species, *Udotea flabellum*, *U. conglutinata* (Ellis and Solander) Lamouroux, *Penicillus capitatus* Lamark, and *Avrainvillea longicaulis* (Kützing) Murray and Boodle, each of which appears to contain unique and biologically active secondary metabolites.

Our field observations indicate that the tropical algae of these three families are avoided by most herbivores, at least by the "generalists" (sensu Emlen, 1973). Few quantitative studies have been done on food preferences of tropical fish and invertebrates. Those dealing with the herbivores and green algae we studied (see Lawrence, 1975; Ogden and Lobel, 1978) noted that the urchin *Echinometra lucunter* (Linnaeus) near St. Croix, Virgin Islands, does not eat *Caulerpa* and *Halimeda*, even though they are available in small amounts on substrate (Juliana and Ambrosetti, 1974; Ogden, 1976) and as drift (D. Abbott et al., 1974). Rates of feeding by *Lytechinus variegatus* (Lamarck) varied in laboratory experiments, with *Caulerpa* being eaten least rapidly when offered alone and most rapidly when offered with five other marine plants; *Halimeda* was consistently the least preferred alga (Lawrence, 1975). Lowe and Lawrence (1976) suggest that *L. variegatus* in Florida may be feeding preferentially on detrital seagrasses. Similarly, Vadas et al. (in press) showed the preferred diet of field populations of *L. variegatus* was detrital *Thalassia*, while siphonaceous greens were largely not eaten (except by one population in which approximately 30% of their diet consisted of these algae). Lowe and Lawrence (1976) suggested a mixed diet might be superior in nutrients for *L. variegatus*.
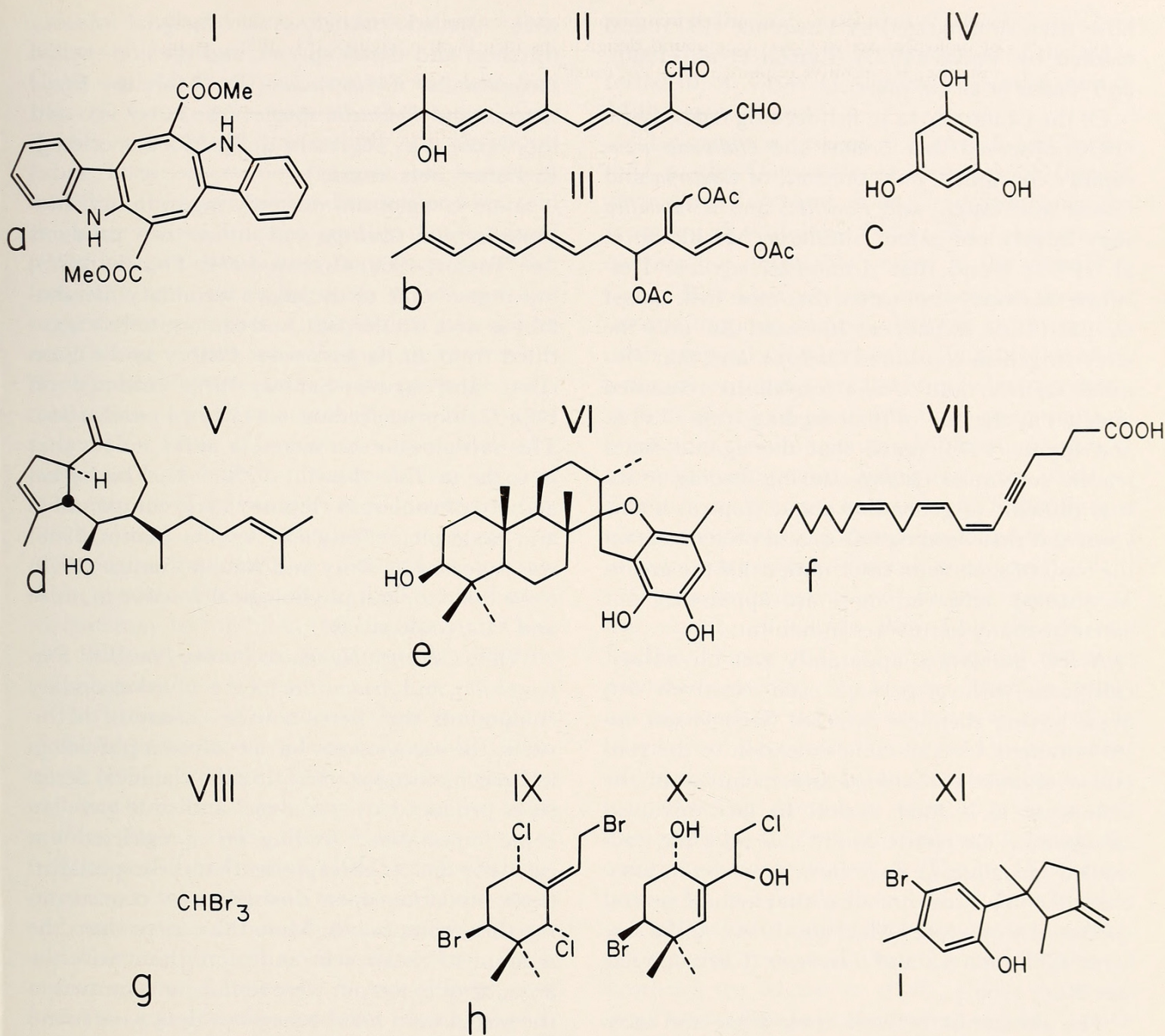
FIGURE 181.—Structures of biologically active metabolites isolated from Carrie Bow Cay marine algae: *a*, caulerpin (compound I) from species of *Caulerpa*; *b*, sesquiterpenoids, rhipocephenal (II) and rhipocephalin (III), from *Rhipocephalus phoenix*; *c*, polyphenol (IV) from *Sargassum* and *Turbinaria*; *d*, pachydictyol A (V) from *Dictyota bartayresii*; *e*, stypotriol (VI) from *Stypopodium zonale*; *f*, acetylene containing lipid (VII) from *Liagora farinosa*; *g*, bromoform (VIII) from *Asparagopsis taxiformis*; *h*, polhyalogenated monoterpenoids, ochtodene (IX) and ochtodial (X), from *Ochtodes secundiramea*; *i*, allolaurinterol (XI) from *Laurencia caraibica*.

Lewis (1958) suggested that *Tripneustes ventrico-sus* (Lamarck) refused *Halimeda* because of its calcified structure, but we suggest this rejection may also be due to the chemical component of *Halimeda*. Green algae not eaten by the urchin *Diadema antillarum* Philippi included *Penicillus* (Ogden et al., 1973; Ogden, 1976) and *Halimeda* (Ogden, 1976). Feeding preferences of sea urchins

have been summarized by Lawrence (1975) and studied by Vadas (1977), Larson et al. (1980), and Vadas et al. (in press).

Of the Chlorophyta in fish-feeding trials, Earle (1972) observed that *Codium* and *Halimeda* were rapidly consumed, only portions of *Caulerpa* and *Udotea* were eaten, and *Penicillus* and *Avrainvillea* were largely not eaten. Similarly, Mathieson et al. (1975) found that *Avrainvillea nigricans* Descaisne was mostly not eaten, that most fish, except the parrotfish, did not eat *Halimeda*, that only the Grey Angelfish consumed *Caulerpa*, and that *Penicillus capitatus* and *Udotea conglutinata* remained uneaten at the end of their feeding trials. Tsuda and Bryan (1973) noted that the siganid fishes readily consumed *Caulerpa* during feeding trials. It is difficult to generalize about tropical herbivores and their feeding habits and preferences on the basis of such scant information. Of the greens we studied, however, most are apparently not eaten by many herbivores in habitat.

A few herbivores apparently can physiologically cope with, or perhaps even selectively eat, algae having chemical defenses. Sacoglossan opisthobranchs are a notable exception to the general avoidance of *Caulerpa* and members of the Codiaceae as a food source. In fact, bivalved sacoglossans are restricted to *Caulerpa*, while non-shelled sacoglossans have been reported in association with a variety of algae that include several species of Codiaceae (MacNae, 1954), and a few other Chlorophyta and *Vaucheria* (Chrysophyta) (see Kay, 1968).

The association between these algae and sacoglossans in the Caribbean has been reported from Puerto Rico (Warmke and Almodóvar, 1963), and in the Pacific from Japan (Hamatani, 1972) and Fiji (Burn, 1966). The distribution of sacoglossans appears dependent on the range of their food source, *Caulerpa* (Burn, 1966), with members of the family Juliidae reflecting the distribution of *Caulerpa* throughout the Indo–West Pacific, the Caribbean, the Mediterranean and Victoria, Australia (Kay, 1968). Specialist herbivores were relatively common at Carrie Bow Cay. Found on *Caulerpa racemosa*

were shelled sacoglossans, *Lobiger souverbeii* (Fischer) and *Oxynoe* species, and the non-shelled sacoglossans, *Elysia cauzae* (Er. Marcus), *Elysia* species, and *Volvatella* species (the latter two and the *Oxynoe* may represent undescribed species, J. R. Lance, pers. comm.).

Some sacoglossans not only ingest intact chloroplasts from *Caulerpa* and utilize their products (see Taylor, 1968; Greene, 1974; Trench, 1975), but ingest some of the alga's secondary metabolites as well. Caulerpicin and caulerpin were identified from *Elysia panamensis* Pilsbry and Olsson (Doty and Aguilar-Santos, 1970) collected off Baja California feeding on *Caulerpa sertularioides*. This sacoglossan can secrete a milky mucus that is toxic to fish (Lewin, 1970). The biological activity of caulerpin (Figures 181a, compound I) and caulerpicin (Doty and Aguilar-Santos, 1966) was reported by Doty and Aguilar-Santos (1970) to be toxic to, and physiologically active in, mice and rats, respectively.

While *Caulerpa, Halimeda, Udotea, Penicillus, Rhipocephalus,* and *Avrainvillea* have evolved secondary compounds that deter a wide variety of herbivores, the sacoglossans have evolved a physiological mechanism for tolerating the chemical deterrents produced by the algae, and thus have become "specialists" feeding on a restricted but exclusive diet. It also appears that these specialists deter predation upon themselves by concentrating these compounds. More than three times the amount of caulerpicin and more than twice the amount of caulerpin were found concentrated in the sacoglossan *Elysia panamensis* than were found in the algal host, *Caulerpa* (Doty and Aguilar-Santos, 1970).

PHAEOPHYTA.—The abundant brown algae at Carrie Bow Cay belong to two families, the Sargassaceae and the Dictyotaceae. Species of *Sargassum* and *Turbinaria* (Sargassaceae) are apparently not eaten by some herbivores, at least in areas where these browns are common.

In the Caribbean, *Sargassum* and *Turbinaria* sometimes grow in areas of the reef where herbivores may have difficulty reaching them or remaining attached to feed. Also, in preliminary

subtidal feeding trials and translocation experiments of *Sargassum* in Caribbean Panama (J. Cubit and M. Hay, pers. comm.) and Islas San Blas (J. Cubit, pers. comm.), these algae were readily consumed, particularly by kyphosid fishes. These observations suggest that herbivory may limit the lower level of distribution of certain *Sargassum* species. It is also possible that increased predation or other factors may keep these fish from the reef where *Sargassum* grows; we also suggest that members of this family may not be eaten owing to their inherent high concentrations of polyphenolic substances based upon the polymerization of phloroglucinol (Figure 181c, compound IV). Types of biological activity shown by polyphenols include antibacterial (Conover and Sieburth, 1964) and antilarval (Conover and Sieburth, 1966). These polyphenols may also be ecologically important in plant-plant interactions; growth of certain phytoplankton and macroalgae may be inhibited (McLachlan and Craigie, 1964) or enhanced (Ragan et al., 1980) by polyphenols.

The presence and absence of these compounds in the Sargassaceae have been reviewed by Glombitza (1977). Pfeffer (1963) suggested that the inability of fish to digest *Sargassum* was due to its tannins (Ogino, 1963). From stomach analysis of tropical reef fish, Randall (1967) concluded *Sargassum* was eaten only by a few larger herbivorous and omniverous fishes—*Kyphosus incisor* (Cuvier and Valenciennes), *K. sectatrix* (Linnaeus), *Pomacanthus arcuatus* (Linnaeus), *P. para* (Bloch), and *Melichthys niger* (Bloch)—and that these kyphosids and *M. niger* feed on drifting algae. Earle (1972) suggested it may be eaten by certain fishes, and W. H. Adey (pers. comm.) reports that the bucktooth parrotfish, *Sparisoma radians* (Cuvier and Valenciennes), readily consumes *Sargassum*. Atkinson et al. (1973) found that *Sargassum*, though available, was not present in the guts of *Diadema antillarum* (see also Lawrence, 1975), while another sea urchin, *Paracentrotus lividus* (Lamarck) has been recorded as feeding on *Sargassum* (Lawrence, 1975). Sammarco et al. (1974) observed lush growth of *Tubinaria* on a patch reef after they

removed *Diadema*; a diet of *Turbinaria* also provided the best growth for *Tripneustes* of the algae tested in St. Croix (J. Ogden, R. Vadas, and S. Miller, pers. comm.).

The common browns at Carrie Bow Cay belong to the Dictyotaceae; members of *Dictyota*, *Dictyopteris*, *Lobophora*, *Padina*, and *Stypopodium* are represented. Although *Padina* and *Lobophora* species are not noticeably grazed in the vicinity of Carrie Bow Cay, we have not found in them the unusual organic compounds that are present in other tropical members of the family; therefore, structure or some other factor may be important, such as increased predation upon potential herbivores, or possibly water soluble compounds or secondary compounds below our level of detection may be present. Interestingly, a Pacific species of *Lobophora* from Palau was found to contain unusual compounds (Fenical, in progress).

Of the several species of *Dictyota* occurring in the vicinity of Carrie Bow Cay (Norris and Bucher, herein: 167), we investigated the most predominant one, *D. bartayresii*, which grows among corals in the spur and groove area of the barrier reef. Recognized in the field by its marked iridescence, *D. bartayresii* in our chemical studies was shown to contain a series of toxic bicyclic diterpenoids, the major component being the compound pachydictyol A (Figure 181d, compound V), previously described by Hirschfeld et al. (1973) from another Dictyotaceae genus, *Pachydictyon* (for review of Dictyotaceae diterpenoid synthesis see McEnroe et al., 1977). Although some sea urchins have been noted to feed on some species of *Dictyota* (Atkinson et al., 1973; Abbott et al., 1974; Lawrence, 1975), as yet none are known to feed specifically on *D. bartayresii*. This alga has been recorded in stomach contents of three species of fish (Randall, 1967; Earle, 1972). It is also possible that pachydictyol A may not function to deter urchin or fish predators, but might be an example of a compound that acts against certain micro-organisms. This metabolite's toxicity to certain fungi suggests it could be defense against microbial pathogens (Fenical, unpublished data).

Another predominant brown alga at Carrie Bow Cay is *Stypopodium zonale*, which grows primarily in open, shallow areas (4–10 m depths) where it is accessible to grazers. Frequently to 20 cm in length and conspicuous in its environment, *S. zonale* is apparently not eaten by most herbivores. When freshly collected *S. zonale* is placed in cool seawater for 10 hours, the water becomes dark brown, apparently from release of pigments and secondary compounds. These substances were toxic to the herbivorous damsel fish, *Eupomacentrus leucostictus*, found at Carrie Bow Cay, and exhibited antimicrobial activity in preliminary testing. Ethanol extracts of *S. zonale* were equally toxic to damsel fish at levels of approximately 3 μg/ml. The toxic components have been found to consist of a mixture of several related C_{27} compounds derived from a mixed biosynthesis of diterpenoid and acetate precursors. One of these compounds, the triol stypotriol (Figure 181*e*, compound VI), has been isolated and structurally defined (Gerwick and Fenical, 1980). We are not aware of published records of *S. zonale* as a food source for fishes or urchins. As in the green alga–sacoglossan relationship, certain mollusks may have co-evolved as specialist predators of *S. zonale*. Recent collections of this alga from the Florida Keys contained large numbers of the sea hare *Petalifera petalifera* Ranger (Fenical, unpublished data), but it was not observed on any other algae and may represent another specialist with a preferred or exclusive food source.

RHODOPHYTA.—Although they have the largest number of species in the environs of Carrie Bow Cay, the red algae are generally smaller in size and individual species are less abundant than either the green or brown algal species. Red algae that are apparently avoided by herbivores at Carrie Bow Cay belong to four families: Helminthocladiaceae, Bonnemaisoniaceae, Rhizophyllidaceae, and Rhodomelaceae. Members of the latter three families are known to produce elaborate halogenated, often toxic, metabolites (Fenical, 1975). With the recent discovery of unique compounds in *Liagora farinosa* (Paul and Fenical, 1980), the Helminthocladiaceae was

added to the expanding list of families known to produce secondary compounds.

The moderately calcified red, *Liagora farinosa* (Helminthocladiaceae), was seasonally abundant in the spur and groove habitats of the barrier reef at Carrie Bow Cay. We noted unusual compounds present on TLC plates, and recently Paul and Fenical (1980) described the major metabolite, an unusual acetylene containing lipid (Figure 181*f*, compound VII), which occurs along with several minor, related compounds in this species. These compounds were observed to be toxic against *Eupomacentrus leucostictus* at the 5–8 μg/ml range in seawater. We did not observe any grazers on *L. farinosa*.

Despite its fine, delicate structure, *Asparagopsis taxiformis* (Bonnemaisoniaceae) does not seem to be utilized as a food source. *Asparagopsis* species produce unique toxins, the major metabolite being the noxious compound bromoform (Figure 181*g*, compound VIII) (McConnell and Fenical, 1976). Several halogenated acetones are also produced by *A. taxiformis* (compounds of this type have been produced synthetically and used as tear gas).

Asparagopsis was not eaten by the fish *Acanthurus triostegus* (Linnaeus) (Randall, 1961), nor has it been reported as being grazed by sea urchins (Lawrence, 1975). We suggest it is not eaten by most herbivores because of its toxic metabolites. These compounds inhibited the growth of all micro-organisms tested, and they were severe lacrymators. Interestingly, though toxic or unpalatable to most grazers, it is consumed by man, for *Asparagopsis taxiformis* is the favorite seaweed food of the Hawaiians (Abbott and Williamson, 1974).

Falkenburgia hillebrandii (Ardissone) Falkenberg, the alternate sporophytic stage in the life history of *Asparagopsis taxiformis* (Chihara, 1961), has also been collected at Carrie Bow Cay. This morphologically different stage also appears to be avoided by grazers. In other studies, McConnell and Fenical (unpublished data) have found *Falkenburgia* from the North Atlantic also to contain bromoform. We suspect that the Carrie Bow Cay *Falkenburgia*, which is generally not eaten by herbi-

vores, also produces this compound. Fish have not been observed to feed on this stage of *Asparagopsis* (Earle, 1972), but it was found in 1% of *Diadema antillarum* guts by Atkinson et al. (1973). Since that was such a small sample, it may have indirectly been consumed while feeding primarily on other turf-forming algae. This possibility, however, will have to be further investigated.

Another red alga containing toxic secondary compounds is *Ochtodes secundiramea* of the Rhizophyllidaceae. *Ochtodes secundiramea* grows in shallow water inside the reef crest at South Water Cay, in areas of strong wave agitation and surge. This alga contains one major and one minor polyhalogenated monoterpenoid, octodene and ochtodial (Figure 181*h*, compounds IX and X) (McConnell and Fenical, 1978). Compound IX, the major metabolite, is strongly antibiotic and made up over 50% of the total organic extract of the alga. During our field studies on freshly collected specimens, we observed iridescence from the large "glandular cells" or "Drüsenzellen" (Kylin, 1956) present in the cortex of *O. secundiramea* (Joly and Ugadim, 1966). Whether these refractive bodies are the site of halogenation in *O. secundiramea* is uncertain, although we observed these bodies were no longer iridescent after the methanol extraction and they appeared to be "empty" on examination with a Wild M5 stereomicroscope. We are not aware of any published accounts of *Ochtodes* as a food source; we did not find it being grazed during our daytime observations in Belize.

Three species of the cosmopolitan genus *Laurencia* (Rhodomelaceae) from Carrie Bow Cay contained interesting secondary metabolites. This genus is known to produce a complex variety of halogen-containing compounds (Fenical and Norris, 1975; Fenical, 1975). We conducted chemical studies on the two abundant species, *Laurencia caraibica* and *L. obtusa* (identified following Taylor, 1960:626), at Carrie Bow Cay. The third species, *L. intricata* Lamouroux, was not abundant enough for further study, even though an initial TLC indicated the presence of secondary compounds.

Laurencia caraibica Silva grows sympatrically with *L. obtusa* in areas of intense water motion, generally along the outer reef crest. This alga produces quantities of the antibiotic cuparane derivative allolaurinterol (Figure 181*i*, compound XI), a compound which has also been isolated as a minor component of *L. subopposita* (J. Agardh) Setchell from California (Wratten and Faulkner, 1977) and *L. filiformis* (C. Agardh) Montagne from the east coast of Australia (Kazlauskas et al., 1976). Izac and Sims (1979) discovered a unique iodinated sesquiterpene in *L. caraibica*, the first report of such a compound and of iodine being found in the genus. We found the same major metabolite in this species, and did not observe this alga being eaten by fish or urchins.

Laurenica obtusa was found in large quantities along the Carrie Bow Cay reef crest (at least during April and May). We found this alga to contain more than 3% (dry weight) of the cytotoxic chamigrene derivative elatol (Figure 182, compound XII), a compound originally isolated from the Australian species *L. elata* (C. Agardh) Hooker and Harvey (Sims et al., 1974). Elatol has subsequently been found to be moderately antibiotic, but more interestingly this compound shows exceptional toxicity against fertilized sea urchin eggs, and totally inhibits cell division (Fig-
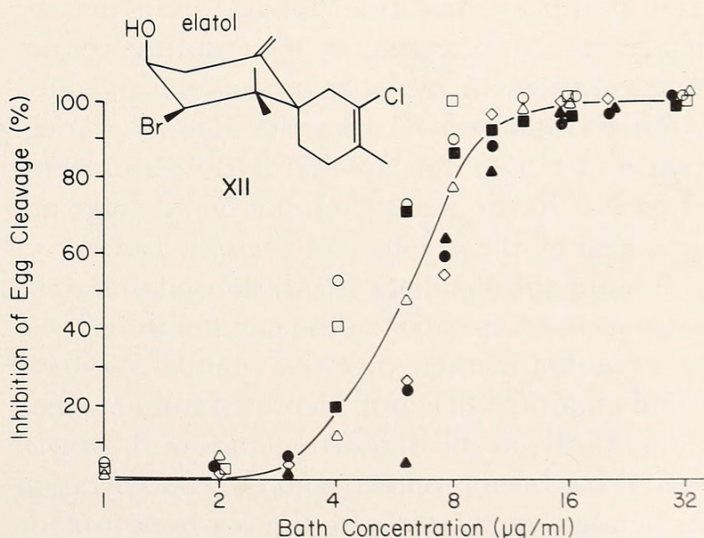

FIGURE 182.—Dose-response curve of elatol (compound XII) from *Laurencia obtusa*, against fertilized eggs of the sea urchin, *Stronglyocentrotus purpuratus* (the seven markers represent individual experiments).

ure 182). The dose-response curve of elatol with fertilized eggs from *Stronglylocentrotus purpuratus* (Stimpson), a California urchin, shown in Figure 182, has been provided by R. Jacobs. The LD_{50} of elatol is estimated at about 7 μg/ml bath concentration. *Laurenica obtusa* is not grazed by *Diadema* (Ogden, 1976), and is avoided by most herbivores. It is interesting to speculate on the ecological role of compounds such as elatol, which are now known to inhibit, or, at certain levels, to kill developing sea urchin eggs. We hypothesize that if such compounds are released or secreted in the vicinity of *Laurencia* stands, they could inhibit sea urchin egg development in situ, and thus give the alga a selective advantage against the settlement and development of potential predators in their vicinity.

In view of the biologically active constituents from *Laurencia*, it is not surprising that the alga has few predators. The sea hares (Anaspidea), particularly some species of *Aplysia*, have specific feeding preferences for *Laurencia*. In our field studies in the Gulf of California, California, the Galápagos Islands and now in Belize, we have observed this grazer-alga relationship between *Laurencia* and *Aplysia*. During our spring studies at Carrie Bow Cay, we typically found *A. dactylomela* (Ranger) grazing on *L. obtusa* on the fore-reef crest. It appears that some *Aplysia* species may be dependent on *Laurencia*, at least during certain stages of their life cycle, as larvae and juveniles. Culture studies on *A. californica* Cooper (Kriegstein et al., 1974) indicate that settling and metamorphosis of the free-swimming larval stage are enhanced by the presence of *Laurencia pacifica*.

Stallard and Faulkner (1974) showed that *Aplysia californica* concentrated the metabolites of *Laurencia pacifica* in their digestive glands. We have found quantities of elatol, identified from *L. obtusa* in our study, in the digestive glands of *A. dactylomela*. It has been proposed that the concentration of the algal metabolites by the sea hare provide a selective advantage against potential predators (Stallard and Faulkner, 1974; Kittredge et al., 1974). Although the defense role of this concentration needs to be tested, known predators of *Aplysia* are few, and opisthobranchs in general are avoided as a food source by Caribbean fish (Ran-

dall, 1967). Opisthobranch gastropods used in feeding-acceptability tests with selected fish by Thompson (1960) were almost invariably refused.

Recently, it was suggested that juveniles of the tropical bridled burrfish, *Chilomycterus antennatus* (Cuvier), in Caribbean Panama, are Batesian mimics of *Aplysia dactylomela* and perhaps avoid predation by mimicking the shape and coloration of the "unpalatable sea hare" (Heck and Weinstein, 1978). We suggest that the avoidance could be due to the concentration of elatol by *A. dactylomela* from *Laurencia obtusa*.

Summary and Conclusions

Our studies of Belize macro-algae, indicate that members of specific algal families—the Caulerpaceae, Codiaceae, Udoteaceae, Dictyotaceae, Sargassaceae, Helminthocladiaceae, Bonnemaisoniaceae, Rhizophyllidaceae, and Rhodomelaceae—produce unusual secondary compounds. The species we studied are not eaten by many herbivorous fishes or sea urchins. These herbivores and the coral reef algae on which they feed appear to represent a co-evolved system of defense and counterdefense. Chemical defense appears successfully to deter the majority of herbivores; however, some specialist grazers have co-evolved physiological mechanisms that enable them to tolerate or possibly even select for some of these same algae. In some specific animal-plant interactions, for example, saccoglossan-*Caulerpa* and *Aplysia*-*Laurencia*, the mollusks not only exclusively select certain algal species for food and show preference for others but they also concentrate the alga's secondary compounds as defense against being preyed upon. Thus, it appears the chemical deterrent against most herbivores may have become a chemical attractant to these specialist species. Published evidence and our own observations, though scant, indicate most herbivorous reef fishes are highly selective in the algae they consume. In tropical reef algal-animal relationships, there is strong evolutionary interaction between herbivores and algae, based on the alga's defenses—structure (Lubchenco, 1978), productivity and growth form (Littler, 1980), life history strategy (Lubchenco and Cubit, 1980), habitat,

and chemistry—and the herbivore's feeding habits (preference for, or not eating of, algae and the peculiarities of their digestive physiology).

Ehrlich and Raven (1965) first attributed to secondary compounds of plants a key role in determining the pattern of insect-plant co-evolution. As suggested by Feeny (1975), we may be witnessing an "evolutionary arms race" in which the algae must deploy part of their metabolic budget on defense against herbivory, and the herbivores must devote a portion of their assimilated energy on ways to locate their algal food, know which species to avoid, and on developing counter measures to tolerate the alga's chemical defense (see for example feeding preference studies of Vadas, 1977; Larson et al., 1980; for additional interpretation of "evolutionary arms race" theory, see Atsatt and O'Dowd, 1976).

The subject of tropical reef algal-animal interactions presents a myriad of problems to be investigated and questions to be answered. Recognizing the speculative nature of this study we concur with Janzen (1977) that there is "quite enough hypothetical biology on the books" and we now need quantitative ecological and behavioral studies "on the pragmatics" of tropical plant-animal interactions.

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