Reports

Dimethyl Sulfide in the Surface Ocean and the Marine Atmosphere: A Global View

Abstract. *Dimethyl sulfide (DMS) has been identified as the major volatile sulfur compound in 628 samples of surface seawater representing most of the major oceanic ecozones. In at least three respects, its vertical distribution, its local patchiness, and its distribution in oceanic ecozones, the concentration of DMS in the sea exhibits a pattern similar to that of primary production. The global weighted-average concentration of DMS in surface seawater is 102 nanograms of sulfur (DMS) per liter, corresponding to a global sea-to-air flux of 39 × 10^{12} grams of sulfur per year. When the biogenic sulfur contributions from the land surface are added, the biogenic sulfur gas flux is approximately equal to the anthropogenic flux of sulfur dioxide. The DMS concentration in air over the equatorial Pacific varies diurnally between 120 and 200 nanograms of sulfur (DMS) per cubic meter, in agreement with the predictions of photochemical models. The estimated source flux of DMS from the oceans to the marine atmosphere is in agreement with independently obtained estimates of the removal fluxes of DMS and its oxidation products from the atmosphere.*

On the basis of mass balance calculations for atmospheric sulfur, the flux of reduced sulfur gases emitted from the oceans to the atmosphere has been postulated by a number of investigators (*1*). Although the range of estimates was rather broad (34 × 10^{12} to 190 × 10^{12} g of sulfur per year), the models were in agreement that this natural, biogenic emission would rival the anthropogenic emission of SO_2 [104 × 10^{12} g of sulfur per year (*2*)]. Dimethyl sulfide (DMS) was discovered in the surface ocean by Lovelock *et al.* (*3*), and preliminary estimates of its sea-to-air flux based on limited data sets have been made (*4–7*).

We present here the first globally representative data set of the distribution of DMS in the surface ocean. New data from the Pacific Ocean complement our earlier results for other ocean areas and make it possible to estimate the global flux of DMS from the world ocean to the marine atmosphere. Our measurements of DMS in the atmosphere over the remote equatorial Pacific are the first data compatible with such a flux and with current photochemical models of the oxidation of DMS.

The DMS was determined in 628 surface seawater samples (collection depths, 0.05 to 3 m) obtained by various methods (sampling with bottles by hand, hydrographic sampling, and continuous pumping systems). No systematic differences between these sampling methods and depths were found. The DMS was determined by gas stripping, cryogenic collection, and gas chromatography with flame photometric detection (*8*). The precision was 6 percent, the accuracy better than 5 percent, and the detection limit 0.5 ng of sulfur (DMS) per liter. For the determination of DMS in air, DMS was collected on gold wool in quartz samplers (*6*). The samples were taken on the forward mast of the ship, at a height of 10 to 15 m above the sea surface under strict precautions to avoid contamination from the ship's emissions. The DMS was determined by gas chromatography with flame photometric detection; the precision and accuracy of this procedure were better than 10 percent at the concentrations observed over the Pacific; the detection limit was 0.1 ng of sulfur (DMS) per cubic meter of air at standard temperature and pressure (STP).

The samples were collected on cruises in the North and South Atlantic Ocean (R.V. *Meteor*, October to November 1980), the Bering Sea (R.V. *Thompson*, May 1981), the Sargasso Sea (R.V. *C. Iselin*, September 1981), the Gulf of Mexico (R.V. *Bellows*, October to November 1981), and the Peru Shelf and the tropical and equatorial Pacific (R.V. *Conrad*, June to August 1982). Detailed accounts of the results of the first four cruises have been prepared (*6, 9*). We discuss here the results from the Pacific Ocean and bring the data from all the cruises together in an effort to achieve a global perspective.

The cruise on the R.V. *Conrad* was divided into two legs, the first one on the Peru-Ecuador Shelf with emphasis on the areas of high biological productivity in the upwelling system off Peru and the second through the equatorial and tropical Pacific to Hawaii (Fig. 1). During leg 1, 159 samples of surface seawater and 29 samples of marine air were analyzed. Figure 1 shows the results of the DMS and chlorophyll a determinations in surface water from the southbound half of this leg. The DMS distribution is characterized by intense "hot spots" some 50 to 200 km in diameter with very high DMS concentrations superimposed on a base level near 100 ng $liter^{-1}$. These hot spots are associated with areas of high primary productivity, as shown by the chlorophyll data, and correspond to the upwelling centers documented along the Peruvian coast [Talara, 3° to 4°S; Pimentel, 6° to 7°S; Chimbote, 9° to 10°S; Callao, 11.5° to 13.5°S; and Pisco, 15° to 16°S (*10*)]. The highest values were observed at the Callao upwelling center, which is the most active area during the fall season when our cruise took place. The lowest values on this leg were observed close inshore at the southern extremity, where intense upwelling brought cold water to the surface. The vertical gradient of DMS, which usually follows the phytoplankton density (*6*), was absent at this station, and the DMS concentrations were comparable to those usually observed at a depth of ~ 50 m. Because of the rapid upwelling at this site, a phytoplankton bloom had not yet had time to develop and no DMS had yet been added to the water as a consequence of its release by phytoplankton (*11, 12*). In cross-shelf sections, the DMS maximum is found offshore of the area of maximum upwelling, close to the positions of maximum chlorophyll concentrations.

In the equatorial Pacific (leg 2), the DMS concentrations near the Ecuador shelf are similar to the average values on the Peru Shelf and decrease toward ~ 80 ng $liter^{-1}$ when one is going from east to west. The same trend is seen in the chlorophyll values and is related to the nutrient contributions by coastal and equatorial upwelling. As on leg 1, the distribution of DMS on leg 2 is characterized by intense patchiness, which creates an apparent scatter in Fig. 1. Because the measurement error is much smaller than the sample-to-sample variations observed, these variations represent real structure in the distribution of DMS, comparable to the patchiness of

phytoplankton distributions. The pattern is further complicated by the fact that different phytoplankton groups release different amounts of DMS per unit biomass (*12*). The most abundant producers are the coccolithophorids (*12*) and the haptophyte *Phaeocystis poucheti* (*9*). Coccolithophorids are abundant in the equatorial upwelling region west of Galápagos (*13*) and may be responsible for the hot spots west of 92°W. In order to investigate the relation between equatorial upwelling, phytoplankton abundance, and DMS, we sampled along a meridional section at 140°W. The upwelling region just north of the equator corresponds to a clear maximum around 1°N both in chlorophyll and in DMS. Going north into the oligotrophic waters of the tropical North Pacific, we encountered DMS concentrations of 50 to 60 ng liter^{-1}, similar to those in the tropical North Atlantic and the Brazil current, both regions of low primary productivity. This general relation between primary productivity (as estimated by phytoplankton biomass) and DMS is borne out by a regression analysis which shows that these values are significantly correlated at the 99.9 percent confidence level (correlation coefficient $r = 0.53$, $N = 225$). On the other hand, a substantial amount of the variability is not accounted for by the regression and is probably related to phytoplankton speciation and physiological differences.

We have combined the DMS data from the Pacific with our earlier data in Table 1. These data are divided into groups corresponding to large-scale ecological regions of planktonic primary production as estimated by Koblentz-Mishke *et al.* (*14*). The first group represents the oligotrophic waters of the central oceans; the second group designates transitional waters of intermediate productivity, in our sample set represented by samples from the temperate North Atlantic. The third group contains the areas of oceanic divergence and upwelling, including the subpolar divergences, which have not yet been sampled. The high abundance of *Phaeocystis* in the circum-Antarctic waters suggests that very high concentrations of DMS may be present there. On the basis of the 628 samples that we analyzed and the areas that these regions represent, we have calculated a global weighted-mean DMS concentration in surface waters of 102.4 ng liter^{-1}. This is substantially higher than the values given earlier (*3, 5*), which were based on very small sample sets.

In order to predict ocean-to-atmosphere fluxes from these concentration data, we use the stagnant-film model (*4, 15*). Since the molecular diffusion coefficient of DMS obtained from the Othmer-Thakar relation (*16*) is the same as that of radon (1.2×10^{-5} cm^2 sec^{-1}), we are able to use the global mean piston velocity given for radon by Peng *et al.* (*17*), 2.8 m day^{-1}. The concentration of DMS in marine air [0 to 500 ng m^{-3} (this report, *6, 12, 18, 19*)] is at least two orders of magnitude below the concentration in equilibrium with surface seawater (~ 30 μg m^{-3}). The sea-to-air flux may there-

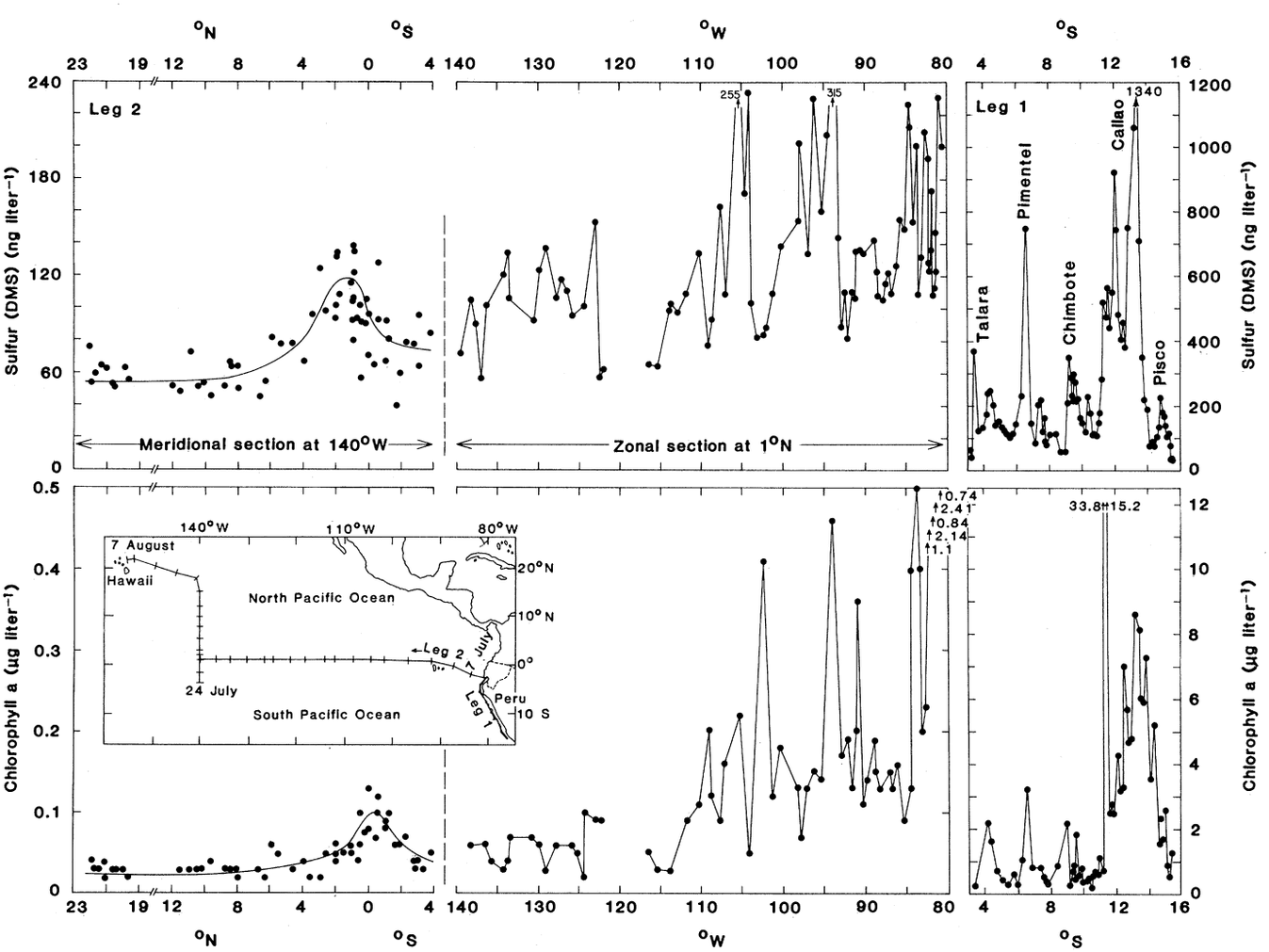

Fig. 1. Concentration of dimethyl sulfide (*DMS*) and chlorophyll a in the surface waters of the Peru Shelf (leg 1) and the equatorial Pacific and tropical North Pacific (leg 2). The data were collected during a cruise of the R.V. *Conrad* (22 June to 7 August 1982) along the cruise track shown in the inset. Tick marks along the leg 2 cruise track are noon positions. Note the difference in concentration scales for the leg 1 and leg 2 data.

fore be calculated as the product of the piston velocity and the DMS concentration in water (*15*). Using the data in Table 1, we predict a global mean emission rate of 290 μg of sulfur (DMS) per square meter per day, which represents a global flux of 38.5×10^{12} g of sulfur per year, about half the global anthropogenic SO_2 emissions (*2, 20*). The uncertainty of this estimate is related primarily to the air-sea exchange model used; our sensitivity analysis based upon the application of different exchange models to the Atlantic data gave an uncertainty of about ±30 percent (*6*). Since over 90 percent of the anthropogenic emissions take place in the Northern Hemisphere, the production of excess particulate sulfate (the sulfate fraction in aerosols not accounted for by sea spray) in the Southern Hemisphere is dominated by DMS of marine origin.

One can test the accuracy of this emission estimate by comparing the atmospheric DMS concentrations that we measured over the remote ocean with those predicted on the basis of the flux given above and the photooxidation of DMS in the atmosphere. Over the remote Pacific, we observed an average concentration of 167 ng m^{-3} (N = 106, standard deviation = 69) with a pronounced diurnal variation (Fig. 2). This concentration is in good agreement with the results of the models of Graedel (*21*)

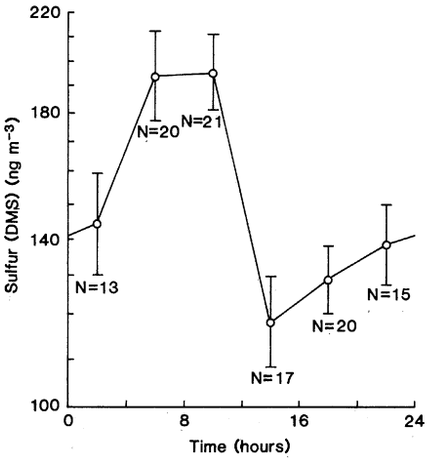

Fig. 2. Diurnal variation in the concentration of dimethyl sulfide (*DMS*) in air over the equatorial Pacific. The data were stratified into 4-hour intervals, and the means and standard errors were plotted at the midpoints of the intervals.

(~ 80 ng m^{-3}) and Rodhe and Isaksen (*20*) (80 to 160 ng m^{-3}) when these models are adjusted for the differences between the DMS flux estimated in this report and the fluxes assumed in the models. The diurnal variation that we observed (a factor of 1.7) is less intense than that predicted by Graedel (a factor of 11) but in excellent agreement with the estimate of Crutzen and Chatfield [1.6 (*22*)], who are using a lower OH radical concentration and a different vertical mixing regime. The phase relation in our observations, with a maximum in the early morning hours and a minimum after noon, is in excellent agreement with both of these models.

Our findings for the remote Pacific are in strong contrast to our earlier data for the Atlantic (*6*) and the Gulf of Mexico (*12*) as well as the data from the first leg of this cruise in air over the sea offshore Peru. These data sets show no diurnality and have much lower average DMS concentrations: 6.1 ng m^{-3} over the Atlantic, 9.7 ng m^{-3} over the Gulf of Mexico, and 40.6 ng m^{-3} (N = 29, standard deviation = 19.0) over the Peru Shelf, even though the latter samples were collected under predominantly longshore air flow over waters with much higher concentrations of DMS than the equatorial and tropical Pacific. We suggest that in continentally influenced air masses there is an additional removal process for DMS that is not directly photochemical. This hypothesis is supported by the fact that continental aerosols were essentially always present in significant amounts during our cruises in the Atlantic (*23*) and on the Peru Shelf (*24*) but were barely detectable over the remote Pacific. Recently, Bingemer has found DMS concentrations comparable to our Pacific data in very clean air over the remote Atlantic (*19*).

Another constraint on the size of the oceanic DMS flux can be placed by the deposition flux of SO_2 and excess (not sea salt) sulfate in unpolluted ocean areas. For the Southern Hemisphere, Rodhe and Isaksen's model (*20*) predicts a flux of about 200 μg of sulfur per square meter per day. In the tropical Atlantic, a mass balance calculation by Kritz (*25*) includes a contribution of ~ 100 μg m^{-2} day^{-1} from biogenic reduced sulfur to the deposition of SO_2 and excess sulfate. Based on aerosol data from marine air in the temperate zone of the Southern Hemisphere, Bonsang *et al.* (*26*) and Andreae (*27*) have derived excess sulfate deposition rates of 209 and 202 μg m^{-2} day^{-1}, respectively. All these removal flux estimates are in excellent agreement with the input flux of DMS into the marine atmosphere as estimated above (290 μg m^{-2} day^{-1}), especially if one considers that additional sinks for DMS exist, for example, its oxidation to methanesulfonic acid (*28*) and dimethyl sulfoxide (*29*).

On the basis of our global data set, we thus present a model for the role of DMS in the atmospheric sulfur cycle that is experimentally constrained and consistent with all available information. Our data indicate that DMS is the dominant

Table 1. The DMS concentrations and sea-to-air flux from the major ecological regions of the world ocean.

Ocean region	N	Average DMS (ng sulfur per liter)	Standard deviation	Area (10^6 km^2)	Flux (10^{12} g sulfur per year)
Oligotrophic areas					
Tropical North Atlantic	17	98.1	44.7		
Gulf of Mexico	4	52.3	9.8		
Gulf Stream and Sargasso Sea	80	80.2	22.8		
Brazil Current	63	46.0	15.3		
Tropical North Pacific	25	59.8	10.8		
Total	189	67.1		148.3	10.2
Transitional areas					
North Atlantic (temperate)	44	66.8	28.3	82.8	5.7
Upwelling areas					
Equatorial Zone					
Atlantic	22	70.1	23.3		
Pacific	106	120.4	46.4		
Peru Shelf	132	230.9	235		
Frontal areas					
Bering Sea	13	150.1	152		
Ushant front	17	156.9	38.0		
Rio de la Plata estuary	5	571.0	237		
Total	295	177.1		86.5	15.7
Coastal and shelf zone					
North Sea and English Channel	27	54.9	28.2		
Eastern coast of South America	39	159.4	12.5		
Ecuador Shelf	34	175.4	123		
Total	100	136.6		49.4	6.9
World ocean total	628	102.4		367.1	38.5

source of biogenic volatile sulfur compounds to the marine atmosphere. Its quantitative importance becomes even more impressive when the DMS emissions from continental sources are added to our estimate of emissions from the sea surface. Adams *et al.* (*30*) have measured the flux of various reduced volatile sulfur compounds from a large variety of ecozones in the United States. From these data, they have extrapolated a global flux estimate of 64×10^{12} g of sulfur per year, of which the average DMS contribution is 21 percent. The extrapolation of the data from the temperate into the tropical zone introduces a substantial amount of uncertainty; further research on sulfur gas emissions in the biologically highly active tropical regions is needed to improve the terrestrial flux estimate. When the estimate of Adams *et al.* (*30*) is added to the marine flux, a DMS flux of 52×10^{12} g year^{-1} and a total biogenic sulfur flux of 103×10^{12} g year^{-1} is predicted, about equal to the anthropogenic SO_2 flux of 104×10^{12} g of sulfur per year (*2*).

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References and Notes

1. Reviewed in A. J. B. Zehnder and S. H. Zinder, in *The Handbook of Environmental Chemistry*, O. Hutzinger, Ed. (Springer, Berlin, 1980), vol. 1, part A, p. 105.
2. C. F. Cullis and M. M. Hirschler, *Atmos. Environ.* **14**, 1263 (1980).
3. J. E. Lovelock, R. J. Maggs, R. A. Rasmussen, *Nature (London)* **237**, 452 (1972).
4. P. S. Liss and P. G. Slater, *ibid.* **247**, 181 (1974).
5. B. C. Nguyen, A. Gaudry, B. Bonsang, G. Lambert, *ibid.* **275**, 637 (1978).
6. W. R. Barnard *et al.*, *J. Geophys. Res.* **87**, 8787 (1982).
7. T. S. Bates and J. D. Cline, *Eos* **63**, 993 (1982).
8. M. O. Andreae and W. R. Barnard, *Anal. Chem.* **55**, 608 (1983).
9. W. R. Barnard, M. O. Andreae, R. L. Iverson, in preparation; M. O. Andreae and W. R. Barnard, in preparation.
10. B. Rojas de Mendiola, in *Coastal Upwelling*, F. A. Richards, Ed. (American Geophysical Union, Washington, D.C., 1981), p. 348.
11. R. A. Rasmussen, *Tellus* **26**, 254 (1974).
12. M. O. Andreae, W. R. Barnard, J. M. Ammons, *Ecol. Bull. (Stockholm)* **35**, 167 (1983).
13. R. Jimenez, in *Coastal Upwelling*, F. A. Richards, Ed. (American Geophysical Union, Washington, D.C., 1981), p. 327.
14. O. J. Koblentz-Mishke, V. V. Volkovinsky, J. G. Kabanova, in *Scientific Exploration of the South Pacific*, W. S. Wooster, Ed. (National Academy of Sciences, Washington, D.C., 1970), p. 183.
15. W. S. Broecker and T.-H. Peng, *Tellus* **26**, 21 (1974).
16. R. C. Reid and T. K. Sherwood, *The Properties of Gases and Liquids* (McGraw-Hill, New York, ed. 2, 1966).
17. T.-H. Peng, W. S. Broecker, G. G. Mathieu, Y.-H. Li, *J. Geophys. Res.* **84**, 2471 (1979).
18. P. J. Maroulis and A. R. Bandy, *Science* **196**, 647 (1977).
19. H. Bingemer, personal communication.
20. H. Rodhe and I. Isaksen, *J. Geophys. Res.* **85**, 7401 (1980).
21. T. E. Graedel, *Geophys. Res. Lett.* **6**, 329 (1979).
22. P. J. Crutzen and R. B. Chatfield, personal communication.
23. M. O. Andreae, *Science* **220**, 1148 (1983).
24. ———, unpublished data.
25. M. A. Kritz, *J. Geophys. Res.* **87**, 8795 (1982).
26. B. Bonsang, B. C. Nguyen, A. Gaudry, G. Lambert, *ibid.* **85**, 7410 (1980).
27. M. O. Andreae, *ibid.* **87**, 8875 (1982).
28. R. Panter and R.-D. Penzhorn, *Atmos. Environ.* **14**, 149 (1980); D. Grosjean and R. Lewis, *Geophys. Res. Lett.* **9**, 1203 (1982).
29. M. O. Andreae, *Limnol. Oceanogr.* **25**, 1054 (1980).
30. D. F. Adams *et al.*, *Environ. Sci. Technol.* **15**, 1493 (1981).
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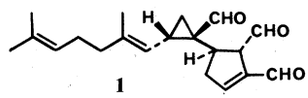
Isolation of Halimedatrial: Chemical Defense Adaptation in the Calcareous Reef-Building Alga *Halimeda*

Abstract. *Halimedatrial, a structurally unprecedented diterpenoid trialdehyde, has been identified as the major secondary metabolite in six species of the calcareous reef-building alga* Halimeda. *In laboratory bioassays, halimedatrial is toxic toward reef fishes, significantly reduces feeding in herbivorous fishes, and has cytotoxic and antimicrobial activities. The widespread occurrence of halimedatrial and its potent biological activities suggest that this metabolite represents a chemical defense adaptation in this pantropical marine alga.*

Calcareous algae of the genus *Halimeda* Lamouroux (Chlorophyta, Udoteaceae) are abundant and widely distributed in tropical marine habitats (*1*). Because of their high calcium carbonate composition (between 50 to 90 percent, dry weight), primary productivity, substrate stabilization, and provision for microhabitats, *Halimeda* species are considered major contributors to the structure of coral reefs (*1–3*).

In many reef systems, *Halimeda* species are most abundant in biomass among the macroalgae exposed to herbivory. The generally low overall algal abundance on tropical reefs has been attributed to the intense grazing activities of herbivorous fishes and sea urchins (*4–8*). Two reports indicate that *Halimeda incrassata* was consumed but not preferred by fishes under certain experimental conditions (*8, 9*). However, our own observations, feeding preference studies, and stomach content analyses indicate that *Halimeda* species are largely avoided by generalist herbivores (*4, 7, 10–16*).

While the basis for the successful adaptation of *Halimeda* species has not been defined, it has been generally accepted that calcification provides a physical deterrent against predation (*4, 5, 10, 17–19*). We here propose and provide evidence that the successful adaptation of *Halimeda* species involves multicomponent strategies of defense, including the protective function of naturally occurring chemical substances. Investigations of the secondary metabolites of numerous Caribbean *Halimeda* species have illustrated the production of a diterpenoid trialdehyde with high biological activity. This compound, halimedatrial (**1**), produces a wide spectrum of delete-



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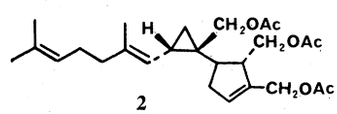
rious biological effects, and is structurally similar to numerous insect antifeedants such as warburganal (*20*) and the iridoid aldehydes (*21, 22*).

Collections made in the Bahama Islands of the widespread Caribbean *Halimeda* species—*H. tuna* (Ellis and Solander) Lamouroux, *H. opuntia* (Linnaeus) Lamouroux, *H. incrassata* (Ellis and Solander) Lamouroux, *H. simulans* Howe, *H. scabra* Howe, and *H. copiosa* Goreau and Graham—were found to contain significant amounts (~ 15 percent of the dichloromethane extracts), of halimedatrial (*23, 24*). The structure of this compound was determined by interpretation of its spectral characteristics and by chemical conversion to the triol triacetate (**2**). Halimedatrial showed



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$[\alpha]_D^{27}$ of −59° (c = 0.9, $CHCl_3$), and could readily be assigned as a bicyclic diterpene trialdehyde by interpretation of its combined spectral features (*25*), particularly its mass spectral and high-resolution nuclear magnetic resonance characteristics. A molecular formula of $C_{20}H_{26}O_3$, reflecting eight degrees of unsaturation, was determined by high reso-