before, but the Si=O vibrations of matrix-isolated SiO and SSiO and the antisymmetric stretch of matrix-isolated SiO_2 occur at 1224, 1265, and 1420 cm^{-1}, respectively,[15-17] and the Si=O stretching frequencies of Cl_2SiO and F_2SiO are 1240 cm^{-1} [17] and 1309 cm^{-1},[18] respectively. All of these results compare well with the bands observed for our trapping product at 1204 (presumably free) and 1186 cm^{-1} (presumably a weak complex with N_2O, not surprising for the undoubtedly highly polar Si=O bond). The ^{18}O isotope shifts of the Si=O stretch in Cl_2SiO and F_2SiO are 37 and 31 cm^{-1}, respectively; these can be compared with the value 35 cm^{-1} observed for our product.

An MNDO[19] calculation of vibrational frequencies and intensities of **3** predicts the Si=O stretch to fall at 1179 cm^{-1} for ^{16}O and 1143 cm^{-1} for ^{18}O; the calculated isotope shift is 36 cm^{-1}. The Si=O stretch is calculated to have the highest intensity of any vibrational mode above 400 cm^{-1}. An identification of additional vibrational transitions is clearly desirable but is hampered by the presence of the unreacted starting material, dodecamethylcyclohexasilane, and the byproduct, decamethylcyclopentasilane.

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Halenaquinone, a Pentacyclic Polyketide from a Marine Sponge

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Tropical marine sponges are a fertile source of secondary metabolites with diverse and often novel molecular architecture.[1] Many of these compounds also exhibit in vitro antimicrobial properties[2] and thus have generated much interest among synthetic and medicinal chemists, as well as among marine ecologists. A majority of known metabolites are terpenoid. Tyrosine and indole-derived structures constitute a second sizable group. Polyketides, on the other hand, are rare and had received little attention beyond research on the fatty acid composition of the Demospongiae[3,4] until the recent biochemical interest in membrane structure and function.[5,6] In this Communication we report

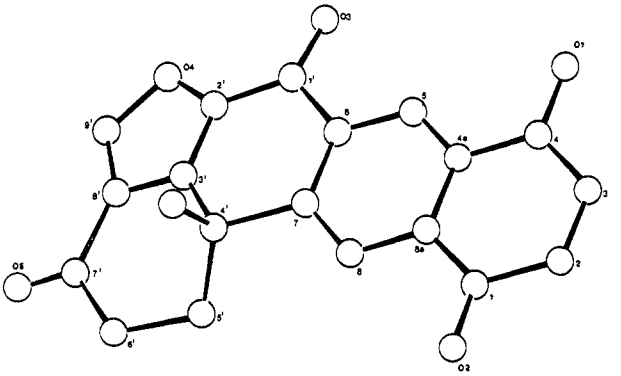
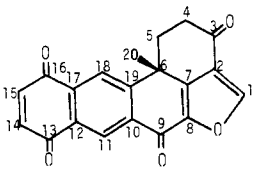


Figure 1. Computer-generated perspective drawing of halenaquinone. Hydrogens are omitted for clarity and no absolute configuration is implied.

isolation and structure of a new pentacyclic polyketide, which possesses in vitro antibiotic activity against *Staphylococcus aureus* and *Bacillus subtilis*.[7]

Frozen *Xestospongia exigua*[8] was lyophilized and successively extracted at room temperature with hexane, benzene, dichloromethane, and ethanol. The residues were scanned by ^1H NMR. The benzene extract was chromatographed on Bio-Beads S-X8[9] (toluene) then Bio-Sil A[9] (CH_2Cl_2/EtOAc, 1:1) and finally by HPLC (Partisil M9,[10] C_6H_6/EtOAc, 2:1). The major metabolite was a yellow solid mp >250 °C dec, $[\alpha]^{25}_D$ +22.2° (*c* 0.124, CH_2Cl_2). A composition of $C_{20}H_{12}O_5$ was secured by high-resolution mass spectrometry (*m/z* 332.06847; calcd for $C_{20}H_{12}O_5$ 332.06847). Successive losses of CO and C_2H_2 from the molecular ion, an IR band at 1680 cm^{-1}, a two-proton singlet at δ 7.13 in the ^1H NMR spectrum, and four ^{13}C signals at δ 183.8(s), 183.3(s), 138.8(d), and 138.7(d) all pointed to a 2,3-unsubstituted-1,4-naphthoquinone, which was subsequently confirmed by treatment with Ac_2O, Zn, and Bu_4NBr, which readily yielded a leucodiacetate, mp 186–188 °C, $[\alpha]^{25}_D$ +62.1° (*c* 0.066, CH_2Cl_2),[11] and which we name halenaquinone (**1**).[12,13]



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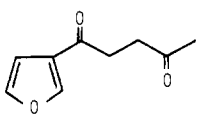

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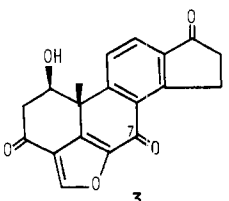

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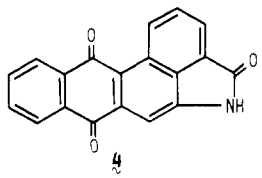

4

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(9) BioRad Laboratories, Richmond, CA.
(10) Whatman, Inc., Clifton, NJ.

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Halenaquinone (1), as defined by x-ray diffraction, contains a 2,4-diketofuran moiety. Both carbonyls are in fact vinylogous esters. The low-field ^{13}C NMR resonance at δ 190.9 must be assigned to the β-substituent in analogy with a δ 192.8 value of C-1 in ipomeanin (2),[14] while the δ 169.5 signal is compatible with the α-keto carbon, comparable to the C-7 resonance at δ 172.5 in demethoxyviridin (3).[15]

Halenaquinone (1) was crystallized from a mixture of benzene/ethyl acetate (2:1), by vapor diffusion with hexane. Successful diffraction[16] revealed all but one non-hydrogen atoms in the two-molecule asymmetric unit. See the supplementary material for additional crystallographic details. A computer-generated perspective drawing of the final X-ray model of halenaquinone (1) is given in Figure 1. The X-ray experiment did not define the absolute configuration so the enantiomer shown is an arbitrary choice.

Halenaquinone (1) not only is a rare polyketide secondary sponge metabolite, but it also represents a new pentacyclic system. The closest literature analogue is benzo[*cd*]naphth[2,3-*f*]indole-4,7,12(5*H*)-trione (4), which is described in the German patent literature as a potential dyestuff.[17]

Acknowledgment. We thank Drs. M. Yunker, G. Schulte, and C. Ireland for collection and Dr. P. Bergquist for identification of the animals, The Colorado State University Regional NMR Center for ^{13}C data, Dr. W. Niemczura for ^{13}C NMR decoupling data, Dr. G. Schulte for rotation data, and Drs. K. Seff and I. Karle for assistance with the initial X-ray diffraction work. We are grateful to the National Science Foundation for support of this work (CHE80-05780) and of the UH NMR instrument (CHE81-00240). Crystallography at Cornell was supported by NIH Grant CA 24487 and by the New York State Sea Grant College Program.

Registry No. 1, 86690-14-4.

(11) Leucodiacetate HRMS: M^+ 418.1086 (calcd for $C_{24}H_{18}O_7$ 418.1052); IR (CH_2Cl_2) 1770, 1705, 1680, 1190 cm^{-1}; UV (MeCN) λ_{max} 220 (ϵ 45 400), 260 (22 700), 282 (15 900), 294 (16 200), 306 (15 700), 317 (17 400), 355 nm (4100); ^{13}C NMR (CD_2Cl_2, 90.5 MHz) (C-1) 148.8 d, (C-2) 122.7 s, (C-3) 191.5 s, (C-4) 34.1 t, (C-5) 36.7 t, (C-6) 35.9 s, (C-7) 143.9 s, (C-8) 147.3 s, (C-9) 171.6 s, (*C-10) 145.8 s, (C-11) 123.8 d, (C-12) 126.2 s, (C-13*) 145.6 s, (C-14$^+$) 118.4 d, (C-15$^+$) 118.7 d, (C-16*) 145.4 s, (C-17) 131.9 s, (C-18) 120.9 d, (C-19) 128.9 s, (C-20) 31.6 q, ($OCOCH_3$) 169.2 s, 169.6 s, 21.0 q, 21.0 q ppm [*, + interchangeable values]; ^1H NMR CD_2Cl_2, 300 MHz) δ 8.94 (1 H, s), 8.25 (1 H, s), 8.01 (1 H, s), 7.38 (2 H, AB q, J = 8 Hz), 3.04 (1 H, ddd, J = 5, 13, 18 Hz), 2.86-2.77 (2 H, complex m), 2.53 (3 H, s), 2.51 (3 H, s), 2.33 (1 H, ddd, J = 5, 13, 13 Hz), 1.67 (3 H, s).

(12) *Halena*, pale yellow in Hawaiian, alludes to the color of **1**.

(13) ^{13}C NMR (Me_2SO-d_6, 75.6 MHz) (C-1) 150.4 d, (C-2) 122.1 s, (C-3) 190.9 s, (C-4) 32.3 t, (C-5) 36.1 t, (C-6) 36.4 s, (C-7) 143.9 s, (C-8) 147.9 s, (C-9) 169.5 s, (C-10) 154.1 s, (C-11) 125.2 d, (C-12) 129.9 s, (C-13) 183.3 s, (C-14) 138.7 d (C-15) 138.8 d, (C-16) 183.8 s, (C-17) 133.3 s, (C-18) 123.5 d, (C-19) 136.3 s, (C-20) 29.7 q ppm; ^1H NMR (Me_2SO-d_6, 300 MHz) δ 8.76 (1 H, s, H-1), 8.66 (1 H, s, H-11), 8.28 (1 H, s, H-18), 7.13 (2 H, s, H-14,15), 3.11 (1 H, ddd, H-5β), 2.94 (1 H, dd, H-4β), 2.74 (1 H, dd, H-5α), 2.22 (1 H, ddd, H-4α), 1.68 (3 H, s); IR (CH_2Cl_2) ν_{max} 1705, 1690, 1680, 1325 cm^{-1}; UV (MeCN) λ_{max} 216 (ϵ 18 100), 232 sh (16 500), 253 (21 600), 260 sh (20 400), 278 (15 900), 325 sh (6000) nm.

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Supplementary Material Available: Tables of fractional coordinates, thermal parameters, bond distances, bond angles, and observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Biosynthesis of Polyprenols in Higher Plants. The Elimination of the *pro*-4*S* Hydrogen Atom of Mevalonic Acid during the Formation of Their (*Z*)-Isoprene Chain[1]

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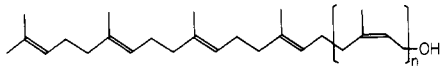
Received June 6, 1983

The stereochemical picture of isoprenoid biosynthesis established from previous studies suggests that the *pro*-4*S* hydrogen of mevalonic acid (MVA) is lost in the formation of an (*E*)-isoprene residue, while the *pro*-4*R* hydrogen is eliminated in the formation of a (*Z*)-isoprene residue.[3-5] No example contravening this has yet been found, and this stereochemistry is believed to be involved in the biosynthesis of all the isoprenoids including polyprenols. We have now found the unusual elimination of the *pro*-4*S* hydrogen of MVA during the formation of the (*Z*)-isoprene chain of the polyprenols, malloprenols, in *Mallotus japonicus* Muell Arg. (Euphorbiaceae).

It has been previously established that the malloprenols are composed of a homologous series of polyprenols as shown in structures **1-3** and are biosynthesized by successive cis addition



1, n = 5
2, n = 6
3, n = 7

of isopentenyl pyrophosphate (IPP) to digeranyl pyrophosphate (GGPP) in that plant.[6]

The labeling pattern in the (*E*)- and (*Z*)-isoprene units of the malloprenols was examined by incorporation of (4*R*)- and (4*S*)-[2-^{14}C,4-^{3}H]MVAs. The potassium salts of these MVAs dissolved in water were fed to *M. japonicus* through cut stalks for 72 h. Malloprenol-9 (**1**), -10 (**2**), and -11 (**3**) were separated in the manner described[6] and their radioactivities are shown in Table I.[7] If the malloprenols are formed from double-labeled MVA following the expected stereochemistry of isoprenoid biosynthesis,[3-5] the $^3H/^{14}C$ ratios in the malloprenols are expected to be as given in column A of Table I. However, the ratios observed for the malloprenols were not coincident with those expected. The $^3H/^{14}C$ ratios were in good agreement with those given in column B. This implies that the *pro*-4*S* hydrogen of MVA is eliminated during the formation of the (*Z*)-isoprene chain of the malloprenols.

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