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]

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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 45400), 260 (22700), 282 (15900), 294 (16200), 306 (15700), 317 (17400), 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 18100), 232 sh (16500), 253 (21600), 260 sh (20400), 278 (15900), 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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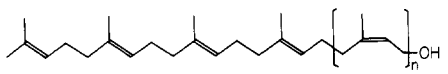
The stereochemical picture of isoprenoid biosynthesis established from previous studies suggests that the *pro*-4*S* hydrogen of mevalonic acid (MVA) is lost in the formation of an (*E*)-isoprene residue, while the *pro*-4*R* hydrogen is eliminated in the formation of a (*Z*)-isoprene residue.[3-5] No 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-^3H]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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Table I. Radioactivity and $^3H/^{14}C$ Ratio in Malloprenols Biosynthesized from (4*R*)-[2-^{14}C,4-^{3}H]MVA and (4*S*)-[2-^{14}C,4-^{3}H]MVA

MVA ($^3H/^{14}C$ ratio)	compd[a]	obsd ^3H, dpm	obsd ^{14}C, dpm	obsd $^3H/^{14}C$ ratio	obsd atom ratio[b] ^3H:^{14}C	calcd atom ratio A[c] ^3H:^{14}C	calcd atom ratio B[d] ^3H:^{14}C
(4*R*)-[2-^{14}C,4-^{3}H]MVA	MPL-9	1045	246	4.25	(9.1 ± 0.2):9	4:9	9:9
(4.22)	MPL-10	2602	600	4.34	(10.3 ± 0.2):10	4:10	10:10
	MPL-11	5666	1343	4.22	(11.0 ± 0.1):11	4:11	11:11
(4*R*)-[2-^{14}C,4-^{3}H]MVA	MPL-10	3797	291	13.1	(9.9 ± 0.2):10	4:10	10:10
(13.2)	MPL-11	4745	359	13.2	(11.0 ± 0.2):11	4:11	11:11
(4*S*)-[2-^{14}C,4-^{3}H]MVA	MPL-9	135	4717	0.03	(0.05 ± 0.02):9	5:9	0:9
(5.4)	MPL-10	88	548	0.16	(0.30 ± 0.02):10	6:10	0:10
	MPL-11	43	1167	0.37	(0.07 ± 0.01):11	7:11	0:11
(4*S*)-[2-^{14}C,4-^{3}H]MVA	MPL-9	658	1133	0.58	(0.40 ± 0.06):9	5:9	0:9
(13.2)	MPL-10	981	3909	0.25	(0.19 ± 0.02):10	6:10	0:10
	MPL-11	922	4703	0.20	(0.17 ± 0.01):11	7:11	0:11

[a] MPL denotes malloprenol. [b] Normalized ratio. The deviations were calculated from the standard deviation in the radioactivity of each sample. [c] Calculated from the expectation that the (*E*)- and the (*Z*)-isoprene residues are formed by loss of the *pro*-4*S* and *pro*-4*R* hydrogens of MVA, respectively, following the usual isoprenoid pathway. [d] Calculated from the expectation that the (*E*)-isoprene residue results from the usual loss of the *pro*-4*S* hydrogen of MVA, whereas the (*Z*)-isoprene unit results from the unusual loss of the *pro*-4*S* hydrogen.

The elimination of the *pro*-4*S* hydrogen might result from an alternative process, which involves the initial addition of an (*E*)-isoprene residue followed by the redox *E*–*Z* isomerization via the corresponding aldehyde, as previously demonstrated for the biosynthesis of the sesquiterpenoids in fungi.[9] However, all the tritiums originating from [2-^{14}C,5-$^3H_2$]MVA were retained in the malloprenols biosynthesized from this double-labeled MVA (Table II).[10] This fact rules out distinctly the participation of the redox *E*–*Z* isomerization in the successive extension of (*Z*)-isoprene units.

The loss of the 4*S* tritium may be due to compartmentalization[11] such that the (*E*)-isoprene residues are assembled in a part of the plant to which is readily accessible external MVA, followed by the addition of (*Z*)-isoprene residues in an area of the plant that external MVA cannot efficiently penetrate. In order to solve this problem, malloprenol-10 (**2**) was biosynthesized from [2-^{14}C,5-$^3H_2$]MVA, and the $^3H/^{14}C$ ratio in the aldehyde derived from the malloprenol was examined. The tritium in the malloprenol-10 (**2**) decreased to nineteen-twentieths in the aldehyde (Table II).[10] This decrease in tritium indicates that one-tenth of the total tritium is located on C-1 of malloprenol-10 (**2**). In addition, the uniform distribution of the radioactivity in each of the isoprene units was examined by determining the labeling pattern in the malloprenols biosynthesized from (4*S*)-[2-^{14}C,4-^{3}H]MVA. The radioactive malloprenol was degraded to ^{14}C-labeled acetone and levulinic acid by $KMnO_4$–$NaIO_4$ oxidation. The molar ratios of the acetone to the levulinic acid were in good agreement with the ratios calculated from the expectation that the (*E*)- and (*Z*)-isoprene units are equivalently formed from external MVA (Table III).[10] These examinations demonstrate that compartmentalization does not affect the incorporation of label in the biosynthesis of the malloprenols in the plant. The stereochemistry of formation of the (*Z*)-isoprene unit of the malloprenol thus differs from that observed for the biosynthesis of other isoprenoids.[3-5]

Quite recently, we also observed elimination of the *pro*-4*S* hydrogen atom of MVA in the formation of the (*Z*)-isoprene residues of polyprenols in *Aleurites cordata* (Euphorbiaceae), *Alnus serrulatoides* (Betulaceae), and *Cleome spinosa* (Capparidaceae).[12] It is suggested therefore that elimination of the *pro*-4*S* hydrogen of MVA might be the usual mode in the formation of the (*Z*)-isoprene chain of polyprenols by successive addition of IPP to GGPP in higher plants.

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Supplementary Material Available: Tables of radioactivity, $^3H/^{14}C$ ratios, and degradation product ratios (2 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of $Na_4[Mo_8O_{24}(OCH_3)_4]\cdot 8MeOH$: A Novel Isopolymolybdate That Decomposes with the Loss of Formaldehyde

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Recent work in our laboratory has focused on the oxidation of methanol to formaldehyde over a variety of molybdate catalysts[1] with special emphasis on MoO_3. Of the physical methods employed to study this reaction, FTIR has been particularly useful in identifying the probable intermediate in this reaction as a surface methoxy group.[2] Efforts have been made to model this system with molecular or ionic species that could be studied by X-ray, single-crystal diffraction techniques. On the basis of the rich and varied chelation chemistry of the oxomolybdenum "core structures"[3,4] and encouraged by the recent crystallographic work on both isopolymolybdates[5,6] and heteropolymolybdates[7] with

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