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CRYSTAL AND MOLECULAR STRUCTURE OF HYATOQUINONE HYDRATE FROM A MARINE SPONGE Hyatella sp.

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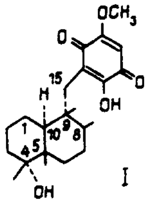
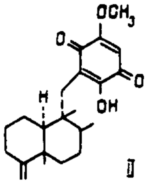
UDC 548.737

The crystal and molecular structures of hyatoquinone hydrate have been established by x-ray structural analysis. The existence of a difference in the spatial orientation of the quinoid fragment in hyatoquinone and in the ilimaquinone studied previously has been shown.

In [1] the isolation of a new quinone from the marine sponge Hyatella sp., which was called hyatoquinone, was reported. On the basis of the results of NMR spectroscopy it was concluded in this paper that a hydroxy group in hyatoquinone was present at C-5. We have made an x-ray structural investigation of this compound, as a result of which the structure of hyatoquinone has been established as (I).



I



II

The spatial structure of the molecule of (I) is given in Fig. 1. The coordinates of the nonhydrogen atoms are given in Table 1, the lengths of the bonds in Table 2, and the valence angles in Table 3. The general conformation of the (I) molecule differs substantially from that of ilimaquinone (II) an x-ray structure study of which was performed previously by a group of American scientists [2]. The main difference consists in the mutual orientation of the quinoid ring and the sesquiterpenoid backbone of the molecule relative to the C-9—C-15 bond. While in compound (II) the substituent at this bond occupies the trans position relative to the C-8 in compound (I) it is turned by 120° and is present in the trans position relative to the C-16 methyl group. This shows the considerable conformational possibilities of molecules with such a structure.

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TABLE 1. Coordinates of the Nonhydrogen Atoms ($\times 10^4$)

Atom	Molecule 1			Molecule 2		
	x	y	z	x	y	z
C1	1696(7)	−770(22)	3377(11)	3333(7)	−2090(20)	6270(10)
C2	2365(7)	−514(24)	2908(11)	2593(8)	−1925(20)	6544(13)
C3	2617(7)	1332(24)	2955(10)	2291(7)	−112(24)	6332(12)
C4	2 63(7)	2715(21)	2661(10)	2741(8)	1235(22)	6805(11)
C5	1369(7)	24 4	3214(10)	3518(8)	1134(23)	6505(9)
C6	816(7)	3693(22)	2821(10)	3966(7)	2468(24)	7040(10)
C7	129(7)	3297(22)	3270(10)	4736(8)	2242(26)	6865(10)
C8	−135(7)	1464(22)	2985(10)	5011(7)	486(22)	7145(11)
C9	373(8)	19(21)	3244(10)	4576(7)	−1111(22)	6704(9)
C10	1140(7)	524(20)	2999(9)	3777(7)	−723(21)	6761(9)
C11	2354(8)	4579(24)	2755(11)	2436(8)	3078(24)	6641(11)
C12	1511(7)	2756(23)	4235(11)	3564(8)	1606(23)	55[illegible](11)
C13	−863(8)	1234(25)	3266(11)	5791(8)	324(22)	6979(11)
C14	331(7)	−539(23)	4269(11)	4891(7)	−146 (23)	5754(10)
C15	155(7)	−1658(21)	2741(9)	4758(7)	−2704(23)	7301(10)
C16	158(7)	−1603(21)	1693(11)	4675(6)	−2787(20)	8291(10)
C17	−435(8)	−1323(23)	1181(10)	5240(8)	−2558(22)	8878(10)
C18	−452(8)	−1258(24)	170(10)	5093(10)	−2569(25)	9878(13)
C19	189(9)	−1311(25)	−291(9)	4447(8)	−2644(25)	10261(11)
C20	759(9)	−1622(24)	193(11)	3913(9)	−2939(25)	9691(12)
C21	791(7)	−2028(19)	1196(9)	4028(8)	−3121(22)	8765(11)
C22	1521(9)	−1427(28)	−1032(14)	3044(10)	−2982(29)	10809(14)
O4	1936(5)	2366(18)	1713(6)	2724(6)	1083(17)	7767(7)
O17	−1662(1)	−1152(17)	1550(6)	5856(5)	−2342(19)	8657(7)
O18	−1628(5)	−1167(18)	−234(7)	5637(6)	−2437(23)	10406(8)
O20	1423(6)	−1685(18)	−104(7)	3232(5)	−3144(19)	9825(8)
O21	1294(5)	−2651(18)	1550(7)	3521(5)	−3731(16)	8216(7)
O-w	−2432(5)	−1051(2)	1036(6)	7061(5)	−2884(23)	9545(8)

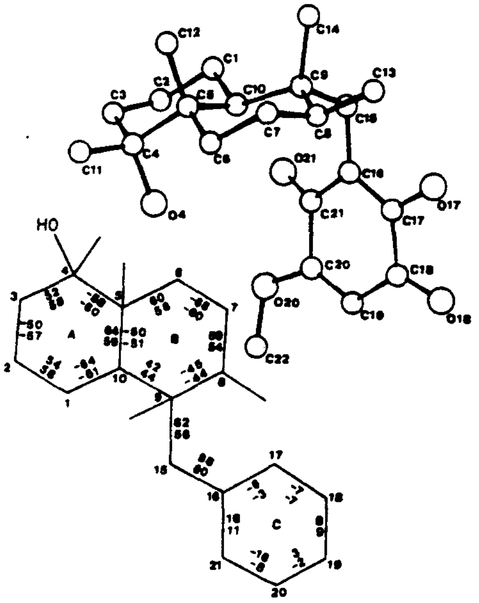

Fig. 1. Spatial structure of compound (I) and the conformational angles in the two symmetrically unconnected molecules 1 (above) and 2 (below).

Some values of the torsional angles characterizing the conformations of the two molecules of (I) present in the independent part of the elementary cell of the crystal are given in Fig. 1. Both trans-linked rings have the chair conformation, the fragment of ring B adjacent to the quinoid ring being flattened in both molecules. The maximum difference in the values of the lengths of the analogous bonds of the two molecules of hyatoquinone amounts to 0.11 Å (the C-20-O-20 bond), that in the values of the valence angles to 9° (the angles at the C-15 atom), and that in the values of the torsional angles to 11° (the O-4—C-4—C-5—C-12 angle).

TABLE 2. Lengths of the Bonds d (Å)

Bond	mol. 1 d	mol. 2 d	Bond	mol. 1 d	mol. 2 d
C1—C2	1,5[illegible](2)	1,52(2)	C9—C10	1,59(2)	1,58(2)
C1—C10	1,55(2)	1,52(2)	C9—C14	1,57(2)	1,5[illegible](2)
C2—C3	1,5[illegible](3)	1,54(2)	C9—C15	1,54(2)	1,54(2)
C3—C4	1,56(2)	1,51(2)	C15—C16	1,54(2)	1,47(2)
C4—C5	1,61(2)	1,58(2)	C16—C17	1.36(2)	1,32(2)
C4—C11	1,55(2)	1,55(2)	C16—C21	1,49(2)	1,45(2)
C4—O4	1,43(2)	1,42(2)	C17—C18	1,49(2)	1,49(2)
C5—C6	1,56(2)	1,54(2)	C17—O17	1,35(2)	1,33(2)
C5—C10	1,54(2)	1,56(2)	C18—C19	1,43(2)	1,39(2)
C5—C12	1,54(2)	1,53(2)	C18—O18	1,24(2)	1,29(2)
C6—C7	1,54(2)	1,53(2)	C19—C20	1,31(2)	1,32(2)
C7—C8	1,55(2)	1,51(2)	C20—C21	1.51(2)	1,48(2)
C8—C9	1,52(2)	1,61(2)	C20—O20	1,37(2)	1,35(2)
C8—C13	1,54(2)	1,54(2)	C21—O21	1,19(2)	1,27(2)
			C22—O20	1,40(2)	1,51(2)

TABLE 3. Valence Angles ω (degrees)

Angle	mol. 1 ω	mol. 2 ω	Angle	mol. 1 ω	mol. 2 ω
C2—C1—C10	110 (1)	110 (1)	C10—C9—C14	112 (1)	114 (1)
C1—C2—C3	113 (1)	112 (1)	C10—C9—C15	110 (1)	109 (1)
C2—C3—C4	115 (1)	109 (1)	C14—C9—C15	102 (1)	109 (1)
C3—C4—C5	109 (1)	112 (1)	C1—C10—C5	110 (1)	110 (1)
C3—C4—C11	111 (1)	110 (1)	C1—C10—C9	114 (1)	112 (1)
C3—C4—O4	103 (1)	112 (1)	C5—C10—C9	117 (1)	118 (1)
C5—C4—C11	114 (1)	111 (1)	C9—C15—C16	116 (1)	125 (1)
C5—C4—O4	110 (1)	109 (1)	C15—C16—C17	121 (1)	122 (1)
C11—C4—O4	108 (1)	102 (1)	C15—C16—C21	121 (1)	124 (1)
C4—C5—C6	107 (1)	110 (1)	C17—C16—C21	117 (1)	114 (1)
C4—C5—C10	106 (1)	106 (1)	C16—C17—C18	123 (1)	121 (1)
C4—C5—C12	110 (1)	110 (1)	C16—C17—O17	123 (1)	125 (1)
C6—C5—C10	110 (1)	109 (1)	C18—C17—O17	114 (1)	114 (1)
C6—C5—C12	110 (1)	106 (1)	C17—C18—C19	119 (1)	124 (2)
C10—C5—C12	114 (1)	115 (1)	C17—C18—O18	118 (1)	117 (2)
C5—C6—C7	108 (1)	112 (1)	C19—C18—O18	123 (1)	119 (2)
C6—C7—C8	110 (1)	108 (1)	C18—C19—C20	118 (1)	116 (2)
C7—C8—C9	113 (1)	114 (1)	C19—C20—C21	125 (1)	120 (2)
C7—C8—C13	108 (1)	112 (1)	C19—C20—O20	128 (1)	132 (2)
C9—C8—C13	114 (1)	112 (1)	C21—C20—O20	107 (1)	108 (1)
C8—C9—C10	111 (1)	109 (1)	C16—C21—C20	116 (1)	124 (1)
C8—C9—C14	113 (1)	110 (1)	C16—C21—O21	123 (1)	119 (1)
C8—C9—C15	109 (1)	106 (1)	C20—C21—O21	121 (1)	117 (1)
			C20—O20—C22	118 (1)	114 (1)

EXPERIMENTAL

Single crystals of the hydrate of (I) ($C_{21}H_{32}O_5 \cdot H_2O$) were obtained by crystallization from aqueous alcoholic solution. They belonged to the monoclinic system, symmetry space group $P2_1$, Z = 4. The parameters of the unit cell of the crystals were measured and refined on a Hilger and Watts automatic four-circle diffractometer, their values being: a = 19.323 (2), b = 7.707 (1), c = 14.712(2) Å, β = 92.15(1)°, V = 2189.4 Å^3, d_{calc} = 1.19 8/cm^3, $\mu_{MoK\alpha}$ = 0.51 cm^{-1}.

The integral intensities of 3067 independent reflections were measured on the same diffractometer by the θ/2θ method in the range from 2θ to 48° [sic], and, of these, 1600 reflections with $I \geq 2\sigma(I)$ were used for refining the structure. In the recalculation of the intensities, corrections for the Lorentz and polarization factors were introduced into the structural factors but no corrections were made for absorption. The structure was determined by the direct method and was refined by the method of least squares in the isotropic and, partially, in the anisotropic, approximation using a weighting scheme to R = 0.104 and R_w = 0.083. The coordinates of the hydrogen atoms of the hydroxy groups and of the water molecules were determined from difference syntheses, while in the other groups they are given geometrically. All the calculations were made by means of the SHELX-76 [3] and SHELX-86 [4] programs on a ES-1061 computer.

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SECONDARY METABOLITES OF Pyricularia oryzae

II. POLYKETIDE METABOLITES

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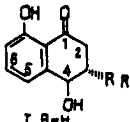
A number of exometabolites have been isolated from the deuteromycete Pyricularia oryzae Cav., of which harman and ~~O-demethyldiaporthin~~ have been isolated from this species for the first time. The latter is the first example of a hexaketide from fungi of the genus Pyricularia, for which only penta- and heptaketides have previously been described.

The isolation and identification of a number of secondary metabolites forming derivatives of o-nitrophenol from the neutral and acid fractions of an extract of the culture fluid of Pyricularia oryzae Cav. has been described previously. In this paper we consider the isolation and identification of five compounds from the neutral fraction of the extract.

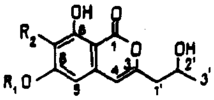
Compounds (I)-(III) were identified by comparing their physicochemical properties with those of substances isolated previously from this fungus. They were metabolites of pentaketide origin and were identical with the isosclerone (4,8-dihydroxy-1(2H)-naphthalenone) (I), 3,4,8-trihydroxy-1(2H)-naphthalenone (II), and 6-hydroxymellein (III), that had been isolated previously from P. oryzae by Japanese workers [2, 7]. The PMR spectra that we obtained from these substances differed from those described previously by a considerably higher resolution and are given in the Experimental part.

Compound (IV), isolated from the neutral fraction, was identified on the basis of its physical properties as harman [3]. Harman is an indole alkaloid that is widely distributed in nature in higher plants. Of microorganisms it has been found in Streptomyces and Nocardia actinomycetes [3] as a result of the screening in the search for substances possessing growth inhibiting activity with respect to plants. In view of the fact that the scheme for isolating metabolites that we selected was designed for acidic and neutral compounds, while harman is a weak base, it may be assumed that its amount in the culture fluid was considerably higher than the amount that we had isolated.



I. R=H

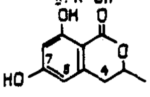
II. R=OH



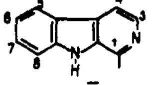
V. R_1=H, R_2=H

VI. R_1=Me, R_2=H

VII. R_1=H, R_2=Me



III



IV

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