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Fungus Pigments. XXVIII.* The Structure of Peniophorin

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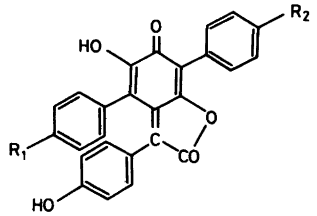
An X-ray analysis of the trimethyl ether of peniophorin has confirmed the originally proposed structure of peniophorin. The unit cell contains two molecules of the compound and has the dimensions $a = 9.451(3)$, $b = 10.719(2)$, $c = 12.261(3)$ Å, $\alpha = 86.14(2)$, $\beta = 71.86(2)$, $\gamma = 81.60(2)°$, space group $P\bar{1}$. The structure was solved by direct methods and refined to an R-value of 0.048 for 1964 reflections.

In a continuing effort to study the structures of fungus pigments, X-ray techniques were recently employed to determine the structures of peniophorinin[1] and xylerythrinin.[2] The structure of peniophorin was studied some years ago[3] by spectroscopic methods, namely UV and NMR. Either structure *1* or *2* was proposed for peniophorin, and some preference was given to *1* for biogenetic reasons. In order to decide between the two structures, an X-ray analysis of the trimethyl ether of peniophorin has been undertaken.

COLLECTION AND REDUCTION OF X-RAY DATA

The isolation of peniophorin and the preparation of the trimethyl ether has been described elsewhere.[3]



1 R_1 = OH R_2 = H

2 R_1 = H R_2 = OH

A crystal was fixed with epoxy cement on the end of a thin glass fiber. A preliminary photographic examination indicated that the crystal was triclinic. Preliminary cell constants were obtained by centering 16 reflections in the range $25 \leq 2\theta \leq 27$ using a Syntex $P2_1$ automatic diffractometer.

The centering and the least-squares cell constant determination was repeated 16 times and the final constants were obtained as an average. The standard deviations in the constants were calculated from the averages and were about half of the deviations in a single determination. The final cell constants are $a = 9.451(3)$, $b = 10.719(2)$, $c = 12.261(3)$ Å, $\alpha = 86.14(2)$, $\beta = 71.86(2)$, $\gamma = 81.60(2)°$; giving a calculated volume of 1167.4(4) Å^3 which is consistent with two molecules per unit cell.

The linear absorption coefficient for Mo$K\alpha$ radiation is 1.0 cm^{-1} and absorption corrections

Table 1. Summary of crystal data and experimental conditions.

Compound	$C_{29}H_{22}O_6$
Molecular weight	466.5
Unit cell dimensions (Å or deg.)	$a = 9.451(3)$ $b = 10.719(2)$ $c = 12.261(3)$ $\alpha = 86.14(2)$ $\beta = 71.86(2)$ $\gamma = 81.60(2)$
Cell volume (Å^3)	1167.4
Z	2
Density calculated (g cm^{-3})	1.33
Space group	$P\bar{1}$
Linear absorption coefficient (cm^{-1})	$\mu = 1.00$ (Mo$K\alpha$)
Radiation (Å)	λ(Mo$K\alpha$) = 0.71069
Scan (° min^{-1})	$\theta - 2\theta$ at 2–29.3
2θ limits (°)	$0 \leq 2\theta \leq 50$
Standard reflections	002, 211

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Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations in parentheses. The anisotropic temperature factor is given by: $\exp\{-2\pi^2[U_{11}(a^*h)^2+\cdots+2U_{23}(b^*c^*kl)]\}$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	.3817(6)	.5614(5)	.1177(4)	.051(3)	.041(3)	.045(3)	−.010(3)	−.017(3)	.007(3)
C2	.4862(5)	.5763(4)	.1824(4)	.042(3)	.036(3)	.034(3)	−.006(2)	−.012(2)	.002(2)
C3	.5001(5)	.4661(4)	.2435(4)	.042(3)	.028(2)	.031(3)	−.006(2)	−.010(2)	.001(2)
C4	.5993(5)	.4154(4)	.3109(4)	.041(3)	.035(3)	.038(3)	−.003(2)	−.013(2)	−.001(2)
C5	.5701(5)	.3043(4)	.3695(4)	.047(3)	.037(3)	.033(3)	−.002(2)	−.016(2)	−.001(2)
C6	.4423(5)	.2381(4)	.3675(4)	.043(3)	.033(3)	.047(3)	−.006(2)	−.014(3)	.003(2)
C7	.3645(5)	.2774(4)	.2813(4)	.036(3)	.033(3)	.039(3)	−.003(2)	−.011(2)	.001(2)
C8	.3963(5)	.3883(4)	.2273(4)	.037(3)	.037(3)	.035(3)	−.002(2)	−.013(2)	.002(2)
C9	.5499(5)	.6948(4)	.1767(4)	.041(3)	.029(2)	.043(3)	−.001(2)	−.014(2)	.005(2)
C10	.5973(6)	.7604(5)	.0731(4)	.060(4)	.044(3)	.042(3)	−.012(3)	−.020(3)	.003(2)
C11	.6561(6)	.8736(4)	.0670(4)	.062(4)	.044(3)	.037(3)	−.020(3)	−.016(3)	.008(2)
C12	.6682(6)	.9190(4)	.1660(4)	.047(3)	.029(3)	.055(3)	−.006(2)	−.021(3)	.004(2)
C13	.6221(6)	.8546(4)	.2700(4)	.059(3)	.029(3)	.040(3)	.000(2)	−.023(3)	.000(2)
C14	.5624(5)	.7441(4)	.2756(4)	.047(3)	.034(3)	.038(3)	.004(2)	−.013(2)	.001(2)
C15	.7495(8)	1.1097(5)	.0698(6)	.135(6)	.050(4)	.084(5)	−.049(4)	−.060(5)	.022(3)
C16	.7259(5)	.4811(4)	.3135(4)	.041(3)	.025(2)	.045(3)	.001(2)	−.018(2)	.000(2)
C17	.8298(5)	.5157(4)	.2118(4)	.046(3)	.039(3)	.049(3)	−.002(2)	−.018(3)	−.003(2)
C18	.9433(6)	.5820(5)	.2139(5)	.047(3)	.051(3)	.055(3)	−.009(3)	−.015(3)	.006(3)
C19	.9556(6)	.6153(5)	.3167(5)	.051(3)	.044(3)	.074(4)	−.013(3)	−.032(3)	.007(3)
C20	.8557(6)	.5815(5)	.4181(5)	.068(4)	.043(3)	.059(4)	−.011(3)	−.035(3)	−.004(3)
C21	.7401(6)	.5135(5)	.4173(4)	.052(3)	.040(3)	.050(3)	−.009(2)	−.017(3)	.001(2)
C22	1.0800(10)	.7277(7)	.4129(7)	.157(8)	.095(5)	.113(6)	−.080(5)	−.095(6)	.035(5)
C23	.6970(6)	.1237(5)	.4472(5)	.067(4)	.035(3)	.062(4)	−.003(3)	−.030(3)	.010(3)
C24	.2551(5)	.2004(4)	.2628(4)	.040(3)	.040(3)	.044(3)	−.012(2)	−.015(2)	.009(2)
C25	.1173(6)	.2553(5)	.2525(5)	.039(3)	.047(3)	.067(4)	−.001(3)	−.014(3)	−.001(3)
C26	.0203(6)	.1812(5)	.2330(5)	.042(3)	.064(4)	.082(4)	−.012(3)	−.022(3)	.001(3)
C27	.0592(6)	.0523(5)	.2241(5)	.055(4)	.054(4)	.077(4)	−.024(3)	−.023(3)	.003(3)
C28	.1944(6)	−.0037(5)	.2340(5)	.061(4)	.044(3)	.063(4)	−.012(3)	−.016(3)	.000(3)
C29	.2928(6)	.0698(5)	.2549(4)	.044(3)	.041(3)	.055(3)	−.010(2)	−.017(3)	.009(3)
O1	.3266(4)	.4460(3)	.1500(3)	.051(2)	.040(2)	.055(2)	−.014(2)	−.029(2)	.010(2)
O2	.3414(4)	.6278(3)	.0486(3)	.070(3)	.054(2)	.064(3)	−.016(2)	−.039(2)	.023(2)
O3	.7194(4)	1.0318(3)	.1701(3)	.087(3)	.045(2)	.059(3)	−.029(2)	−.037(2)	.010(2)
O4	1.0729(5)	.6821(4)	.3093(4)	.090(3)	.084(3)	.095(3)	−.047(3)	−.046(3)	.013(3)
O5	.6518(4)	.2583(3)	.4400(3)	.071(2)	.030(2)	.056(2)	−.009(2)	−.038(2)	.006(2)
O6	.4025(4)	.1531(3)	.4382(3)	.072(3)	.052(2)	.056(2)	−.025(2)	−.028(2)	.024(2)

	x	y	z		x	y	z
H10	.594(5)	.723(4)	.001(4)	H221*	.975	.793	.450
H11	.703(5)	.913(4)	−.022(4)	H222*	1.082	.650	.476
H13	.623(5)	.889(4)	.342(4)	H223*	1.172	.780	.409
H14	.516(5)	.706(4)	.360(4)	H231	.804(5)	.111(4)	.455(4)
H151	.768(5)	1.179(4)	.090(4)	H232	.718(5)	.084(4)	.362(4)
H152	.664(5)	1.127(4)	.042(4)	H233	.640(5)	.099(4)	.502(4)
H153	.864(5)	1.054(4)	.000(4)	H25	.085(5)	.341(4)	.267(4)
H17	.817(5)	.495(4)	.145(4)	H26	−.085(5)	.223(4)	.236(4)
H18	1.002(5)	.611(4)	.151(4)	H27	−.004(5)	.003(4)	.207(4)
H20	.853(5)	.611(4)	.503(4)	H28	.233(5)	−.092(4)	.213(4)
H21	.661(5)	.497(4)	.493(4)	H29	.396(5)	.029(4)	.261(4)

* Atomic coordinates of H221, H222 and H223 were not refined.

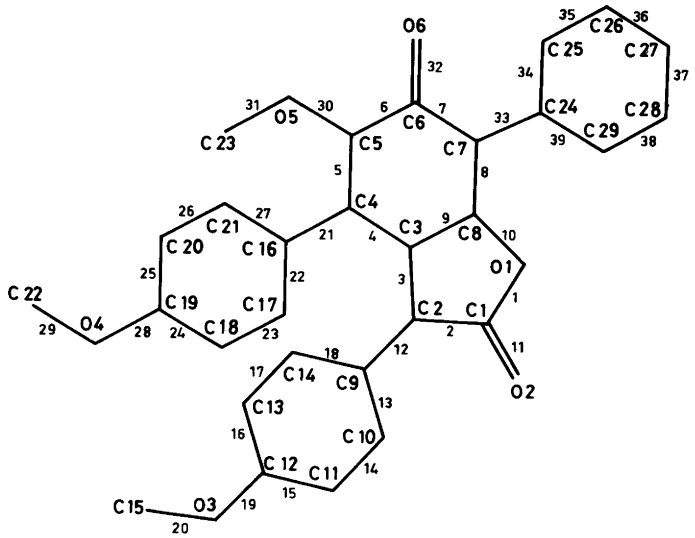

Fig. 1. The numbering of the atoms in peniophorin trimethyl ether.

were therefore considered unnecessary. Intensities were measured using the $\theta-2\theta$ scan technique. A total of 4162 independent data were collected with Mo$K\alpha$ radiation. The intensities of two standard reflections were monitored throughout data collection and showed no significant decrease in intensity during the period of data collection. Details of the experimental conditions, together with the crystal data, are presented in Table 1.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods using the program MULTAN 78[4] and refined by least-squares techniques on F. The first trial structure in the space group $P\bar{1}$ showed all nonhydrogen atoms and an isotropic refinement gave a conventional agreement factor $R = 0.117$ for 1946 reflections ($I > 3\sigma(I)$). The same atoms were refined anisotropically and from a resulting difference Fourier synthesis all hydrogen atoms were located.

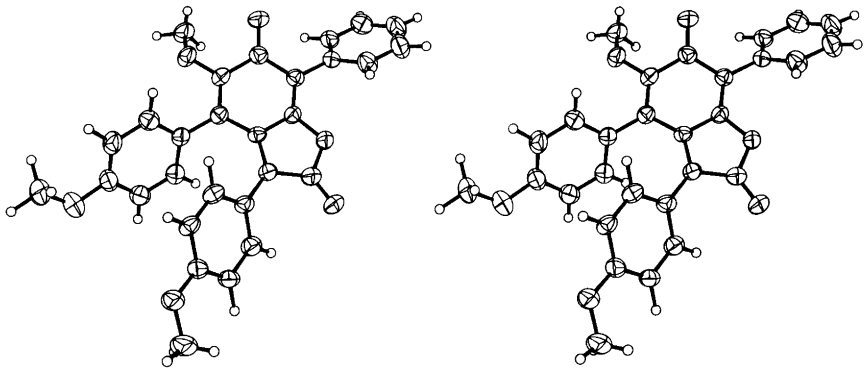

Fig. 2. A stereoscopic pair of the peniophorin trimethyl ether molecule. Thermal ellipsoids involving nonhydrogen atoms are scaled to include 50 % probability. Hydrogen atoms are shown as spheres of 0.1 Å radius.

Table 3. Bond distances (Å) and angles (°) involving the nonhydrogen atoms.

1 = 1.397(15)	16 = 1.384(20)	31 = 1.449(12)
2 = 1.477(14)	17 = 1.374(13)	32 = 1.230(19)
3 = 1.368(18)	18 = 1.399(14)	33 = 1.491(16)
4 = 1.459(17)	19 = 1.376(12)	34 = 1.389(15)
5 = 1.367(18)	20 = 1.416(21)	35 = 1.379(16)
6 = 1.495(15)	21 = 1.484(15)	36 = 1.380(12)
7 = 1.472(16)	22 = 1.392(22)	37 = 1.368(16)
8 = 1.347(17)	23 = 1.378(15)	38 = 1.394(16)
9 = 1.442(16)	24 = 1.376(12)	39 = 1.395(11)
10 = 1.381(17)	25 = 1.370(22)	
11 = 1.187(16)	26 = 1.403(16)	
12 = 1.472(14)	27 = 1.392(12)	
13 = 1.388(20)	28 = 1.382(15)	
14 = 1.395(14)	29 = 1.416(15)	
15 = 1.381(14)	30 = 1.355(16)	

1,2 = 108.6(4)	7,33 = 120.7(4)	23,24 = 120.5(5)
1,10 = 106.8(4)	8,9 = 126.5(5)	24,25 = 120.1(6)
1,11 = 119.7(5)	8,10 = 123.3(5)	24,28 = 115.9(5)
2,3 = 106.6(4)	8,33 = 124.8(5)	25,26 = 120.0(6)
2,11 = 131.7(5)	9,10 = 110.1(4)	25,28 = 124.0(6)
2,12 = 121.4(4)	12,13 = 120.5(5)	26,27 = 120.1(4)
3,4 = 133.4(5)	12,18 = 120.7(4)	28,29 = 117.1(5)
3,9 = 107.6(5)	13,14 = 121.0(5)	30,31 = 119.7(4)
3,12 = 132.0(5)	13,18 = 118.8(5)	33,34 = 121.8(4)
4,5 = 116.4(5)	14,15 = 118.8(4)	33,39 = 119.1(4)
4,9 = 118.9(4)	15,16 = 121.1(5)	34,35 = 120.1(5)
4,21 = 121.3(4)	15,19 = 123.3(4)	34,39 = 119.2(5)
5,6 = 122.6(5)	16,17 = 119.9(5)	35,36 = 120.3(5)
5,21 = 122.3(5)	16,19 = 115.5(5)	36,37 = 120.6(6)
5,30 = 118.6(5)	17,18 = 120.6(4)	37,38 = 119.7(5)
6,7 = 119.0(4)	19,20 = 118.0(5)	38,39 = 120.1(5)
6,30 = 118.6(4)	21,22 = 120.5(5)	
6,32 = 119.9(5)	21,27 = 120.8(4)	
7,8 = 114.4(5)	22,23 = 120.6(5)	
7,32 = 121.1(5)	22,27 = 118.7(5)	

In the final refinements hydrogen atoms were given fixed isotropic temperature factors ($U = 0.07$). After alternating full-matrix refinements of nonhydrogen and hydrogen atoms the agreement factors were $R = 0.048$ and $R_w = 0.053$ $[w = 1/\sigma^2(F_o^2)]$. The final positional and thermal parameters are given in Table 2. All calculations were performed with a UNIVAC 1108 computer using the X-RAY 76 program system.[5] A listing of structure factors is available from the authors upon request.

DISCUSSION

The unit cell comprises two discrete molecules, which are related by inversion symmetry. A schematic drawing of the molecule showing the atom numbering scheme is presented in Fig. 1 and a stereo pair drawing is given in Fig. 2. The found structure confirms the earlier tentative proposal (*1*).[3] Peniophorin is thus 5-hydroxy-3,4-di(*p*-hydroxyphenyl)-7-phenylbenzofuran-2,6-dione.

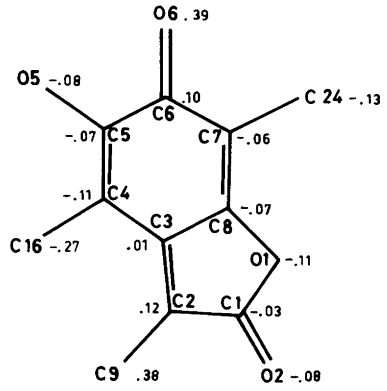

Fig. 3. Deviations (Å) of the atoms from the least-squares plane for benzofuran-2,6-dione.

The bond lengths and angles are in the usual range (see Table 3). The carbon hydrogen bond distances range from 0.79 to 1.25 Å. Disorder was detected in the C22-methyl group, where the hydrogen atoms were not refined. The planarity of the central fragment of the molecule, consisting of atoms C1 – C9, C16, C24, O1, O2, O5 and O6 was tested by a least-squares plane calculation. Fig. 3 shows the deviations from planarity. The three phenyl rings are tilted out of the molecular plane for steric reasons. The torsion angles around the bonds 12, 21 and 33 are 42(1), 55(1) and 45(1)°, respectively. The shortest intermolecular contact distance is 3.207(2) Å, between C15 and O2.

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