

Fungus Pigments. XXVI.* A Revised Structure of Peniophorinin

JARL GRIPENBERG, LASSI HILTUNEN, LAURI NIINISTÖ, TAPANI PAKKANEN and TUULA PAKKANEN

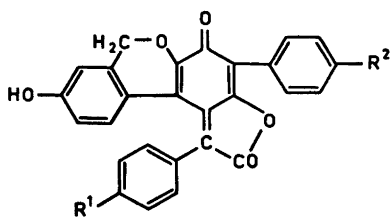
Department of Chemistry, Helsinki University of Technology, Otaniemi, SF-02150 Espoo 15, Finland

An X-ray analysis of the dimethyl ether of peniophorinin has revealed that the originally proposed structure of peniophorinin has to be revised to 9-hydroxy-1-(*p*-hydroxyphenyl)-4-phenyl-6*H*-benzofuro[5,4-*c*][1]benzopyran-2,5-dione (3).

The unit cell contains four molecules of the compound and two benzene solvent molecules, and it has the following dimensions $a = 13.695(8)$ Å, $b = 6.622(3)$ Å, $c = 27.933(13)$ Å, $\beta = 98.10(4)^\circ$; space group is $P2_1/n$. The structure was solved by direct methods and refined to an R -value of 0.048 for the 1864 diffractometer measured reflections.

Some years ago, either structure 1 or 2 was proposed for peniophorinin,¹ one of the pigments produced by the wood attacking fungus *Peniophora sanguinea* Bres. Some preference was given for 1. The possibility that the oxygen atom and the CH₂-group in the pyran ring should be in the reverse order, as in 3 or 4, was dismissed as biogenetically highly unlikely.

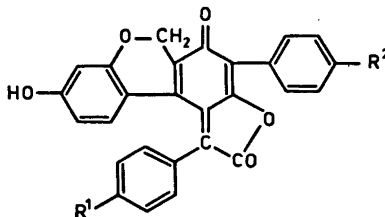
In order to decide between the two structures 1 and 2 an X-ray analysis of the dimethyl ether of peniophorinin¹ has been undertaken.

* Part XXV *Acta Chem. Scand. B* 32 (1978) 75.

1 $R^1 = \text{OH}; R^2 = \text{H}$
2 $R^1 = \text{H}; R^2 = \text{OH}$

COLLECTION AND REDUCTION OF X-RAY DATA

The crystals of the dimethyl ether of peniophorinin were prepared from a benzene solution by cooling. A preliminary photographic examination indicated that the crystals were monoclinic. Intensity data were recorded on a Syntex P2₁ automatic diffractometer. Cell constants at 25°C and an orientation matrix were refined using 12 centered reflections. Three-dimensional intensity data were recorded using the $\omega-2\theta$ scanning mode with scan speed varying from 1 to 29.3° min⁻¹ depending on the peak intensity of the reflections. Full details of the experimental conditions together with the crystal data are presented in Table 1. During the data collection a standard reflection was examined regularly. The variations in the intensity were random. Of the 4964 symmetry independent reflections measured (2θ max = 50°) 1864 had intensities larger than three times their standard deviations. These were regarded as "observed" reflections, and the remaining were excluded from further calculations. The intensities were corrected for Lorentz and polarization effects; no absorption correction



3 $R^1 = \text{OH}; R^2 = \text{H}$
4 $R^1 = \text{H}; R^2 = \text{OH}$

Table 1. Summary of crystal data and experimental conditions.

Compound	$C_{29}H_{20}O_4 \cdot \frac{1}{2}C_6H_6$
Molecular weight	503.5
Unit cell dimensions (Å or deg.)	$a = 13.695(8)$ $b = 6.622(3)$ $c = 27.933(13)$ $\beta = 98.10(4)$
Cell volume (Å ³)	2507.7
Z	4
Density calculated (g cm ⁻³)	1.33
Space group	$P2_1/n$
Linear absorption coefficient (cm ⁻¹)	$\mu = 0.99$ (MoK α)
Radiation (Å)	λ (MoK α) = 0.71069
Scan (° min ⁻¹)	$\omega - 2\theta$ at 1 - 29.3
2 θ limits (°)	$5 \leq 2\theta \leq 50$
Standard reflection	117, recorded every 40 observations

was applied. The space group was deduced from systematic absences to be $P2_1/n$.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods using the program MULTAN² and refined by least-squares techniques on F . Scattering factors for neutral nonhydrogen atoms were taken from Cromer and Mann³ while those for H were from Stewart *et al.*⁴ The trial structure revealed also two benzene molecules in the unit cell.

A refinement varying positional and isotropic thermal parameters for all 38 nonhydrogen atoms gave a conventional agreement factor $R = 0.103$. In further refinement cycles anisotropic thermal parameters were used and the R -value decreased to 0.080. Idealized coordinates for the hydrogen atoms were calculated (C-H 1.09 Å) and the final results were obtained by alternating refinements of nonhydrogen and hydrogen atoms. Isotropic thermal parameters were used for the hydrogen atoms. The final agreement values are $R = 0.048$ 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 crystal structure consists of discrete molecules. A schematic drawing of the molecule showing the atom numbering scheme is presented in Fig. 1, while a stereo pair drawing is given in Fig. 2. The coordinates and the thermal parameters of the atoms are listed with standard deviations in Table 2. The bond distances and angles are given in Tables 3 and 4. The twenty C-H bond distances range from 0.91 to 1.15 Å; the mean value is 1.00 Å. The structure does not show any unusual bond

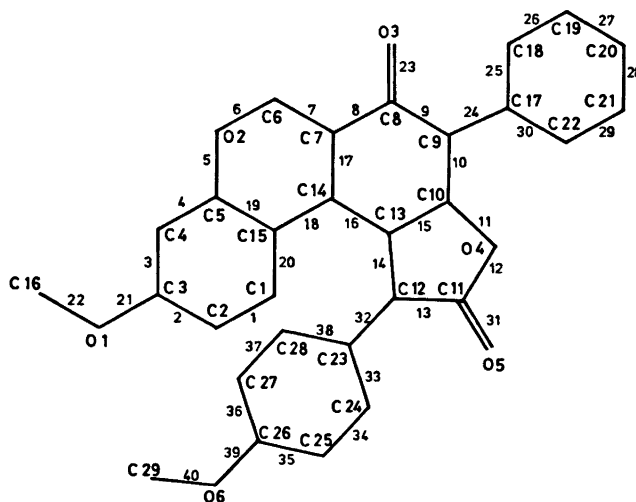
*Fig. 1.* The numbering of the atoms in the peniophorinin dimethyl ether molecule.

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
C1	.0059(4)	.1389(8)	.1770(2)	.0431(33)	.0334(33)	.0395(35)	-.0035(29)	.0099(27)	-.0031(28)
C2	-.0803(4)	.2202(9)	.1893(2)	.0391(33)	.0486(40)	.0476(35)	-.0074(31)	.0110(27)	.0025(32)
C3	-.0812(4)	.4216(9)	.2045(2)	.0346(31)	.0474(37)	.0391(33)	-.0001(30)	.0077(25)	.0034(31)
C4	.0035(4)	.5375(8)	.2077(2)	.0462(33)	.0329(33)	.0398(32)	-.0029(29)	.0055(26)	-.0020(28)
C5	.0904(3)	.4482(8)	.1954(2)	.0305(30)	.0360(34)	.0318(30)	.0006(27)	.0031(23)	.0108(28)
C6	.2625(4)	.4591(9)	.2144(2)	.0320(29)	.0359(35)	.0516(35)	.0006(27)	-.0007(25)	-.0038(31)
C7	.2697(4)	.2775(8)	.1835(2)	.0316(29)	.0282(31)	.0330(30)	.0018(26)	.0020(23)	-.0016(26)
C8	.3708(4)	.2068(8)	.1778(2)	.0364(30)	.0360(35)	.0378(32)	-.0017(28)	.0036(25)	.0063(29)
C9	.3813(4)	.0102(8)	.1549(2)	.0294(28)	.0313(33)	.0378(31)	-.0021(26)	.0041(23)	.0059(27)
C10	.2974(4)	-.0856(8)	.1375(2)	.0383(31)	.0302(31)	.0288(30)	.0024(27)	.0054(23)	.0004(27)
C11	.1940(4)	-.2980(9)	.0924(2)	.0364(31)	.0451(37)	.0381(32)	.0000(29)	.0031(26)	-.0047(30)
C12	.1357(4)	-.1208(8)	.1050(2)	.0331(29)	.0291(31)	.0327(31)	.0002(26)	.0016(24)	.0004(26)
C13	.1968(3)	-.0029(8)	.1360(2)	.0289(28)	.0297(31)	.0320(30)	-.0026(25)	.0027(23)	.0036(27)
C14	.1862(3)	.1778(8)	.1648(2)	.0296(29)	.0297(31)	.0303(29)	.0019(25)	.0035(23)	.0024(25)
C15	.0923(4)	.2510(8)	.1783(2)	.0349(30)	.0308(33)	.0304(29)	.0010(27)	.0047(23)	.0028(28)
C16	-.1659(4)	.6722(11)	.2437(2)	.0401(35)	.0772(52)	.0617(43)	.0186(36)	.0157(31)	-.0086(40)
C17	.4819(3)	-.0674(9)	.1501(2)	.0258(27)	.0451(35)	.0364(31)	.0026(27)	.0000(23)	-.0078(30)
C18	.5161(4)	-.2481(9)	.1710(2)	.0290(28)	.0443(35)	.0466(34)	.0021(28)	-.0009(25)	.0014(31)
C19	.6093(4)	-.3162(10)	.1657(2)	.0432(38)	.0597(45)	.0685(46)	.0148(35)	.0003(33)	-.0007(39)
C20	.6703(4)	-.2082(13)	.1400(2)	.0307(33)	.0995(62)	.0653(45)	.0310(40)	.0015(31)	-.0133(45)
C21	.6373(4)	-.0266(12)	.1197(2)	.0403(36)	.0861(57)	.0691(46)	.0022(40)	.0194(33)	-.0003(44)
C22	.5438(4)	.0467(10)	.1246(2)	.0481(35)	.0568(42)	.0555(39)	.0038(35)	.0130(30)	.0113(36)
C23	.0354(4)	-.0863(8)	.0800(2)	.0316(29)	.0342(33)	.0317(30)	-.0022(27)	.0000(23)	-.0065(28)
C24	.0072(4)	.1065(9)	.0636(2)	.0335(32)	.0400(37)	.0419(35)	-.0007(28)	.0019(26)	-.0091(29)
C25	-.0846(4)	.1414(9)	.0374(2)	.0448(35)	.0328(33)	.0469(36)	.0000(29)	.0054(29)	.0031(29)
C26	-.1500(4)	-.0170(10)	.0269(2)	.0288(29)	.0540(41)	.0422(33)	-.0007(31)	.0037(25)	-.0032(33)
C27	-.1251(4)	-.2097(9)	.0431(2)	.0356(32)	.0385(37)	.0466(35)	-.0122(29)	.0001(26)	.0011(31)
C28	-.0320(4)	-.2451(9)	.0694(2)	.0462(35)	.0346(34)	.0437(35)	-.0020(29)	-.0011(28)	.0025(31)
C29	-.3073(4)	-.1248(11)	-.0158(3)	.0432(36)	.0732(51)	.0777(48)	.0027(37)	-.0097(32)	.0028(41)
C30*	.5694(6)	-.5476(13)	.0388(3)	.0825(57)	.0783(59)	.0815(60)	-.0094(50)	.0054(45)	.0136(51)
C31*	.4835(7)	-.4559(14)	.0461(3)	.0920(60)	.0959(67)	.0704(56)	-.0084(56)	.0243(49)	-.0190(52)
C32*	.4144(6)	-.4050(11)	.0075(4)	.0729(51)	.0518(46)	.1198(72)	.0030(42)	.0401(53)	-.0126(51)
O1	-.1678(3)	.4886(6)	.2172(1)	.0354(22)	.0528(27)	.0705(28)	.0046(21)	.0173(20)	-.0096(25)
O2	.1729(2)	.5695(5)	.1995(1)	.0342(20)	.0285(21)	.0576(25)	-.0016(18)	.0089(18)	-.0054(20)
O3	.4425(2)	.3102(6)	.1942(1)	.0335(20)	.0432(25)	.0655(28)	-.0057(19)	-.0025(19)	-.0039(22)
O4	.2931(2)	-.2671(6)	.1124(1)	.0312(21)	.0362(23)	.0499(24)	.0026(18)	.0000(17)	-.0112(21)
O5	.1721(3)	-.4466(6)	.0695(1)	.0463(23)	.0423(25)	.0680(28)	.0025(21)	-.0010(20)	-.0178(23)
O6	-.2367(3)	.0314(6)	-.0013(1)	.0351(21)	.0525(28)	.0739(29)	-.0050(21)	-.0143(20)	.0035(25)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H1	.008(2)	.000(5)	.167(1)	.015(10)	H12	.679(4)	.047(8)	.099(2)	.071(17)
H2	-.136(3)	.137(7)	.190(2)	.049(14)	H13	.517(3)	.187(7)	.108(2)	.052(15)
H3	-.119(3)	.675(7)	.272(2)	.049(14)	H14	.053(3)	.210(6)	.071(1)	.026(11)
H4	-.148(3)	.787(8)	.221(2)	.064(16)	H15	-.099(2)	.264(6)	.023(1)	.013(10)
H5	-.227(3)	.695(7)	.254(2)	.037(13)	H16	-.166(3)	-.322(7)	.039(1)	.036(12)
H6	.009(3)	.689(6)	.221(1)	.037(13)	H17	-.016(3)	-.385(6)	.083(1)	.024(11)
H7	.268(3)	.396(7)	.253(2)	.055(15)	H18	-.335(4)	-.180(8)	.013(2)	.073(17)
H8	.318(3)	.554(7)	.212(2)	.052(14)	H19	-.274(4)	-.236(9)	-.036(2)	.080(18)
H9	.478(3)	-.327(7)	.193(2)	.056(15)	H20	-.364(4)	-.057(9)	-.040(2)	.095(21)
H10	.629(3)	-.448(7)	.175(1)	.043(13)	H21*	.353(4)	-.357(9)	.012(2)	.097(21)
H11	.734(4)	-.258(9)	.136(2)	.080(18)	H22*	.621(4)	-.576(10)	.066(2)	.116(24)
					H23*	.472(5)	-.420(12)	.080(2)	.147(29)

* Atomic coordinates and thermal parameters of the benzene solvent atoms.

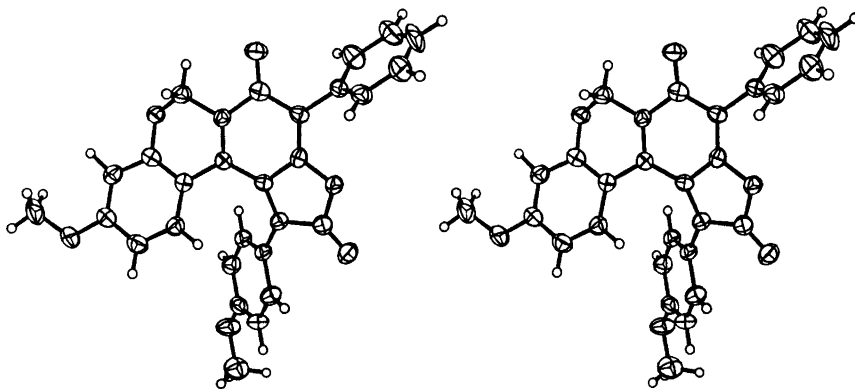


Fig. 2. The configuration of the peniophorinin dimethyl ether molecule. The thermal ellipsoids for the nonhydrogen atoms are scaled to 50 % probability. Hydrogen atoms are shown as spheres of 0.1 Å radius.

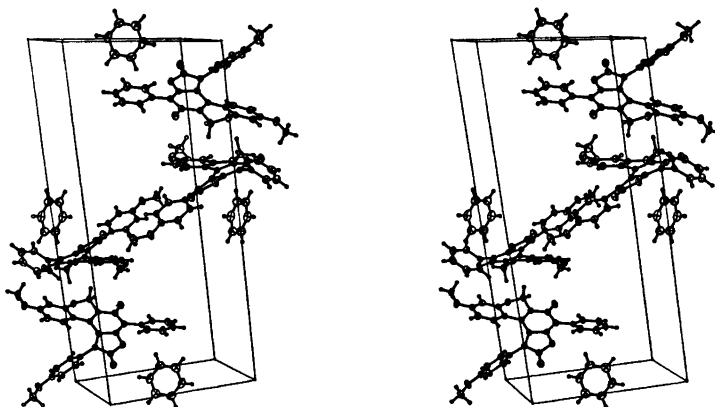


Fig. 3. A stereoscopic pair of the unit cell showing the peniophorinin dimethyl ether and the benzene solvent molecules. The monoclinic *b*-axis points out from the page and the *c*-axis up in the page. Thermal ellipsoids involving nonhydrogen atoms are scaled to include 30 % probability.

lengths or angles. The central fragment of the molecule, consisting of atoms C7–C14, O3, O4, and O5 is planar due to the double bonds C7–C14, C9–C10 and C12–C13. Nearly tetrahedral bond angles around the atom O2 (C5–O2–C6 112.6°) and around C2 (O2–C2–C7 111.5°) force the benzene ring C1–C5, C15 out of the plane of the central fragment. The two other benzene rings are also tilted out of this plane for steric reasons. The solvent benzene molecule does not show disorder although the thermal parameters of the solvent atoms are slightly larger than those of the main structure. The location of the solvent molecules and molecular packing in the unit

cell is shown in a stereo pair drawing (Fig. 3).

In order to verify the positions of the oxygen atom (O2) and the CH₂ group (C6) in the pyran ring we made an attempt to refine a trial structure corresponding to the parent compound *1*. The resulting abnormal temperature factors, the excess of electron density on the carbon atom and the respective lack of density on the oxygen atom together with the collapse of the hydrogen atoms to the CH₂ carbon demonstrate that the CH₂ group and the oxygen atom are correctly placed in our structure.

The correct structure of peniophorinin is thus **3** (9-hydroxy-1-(*p*-hydroxyphenyl)-4-

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

1	1.385(8)	21	1.359(7)
2	1.402(9)	22	1.424(8)
3	1.384(8)	23	1.232(8)
4	1.413(8)	24	1.494(7)
5	1.379(6)	25	1.382(8)
6	1.437(6)	26	1.382(8)
7	1.493(8)	27	1.373(10)
8	1.490(7)	28	1.378(11)
9	1.468(8)	29	1.393(9)
10	1.343(7)	30	1.402(8)
11	1.390(6)	31	1.190(7)
12	1.409(6)	32	1.469(7)
13	1.490(8)	33	1.390(8)
14	1.363(7)	34	1.382(7)
15	1.477(7)	35	1.384(8)
16	1.463(7)	36	1.379(8)
17	1.361(7)	37	1.398(7)
18	1.473(7)	38	1.404(8)
19	1.393(8)	39	1.368(6)
20	1.393(7)	40	1.435(8)
1,2	119.3(5)	14,16	136.1(5)
1,20	122.5(5)	14,32	131.5(5)
2,3	120.3(5)	15,16	116.9(4)
2,21	115.8(5)	16,17	117.8(4)
3,4	118.6(5)	16,18	124.7(4)
3,21	123.9(5)	17,18	117.3(5)
4,5	116.3(5)	18,19	117.2(5)
4,19	122.2(5)	18,20	125.9(5)
5,6	112.6(4)	19,20	116.9(5)
5,19	121.4(4)	21,22	117.5(4)
6,7	111.5(4)	24,25	121.4(5)
7,8	116.9(4)	24,30	119.5(5)
7,17	119.6(5)	25,26	120.0(5)
8,9	118.3(4)	25,30	119.1(5)
8,17	123.4(5)	26,27	121.7(6)
8,23	119.3(5)	27,28	118.6(6)
9,10	116.6(5)	28,29	121.1(6)
9,23	122.3(5)	29,30	119.5(6)
9,24	119.5(4)	32,33	119.8(5)
10,11	124.5(5)	32,38	121.9(5)
10,15	125.6(5)	33,34	121.1(5)
10,24	123.9(5)	33,38	118.3(4)
11,12	107.3(4)	34,35	119.9(5)
11,15	109.4(4)	35,36	120.7(5)
12,13	108.0(4)	35,39	115.4(5)
12,31	119.4(5)	36,37	119.4(5)
13,14	107.6(4)	36,39	123.9(5)
13,31	132.6(5)	37,38	120.7(5)
13,32	120.3(4)	39,40	119.4(5)
14,15	107.0(4)		

Table 4. Bond distances (Å) and angles (°) involving the solvent atoms.

C30-C31	1.364(13)	C32-C30-C31	119.9(7)
C30-C32	1.381(14)	C32-C31-C30	120.4(8)
C31-C32	1.372(12)	C31-C32-C30	119.7(8)

phenyl-6*H*-benzofuro[5,4-*c*][1]benzopyran-2,5-dione), and it is clear that the original dismissal of the structures with the reverse order of the pyran ring was unfounded. This dismissal was based on the fact that all other pigments produced by *Peniophora sanguinea*, whose structure was known at that time⁶⁻⁸ have an oxygen atom attached to the quinonoid ring. It thus appeared logical to assume that peniophorin was a dehydrogenation product of a methyl ether of peniophorin, for which view even experimental, although in the event unsuccessful, confirmation was sought.¹

A close connection between peniophorin and peniophorin has recently found further support by the work of v. Massow and Noppel.⁹ They have demonstrated that 4-hydroxypulvinic acid is an efficient precursor for both peniophorin and peniophorin. According to them 4-hydroxypulvinic acid reacts further with tyrosin to give the pigments with loss of the carboxyl group of tyrosin. The obvious assumption that this carbon atom is retained in the formation of peniophorin forming the CH₂-group of the pyran ring is rendered impossible by v. Massow's result that L-tyrosin[1-¹⁴C] was incorporated to the same degree in both peniophorin and peniophorin.¹⁰ The extra carbon atom of the pyran ring in peniophorin has thus to come from an extraneous one-carbon entity.

REFERENCES

- Gripenberg, J. *Acta Chem. Scand.* 24 (1970) 3449.
- Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A* 27 (1971) 368.
- Cromer, D. T. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
- Stewart, R. F., Davidson, E. and Simpson, W. *J. Chem. Phys.* 42 (1965) 3175.
- Stewart, J. M. *The X-Ray System, Version of 1976*, Technical Report TR-446, Computer Science Center, University of Maryland, College Park 1976.
- Gripenberg, J. and Martikkala, J. *Acta Chem. Scand.* 23 (1969) 2583.
- Gripenberg, J. and Martikkala, J. *Acta Chem. Scand.* 24 (1970) 3444.
- Gripenberg, J. *Acta Chem. Scand.* 25 (1971) 2999.
- v. Massow, F. and Noppel, H. E. *Phytochemistry* 16 (1977) 1699.
- v. Massow, F. *Phytochemistry* 16 (1977) 1695.

Received June 21, 1978.