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Fungus Pigments. XXVII.* Xylerythrinin

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An X-ray analysis of the methyl ether of xylerythrinin, a new pigment isolated from wood attacked by *Peniophora sanguinea* Bres., has shown that xylerythrinin is 1-(*p*-hydroxyphenyl)-4-phenyl-7*H*-benzofuro[5,4-*c*][2]benzopyran-2,5-dione (*4*).

The compound crystallizes in the space group $P\bar{1}$. The asymmetric unit contains one xylerythrinin methyl ether molecule and a disordered chloroform solvent molecule. Cell dimensions are $a = 9.614(6)$ Å, $b = 10.035(6)$ Å, $c = 15.574(10)$ Å, $\alpha = 89.65(5)°$, $\beta = 78.82(5)°$, $\gamma = 63.20(5)°$. The structure was solved by direct methods and refined to an R of 0.097 by least-squares techniques. 2160 reflections, collected on an automatic diffractometer, were used in the refinement.

In an attempt to recover more xylerythrin (*1*) from the mother liquors [1] by chromatography, a new pigment was found, giving on TLC a spot, just below that of xylerythrin. By a combination of chromatography and crystallization the new pigment could be obtained in a pure state, and the name xylerythrinin is proposed for this compound. It gave readily a monomethyl ether and a monoacetate. Analytical data indicated a composition $C_{27}H_{16}O_5$ for xylerythrinin. The UV spectra of xylerythrinin and its derivatives corresponded closely to the spectra of peniophorinin and its derivatives.[2] Very characteristic is furthermore a two-proton singlet at $\delta \sim 5.20$ in the ^{1}H NMR spectra. In peniophorinin and its derivatives a similar signal is found at $\delta \sim 5.00$, which has been attributed to the protons at 2-C of a 2*H*-pyran ring.[2] Peniophorinin has recently been shown to have the structure *3*,[3] and xylerythrinin could thus be a desoxypeniophorinin, although a reverse order of the oxygen atom and the CH_2-group in the pyran ring, as originally suggested for peniophorinin,[2] should also be taken into account.

In order to establish the structure of xylerythrinin an X-ray analysis of the methyl ether has been undertaken.

COLLECTION AND REDUCTION OF X-RAY DATA

The preparation of the crystals of the methyl ether of xylerythrinin is described in Experimental. A preliminary investigation employing photographic techniques indicated that the

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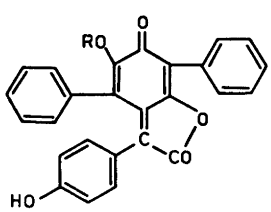

1 R = H
2 R = CH_3

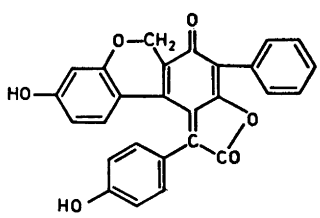

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Table 1. Summary of crystal data and experimental conditions.

Compound	$C_{28}H_{18}O_5 \cdot CHCl_3$
Molecular weight	553.8
Unit cell dimensions (Å or deg.)	$a = 9.614(6)$ $b = 10.035(6)$ $c = 15.574(10)$ $\alpha = 89.65(5)$ $\beta = 78.82(5)$ $\gamma = 63.20(5)$
Cell volume (Å^3)	1310.0
Z	2
Density calculated (g cm^{-3})	1.40
Space group	$P\bar{1}$
Absorption coefficient (cm^{-1})	$\mu = 3.90$ (Mo$K\alpha$)
Radiation (Å)	λ(Mo$K\alpha$) = 0.71069
Scan (°min^{-1})	$\theta - 2\theta$ at 1 – 29.3
2θ limits (°)	$5.0 \leq 2\theta \leq 55$
Standard reflection	355

crystals were triclinic. The unit cell was determined at 25 °C from a least-squares refinement of the angular settings of 14 reflections with a Syntex $P2_1$ single crystal automatic diffractometer. The crystal data and the experimental conditions are summarized in Table 1.

The intensity data were collected on the same diffractometer with graphite-monochromatized Mo$K\alpha$-radiation by the $\theta - 2\theta$ method and at a variable scan rate of 1 – 29.3° min^{-1}. All reflections up to 2θ of 55° were measured and of those, 2160 with $I > 3\sigma(I)$ were used in the subsequent calculations. The net intensities were corrected for Lorentz and polarization effects, but not for absorption.

STRUCTURE DETERMINATION

The structure was solved by direct methods using the program MULTAN.[4] The positional and anisotropic thermal parameters of the nonhydrogen atoms were refined using the full-matrix least-squares method leading to an R-value of 0.109. The hydrogen atoms were located on a difference Fourier map, and they were included in the final cycles of refinement with isotropic temperature factors. The final R index was 0.097.

The unit cell contains two chloroform molecules, which were located in the early stages of the refinement. The relatively high final R-value is due to disorder in the chloroform molecules. The carbon and chlorine atoms have large temperature factors and the difference Fourier map shows minor peaks near the central carbon atom. These peaks cannot be correlated with an other orientation of the chloroform molecule. It should be noticed, however, that no disorder occurs in the region of the unit cell which is of chemical interest, namely in the xylerythrinin methyl ether molecule.

All calculations were performed with a Univac 1108 computer using the X-RAY 76 program system.[5] A list of structure factors is available from the authors upon request.

DISCUSSION

The molecular structure and atomic numbering is shown in Fig. 1. The unit cell contains two discrete xylerythrinin methyl ether molecules. A stereopair drawing of the molecule is presented in Fig. 2. The atomic coordinates, temperature factors, bond lengths and angles with standard deviations are given in Tables 2 – 4, respectively. The C – H bond distances range from 0.80 Å to 1.17 Å; the mean value is 1.01 Å. The central part of the molecule, which contains atoms C7 – C14 and O2 – O4 is forced planar by the sp^2-hybridized carbon atoms C7 – C14. The benzene ring C1 – C5,C15 is tilted out of the plane by the CH_2 group and the oxygen atom in the adjacent ring. Similarly

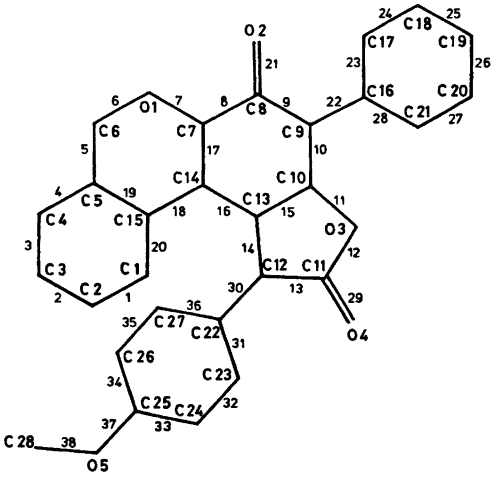


Fig. 1. The numbering of the atoms in the xylerythrinin methyl ether molecule.

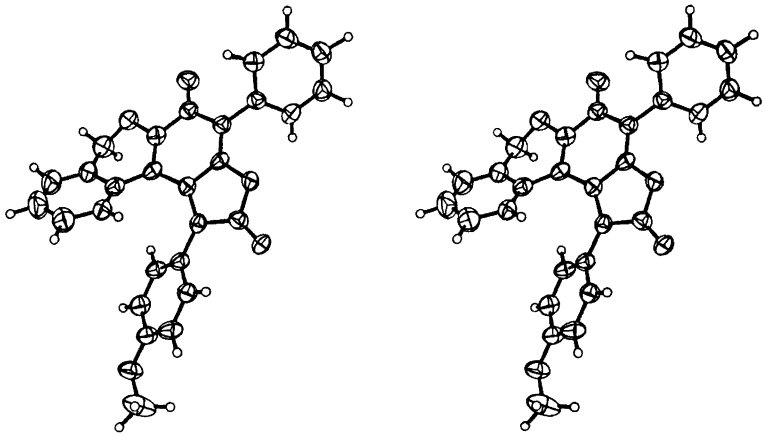


Fig. 2. A stereoscopic pair of the xylerythrinin methyl ether. The thermal ellipsoids for nonhydrogen atoms are scaled to enclose 50 % probability. Hydrogen atoms are shown as spheres of 0.1 Å radius.

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	.4603(11)	1.2372(10)	.2149(6)	.051(6)	.051(6)	.048(6)	−.023(5)	−.008(4)	.012(5)
C2	.3770(13)	1.3664(12)	.1753(7)	.068(7)	.068(8)	.076(8)	−.023(6)	−.011(6)	.016(6)
C3	.4286(15)	1.3737(15)	.0862(8)	.085(9)	.093(10)	.081(9)	−.026(8)	−.018(7)	.046(8)
C4	.5586(14)	1.2546(14)	.0370(7)	.076(8)	.091(9)	.060(7)	−.033(7)	−.008(6)	.033(7)
C5	.6437(11)	1.1289(11)	.0762(6)	.054(6)	.075(8)	.040(5)	−.029(6)	−.010(5)	.020(5)
C6	.7956(12)	.9950(13)	.0290(6)	.062(7)	.093(9)	.036(5)	−.033(6)	−.003(5)	.012(5)
C7	.8600(11)	.9143(10)	.1640(5)	.049(6)	.054(6)	.035(5)	−.024(5)	−.004(4)	−.002(5)
C8	.9916(11)	.8158(10)	.2066(6)	.041(6)	.048(6)	.043(5)	−.019(5)	−.001(5)	.001(4)
C9	.9464(10)	.7789(10)	.2967(6)	.042(6)	.050(6)	.040(5)	−.022(5)	−.007(4)	.005(4)
C10	.7893(10)	.8322(10)	.3291(5)	.047(6)	.052(6)	.029(5)	−.030(5)	−.001(4)	.002(4)
C11	.5598(10)	.8643(10)	.4190(6)	.041(5)	.053(6)	.041(5)	−.019(5)	−.009(4)	.003(4)
C12	.5180(10)	.9440(9)	.3398(5)	.044(5)	.041(5)	.034(5)	−.019(4)	−.005(4)	.004(4)
C13	.6598(10)	.9284(9)	.2875(5)	.045(5)	.044(6)	.032(5)	−.021(5)	−.007(4)	.002(4)
C14	.6997(10)	.9828(10)	.2034(5)	.048(5)	.052(6)	.032(5)	−.029(5)	.001(4)	−.001(4)
C15	.5916(11)	1.1159(11)	.1662(6)	.048(6)	.058(6)	.040(5)	−.029(5)	−.005(4)	.005(5)
C16	1.0705(10)	.6825(10)	.3448(6)	.036(5)	.040(5)	.048(5)	−.014(4)	−.004(4)	.000(4)
C17	1.1948(11)	.7171(11)	.3501(6)	.051(6)	.058(7)	.066(7)	−.029(5)	−.017(5)	.011(5)
C18	1.3117(12)	.6273(12)	.3959(7)	.054(6)	.066(8)	.089(8)	−.030(6)	−.034(6)	.017(6)
C19	1.3104(12)	.5017(12)	.4327(7)	.050(6)	.062(7)	.056(6)	−.013(5)	−.015(5)	.009(5)
C20	1.1893(12)	.4681(12)	.4249(6)	.053(6)	.066(7)	.051(6)	−.019(6)	−.004(5)	.016(5)
C21	1.0709(11)	.5569(10)	.3828(6)	.057(6)	.048(6)	.052(6)	−.028(5)	−.002(5)	.007(5)
C22	.3552(10)	1.0077(10)	.3270(5)	.040(5)	.052(6)	.034(5)	−.024(5)	−.003(4)	.002(4)
C23	.2236(11)	1.0725(11)	.3982(6)	.045(6)	.063(7)	.039(5)	−.024(5)	−.008(4)	.008(5)
C24	.0663(11)	1.1325(11)	.3887(6)	.043(6)	.077(7)	.042(5)	−.029(5)	.003(4)	−.007(5)
C25	.0393(10)	1.1251(11)	.3051(6)	.042(6)	.068(7)	.049(6)	−.030(5)	−.008(4)	.005(5)
C26	.1656(11)	1.0619(11)	.2323(6)	.057(6)	.070(7)	.039(5)	−.034(6)	−.011(5)	.005(5)
C27	.3213(10)	1.0037(10)	.2438(5)	.044(5)	.062(6)	.035(5)	−.029(5)	.000(4)	−.003(4)
C28	−.2456(12)	1.2277(15)	.3599(8)	.043(6)	.132(11)	.073(8)	−.018(7)	−.011(6)	−.024(8)
C29*	.1853(26)	.5398(28)	.8561(16)	.164(19)	.259(26)	.272(27)	−.056(19)	−.040(18)	−.210(24)
O1	.9146(7)	.9438(8)	.0830(4)	.048(4)	.092(5)	.033(4)	−.027(4)	.004(3)	.020(3)
O2	1.1295(8)	.7660(8)	.1671(4)	.043(4)	.090(6)	.050(4)	−.025(4)	.000(3)	.007(4)
O3	.7268(7)	.7983(7)	.4093(4)	.044(4)	.062(4)	.036(3)	−.021(3)	−.008(3)	.015(3)
O4	.4799(7)	.8473(8)	.4832(4)	.051(4)	.081(5)	.043(4)	−.033(4)	−.003(3)	.023(3)

Table 2. Continued.

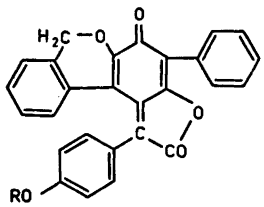
O5	−.1092(7)	1.1746(8)	.2866(4)	.041(4)	.096(6)	.059(4)	−.030(4)	−.015(3)	.005(4)
Cl1*	.1364(7)	.6432(8)	.9447(5)	.163(5)	.209(6)	.237(7)	−.043(5)	−.064(5)	−.069(6)
Cl2*	.0409(11)	.5298(9)	.8232(7)	.364(11)	.238(8)	.434(13)	−.169(8)	−.270(11)	.027(8)
Cl3*	.3660(9)	.4080(8)	.8194(6)	.209(7)	.181(7)	.331(10)	−.040(6)	.032(7)	−.103(7)

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
H1	.435(8)	1.236(8)	.272(4)	.048(21)	H10	1.181(11)	.377(10)	.456(6)	.097(33)
H2	.273(13)	1.464(13)	.223(7)	.147(44)	H11	.997(7)	.523(7)	.372(4)	.037(19)
H3	.362(9)	1.464(9)	.057(5)	.075(27)	H12	.237(10)	1.055(10)	.447(6)	.089(30)
H4	.609(10)	1.275(10)	−.017(6)	.086(30)	H13	−.021(9)	1.172(9)	.440(5)	.065(25)
H5	.842(9)	1.032(9)	−.023(5)	.076(27)	H14	.152(9)	1.056(8)	.167(5)	.061(24)
H6	.798(8)	.895(7)	.013(4)	.040(20)	H15	.411(10)	.955(9)	.188(5)	.076(27)
H7	1.173(11)	.830(10)	.335(6)	.107(34)	H16	−.217(10)	1.137(10)	.403(6)	.091(31)
H8	1.403(12)	.640(11)	.400(6)	.115(36)	H17	−.345(11)	1.272(10)	.325(6)	.097(32)
H9	1.393(10)	.432(10)	.472(6)	.085(29)	H18	−.260(9)	1.304(9)	.398(5)	.063(24)

* Atomic coordinates and thermal parameters of the chloroform solvent atoms. The hydrogen atom of the chloroform molecule could not be located.

the benzene rings C16−C21 and C22−C27 are not parallel with the central fragment for steric reasons.

An important feature in the structure of a related molecule, peniophorinin,[3] is the order of the oxygen atom and the CH_2-group in the pyran ring. The order in the present molecule was found reversed to that of peniophorinin.



4 R = H

5 R = CH_3

The structure of xylerythrinin methyl ether is thus *5*, and hence *4* represents the structure of xylerythrinin, the systematic name being 1-(*p*-hydroxyphenyl)-4-phenyl-7*H*-benzofuro[5,4-*c*][2]benzopyran-2,5-dione. Xylerythrinin is thus not a desoxypeniophorinin, but can be regarded as a dehydrogenated 5-*O*-methylxylerythrin (*2*), a compound also produced by the fungus.[1] Evidently the order in which the pyran ring is incorporated into the ring systems represented by xylerythrinin and peniophorinin has very little influence on the UV-spectra.

EXPERIMENTAL

For analytical details see Ref. 6.

Isolation of xylerythrinin. The combined mother liquors from several preparations of xylerythrin[1] were chromatographed on silica gel with chloroform as eluent. Fractions showing on TLC a spot a little below that of xylerythrin were combined and rechromatographed. Those fractions where this spot was clearly stronger than that of xylerythrin were again combined and most of the solvent evaporated. Upon addition of benzene, *xylerythrinin* was obtained as dark red, almost black crystals, m.p. 273−275 °C. IR: 3290, 1780, 1615, 1595, 1575, 1505, 1270, 1220, 1195, 1145, 1130, 750 cm^{-1}. UV(dioxane): λ_{max} 273(4.39), 365(3.88), 437(4.29); λ_{min} 249(4.17), 329(3.78), 380(3.85) nm(log ε). ^1H NMR ($CDCl_3$): δ 5.20 (2 H, s), 5.50 (1 H, s; exch. D_2O), 6.50−7.50 (13 H, m).

Xylerythrinin methyl ether was obtained by methylation of xylerythrinin (30 mg) with methyl iodide and potassium carbonate in DMF. Final purification was achieved by preparative TLC ($CHCl_3$ as eluent) giving red crystals with m.p. 224−226 °C. Anal. $C_{28}H_{18}O_5$: C, H. IR: 1770, 1640, 1595, 1505, 1260, 1150, 1135, 765 cm^{-1}. UV(dioxane): λ_{max} 272(4.46), 367(3.94), 433(4.33); λ_{min} 248(4.22), 332(3.81), 377(3.90) nm(log ε). ^1H NMR ($CDCl_3$): δ 3.78 (3 H, s), 5.24 (2 H, s), 6.60−7.60 (13 H, m).

Xylerythrinin acetate. Xylerythrinin (30 mg) was acetylated with acetic anhydride and a drop of pyridine. After 2 h at room temperature the mixture was poured onto ice. The acetate was purified by preparative TLC (NaH_2PO_4-impregnated plate; eluent $CHCl_3$) and recrystallized from chloroform/methanol, m.p. 216−217 °C. Anal. $C_{29}H_{18}O_6$: C, H. IR: 1760−1770, 1645, 1630, 1195, 1180, 1155, 1135, 930,

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

1	1.396(14)	20	1.381(10)
2	1.393(17)	21	1.215(11)
3	1.368(14)	22	1.489(12)
4	1.373(15)	23	1.403(17)
5	1.519(11)	24	1.405(15)
6	1.456(13)	25	1.386(18)
7	1.354(11)	26	1.376(19)
8	1.485(13)	27	1.374(14)
9	1.482(13)	28	1.388(15)
10	1.342(12)	29	1.199(11)
11	1.388(10)	30	1.455(13)
12	1.409(11)	31	1.405(11)
13	1.488(12)	32	1.390(14)
14	1.387(13)	33	1.385(14)
15	1.456(12)	34	1.394(11)
16	1.465(12)	35	1.388(14)
17	1.382(12)	36	1.403(13)
18	1.474(12)	37	1.373(12)
19	1.420(13)	38	1.450(12)
1,2	119.7(8)	14,16	133.7(8)
1,20	120.5(8)	14,30	133.1(8)
2,3	120.6(11)	15,16	118.5(8)
3,4	120.0(10)	16,17	114.7(7)
4,5	124.2(8)	16,18	126.2(7)
4,19	120.8(8)	17,18	118.3(8)
5,6	110.7(8)	18,19	116.1(7)
5,19	115.0(8)	18,20	124.7(8)
6,7	113.0(8)	19,20	118.3(8)
7,8	112.3(7)	22,23	119.0(9)
7,17	121.9(8)	22,28	122.6(10)
8,9	117.2(7)	23,24	119.3(10)
8,17	125.5(8)	23,28	118.4(9)
8,21	120.2(8)	24,25	121.3(12)
9,10	115.8(8)	25,26	118.3(10)
9,21	122.5(8)	26,27	121.4(11)
9,22	120.9(7)	27,28	121.3(12)
10,11	123.3(8)	30,31	121.5(8)
10,15	127.1(8)	30,36	121.9(7)
10,22	123.3(8)	31,32	123.2(9)
11,12	107.7(6)	31,36	116.5(8)
11,15	109.6(7)	32,33	118.0(7)
12,13	108.3(7)	33,34	121.1(9)
12,29	119.6(8)	33,37	124.2(7)
13,14	106.5(7)	34,35	119.6(9)
13,29	132.1(8)	34,37	114.6(9)
13,30	120.2(8)	35,36	121.6(7)
14,15	107.8(7)	37,38	117.9(8)

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

C29–Cl1	1.590(27)	Cl1–C29–Cl2	115.8(13)
C29–Cl2	1.613(32)	Cl1–C29–Cl3	122.3(18)
C29–Cl3	1.627(20)	Cl2–C29–Cl3	118.5(17)

775 cm^{-1}. UV(dioxane): λ_{max} 265(4.37), 397(4.33), 480 sh(3.03); λ_{min} 242(4.18), 331(3.78) nm (log ε). ^1H NMR ($CDCl_3$): δ 2.27 (3 H, s), 5.23 (2 H, s), 6.40–7.60 (13 H, m).

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