

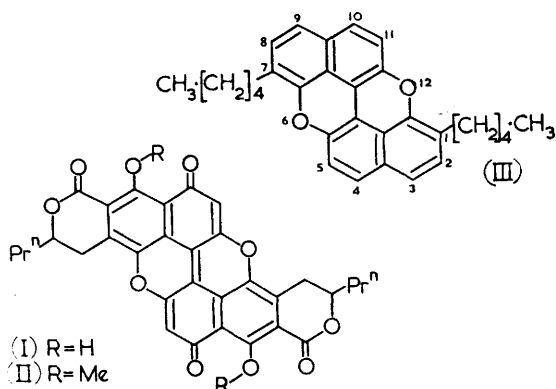
The Structure of Xylindein

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XYLINDEIN, the green pigment of *Chlorociboria aeruginosa* (formerly described as *Peziza aeruginosa* or *Chlorosplenium aeruginosum*) was first isolated from wood infected with the fungus¹ but is more conveniently obtained from *C. aeruginosa* cultures grown on a cellulose base in aqueous malt extract. Xylindein was investigated by Kögl and his co-workers who assigned² to it a formula $C_{34}H_{26}O_{11}$ but were unable to determine its structure although they established³ the existence in the molecule of two lactone groupings and an extended quinone system.

We have evidence that the pigment as obtained by simple extraction either of cultures or of the infected wood is not as a rule homogeneous, the major component, for which we retain the name xylindein, being accompanied by smaller amounts of closely related substances whose presence may account for some of the difficulties experienced by earlier workers. The molecular weight of xylindein obtained by extracting the culture mycelium with phenol was found by mass spectrometry to be 568—570 (quinone-quinol) and this, together with the analytical values for xylindein derivatives, accords best with a formula $C_{32}H_{20}O_{10}$. As a result of our investigations we now propose structure (I) for xylindein.



Xylindein shows infrared bands at 1720 and 1625 cm^{-1} which we assign, respectively, to the two identical $\alpha\beta$ -unsaturated δ -lactone groupings and a hydrogen-bonded extended quinone system. It contains two hydroxyl groups [diacetate, dimethyl ether

(II)] which appear to be situated *peri* to the quinone carbonyl group (boroacetate reaction and infrared absorption). The light-absorption curve of xylindeol dimethyl ether, the product of reduction of the ether (II) with lithium aluminium hydride, has maxima at 563, 522, and 490 $m\mu$. The close similarity in form between this spectrum and that of *peri*-xanthoxanthene-4,10-quinone⁴ (λ_{max} , 522, 484, and 451 $m\mu$) strongly supports the view that the central chromophore of xylindein is that of 3,9-dihydroxy-*peri*-xanthoxanthene-4,10-quinone. Moreover, zinc-dust distillation of tetra-*O*-acetyldihydro-xylindein yields a yellow, crystalline product shown by high-resolution mass spectrometry⁵ to be either 1,7-din-pentyl-*peri*-xanthoxanthene (III) or the 5,11-isomer; of these, only the former is compatible with the chemical behaviour of xylindein. Further support is found in a comparison of the light absorption of the zinc dust distillation product (λ_{max} , 444, 416, 391, and 368 $m\mu$) with that of *peri*-xanthoxanthene (λ_{max} , 439.5, 412, 389, and 368 $m\mu$).

Kögl considered that xylindein contained two enolic lactone groupings, but the dominant mass peak at 568 in the mass spectrum of xylindein and the absence of ketonic infrared absorption in chromatographically pure xylindeic acid dimethyl ester indicate that they are saturated. Chromic acid oxidation of xylindein gives 1.3—1.5 mol. of volatile acid containing *n*-butyric acid as major component with only minor amounts of propionic and acetic acid. Clearly the *n*-butyric acid must originate in that part of the xylindein molecule which yields the *n*-pentyl group in the degradation product (III), and its production thus indicates that in xylindein there are two 3,4-dihydro-3-*n*-propylisocoumarin systems. The absence of infrared absorption corresponding to a phenol acetate grouping in the acetate of dihydro-3,4,9,10-tetra-*O*-methylxylindeol (ν_{max} , 1732 cm^{-1}) shows that the lactone systems cannot be of the dihydrocoumarin type and the change in the 340 $m\mu$ region of the absorption spectra of xylindein derivatives on reduction of the lactone groupings is evidence for the attachment of the carbonyl groups in them to the chromophore. We regard the lactones, therefore, as being of the dihydroisocoumarin type and formulate xylindein as (I).

¹ Döbereiner, *Schweiggers Journal*, 1813, 9, 160; Rommeir, *Compt. rend.*, 1868, 60, 108; Liebermann, *Ber.*, 1874, 7, 1102.

² Kögl and von Taucffenbach, *Annalen*, 1925, 445, 170.

³ Kögl and Erxleben, *Annalen*, 1930, 484, 65.

⁴ Pummerer, Rieche, von Krudener, Pfeiffer, Prell, Tuchmann, and Wilsing, *Annalen*, 1933, 503, 40.

⁵ Benyon, Proc. Xth Colloquium Spectroscopium Internationale, Maryland, 1962.

The structure can be built up from two acetate-derived naphthalene units and a successful model coupling of units of this type will be reported later.

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The Free-radical Reactions of Co-ordination Compounds: Pentane-2,4-dione Chelates

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SOME ionic substitutions of pentane-2,4-dione chelates have been reported;¹ we now relate some results on the free-radical reactions of the organic portions of these compounds, involving hydrogen-atom abstraction; both the ease of carbon-hydrogen bond breaking and the structure of the intermediate radicals have been determined.

When *t*-butyl peroxide is heated in a substrate, the *t*-butoxy-radicals obtained either abstract a hydrogen atom to form *t*-butyl alcohol or decompose to acetone and a methyl radical. Thus the alcohol : acetone ratio indicates the strength of the carbon-hydrogen bond being broken.²

Such measurements on a number of pentane-2,4-dione chelates and other compounds in bromobenzene (see Table) show the great effect of the structure of the chelates and the properties of the metal. The rate ratios from the substituted toluenes were used to determine the Hammett³ ρ value for the reaction (-0.77). The Hammett³ m - σ values for the chelate rings were calculated from this ρ value, and these are also listed in the Table.

Correlation of the rates with such properties of the metals as electronegativity, ionisation potential, ionic radius, and ligand-field effect shows that the rates increase with the increasing energy of the metal-oxygen bond. The increase of rate with increasing number of *d*-electrons of the metal ion suggests that the back-donation of electrons from the metal to the organic ligand is very important in determining the relative reactivities. This is true because the more reactive the chelate the greater the electron density at the site of the radical reaction.⁴

The studies on the site of attack with a *t*-butoxy-radical have shown that a hydrogen atom is abstracted from the 1-position of the chelate (from a methyl group). It had been previously found that a hydrogen atom is abstracted from the 3-position of unco-ordinated pentane-2,4-dione under the same conditions.⁵ Thus, co-ordination changes the site of radical attack. The intermediate chelate radical has been found to add to other intact chelate molecules

Reactivities and Hammett σ values of chelates and some aromatic compounds

Compound	Rate ratios*	m - σ values†
Pentane-2,4-dione	5.00	—
Na(C ₅ H ₇ O ₂)‡	0.515	+0.681
Mg(C ₅ H ₇ O ₂) ₂	8.85	-0.528
Cr(C ₅ H ₇ O ₂) ₃	5.70	-0.053
Co(C ₅ H ₇ O ₂) ₃	27.9	-0.947
Mn(C ₅ H ₇ O ₂) ₃	11.6	-0.455
Fe(C ₅ H ₇ O ₂) ₃	6.54	-0.130
Al(C ₅ H ₇ O ₂) ₃	5.62	-0.043
Cu(C ₅ H ₇ O ₂) ₂	21.0	-1.02
Be(C ₅ H ₇ O ₂) ₂	31.8	-1.25
Ni(C ₅ H ₇ O ₂) ₂	9.14	-0.548
Co(C ₅ H ₇ O ₂) ₂	4.59	-0.157
Zn(C ₅ H ₇ O ₂) ₂ ‡	2.76	+0.125
Mn(C ₅ H ₇ O ₂) ₂	19.7	-0.981
Cu(C ₅ H ₆ O ₂ -3-Me) ₂	77.7	—
Cu(C ₃ H ₆ ClO ₂) ₂	45.1	—
Cr(C ₃ H ₃ O ₂) ₃	10.1	—
Toluene	1.55	—
<i>m</i> -Xylene	1.73	0.000
<i>p</i> -Bromotoluene	1.01	—
<i>p</i> -Tolunitrile	0.507	—

* Calc. from the ratios of *t*-butyl alcohol : acetone obtained.

† Corr. for the no. of chelate rings.

‡ Min. values because of poor solubility in bromobenzene.

in the 3-position; therefore, the product obtained after hydrolysis of the reaction mixture is the 1,3'-dimer; 3-acetyloctane-2,5,7-trione. It was determined that the best method of hydrolysis was by using an ion-exchange resin. The authentic dimer was prepared by the reaction of 1-bromopentane-2,4-dione and the sodium salt of pentane-2,4-dione. It was also synthesised from the 1,3-dipotassio-derivative of pentane-2,4-dione and 3-chloropentane-2,4-dione.⁶

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¹ For a review see Collman and Kittleman, *Inorg. Chem.*, 1962, 1, 499.

² Williams, Oberright, and Brooks, *J. Amer. Chem. Soc.*, 1956, 78, 1190.

³ Jaffe, *Chem. Rev.*, 1953, 53, 191.

⁴ Russell, *J. Org. Chem.*, 1958, 23, 1407.

⁵ Gritter, Ph.D. Dissertation, University of Chicago, 1955.

⁶ Hauser and Harris, *J. Amer. Chem. Soc.*, 1958, 80, 6360.