

A REVISED STRUCTURE FOR PLUMBAZEYLANONE

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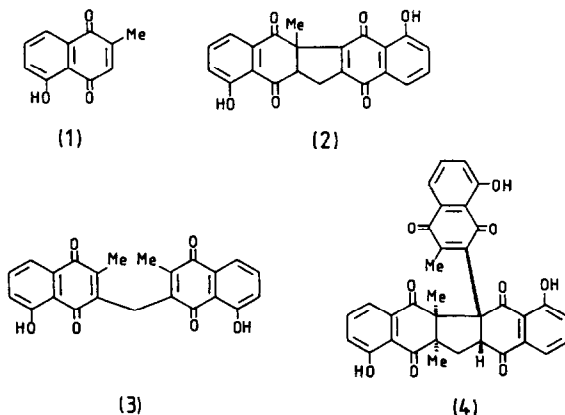
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Abstract: The structure of plumbazeylanone has been revised, by X-ray crystallography, to 1,2,3,4-tetrahydro-5-hydroxy-1,4-diketo-2-methyl-2,3-di(5'-hydroxy-2'-methyl-1,4-naphthoquinon-3'-yl)naphthalene.

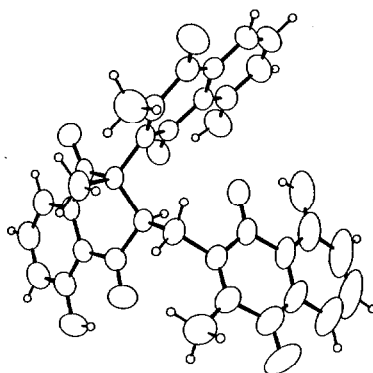
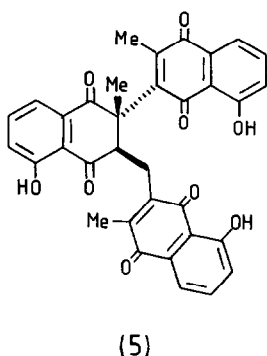
Plumbago zeylanica (Plumbaginaceae) produces plumbagin (1) and several related quinones¹ including, in particular, the dimers zeylanone (2),² and methylene-3,3'-biplumbagin (3)³ which contains an additional carbon atom.

Earlier, we reported⁴ the isolation of plumbazeylanone (4), a plumbagin trimer containing an additional carbon atom and, like (2), optically inactive. The structure suggested was



based on spectroscopic data, analogy with (2), and a possible mode of biosynthesis, and we added "final elucidation of the structure is being sought by X-ray analysis".

Plumbazeylanone decomposes on sublimation,⁵ one product being plumbagin (1). Another has now been identified as (3) which immediately cast doubt on structure (4) and made X-ray analysis even more desirable. Plumbazeylanone crystallises easily but the crystals are usually disordered. After many trials it was eventually found that suitable crystals could be obtained by very slow crystallisation from toluene. Subsequent X-ray crystallographic analysis then revealed that plumbazeylanone has the linear trimeric structure (5). A perspective drawing is shown below.



The plumbazeylanone-toluene solvate, $C_{34}H_{24}O_9 \cdot C_7H_8$, crystallises in the triclinic space group $P\bar{1}$ with cell dimensions $a = 9.489(6)$, $b = 13.020(13)$, $c = 14.773(22)$ Å, $\alpha = 96.22(10)^\circ$, $\beta = 98.60(9)^\circ$, $\gamma = 113.15(6)^\circ$ and $Z = 2$. The X-ray intensities were measured with Mo-K α radiation on a four-circle diffractometer. The crystal structure was solved by MITHRIL⁶ and refined with SHELX.⁷ Final R is for 0.075 for 4844 reflexions.

¹ R.H. Thomson, Naturally Occurring Quinones III, Chapman and Hall, London, 1987.

² A.V.B. Sankaram and A.S. Rao, Tetrahedron, 1979, **35**, 1777.

³ G.M.K.B. Gunaherath, A.A.L. Gunatilaka, and R.H. Thomson, J.C.S. Perkin Trans. 1, in the press.

⁴ G.M.K.B. Gunaherath, A.A.L. Gunatilaka, and R.H. Thomson, Tet. Lett., 1984, **25**, 4801.

⁵ Plumbazeylanone in a tube maintained at 4.5 mm Hg was inserted into a preheated chamber at 240°C and left for 5 min.

⁶ C.J. Gilmore, J. Appl. Crystallogr., 1984, **17**, 42.

⁷ G.M. Sheldrick, 'SHELX, A Program for Crystal Structure Determinations', University of Cambridge, 1976.

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