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TRIANELLINONE, A NOVEL NATURAL TRIQUINONE

R.G.Cooke, J.G.Down*
Department of Organic Chemistry, University of Melbourne,
Parkville, Australia, 3052.

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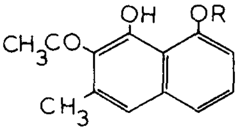
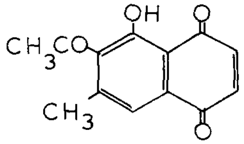
Previous chemical investigations of plants in the sub-tribe Dianellinae have revealed the presence of a family of naphthols and naphthoquinones[1,2]. These are dianellin (I,R=biose), dianellidin (I,R=H), stypandrone (II), and dianellinone (III).



I



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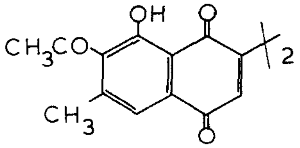
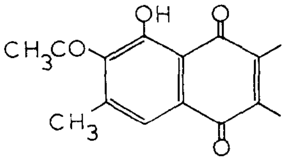


III

Further fractionation of the benzene extracts of Dianella revoluta has yielded a new pigment, trianellinone. This is an orange-yellow solid decomposing without melting above 300°C. It shows λ_{max} (EtOH) 228, 280, 410 mμ (c.f. dianellinone 223, 275(sh), 429 mμ, in dioxan). The n.m.r. spectrum (in CF_3COOH) consists of three singlet absorptions at 2.25, 7.10 and 7.43 τ , of relative intensity 1 : 3 : 3 (c.f. dianellinone 2.24, 2.64, 7.16 and 7.49 τ , relative intensity 1 : 1 : 3 : 3). These data suggest a structural unit (IV) in which both positions of the quinone ring are substituted.



IV

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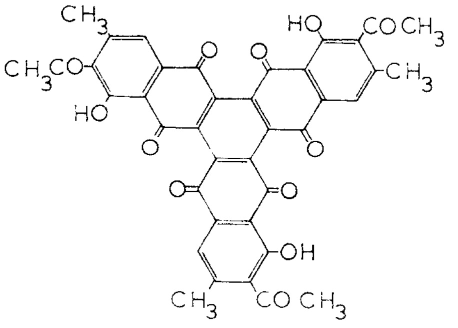
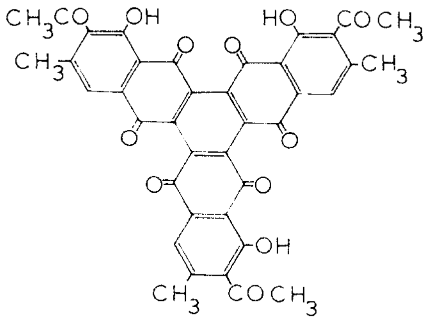
* Present address : Pharmacology Department, South Parks Rd., Oxford, England.



V



VI

Mass spectrometry gives the molecular weight 684.130 (= $C_{39}H_{24}O_{12}$). This indicates three units of type (IV), which may be arranged in either of two ways to form the regular structure (V), or the irregular structure (VI). The pigment forms a trimethyl ether (M.Wt. = 726 by mass spectrometry), the spectroscopic properties of which are consistent with structures (V) or (VI) for trianellinone. There was no evidence of any rearranged product as is found on normal methylation of dianellinone[2] or diospyrin[3]. The n.m.r. spectrum of this derivative (in CF_3COOH) shows methoxyl absorption peaks at 5.76 and 5.78 τ , of relative intensity 1 : 2. Similarly the n.m.r. spectrum of trianellinone recorded in $CDCl_3$ shows two absorptions for H-bonded hydroxyl groups at -1.74 and -1.64 τ , again with relative intensity 1 : 2 . These observations indicate the irregular structure (VI), because all like substituents would be identical in regular structure (V).

Triphthaloylbenzene was prepared by the method of Scoll *et.al.*[4] and was found to exhibit carbonyl absorption at 5.95 μ , in close agreement with that for trianellinone. Finally the same synthetic method was adapted to prepare the pigment from a mixture of stypandrone and dianellinone. It was necessary to employ a nitrogen atmosphere because both quinones are sensitive to oxygen in basic solutions. The synthetic pigment was isolated by preparative thin layer chromatography and proved identical with trianellinone.

Trianellinone is unlikely to be an artefact arising from the coexistence of stypandrone and dianellinone in the one extract. *Stypandra grandis* has yielded both stypandrone and dianellinone but no trianellinone, while *Dianella revoluta* has yielded dianellinone and trianellinone but no stypandrone. A mixture of stypandrone and dianellinone generated no trianellinone after two weeks boiling under reflux in benzene.

References

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