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DIANELLIDIN, STYPANDROL AND DIANELLINONE: AN OXIDATION-RELATED SERIES FROM *DIANELLA REVOLUTA*

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Key Word Index—*Dianella revoluta*; Liliaceae; Blue-flax lily; naphthols; binaphthols; binaphtho-1,4-quinones; dianellidin; stypandrol; dianellinone.

Abstract—Dianellidin, stypandrol and dianellinone were isolated from *Dianella revoluta* and were considered with respect to their biosynthetic relationship and to the toxicity of *Stypandra imbricata*.

INTRODUCTION

Dianella revoluta R.Br. (Blue-flax lily) is a member of the Liliaceae and is widespread in Australia. All species of *Dianella* have stiff, grass-like leaves and panicles of blue flowers followed by deep-blue fruits. Several species of *Dianella* have been suspected of causing poisoning in livestock and physiological disturbances in man when ingested [1].

Dianella revoluta has previously been investigated and found to contain the 2,2'-binaphtho-1,4-quinone, dianellinone (1) and the related triquinone, trianellinone (2) [2, 3]. It has been suggested that binaphtho-1,4-quinones such as dianellinone (1) and the related mamegakinone (3) (isolated from species of *Diospyros* [4]) are biogenetically derived from the respective naphthalene-diols (4) and (5) via oxidative coupling to the binaphthalene-tetrols (6) and (7) [2, 5]. The isolation of the three related title compounds 4, 6 and 1 from one plant source lends support to the biosynthetic postulations.

RESULTS AND DISCUSSION

The naphthalene-1,8-diol, dianellidin (4), the proposed precursor to dianellinone (1) has also been suggested as a possible precursor to non-acetylated analogues following initial oxidative de-acetylation to form the naturally occurring quinone, plumbagin (8) [6].

Dianellidin (4) has been isolated from many plant sources [6–8] including *Maesopsis eminii* where it was called musizin [9]. It has not previously been isolated from *Dianella revoluta* which led Cooke *et al.* [2] to suggest the importance of the biosynthetic steps which utilise dianellidin or its glycosides in the formation of stypandrone (9) and dianellinone (1).

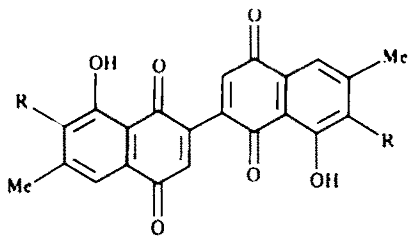
Recently, both dianellidin (4) and the postulated product of oxidative coupling, the binaphthalene-tetrol, stypandrol (6) were isolated from toxic specimens of *Stypandra imbricata* [10]. With occurrences restricted to south-west Australia, *Stypandra imbricata* is colloquially referred to as 'blind-grass'. It is also a member of the Liliaceae and ingestion of the toxic plant by livestock leads to a number of clinical and pathological effects culminating either in death or blindness [11, 12]. The toxic effects of *Stypandra imbricata* have been shown to be caused by the binaphthalene-tetrol, stypandrol (6).

In the analogous oxidation-related series of compounds 5, 7 and 3 from *Diospyros* species, it is also the binaphthalene-tetrol which is biologically active. In this case, diospyrol (7) demonstrates anthelmintic activity [13].

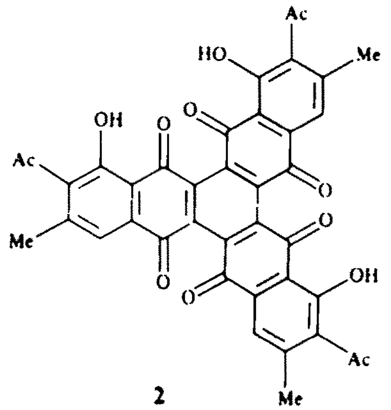
Chloroform extracts of dried roots from *Dianella revoluta* have now yielded dianellidin (4) and stypandrol (6) as well as the previously isolated dianellinone (1). The extracts and subsequent chromatographic fractions are readily screened for the presence of these compounds by TLC. Exposure of developed plates ($CHCl_3$–EtOH, 9:1) to iodine vapour immediately visualizes the pale yellow dianellidin and stypandrol as persistent, grey coloured spots (R_f 0.9 and 0.1 respectively). Subsequent exposure to ammonia vapour or spraying with 1 M aqueous sodium hydroxide readily visualizes the dianellinone as a purple spot (R_f 0.7).

Following TLC identification each of the three compounds was isolated by flash column chromatography [14] and the melting points and spectroscopic properties compared to authentic samples and literature reports. Also, the product obtained on acetylation of the sample of stypandrol (6) from *Dianella revoluta* was exactly the same as the tetra-acetate of an authentic sample of stypandrol obtained from *Stypandra imbricata*.

Dianellidin (4) and dianellinone (1) have been found in appreciable quantities in *Dianella revoluta* (0.02% and 0.03% yields respectively) whereas stypandrol has only been found in very small amounts (< 0.001%). This may indicate that the oxidation of stypandrol (6) to dianellinone (1) is a favoured, rapid reaction within the biosynthetic scheme. If this reaction is blocked then a build-up of the toxic stypandrol (6) might be expected. Such a mechanism may be responsible for the toxicity of this plant as well as *Stypandra imbricata*. Indeed, from toxic samples of *Stypandra imbricata*, stypandrol (6) is isolated in much higher yields (0.02%) whereas dianellinone (1) has not yet been detected. However, in non-toxic samples of *Stypandra imbricata*, only dianellinone (1), and not dianellidin (4) or stypandrol (6), has been isolated. The factors which may affect the further metab-



R	
1	Ac
3	H



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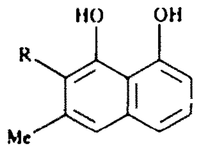
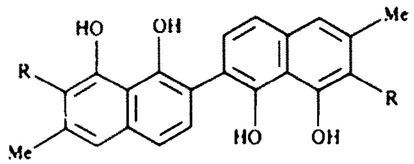
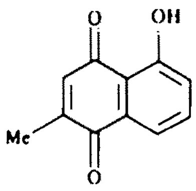


R	
4	Ac
5	H



R	
6	Ac
7	H



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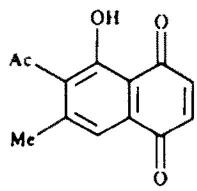

9

olism of stypandrol (**6**) to the non-toxic dianellinone (**1**) are currently being investigated.

EXPERIMENTAL

Dianella revoluta was collected from various localities around Perth, Western Australia and was authenticated by the Western Australian Herbarium. The 80 MHz ^{1}H and 20.1 MHz ^{13}C NMR and mass spectra were recorded at the Organic Chemistry Department of the University of Western Australia. Kieselgel 60G (Merck) and Kieselgel 60 (Merck) were used as adsorbents for TLC and flash CC respectively. Light petroleum used in chromatography refers to the fraction of br 60–80°.

Extraction of Dianella revoluta. The dried, milled roots of *Dianella revoluta* (300 g) were exhaustively extracted at room temp. by percolation of $CHCl_3$ through a column of the plant material. Evaporation of the solvent afforded a red solid mixture (*ca* 3 g). The total extract was adsorbed on silica gel and flash chromatographed using light petroleum and $CHCl_3$ as the eluents. Dianellidin (**4**) was obtained using light petroleum–20% $CHCl_3$ the eluent. The yellow crystals were readily sublimable (*ca* 90°/10 min) mp 161–162°, lit. [6] mp 164°, 0–0.02% yield. Dianellinone (**1**) was obtained using 40% $CHCl_3$ in light petroleum as the eluent. Recrystallization from $CHCl_3$–Et_2O

afforded orange needles which decomposed without melting from 265 to 350°, lit. [2] mp 285–295°, 0.03% yield. Stypandrol (6) was obtained as a diffuse band using $CHCl_3$ as the eluent. Recrystallization from $CHCl_3$ afforded the stypandrol as very small orange needles, mp 265–266° (dec.), < 0.001% yield. Acetylation of stypandrol was as previously reported [10] affording colourless needles of stypandrol-tetraacetate, mp 241-242°. The spectroscopic properties of dianellidin (4), dianellinone (1) and stypandrol (6) were identical to literature reports [2, 6, 10].

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