

## The Structure of Isopannarin

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### Abstract

The structure proposed by Yosioka for the product obtained by the treatment of the depsidone pannarin (2-chloro-3-hydroxy-8-methoxy-1,6,9-trimethyl-11-oxo-11*H*-dibenzo[*b,e*][1,4]dioxepin-4-carbaldehyde) (2) with concentrated sulfuric acid is revised to 5-chloro-6-hydroxy-4'-methoxy-2',4,5'-trimethyl-3,6'-dioxo-2,3-dihydrospiro[benzofuran-2,1'-cyclohexa-2',4'-diene]-7-carbaldehyde (5).

A number of years ago we revised the structure (1), proposed by Yosioka<sup>1</sup> for the lichen depsidone pannarin, to (2).<sup>2</sup> Yosioka observed that pannarin on brief treatment with concentrated sulfuric acid underwent isomerization to a yellow product, isopannarin, for which he proposed the unusual structure (3). On methanolysis,<sup>1</sup> isopannarin yielded pannarin methoxide, previously shown to have structure (4).<sup>2</sup>

Since more pannarin has recently become available we have now repeated the work of Yosioka and are therefore able to comment on the structure of isopannarin. This compound exhibited spectroscopic properties in keeping with the linearly conjugated grisadienedione structure (5). Thus the electronic spectrum was similar to that of compounds (6) and (7).<sup>3</sup> The chemical shifts of the vinylic methyl groups in the <sup>1</sup>H n.m.r. spectrum of compound (5) were similar to those found in the spectra of compounds (6) and (7). The chemical shifts of the singlet at  $\delta$  6.77, ascribed to the dienone vinyl proton, was also in keeping with typical values for similar compounds.<sup>3</sup> The infrared spectrum (Nujol) exhibited a  $\beta$ -coumaranone carbonyl band at 1710 cm<sup>-1</sup>, a bonded aldehyde carbonyl band at 1668 cm<sup>-1</sup>, a dienone carbonyl band at 1645 cm<sup>-1</sup>, and a double bond stretching band at 1608 cm<sup>-1</sup>.

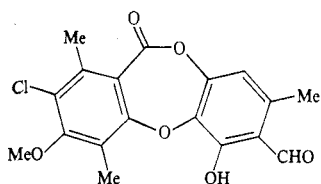
Plausible intermediates involved in the formation of the grisadienedione (5) might be the ketene (8),<sup>3</sup> or the acylium ion (9) which would undergo intramolecular *ipso*-substitution.<sup>4</sup>

<sup>1</sup> Yosioka, I., *J. Pharm. Soc. Jpn.*, 1941, **61**, 332.

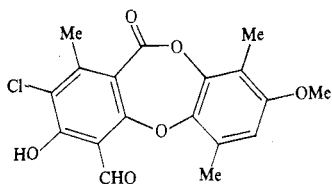
<sup>2</sup> Jackman, D. A., Sargent, M. V., and Elix, J. A., *J. Chem. Soc., Perkin Trans. I*, 1975, 1979.

<sup>3</sup> Sala, T., and Sargent, M. V., *J. Chem. Soc., Perkin Trans. I*, 1981, 855.

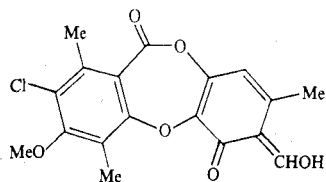
<sup>4</sup> Sargent, M. V., *J. Chem. Soc., Perkin Trans. I*, 1982, 403.



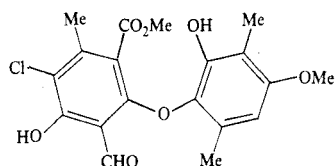
(1)



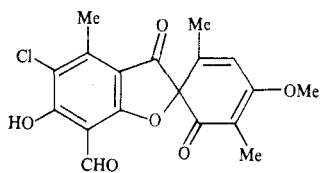
(2)



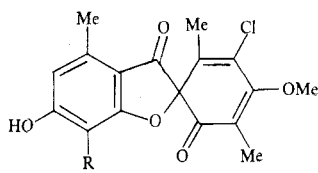
(3)



(4)

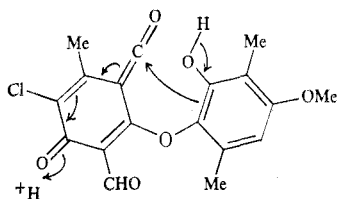


(5)

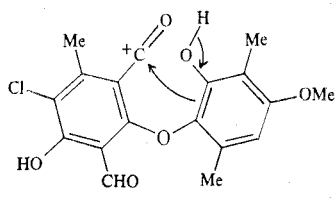


(6) R = H

(7) R = Me



(8)



(9)

## Experimental

### Extraction of *Pannaria elatior*

The lichen (9.4 g), collected in North Queensland and determined by Dr J. A. Elix in whose herbarium a specimen is lodged, was extracted in a Soxhlet apparatus with light petroleum. Removal of the solvent and crystallization of the residue from dichloromethane/light petroleum afforded pannarin (2) (350 mg) as needles, m.p. and mixed m.p. 216–217°. The  $^1\text{H}$  n.m.r. and mass spectra were identical with those of an authentic sample.

*5-Chloro-6-hydroxy-4'-methoxy-2',4,5'-trimethyl-3,6'-dioxo-2,3-dihydrospiro[benzofuran-2,1'-cyclohexa-2',4'-diene]-7-carbaldehyde (Isopannarin) (5)*

Pannarin (130 mg) was dissolved in concentrated sulfuric acid (5 ml) and the solution was stirred for 1 min and then poured onto ice. The precipitate was isolated with ethyl acetate which was washed with saturated sodium hydrogen carbonate solution, with water, and with saturated brine. The crude product crystallized from dichloromethane as yellow plates (105 mg) of *isopannarin* (5), m.p.

303–305° (dec.) [lit.<sup>1</sup> 225° (dec.)] (Found: Cl, 9.5%; M<sup>+</sup>, 362/364. C<sub>18</sub>H<sub>15</sub>ClO<sub>6</sub> requires Cl, 9.8%; M, 362/364).  $\lambda_{\max}$  (EtOH) 216, 260, 295 (infl.), 316 and 360 nm ( $\epsilon$  16900, 15400, 13200, 15700 and 6900).  $\delta$  (CD<sub>3</sub>SOCD<sub>3</sub>, 80 MHz) 1.61 and 1.79 (each 3H, s, dienone Me), 2.38 (3H, s, ArMe), 3.99 (3H, s, OMe), 6.77 (1H, s, olefinic H) and 9.89 (1H, s, CHO).

*Methyl 3-Chloro-5-formyl-4-hydroxy-6-(2-hydroxy-4-methoxy-3,6-dimethylphenoxy)-2-methylbenzoate (Pannarin Methoxide) (4)*

The grisadienedione (5) (25 mg) and sodium methoxide [from sodium (50 mg)] in dry methanol (10 ml) were heated under reflux under dry nitrogen for 2 h. Acidification and isolation with ethyl acetate gave the crude product which formed prisms (from dichloromethane/light petroleum), m.p. 197–198° (lit.<sup>2</sup> 197–198°), identical (mass and <sup>1</sup>H n.m.r. spectra) with an authentic sample.

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