

NEW SYNTHESSES OF XANTHOTOXOL AND XANTHOTOXIN¹

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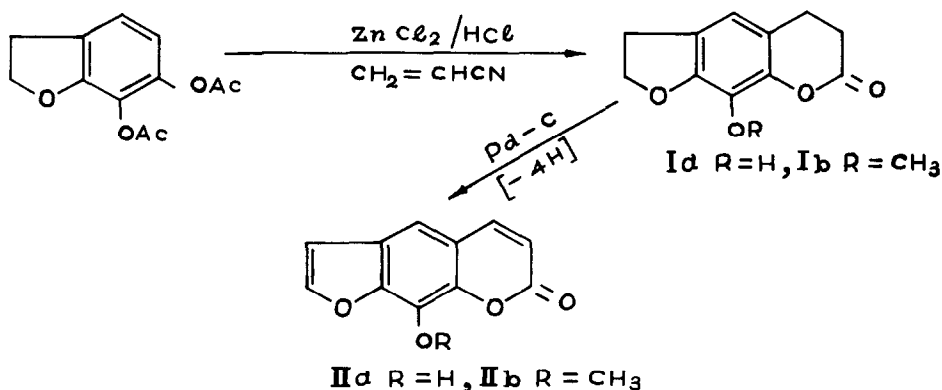
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Xanthotoxol and xanthotoxin are furocoumarins that occur in a number of indigenous plants (2). Xanthotoxin has been found to be having skin photosensitising activity, whereas xanthotoxol is practically inactive (3).

Constitution of xanthotoxin was established by Thomas (4). Synthesis of xanthotoxol was achieved by E. Späth (2a) in a poor yield. Xanthotoxin has been synthesised by various workers (5). We are reporting here new syntheses of xanthotoxol and xanthotoxin in good overall yield starting from pyrogallol by the general method developed in our laboratory (6) (1).

6,7-Diacetoxy-2,3-dihydrobenzofuran (7) was condensed with acrylonitrile using anhydrous zinc chloride and hydrogen chloride as condensing agent to produce 2,3,5,6-tetrahydroxanthotoxol Ia, which was crystallised (8) to m.p. 130-131° (benzene) (66%); ν_{\max} (Nujol) 1770 cm^{-1} (lactone). τ (CDCl_3) 7.2-6.8 (6H, m), 5.4 (2H, t, $-\text{OCH}_2-$), 3.4 (1H, s, aromatic). Ia was dehydrogenated



with palladised charcoal in boiling diphenyloxide to produce xanthotoxol IIa, which was crystallised to m.p. 245° (acetic acid) [Lit.(2a) m.p. 249°] (40%). ν_{\max} (Nujol) 1709 cm^{-1} (coumarin). $\lambda_{\max}^{\text{ethanol}}$ μ (log ϵ) 251 (4.24), 268(4.25), 308(4.08). Ia was methylated with diazomethane to 2,3,5,6-tetrahydroxanthotoxin Ib, m.p. 79° (pet.-ether) (84%). ν_{\max} (Nujol) 1770 cm^{-1} (lactone). Ib on dehydrogenation with palladised charcoal in boiling diphenyl oxide furnished xanthotoxin IIB, which was purified to m.p. 146° (benzene - pet.-ether) (45%) [Lit.(5a) m.p. 146°]. ν_{\max} (Nujol) 1718 cm^{-1} (coumarin). $\lambda_{\max}^{\text{ethanol}}$ μ (log ϵ) 218 (4.44), 249 (4.44), 299 (4.08). IIA was also methylated with diazomethane to the same product IIB.

REFERENCES AND NOTES

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8. The melting points of all compounds are uncorrected, and they have composition (C,H) in agreement ($\pm 0.3\%$) with calculated value.

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