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THE STRUCTURE OF PALASONIN

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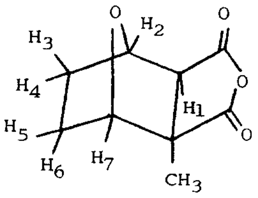
Palasonin, a principle isolated from the seeds of Butea frondosa, has been shown to be exo-cis-3,6-epoxy-1-methylhexahydrophthalic anhydride (desmethylcantharidin) (I).

Raj and Kurup (1) recently examined the seeds of Butea frondosa, an Indian tree, for anthelmintic substances and described the isolation of a compound m.p. 106-108° which they named palasonin. Elemental analysis, IR and NMR spectra, and the formation of several derivatives led them to the conclusion that palasonin had the molecular formula $C_{16}H_{22}O_6$ and possessed an orthodicarboxylic acid, a lactone, and a gem dimethyl group.

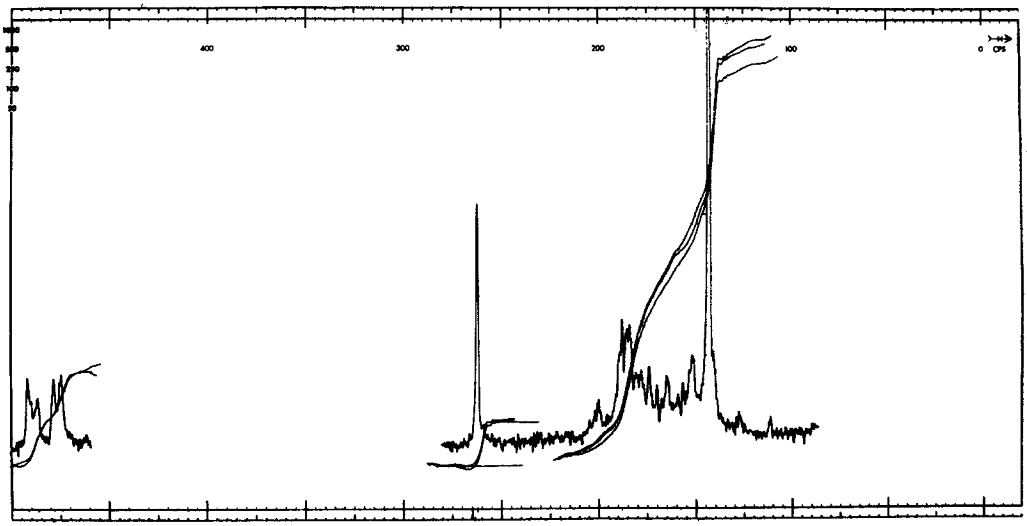
By a similar procedure we obtained a compound m.p. 109-111°. Found: C, 59.45; H, 5.32. Calc. for $C_9H_{10}O_4$: C, 59.33; H, 5.53. The IR and NMR spectra were identical to those published for palasonin. IR, 1780, 1850 cm.$^{-1}$ (anhydride), NMR (100 Mc/sec, $CDCl_3$) (Fig. 1), 1 H double doublet 5.11 τ (J_{23} 5 cps, J_{27} 1.5 cps) (O-C(H)-C(H)-), 1 H double doublet 5.24 τ (J_{75} 4 cps, J_{72} 1 cps) (O-C(H)-C(CH_3)-), 1 H singlet 7.38 τ (H-C-C=O), 4 H complex multiplet 8.35 τ (H-C(H)-C(H)-H), 3 H singlet 8.57 τ ($-CH_3$). The assignment of the smaller coupling in the doublet of doublets is not certain. Bridgehead interactions are the most probable (2,3) although a recent publication (4) claimed a 1-3 interaction, i.e. J_{25} of 1 cps, in a similar structure. The mass spectrum exhibited a molecular ion peak at m/e 182 and the expected fragmentation pattern. The exo anhydride structure was preferred for two main reasons.

(a) The methine proton H_1 appears as a singlet at 7.38τ. A model indicates an almost 90° dihedral angle between this endo proton and the adjacent proton H_2, justifying the absence of coupling.

(b) The NMR spectrum in benzene showed an 88 cps shift of the methyl protons



(I)



(FIG. 1)

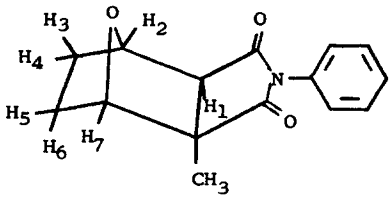
to a higher τ value over the spectrum in $CDCl_3$. Cantharadin showed a similar shift of 78 cps (5).

Optical activity was demonstrated as a small positive Cotton effect at 227 mμ. The IR, NMR and mass spectra of cantharidin closely resembled the spectra of palasonin.

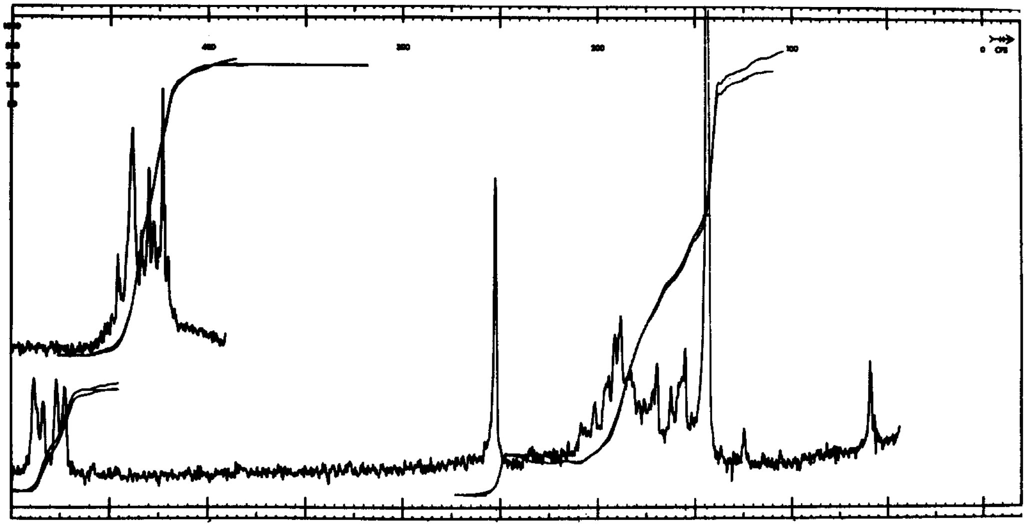
Further structural evidence was obtained from the phenylimide derivative (II) m.p. 204-205°. Found: C, 70.23; H, 5.66; N, 5.56. Calc. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. IR 1700, 1770 $cm.^{-1}$ (imide), no other carbonyl.

NMR (100 Mc/sec, $CDCl_3$) (Fig. 2), 5 H complex multiplet 2.67 τ (aromatic protons), 1 H double doublet 5.15 τ (J_{23} 5 cps, J_{27} 1.5 cps) (O-$\underset{H}{\overset{|}{C}}$-$\underset{H}{\overset{|}{C}}$-), 1 H double doublet 5.25 (J_{75} 4 cps, J_{72} 1 cps) (O-$\underset{H}{\overset{|}{C}}$-$\underset{CH_3}{\overset{|}{C}}$-), 1 H singlet 7.48 τ (H-$\underset{|}{\overset{|}{C}}$-$\overset{|}{C}$=O), 4 H complex multiplet 8.18 τ (H-$\underset{H}{\overset{|}{C}}$-$\underset{H}{\overset{|}{C}}$-H), 3 H singlet 8.57 τ (-CH_3). The mass spectrum showed a molecular ion peak at m/e 257 with a feasible fragmentation pattern.

Palasonin is of some biogenetic interest in that it is closely related to cantharidin, a vesicant principle found only in certain beetles.



(II)



(FIG. 2)

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