

New Phytoecdysones from *Dacrydium intermedium*

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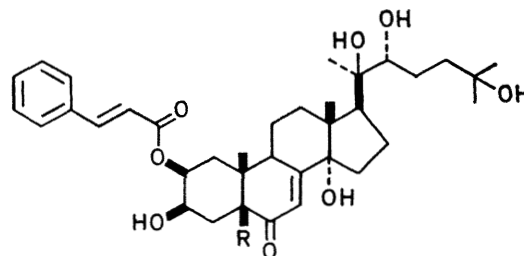
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Summary Two new phytoecdysones from *Dacrydium intermedium* are shown to be crustecdysone 2-cinnamate (I) and polypodine B 2-cinnamate (II).

THE bark of the tree *Dacrydium intermedium* Kirk. contains a remarkably high concentration of crustecdysone¹ (ca. 1%) together with smaller amounts of polypodine B² (ca. 0.3%) and related phytoecdysones now identified as crustecdysone 2-cinnamate (I) (ca. 0.1%) and polypodine B 2-cinnamate (II) (ca. 0.1%). The crude ecdysone mixture, isolated as previously described,¹ was partially separated by column chromatography on silicic acid (Mallinckrodt, 15% water) using CHCl₃-96% EtOH (19:1) as eluting solvent. The cinnamate ester fraction so obtained was finally separated by preparative t.l.c. on unactivated silica gel (Merck type HF 254) with CHCl₃-96% EtOH (9:1) as developing solvent.

Crustecdysone 2-cinnamate (I), m.p. 254–256° shows absorptions [λ_{\max} (ethanol) 276 (ϵ 21,000), 223 (19,200), 217 nm (20,100)] due to the cinnamate moiety and a shoulder absorption (248 nm) attributed to the 7-en-6-one grouping.¹ Its i.r. spectrum has absorptions (KBr) at 1700 (ester) and 1645 cm⁻¹ (ketone). In its mass spectrum ester (I) shows a weak peak at m/e 610 (M^+), further peaks at m/e 592, 574, and 556 (C₃₆H₄₄O₅ by high resolution) attributed to the loss of one, two, and three molecules of water, respectively, and intense peaks at m/e 148, 147, and 131 ascribed to cinnamic acid, cinnamoyloxy, and cinnamoyl ions, respectively. In its n.m.r. spectrum (C₅D₅N) the cinnamate ester (I) shows a signal centred at δ 7.38 due to aromatic protons (5H) and a pair of doublets at 6.60 and 7.92 (2H, J 16 Hz) which is assigned to the conjugated vinylic protons of the cinnamate moiety. The signal of the axial C-2 proton of ester (I), identified by its width at half-height (ca. 16 Hz)¹ was found to be 1.32 p.p.m. downfield from the corresponding signal of the C-2 proton of

crustecdysone and the ester group is assigned to the C-2 position. The slow rate of acetylation of ester (I) as compared with that of crustecdysone^{1,3} is also consistent with this assignment. Polypodine B 2-cinnamate (II), m.p. 268–270° has similar spectral properties to ester (I) but in its mass spectrum the highest peak identified was m/e 608 ($M - 18$).



(I) R = H
(II) R = OH

Hydrolysis of esters (I) and (II) with sodium bicarbonate in aqueous methanol gave cinnamic acid and alcohols identical with authentic crustecdysone and polypodine B, respectively. Finally, crustecdysone 2-cinnamate and polypodine B 2-cinnamate were synthesised from the authentic alcohols and cinnamoyl chloride in pyridine. Chromatography gave products identical with the natural esters in each case. In the housefly bioassay⁴ these esters showed 1/10th the moulting hormone activity of crustecdysone.

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