Structures of Hallactones A and B, Insect Toxins from *Podocarpus hallii*

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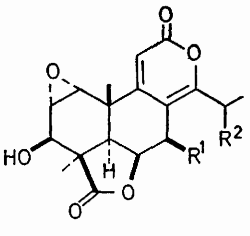
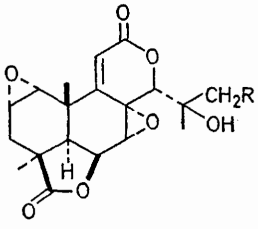
Summary Hallactones A and B, which are toxic to house-fly larvae, are shown to be the norditerpene lactones (**1**) and (**4**) respectively.

A recent communication[1] reported the isolation of nagilactone C (**2**) from leaves of *Podocarpus nivalis* Hook. and *P. hallii* Kirk as the component responsible for the mortality of house-fly larvae (*Musca domestica* L.) reared on a diet containing the plant material. Further examination of the mother liquors from the *P. hallii* extraction has yielded two new lactones with similar toxicity and we suggest structures (**1**) and (**4**), respectively, for these lactones.



(1) $R^1 = H$, $R^2 = Me$
(2) $R^1 = OH$, $R^2 = Me$
(3) $R^1 = R^2 = H$



(4) $R = SO_2Me$
(5) $R = SOMe$

Hallactone A (**1**), m.p. 266—268° (decomp.), has the formula $C_{19}H_{22}O_6$ from elemental analysis and the high resolution mass spectrum. U.v. and i.r. spectra give data consistent with the presence of an α-pyrone ring, and γ-lactone and OH groups and are similar to those recorded for nagilactones C (**2**) and D (**3**).[2] Comparison of the n.m.r. spectra of nagilactone D and hallactone A indicates that hallactone A differs only in the nature of the side chain ($2\times$ 3H doublets at δ 1·22 and 1·10, J 4 Hz). Comparison of the ring proton coupling constants confirms the relative stereochemistry of hallactone A, which is the $\Delta^{8,14}$-isomer of ponalactone A.[3]

Hallactone B (**4**), m.p. 325—330° (decomp.), has the formula $C_{20}H_{24}O_9S$ from elemental analysis. The u.v. and i.r. spectra show the usual absorptions due to $\alpha\beta$-unsaturated lactone, γ-lactone, and OH groups, and in addition the i.r. spectrum shows two strong bands (ν_{max} 1310 and 1140 cm^{-1}) characteristic of sulphones.[4] The n.m.r. spectrum of hallactone B gave peaks with chemical shifts and coupling constants similar to those recorded for the terpene sulphoxide, podolactone C (**5**),[5] and identical to those found in the spectrum of the sulphone derivative prepared from podolactone C by oxidation with *m*-chloroperoxybenzoic acid.[5] Satisfactory comparison of the natural and derived products confirmed the absolute structure of hallactone B as shown in (**4**). The mass spectrum of hallactone B did not show a molecular ion but gave peaks at *m/e* 361 (M^+-SO_2Me) and 304 (base peak, $C_{16}H_{16}O_6$) resulting from a side-chain fission as in podolactones A, B, and C.[5,6]

Hallactones A and B are toxic to house-fly larvae when incorporated into a defined diet. Hallactone A in particular shows complete mortality at a concentration of 20 p.p.m. and adverse effects to pupation and adult emergence at concentrations down to 2 p.p.m.

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