Cytotoxic bispyrones from *Onchidium sp.*: absolute stereochemistry of onchitriols I and II

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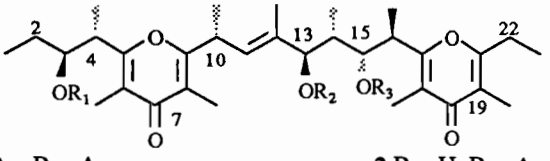
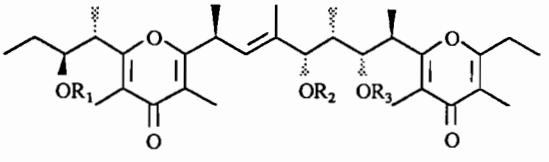
The *Onchidiaceae*, shell-less molluscs inhabiting the rocky intertidal zones of many tropical shorelines, are known to produce cytotoxic pyrone-containing propionate and acetate metabolites. Peroniatriol I and II were isolated by Ireland[1] *et al.* after saponification of the extracts from *Peronia peronii*; elucidation of their structure and relative stereochemistry was based on those of ilikopyrone[2] and corrected by partial synthesis[3].

We now report the isolation, by reverse phase hplc, of cytotoxic extract of *Onchidium* sp. collected in New Caledonia of the metabolites identified as the acetates and propionates **1-4** and **6-9**.

The skeletal structure of **1-4** and **6-9**, and the exact positions of the acetate and propionate groups, were deduced by MS (EI and FAB) and NMR (homonuclear and heteronuclear correlations). Upon saponification in 1% KOH/MeOH at r.t. **1-4** gave onchitriol I and **6-9** gave onchitriol II (**10**). NMR studies of the mono, di, tri (R) and (S) O-methylmandelates, dioxolane formation and reducive ozonolysis showed the absolute stereochemistry of **5** to be 3*S* , 4*R* , 10*R* , 13*R* , 14*R* , 15*R* , 16*R* and that of **10** 3*S* , 4*R* , 10*S* , 13 *S* , 14 *R* , 15*R* , 16*R*.

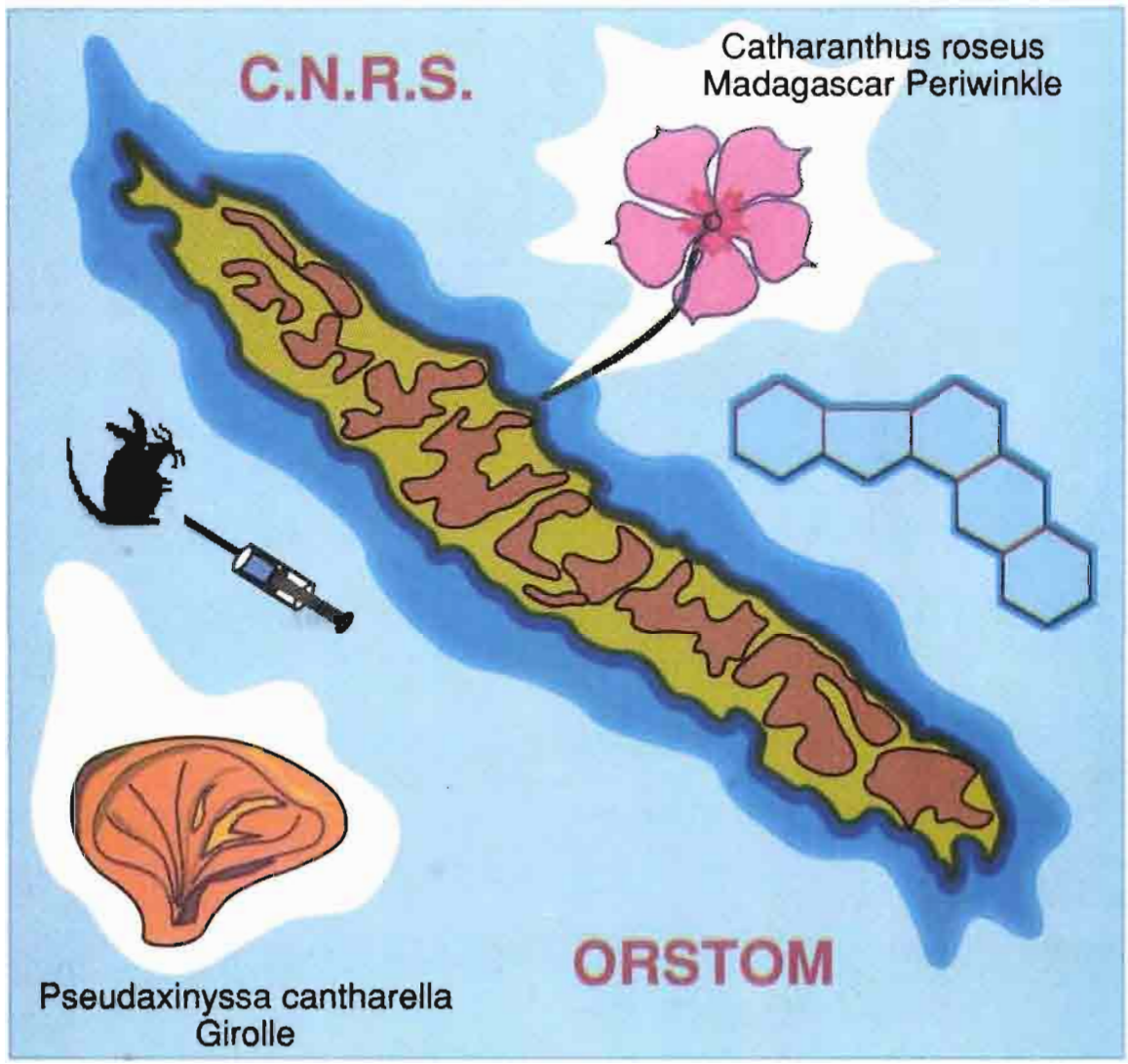


1 R_1=H, R_2=R_3=Ac
2 R_1=H, R_2=Ac, R_3=Pr
3 R_1=H, R_2=Pr, R_3=Ac
4 R_1=Ac, R_2=R_3=Pr
5 R_1=R_2=R_3=H



6 R_1=H, R_2=H, R_3=Ac
7 R_1=H, R_2=H, R_3=Pr
8 R_1= R_3=Ac, R_2=H
9 R_1= R_2=R_3=Ac
10 R_1=R_2=R_3= H

References:
1. M. Ireland and J.E. Biskupiak, Tetrahedron Lett., 26, 4307 (1985)
2. M. Ireland, J.E. Biskupiak, G.J. Hite, R. Rapposch, P.J. Scheuer and J.R. Ruble, J. Org. Chem., 49, 559 (1984)
3. H. Arimoto, S. Nishiyama and S. Yamamura, Tetrahedron Lett., 31, 5491 (1990)



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