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Stereospecific Syntheses
from Podocarpic Acid

A Thesis
presented to the University of Auckland
for the Degree of

Doctor of Philosophy

by
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ABSTRACT

The triterpene precursor, 12-methoxypodocarpa-8,11,13-trien-3-one (46)*, has been prepared via the 3α-alcohol (48) formed by opening of the 3α,4α-epoxide (13) with lithium diethylamide.

The total synthesis of the methyl ether of the natural product, (+)-hinokione, has been achieved by a similar sequence involving prior addition of an isopropyl group at C13 of the methoxy acid (4). (Scheme 1).

A study of the boron trifluoride rearrangements of the three epoxides (12), (13), and (14), has been made using benzene and dimethyl sulfoxide as solvents.

The stereochemistry of a series of 6-bromo-7-cxo derivatives of diterpenoids possessing an aromatic ring-C is discussed and the assignment of configuration of the 6-bromo substituents from n.m.r. and n.o.e. data is examined.

* The numbering system used throughout this thesis is that proposed by J. W. Rowe (personal communication to Professor R. C. Cambie) in "The Common and Systematic Nomenclature of Cyclic Diterpenes", 3rd Revision, Oct. 1968, to be submitted to the IUPAC Commission on Organic Nomenclature.
A preliminary investigation into the possibility of preparing a 9α-methyl steroidal analogue by addition of a cyclopentanone ring across positions 3 and 4 of ring-A of the podocarpic system is also reported.