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RING C TRANSFORMATIONS
OF
PODOCARPIC ACID

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

by

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ABSTRACT

This thesis describes further studies on the utilisation of the diterpenoid natural product, 12-hydroxypodocarpa-8,11,13-trien-19-oic acid* (podocarpic acid) (1). In particular it describes transformations of the C-ring to give suitable intermediates for the synthesis of optically active steroids and terpenoids.

An investigation has been carried out on the Birch reduction of 12-methoxypodocarpa-8,11,13-trien-19-ol (8), and conditions for the optimum formation of the ketonic products (10) and (12) are suggested.

The enones (25) and (26) have been synthesised from 12-hydroxypodocarpa-8,11,13-trien-19-oic acid (1) by sequences involving reduction of the aromatic ring followed by ring C transformations.

Methyl 12-hydroxypodocarpa-8,11,13-trien-19-oate (3) has been converted in ca. 60% yield to the dextrorotatory C 13 methyl ether (62), which has then been reduced in good yield to the enone (163). Potential routes for conversion of the enones (25), (26), and (163)

* 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 (see page 144).

into steroidal analogues are described.

Initial steps in the transformation of the C 13 methyl ether (62) into an intermediate (176) suitable for the synthesis of (+)- α -onocerin (80) have been investigated.

A preliminary study on the synthesis of the C 14 phenol (190) or its methyl ether (191) is also reported.