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SYNTHETIC STUDIES UTILIZING PODOCARPIC ACID

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

by

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TABLE OF CONTENTS

ABSTRACT ii

INTRODUCTION 1
Approaches to Steroid Synthesis from 12-Hydroxypodocarpa-8,11,13-trien-19-oic Acid 2
Conversion of 12-Hydroxypodocarpa-8,11,13-trien-19-oic Acid to 3-Oxygenated Diterpenes 5

DISCUSSION 7
The Mechanism of Lactone Formation During the Reaction of 12-Methoxypodocarpa-8,11,13-trien-19-oic Acid with Lead Tetraacetate 7
Steroid Synthesis from 12-Hydroxypodocarpa-8,11,13-trien-19-oic Acid 18
The Reactions of Ring A Epoxides of 12-Methoxypodocarpa-8,11,13-trien-19-oic Acid 40
Ring B Lactones of 12-Methoxypodocarpa-8,11,13-trien-19-oic Acid 54
Ring B Conformation in 12-Methoxypodocarpa-8,11,13-trien-19-oic Acid Derivatives 68

CONCLUSION 82

EXPERIMENTAL 83

Contd....
ABSTRACT

The ketoester, 3-ethoxycarbonyl-12-methoxy-5βH-18,19-bisnor-
podocarpa-8,11,13-trien-4-one (80),* has been prepared from
12-hydroxypodocarpa-8,11,13-trien-19-oic acid (1), via the C 4
ketones (76) and (77). Both of these isomers were obtained from the
methoxyalkene (11), which was isolated in a pure form during selective
epoxidation of the methoxyalkene mixture (11 - 13) obtained from the
decarboxylation of 12-methoxypodocarpa-8,11,13-trien-19-oic acid (2)
with lead tetraacetate.

This reaction has been investigated, and a mechanism accounting
for the formation of nondecarboxylation products is proposed.

The unsaturated ketoester (102) was prepared in low yield via the
saturated C 12 ketone (24), obtained from 12-hydroxypodocarpa-8,11,13-
trien-19-oic acid (1) by Birch reduction of the aromatic ring.

A number of ring A epoxide derivatives of the acid (1) were
prepared and cleaved by a variety of reagents to give the 3-oxygenated
derivatives (145), (146), and (152), together with compounds possessing
a contracted ring A. Some ring B lactone derivatives of the acid (1)

* The numbering used throughout this thesis is that proposed by J.W. Rowe
(personal communication to Dr. 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.
were prepared, and their stereochemistry and conformation were
determined by n.m.r. spectroscopy. The conformation of some ring B-
substituted derivatives was also determined by n.m.r. methods.

The bromination of some 7-ketopodocarpa-8,11,13-triene derivatives
was investigated, and reasons are advanced for the non-stereospecific
reactions observed in some cases.