

http://researchspace.auckland.ac.nz

ResearchSpace@Auckland

## Copyright Statement

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage. <u>http://researchspace.auckland.ac.nz/feedback</u>

### General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.

# SYNTHETIC STUDIES WITH DITERPENOIDS

A Thesis

Presented to the University of Auckland for the Degree of

# DOCTOR OF PHILOSOPHY

by

Glen Richard Ryan

Department of Chemistry, UNIVERSITY OF AUCKLAND.

October, 1988

#### TABLE OF CONTENTS

ABSTRACT	i
CHAPTER ONE: SYNTHESIS OF POTENTIAL AMBER ODORANTS	
FROM ABIETIC ACID.	
Introduction	1
Discussion - part 1: 5-membered ring-C compounds	10
- part 2: 6-membered ring-C compounds	44
Experimental - part 1: 5-membered ring-C compounds	58
- part 2: 6-membered ring-C compounds	93
Appendix - crystallography	112
References	124
Diagrams	130
CHAPTER TWO: SYNTHESIS OF NAGILACTONE PRECURSORS	
FROM TOTAROL.	
Introduction	138
Discussion	143
Experimental	158
Appendix - crystallography	166
References	185
Diagrams	187
CHAPTER THREE: SYNTHESIS OF AMBER ODORANTS FROM	
PODOCARPIC ACID.	
Introduction	190
Discussion	193
Experimental	203
Appendix - crystallography	220
References	226
Diagrams	228
ACKNOWLEDGEMENTS	231

#### ABSTRACT

Chapter one of this thesis reports an investigation of the synthesis of potential amber odorants from abietic acid. The acid catalysed rearrangement of abietic acid afforded two isomeric dienes the structures of which have been elucidated. Compounds containing the diene functionality were found to be unstable. However, removal of the diene system afforded stable compounds which are suited to further synthetic modification. Although the skeletal features possessed by a class of amber odorants were successfully introduced stereochemical control proved difficult. The stereochemistry of two intermediates was unambiguosly assigned by single-crystal X-ray diffraction experiments.

The second chapter describes the successful conversion of totarol into conjugated dienolides possessing the B/C-ring present in type A and type C nagilactones. Consequently totarol may be considered as a useful model for the preparation of the biologically active nagilactones. In the course of this work several unusual rearrangements were observed. The products of rearrangement were characterised by 2-D n.m.r. and single crystal X-ray diffraction experiments and reaction mechanisms are proposed.

The third chapter of this thesis reports the synthesis of the amber odorant,  $\gamma$ -bicyclohomofarnesal, from podocarpic acid. Analogues in which C-19 is functionalised were also prepared. However these compounds were odorless.

i