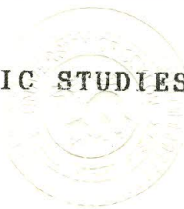


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COUMARINS OF *MURRAYA* SPECIES
AND SYNTHETIC STUDIES ON PHEROMONES



A THESIS SUBMITTED BY

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IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

OF THE

UNIVERSITY OF PERADENIYA

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August 1987

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409925

ABSTRACT

This thesis consists of two parts.

Part I describes studies on *Murraya gleniei*, whose extracts showed insecticidal activities.

M. gleniei leaves contained a new coumarin, 5,6,7-trimethoxy-8-(2',3'-dihydroxyisopentyl)coumarin (murragleinin) and eight more coumarins, phebalosin, meranzin, *epi*-sibiricin, murralongin, meranzin hydrate, scopoletin, murrangatin, and *epi*-mexoticin, together with skimmianine, exoticin and stigmasterol. Its root bark contained the new coumarins, 5,7-dimethoxy-8-(3'-methyl-1'-butenyl)coumarin (gleinene), 5,7-dimethoxy-8-(3'-methyl-1',3'-buta-dienyl)coumarin (gleinadiene), a new dimeric coumarin, 2',3-di(5",7"-dimethoxycoumarin-8"-yl)-1,4,-dimethyl-4-(1'-ethenyl)cyclohexene with eight coumarins found in the leaves, four more coumarins, toddalenone, coumurrayin, omphamurin and *threo*-murrangatin and two sesquiterpenoids, bulnesol and qualol. The stem bark of *M. gleniei* contained the dimeric coumarin and seven other coumarins present in the root bark together with one more coumarin, umbelliferone.

The insecticidal activity of these extracts was due to the presence of phebalosin.

The acid catalysed rearrangements of (-)-phebalosin, (+)-*erythro*-murrangatin, *threo*-murrangatin and *epi*-mexoticin

were studied. (-)-Phebalosin gave (-)-murrangatin and murralongin, while (+)-*erythro*-murrangatin gave murralongin, suggesting that the structure of murralongin needed revision to 7-methoxy-8-(1'-formyl-2'-methylprop-1'-enyl)coumarin. *threo*-Murrangatin, however, gave with acid, 3-formyl-3-methyl-2-(7'-methoxycoumarin-8'-yl)-5-isopropyltetrahydrofuran. The *erythro*- and *threo*- isomers behaved differently with acidic acetone, the former giving an acetonide while the latter gave 3-formyl-2-(7'-methoxycoumarin-8'-yl)-3,5,5-trimethyltetrahydrofuran. Differences in reactivity are explained on the stereoelectronic requirements of the pinacol rearrangement. Acid rearrangement of *epi*-mexoticin gave 2'[[1',1'-dimethyl-2'-(5'',7''-dimethoxycoumarin-8''-yl)ethyl]-4-[5'',7''-dimethoxycoumarin-8''-yl)methyl]-5,5-dimethyl-1,3-dioxalane.

Part II of the thesis discusses the synthesis and attempted synthesis of some insect pheromones.

trans- β -Farnesene was synthesized from 2-methyl-6-methylene-1,7-octadien-3-ol in four steps in 57% yield. An intermediate in the synthesis was converted into 2,6-dimethyl-10-methylene-1,6,11-dodecatrien-3-ol in 45% yield in an attempt to synthesize β -sinensal.

An attempted synthesis of lineatin from carvone using an intramolecular photosensitized (2+2) addition for the formation of the cyclobutane ring gave hydroxylineatin in 7 steps in an overall yield of 6%.