NATURAL PRODUCT ISOLATION

AND

TERPENE BIOTRANSFORMATIONS

BY

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ABSTRACT

This thesis is divided into two parts. In part 1 (Chapters 1-3) the transformation of terpenoids by the fungus Beauveria bassiana ATCC 7159 is discussed. Part 2 is composed of Chapters 4 and 5 and there the isolation of natural products from Russelia equisetiformis is described.

In Chapter 1, the biotransformation reactions by B. bassiana is reviewed, as well as the mechanisms of some enzyme-mediated reactions.

The isolation and characterisation of cadina-4,10(15)-dien-3-one and two other sesquiterpenes, namely cadin-4-en-1β-ol and squamulosone, are reported for the first time from Hyptis verticillata (chapter 2). The bioconversion of
cadina-4,10(15)-dien-3-one and its synthetic alcohol cadina-4,10(15)-dien-3α-ol and the optimisation of fermentation conditions were also examined. Incubation of cadina-4,10(15)-dien-3-one with *B. bassiana* ATCC 7159 resulted in the production of nine novel sesquiterpenes. These metabolites were identified as (4S)-cadin-10(15)-en-3-one, (4S)-cadin-10(15)-en-3α-ol, (4R)-cadin-10(15)-en-3α-ol, (4S)-cadin-10(15)-en-3β-ol, (4S)-cadin-10(15),12-dien-3β-ol, (4S)-13-hydroxycadin-10(15)-en-3-one, (4S)-12-hydroxycadin-10(15)-en-3-one, (4R)-cadin-10(15)-en-3β,14-diol and cadina-4,10(15)-dien-3α-ol. The allylic alcohol cadina-4,10(15)-dien-3α-ol was also biotransformed to afford cadina-4,10(15)-dien-3-one, (4S)-cadin-10(15)-en-3-one and (4S)-12-hydroxycadin-10(15)-en-3-one. The insecticidal potential of all the sesquiterpenes and phytotoxicity of the isolated metabolites have been evaluated.

The isolation and bioconversion of terpenes from *Stemodia maritima* is discussed in Chapter 3. The compounds isolated from this plant were stemodinone, stemodin, stemarin, stemolide and stemodinoside A. The biohydroxylation of stemodin and stemodinone by *B. bassiana* gave exclusively stemodane-2α,13,18-triol and 13,18-dihydroxystemodan-2-one respectively. Stemarin was converted to the novel stemarane-1β,13,19-triol and 13-hydroxystemaran-19-oic acid. The synthesis and biotransformation of novel carbonate, carbamate, phosphate and ester derivatives of stemodin were studied in this chapter.