

ABSTRACT

PRENYLATED BENZOPHENONES FROM CARIBBEAN *CLUSIA*, *HYPERICUM* AND *VISMIA* SPECIES

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Over the past decade the Clusiaceae family has been the focus of much research due to the complexity and significant biological activities displayed by several metabolites isolated from the family. Prenylated benzophenones are structurally the most complex metabolites found in the Clusiaceae family. The absolute stereochemistry of most of these prenylated benzophenones remains unknown. The objectives of this study were to elucidate, using standard NMR techniques, the structures of the prenylated benzophenones of *Clusia*, *Hypericum* and *Vismia* species, to investigate the stereochemistries of these metabolites and to synthesize some of these prenylated benzophenones.

This thesis is divided into two parts, Part I and Part II. Part I consists of a review of the metabolites of the Clusiaceae (Guttiferae), and examines the biogenetic origin of these metabolites. Part I also describes the isolation and structure elucidation of several new and known prenylated benzophenones from two genera of the Clusiaceae, namely, *Clusia* and *Hypericum*. Seven compounds were isolated from *Clusia havetioides* var. *stenocarpa*, of which three (3) are new, 28,29-epoxyplukenetione A, 33-hydroperoxyisoplukenetione C and 15,16-dihydro-16-

hydroperoxyplukenetione F (compounds A, B and C respectively) and four (4) are known, sampsonione G, plukenetione C, plukenetiones F and G, plukenetione A (compounds D-H). Two new tautomeric pairs, 13-hydroxy-7-*epi*-clusianone and 13-acetoxyclusianone (compounds I and J) and two known tautomers, clusianone and 7-*epi*-clusianone (compounds K and L), as well as the new prenylated benzophenone derivative (compound M) possessing an adamantane cage were isolated from *Hypericum hypericoides* (St Andrew's Cross). These structures were solved by the use of 1D and 2D NMR experiments.

Part I culminates with an examination of the stereochemistry of several bicyclononane, adamantane and homoadamantane-type natural products isolated from Clusiaceae. The discussion attempts to provide a unified perspective of the stereochemistry of these natural products. X-ray crystallographic data of compound I is also presented.

Part II describes the isolation and structural elucidation of two prenylated benzophenones, of which one is new isovismiapphenone D (compound N) and one is known vismiapphenone F (compound O), from *Vismia guianensis*. Part II also contains a brief review of the methods used to prepare some metabolites of *Vismia*, the vismiapphenones, and outlines the methods used towards the synthesis of vismiapphenones D-G and isovismiapphenone D.