

ISOLATION AND SPECTRAL STUDIES OF SOME

QUINONE-METHIDES OF *CASSINE BALAE* AND

OXINDOLE ALKALOIDS OF *NEISOSPERMA OPPOSITIFOLIA*

A THESIS PRESENTED BY

H. CHANDRASIRI FERNANDO

IN PARTIAL FULFILMENT OF THE REQUIREMENT

FOR THE AWARD OF

THE DEGREE OF

MASTER OF PHILOSOPHY

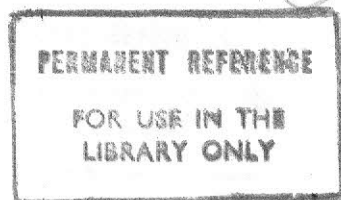
OF

UNIVERSITY OF PERADENIYA

SRI LANKA

426049

January 1990



Research Laboratory

Department of Chemistry

### ABSTRACT

The first part of this thesis describes the isolation and spectral analysis of some quinone-methide and 14(15)-ene-quinone-methide triterpenoids isolated from *Cassine balaë* of the family Celastraceae.

The three new 14(15)-ene-quinone-methide triterpenoids, balaenonol, balaenol and isobalaendiol isolated were shown to be 3,21 $\beta$ -dihydroxy-2,22-dioxo-3,5,7,10(1),14(15)-pentaen-(14 $\rightarrow$ 15)-D:A-*friedo*-24,29-dinoroleanane, 3,21 $\beta$ -dihydroxy-2-oxo-3,5,7,10(1),14(15)-pentaen-(14 $\rightarrow$ 15)-D:A-*friedo*-24,29-dinoroleanane and 3,21 $\beta$ ,22 $\beta$ -trihydroxy-2-oxo-3,5,7,10(1),14(15)-pentaen-(14 $\rightarrow$ 15)-D:A-*friedo*-24,30-dinoroleanane, respectively on the basis of spectroscopic evidence. In this study the structure of a previously isolated ene-quinone-methide identical with balaenonol has been revised.

In addition, the following quinone-methide triterpenoids have been isolated and their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra including HOMOCOSY and HETEROCOSY spectra are discussed; pristimerin, tingenone, 22 $\beta$ -hydroxytingenone and 15 $\alpha$ ,22 $\beta$ -dihydroxytingenone. These studies also led to the revision of some previous NMR spectral assignments of pristimerin.

The co-occurrence of the new quinone-methide triterpenoid,  $15\alpha,22\beta$ -dihydroxytingenone:  $3,15\alpha,22\beta$ -trihydroxy-2,21-dioxo-3,5,7,10(1)-tetraen-D:A-*friedo*-2,29-dinor-oleanane, with 14(15)-ene-quinone-methides is biogenetically important due to it can be the probable biosynthetic intermediate in the transformation of quinone-methides to 14(15)-ene-quinone-methides through dehydroxylation and rearrangement.

The second part of this thesis constitutes the investigation of the stem bark of *Neisosperma oppositifolia* of the family Apocynaceae for its alkaloidal constituents and describes the isolation of pentacyclic ajmalicinoid indole alkaloides, isoreserpiline, reserpiline and tetracyclic indole alkaloid, ochroposinine with two pentacyclic oxindole alkaloids, isocarapanaubine and a new stereoisomer of isocarapanaubine, named neisosposinine. The structure elucidation of neisosposinine was based on detailed spectral data with those recorded in this study for isocarapanaubine. This constitutes the report of the occurrence of oxindole alkaloids in this genus and may be of chemotaxonomic importance.