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CHEMISTRY OF SOME QUINONE-METHIDES

OF *KOKOONA ZEYLANICA* AND

QUINONES OF *PLUMBAGO ZEYLANICA*

A THESIS PRESENTED BY

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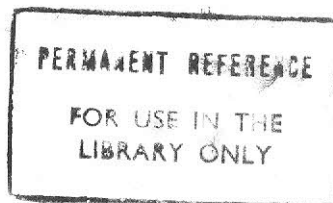
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ABSTRACT

This thesis consists of two parts.

The first part describes the isolation and characterisation of four novel phenolic friedo-oleanane triterpenoids from Kokoona zeylanica Thw. (Celastraceae) along with the identification of some known triterpenoid quinone-methides, (-)-4<sup>β</sup>-O-methylepigallocatechin, an unusual catechin that has been encountered previously only twice, in both instances in plants belonging to family Celastraceae and dulcitol, a hexitol which is frequently found in family Celastraceae and some genera of Scrophulariaceae.

Presence of pristimerin, (-)-4<sup>β</sup>-O-methyl-epigallocatechin and dulcitol in K. zeylanica is of chemotaxonomic significance. Isolation of phenolic triterpenoids, in which the A ring of the D:A-friedo-oleanane skeleton has undergone aromatization, constitutes the first report of natural occurrence for this type of compounds. The presence of these phenolic constituents in Celastraceae is of some biosynthetic interest.

Co-occurrence of these with pristimerin, celastrol and 6-oxo-friedo-oleanane triterpenoids suggests a common biogenesis. A possible biogenesis to these compounds from friedelin via polpunonic and salaspertemic acids have been postulated.

The second part constitutes the isolation and identification of some known and novel quinones and naphthalenones from Plumbago zeylanica (Plumbaginaceae), a plant with a variety of applications in the indigenous system of medicine. Among the quinones encountered in this study, zeylanone and isozeylanone have been reported recently only once in P. zeylanica and this is the first report of the occurrence of martitinone in a plant other than Diospyros maritima (Ebenaceae).

3,3'-Methylenediplumbagin and plumbazeylanone are novel dimer and trimer of plumbagin, respectively. Structure elucidation of the former was based on spectral data and synthesis of its dimethyl derivative, while the latter was based exclusively on spectral characterisation including  $^{13}\text{C}$  nmr assignments.

The structure of the novel naphthalenone, 1,2(3)-tetrahydro-3,3'-biplumbagin was mainly based on  $^1\text{H}$  nmr spectral comparisons with plumbagin and isoshinanolone and the absolute configurations at chiral centres came from its CD curves and  $^1\text{H}$  nmr data.

Presence of naphthalenones, in this plant supports the biogenesis of quinones from acetate polymalonate units. The possible biogenesis of plumbagin, isoshinanolone and other compounds is briefly discussed.

