STRUCTURAL STUDIES OF A POLYSACCHARIDE FROM *LITSEA GLUTINOSA* AND THE SYNTHESIS OF SOME ACRIDONES AND COUMARINS

A THESIS SUBMITTED BY

H. M. T. BANDARA HERATH

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SRI LANKA

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Research Laboratory
Department of Chemistry

ABSTRACT

This thesis consists of three parts.

Part-1 describes the structural studies of an arabinoxylan isolated from *Litsea glutinosa* (Lour).

Arabinose and the xylose were the major neutral sugars present in the water soluble polysaccharide isolated from the mucilaginous bark of *Litsea glutinosa* (Lauraceae). The molar ratio of D-xylose : L-arabinose was 1.0 : 3.5. Methylation analysis, partial hydrolysis and ^{1}H, ^{1}H-^{1}H 2D-COSY, and ^{13}C-nmr spectroscopy indicated a backbone of (1-4)-linked ß-D-xylopyranosyl residues substituted at both positions 2 and 3 with side chains composed of either single or (1-3)-linked arabino- furanosyl residues. Both α-L- and ß-L- arabinofuranosyl residues were present. Side chains composed of two ß-L-arabinofuranosyl residues are probably attached at *O*-2 of some xylosyl residues.

Part-2 of the thesis discusses the total synthesis of twenty acridone alkaloids, eleven of which are new acridones.

1,3-Dihydroxy-9-acridone (31) was synthesised from methyl anthranilate and phloroglcinol. Selective methylations of compound (31), gave 1-hydroxy-3-

methoxy-10-methyl-9-acridone (32), 1,3-dimethoxy-10-methyl-9-acridone (33) and 1,3-dihydroxy-10-methyl-9-acridone (34). The iodination of (31) afforded a new acridone, 1,3-dihydroxy-2,4-diiodo-9-acridone (35) while compounds (32), (33) and (34) gave 1-hydroxy-2-iodo-3-methoxy-10-methyl-9-acridone (36), 2-1odo-1,3-dimethoxy-10-methyl-9-acridone (37) and 1,3-dihydroxy-2-iodo-10-methyl-9-acridone (38) respectively. Methylation of compound (35) gave another new acridone, 2,4-diiodo-1,3-dimethoxy-10-methyl-9-acridone (39). The palladium catalysed Heck condensation reaction of compounds (36), (38) and (39) with 2-methyl-3-butene-2-ol afforded three new acridone alkaloids, 1-hydroxy-2-(3-hydroxy-3-methyl-1-butenyl)-3-methoxy-10-methyl-9-acridone (40), 1,3-dimethoxy-2-(3-hydroxy-3-methyl-1-butenyl)-10-methyl-9-acridone (42) and 2,4-bis(3-hydroxy-3-methyl-1-butenyl)-1,3-dimethoxy-10-methyl-9-acridone (43) respectively, while compound (37) affoded a naturally occurring acridone, isonoracronycine (41). Methylation of (41) gave isoacronycine (44).

Methyl-6-amino-2,3-dimethoxybenzoate (51) which was synthesised from 6-formyl-2,3-dimethoxybenzoic acid (45), was treated with phloroglucinol to give two new acridone alkaloids, 1,3,8-trihydroxy-7-methoxy-9-acridone (52) and 1,3-dihydroxy-7,8-dimethoxy-9-acridone (53). The selective methylation of (52) and

(53) gave another four new acridones, 1,8-dihydroxy-3,7-dimethoxy-9-acridone (54), 1,8-dihydroxy-3,7-dimethoxy-10-methyl-9-acridone (55), 1-hydroxy-3,7,8-trimethoxy-10-methyl-9-acridone and 1,3,7,8-tetramethoxy-10-methyl-9-acridone (57).

Part-3 of the thesis deals with the total synthesis of (*E*)-suberenol (3) from 4-bromoresorcinol and describes the use of (*E*)-suberenol as a precursor for the synthesis of related coumarin derivatives.

The synthesis of three naturally occurring coumarins, cyclobisuberodiene (9), dihydrosuberenol (11) and ethylsuberenol (12) and three new coumarins, (*E*)-suberodiene (8), (*E*)-suberenene (10) and methylsuberenol (13), a new coumarin dimer (14) and three new acridone-coumarin dimers (Acrimarins), 1,3-dihydroxy-2-[1-7-(methoxy-2-oxo-2*H*-chromen-6-yl)-3-methyl-2-butenyl]-10-methyl-9-acridone (15), 1-hydroxy-3-methoxy-2-[1-7-(methoxy-2-oxo-2*H*-chromen-6-yl)-3-methyl-2-butenyl]-10-methyl-9-acridone (16) and 1,3-dihydroxy-2-[1-7-(methoxy-2-oxo-2*H*-chromen-6-yl)-3-methyl-2-butenyl]-9-acridone (17) are described in this part of the thesis.