

ABSTRACT

This thesis is mainly concerned with the chemistry of 2,2-dimethylchromenes isolated from Eupatorium riparium L. (Compositae) and Spathelia sorbifolia L. (Rutaceae). Studies related to the synthesis of chromenes via rearrangement of aryl propargyl ethers are also discussed.

Part I includes a discussion of the biogenesis of 2,2-dimethylchromenes and of other phenolic terpenoids as well as a review of the chemistry of 2,2-dimethylchromenes. Various synthetic approaches to the introduction of C₅ units in phenols are also reviewed.

The isolation and structural elucidation of methyl-ripariochromene A and of acetovanillochromene from E. riparium are discussed in Part II. Methylripariochromene A is shown by degradation and the synthesis of its dihydro derivative to be 6-acetyl-7,8-dimethoxy-2,2-dimethylchromene. Attempts at the synthesis of methylripariochromene A are also described. Acetovanillochromene by synthesis is shown to be 6-acetyl-7-methoxy-2,2-dimethylchromene. Reference is also made to studies on the Eupatorium genus by other workers which resulted in the isolation of various natural products.

Spathelia sorbifolia L. (Rutaceae) had earlier afforded the chromeno-chromone, sorbifolin. More careful separation of

the extract now leads to the isolation of the known alloptaeroxylin and several new chromeno-chromones. These include an isomer of alloptaeroxylin, spatheliachromene, whose structure is proven by synthesis, as well as methylisospatheliachromene and spatheliabischromene, the structures of which are established by correlation with their hydrogenated derivatives. Two derivatives of spatheliachromene, the 8-(3',3'-dimethylallyl)- and the δ^- (β,β -dimethylacrylyl)- derivatives were also isolated, the former lending itself to synthesis. Attempts at the synthesis of all these compounds as well as an investigation into the general methods of prenylation of 2,2-dimethylchromenes are also treated in Part III. A brief discussion of the interpretation of the mass spectral data of some of these chromeno-chromones is given, and other naturally occurring chromones isolated since Dean's review are mentioned.

Recently, 2,2-dimethylchromenes have been synthesised in very high yield by several workers including the author, via the rearrangement of aryl dimethylpropargyl ethers. In Part IV, the mechanism of this reaction is discussed. Studies carried out with the aim of determining the factors affecting the rearrangement are described in this final section of this thesis.