ABSTRACT

This thesis describes studies directed towards the synthesis of rotenoids — compounds possessing the benzopyran-benzopyran moiety (A-1). The rotenoids are important commercial insecticides of plant origin.

Chapter one reviews their pharmacology and existing methods of synthesis.

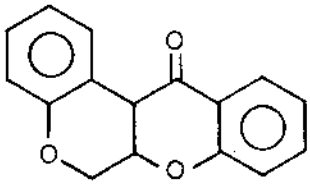
Chapter two outlines existing pathways to 3-hydroxycoumarins and presents an improved synthesis of 3-hydroxy-6,7-dimethoxycoumarin (A-3). An efficient pathway to the compound (A-3) was required since 3-hydroxy-4-aroyl-6,7-dimethoxycoumarins (A-2; R=H), products of Fries rearrangement of aryl esters of the compound (A-3), were seen as possible precursors of 6-oxorotenoids (rotenonoids).

Chapter three describes the esterification of compound (A-3) and the response of these esters to conditions of thermal and photochemical Fries rearrangement. The desired 3-hydroxy-4-aroylcoumarins (A-2; R=H) were isolated from the photochemical reaction and not from the thermal; during one attempted thermal Fries reaction, a very small amount of a rotenonoid was produced. Some of the chemistry of the compounds (A-2) is also discussed.

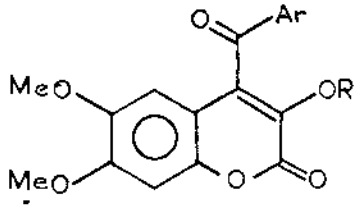
Conversion of the coumarins (A-2) to the corresponding 2-carboxy-3-aroylbenzofurans is next described. This work was done in an effort to prepare β-rotenonoids (A-4; X,Y=O) which are known to rearrange to rotenonoids in weak alkaline solution.

Part A of chapter four relates to the preparation of [1]-benzofurano-[2,3-c]-[6H,12H-1]-benzoxepin-6-ones (A-4; X=Y=H, R=OMe) by the acid-catalysed rearrangement of some 2-carboethoxy-3-aryloxymethylbenzofurans (A-5; R=-OAr) to 2-carboethoxy-3-(2′-hydroxyarylmethyl)benzofurans followed by their lactonisation. The benzoxepins (A-4; X=H, Y=Br) prepared by bromination of the compounds (A-4; X=Y=H) showed a strong susceptibility to nucleophilic substitution, thus giving support to the idea that they are potential precursors of 8-rotenonoids.

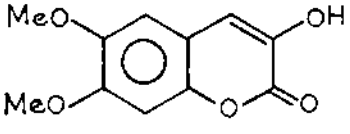
Part B of the same chapter deals with reactions of the compound (A-5; R=Br) with 2-aminopyridine and highlights an instance of alkylation of 2-aminopyridine occurring at the exocyclic nitrogen without previous deprotonation.



(A-1)



(A-2)



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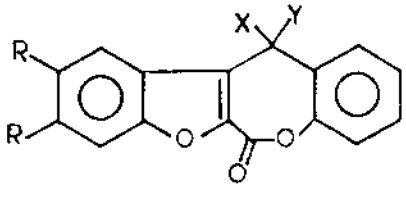
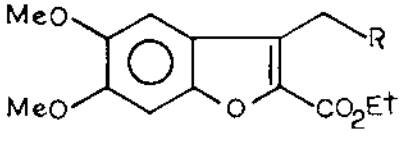


(A-4)



(A-5)