ABSTRACT

SYNTHESIS OF ROTENONOIDS AND AZAROTENONOIDS

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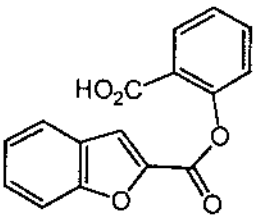
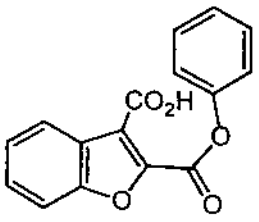
In this thesis, the focus is on synthesis of rotenonoids (6-oxo-analogues of rotenoids) and their nitrogen analogues – azarotenonoids. Rotenonoids have been known to co-occur with rotenoids in plants from the *Leguminosae* family and are available in much less quantity (than rotenoids) from natural sources. Due to their potent insecticidal and piscicidal activity, and the wide range of biological properties exhibited by rotenoids, much attention has been focused on devising efficient synthetic pathways to the rotenonoids. Synthesis of rotenonoids and azarotenonoids would make for useful structure/activity relation studies.

A review of synthetic pathways to rotenoids is described in chapter one. Rotenonoids are usually obtained *via* oxidation of rotenoids. This is a rather inefficient route, however, as rotenoids are quite difficult to synthesize and are usually obtained in low yields. This and other strategies designed to synthesize rotenonoids are detailed in chapter one. Sulfur analogues of rotenoids (thiorotenoids) have also been studied, and a few synthetic pathways to them have been outlined in chapter one.

It has been reported that β-rotenonoids rearrange to the corresponding rotenonoids when treated with aqueous base. In chapter two, efforts to obtain a β-rotenonoid by intramolecular acylation of compounds of types **A** and **B** are described.



A



B

Precursors **A** and **B** were obtained by treatment of readily synthesized and appropriately substituted benzofuran carboxylic acids with salicylic acid or phenol.

Investigation into the oxidation of a (1)-benzofuran-(2,3-*c*)-(6H, 12H)-(1)-benzoxepin-6-one to the corresponding β-rotenonoid is detailed in chapter three. Synthesis of a 2,3-dimethoxyrotenonoid *via* initial allylic oxidation of the benzoxepinone and subsequent base rearrangement is also reported.

A five step synthetic pathway to *N*-methyl-2,3-dimethoxy-β-azarotenonoid is described in chapter four. The key reaction involved in this synthesis is an acid catalysed cyclodehydration.

Synthesis of six novel 3,1-benzoxazin-4-ones is also reported in chapter four. 3,1-Benzoxazinones are known to be potent serine protease inhibitors and are potentially useful in combating viral infections such as herpes simplex type 1.