Abstract
This thesis deals with synthetic studies towards Quassinoids and some aspects of the Chemistry of unsaturated sugar. The thesis consists of two chapters. In chapter I, approaches towards the synthesis quassinoids in general bruceantin, in particular are presented, while chapter II contains the chemistry of unsaturated sugars. Each chapter is subdivided into three sections, comprising introduction, results and discussion and experiments, respectively.

The introductory section of chapter I briefly covers the biological activity of quassinoids and synthetic strategies culminating in the synthesis of bruceantin.

Quassinoids are a group of diterpenes isolated from the bitter principles of Simaronbaceae family. They have been shown to possess antitumour and many other medicinal properties. Bruceantin (1) is one of the most active member of the group and has been the subject of extensive synthetic and pharmacological investigations.

We conducted model studies towards the construction of BCD rings of the Quassinoids and towards this end, envisaged a strategy in which an intramolecular hetero Diels - Alder reaction find the key step. After a retrosynthetic analysis, we selected 4-(2-methyl-2-cyclohexen-1-yl) butyraldehyde (42) as the starting material. Compounds 42, when subjected to tandem Knoevenegal - hetero Diels - Alder reaction, failed to give any cycloadduct, but furnished only a condensation products. Several attempts to prepare the cycloadduct 53 were not fruitful.
In another approach, the BCD ring system was proposed to be synthesized by the nucleophilic ring opening of an appropriately substituted cyclopropane. We chose the diazosulfone ester 56 prepared from 2-methyl-2-cyclohexenol (43) as the substrate for this investigation. This compound, under several conditions tried, did not undergo intramolecular cyclopropanation. Another compound 62, prepared from 43, furnished the cyclopropane 64 in low yields when heated with excess of Cu powder in xylene. However, 64 could not be reproducible made and further studies in this direction could not carried out. Preliminary studies carried out using an intramolecular Michael reaction were also unsuccessful. In the light of these failures, further studies towards the synthesis of Quassinoids were not pursued.

Introduction to chapter II covers the various reactions glycals and 2,3-unsaturated sugars. Some of the general methods available for the synthesis of medium sized oxygen containing rings are also discussed.

We envisaged an insertion homologation strategy for the construction of functionalized seven membered oxygen heterocycles. Out strategy consisted of addition of dihalocarbenes to glycals and solvolyzing the resultant strained dihalo cyclopropanes. To this end, we investigated the addition of dibromo and dichloro carbenes to glycals 31, 32, 33 and 34. With dichlorocarbene, only a single adduct was furnished in each case. Glycals 31, 32 and 34 gave single dibromo cyclopropanes
with dibromocarbene while, 33 gave two adducts 41 and 42 in a 7:1 ratio.

We conducted solvolysis experiments with adducts 34 and 39 under several conditions. Solvolysis under basic conditions produced ring expanded products. Reactions of the dihalocyclopropanes with tributyl tinhydride and lithium aluminium hydride were examined next. Compound 34 gave cyclopropane 57 upon reduction LAH. While 39 produced a mixture of 35, 57 and 59. Direct cyclopropanation of glycals was also attempted and this produced cyclopropane having an opposite stereochemistry compared to the products of reductive dehalogenation. The utility of cyclopropanated sugars in the synthesis of glycosides has been examined with 57. NBS and Hg(OAc) have been used as electrophiles in these reactions, leading to 2-deoxy glucopyranosides 67 and 75, respectively.

Partially protected 1,5-anhydroaditols have been prepared by hydroboranation of glycals. Finally, the third section in both chapters I and II contains all the relevant experimental details, followed in each case by appropriate references.