INTRODUCTION

Part I deals with the exploration of various methods for the building up of gross structure of dihydroxanthatin, one of a few mono-cyclic sesquiterpenes, biogenetically related to guaianolides. As its molecular framework reveals, it contains quite a number of asymmetric centres. Synthetic studies have been complicated because of the stereochemical difficulties associated with the γ-lactone ring, as revealed by the recent investigations of Herz and his collaborators. This part of the thesis is mainly concerned with the development of characteristic C₄-chain and various methods have been tried with a model compound. Although success has been achieved in the case of model compounds, curiously enough, all reactions have failed when applied to the requisite intermediate for building up of the C₄-chain. All these reactions have been elaborately dealt with and possible reasons have been suggested in the case of the actual compound. It may be emphasised that behaviour of the cycloheptane ring is significantly different from that of the cyclohexane ring, particularly if other functional groups are present.

Part II of this thesis is concerned with the synthesis of vetivenes and related bodies, the lesser known
sesquiterpenoids affording the well known azulene, vetivazulene. In this chapter, the general chemistry of the azulenes has been discussed with particular reference to their naturally occurring precursors. Although synthetic studies in this field have been quite prolific, synthesis of the hydroazulenes, closely related to the natural products is rather difficult because of the complicated factors of stereoisomerism arising from the presence of quite a number of the asymmetric centres in the molecule. The problem is further complicated by the presence of a seven-membered ring, the behaviour of which has not been completely understood, compared to the knowledge of cyclohexane series. Experimental portion of this part deals with an attempt towards the synthesis of vetivones. The scheme, however, could not be pushed to a successful finish, but the fundamental carbon skeleton has been developed, where there is a scope for subsequent introduction of functional groups, as are occurring in natural derivatives. Because of recent discovery of a few important members having this type of carbon-skeleton, degradative studies have recently assumed quite a good deal of importance, but the synthetic studies again are lacking far behind because of the stereochemical difficulties as mentioned before. Although the final compound could not be characterised definitely, but the formation of the desired product is quite convincing.
Part III deals with the chemistry of guaianolides and is divided into two Sections, A and B. The chemistry of guaianolides is barely ten years old and in early fifties, it created a lot of interest because of its formal relationship with santonins in having a γ-lactonic moiety attached to the hydroazulenic ring in place of the decalin system, evidently arising from the same biogenetic precursor. This aspect has been fully corroborated from subsequent studies, particularly the brilliant scheme put forward by Hendrickson.

Section A is concerned with the chemistry of guaianolides proper as distinct from pseudoguaianolides described in Section B. As the chemistry of guaianolides was being developed, it became increasingly clear that not only the stereochemistry is difficult to rationalize but it is further complicated by the migration of a methyl group leading to the formation of a new basic carbon skeleton for pseudoguaianolides. Thanks to the brilliant researches of Herz and his collaborators, the chemistry of pseudoguaianolides is now better understood. The remarkable application of nuclear magnetic resonance spectroscopy in this field has to be specially made mention of: Although it has been possible to arrive at the correct structures of well known guaianolides like helenalin, tenulin and mexicanins, still the number of the guaianolides are quite a
few as mentioned in Section A. It is not unlikely that some of the structures described in Section A may undergo revision with better refinement of physico-chemical methods as applied to structural elucidation of natural products.

In conclusion, it is my pleasant duty to place on record my grateful thanks to Professor P. C. Dutta, D.Sc., for his valuable advice and guidance. My thanks are also due to Dr. U. R. Ghatak, M.Sc., D.Phil. for his kind help and encouragement.

Analyses recorded in this thesis were carried out by Mrs. Chhabi Dutta, M.Sc. in the micro-analytical laboratory of this department and I am thankful to her for the same. Thanks are also due to Dr. Sukh Dev, Assistant Director, National Chemical Laboratory, Poona, Dr. A. Wettstein, Ciba Ltd., Basle, Switzerland, Dr. S. A. Narang, formerly Post-doctoral Fellow at John Hopkins University and to Dr. P.K. Ramachandran, formerly Post-doctoral Fellow at University of Utah, U.S.A. for V.P.C. studies. I would like further to appreciate the kind help of Mr. Ashutosh Ghosal, B.Sc. for ultraviolet and of Mr. Kanak Medhi, M.Sc. for infra-red spectra recorded in this thesis.