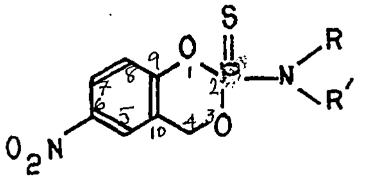
SYNOPSIS

The work embodied in this dissertation is related to the investigation of some nitro-saligenin cyclic amidophosphorothionates with reference to their chemical, biochemical, insecticidal, fungicidal and other toxicological properties besides structural elucidations by chemical analyses and spectroscopic methods.

At the outset, in Part - I of this dissertation, a general introduction including anticholinesterase activities, chemical hydrolysis, NMR, IR, and Mass spectra of some organophosphorus pesticides has been presented. Common or trade names, chemical structures and other properties of some of them have been given in Appendix - I

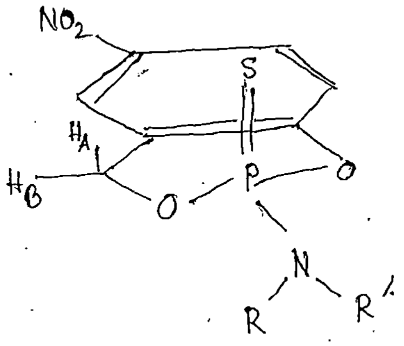
Part - II of this thesis has been devoted to a short review describing the chemical, bio-chemical, insecticidal, fungicidal and other toxicological properties of saligenin cyclic phosphorus compounds with special emphasis on salithion (2-methoxy-4H-1,3,2-benzodioxaphosphorin-2-sulphide) discovered in 1963 by Prof. Eto., Prof. Oshima and their co-workers. Investigations have revealed that the biological activities of these compounds are greatly influenced by the exocyclic substituents on the phosphorus atom, and also by the substituents in benzene ring and/or in hetero-cyclic ring.

It was reported by Prof. Eto and his co-workers that 2-methocy-6-nitro-4H-1,3,2-benzodioxaphosphorin-2-sulphide (BD-8) was obtained as a paste after purification through silicic acid column chromatography and found to have about sixty times less insecticidal activity compared to salithion. However, it has been observed in this laboratory that the methoxy compound (BD-8) is a solid (m.p. 84°C), and has about 1.5 - 2 times greater oral insecticidal activity to *Periplaneta americana* than salithion. Moreover, introduction of an amide group in place of an alkyl ester group often gives organophosphorus esters fungicidal, nematocidal and other biological activities. There are many examples in literature which show that some phosphoramidothionates, phosphoramides or phosphonamides in which the phosphorus atom is attached directly to the nitrogen atom of an amine or a hetero-cyclic compound such as phthalamide, imidazole or triazole have very good fungicidal activity. These observations prompted us to undertake a systematic work on some nitro-saligenin cyclic alkylamidophosphorothionates. The work embodied in Part - III of this dissertation is related to the investigation of some 2-alkylamido-6-nitro-4H-1,3,2-benzodioxaphosphorin-2-sulphides having the general structure (A)



where -NRR' = cyclohexylamido, morpholino, diethylamido, dimethylamido, isopropylamido, pyrrolidino, piperidino, or nonylamido group.

Part - III deals with the work related to the synthesis and structure determination of these cyclic phosphoramidothionates. The structures of these compounds have been established by chemical analyses, UV, IR, Mass and ^{1}H, ^{13}C, ^{31}P - NMR spectral data. All compounds show common IR bands for P-O-C (alkyl), P-O-C (aryl) and for nitro group. They show common parent molecular ion in mass spectra; all compounds show an ion due to $(M - SH)^{+}$. From the study of the PMR spectral data of some 2-alkoxy/phenoxy/alkylamido 6-nitro-4H-1,3,2-benzodioxaphosphorin-2-sulphides it is fairly evident that the chemical shift difference of the protons H_A and H_B increases in going from 2-alkoxy to 2-alkylamido compounds, and that the 2-substituent at the same time increases in bulk, and probably spends more time in the conformation with the least steric interactions. The structure II appears to explain, to a reasonable extent, the reversal of the expected proton chemical shift order for the quasi-axial and quasi-equatorial protons, due to the position of the magnetically anisotropic P = S bond relative to the $-CH_2-$ group in the dioxaphosphorin ring.



^{13}C and ^{31}P NMR spectral data of some of these compounds, the temperature dependant of ^{1}H NMR spectra of the methoxy compound (BD-8) have been presented. It has been observed that as the temperature is varied, the rates of inter-conversions

of the conformers and their relative populations are also varied. This suggests that the methylene protons (H_{4A} & H_{4B}) are not equivalent to each other, and the dioxaphosphorin ring is conformationally mobile in solution.

All the compounds show good fungicidal activity against *Helminthosporium* spp. ; the isopropylamidophosphorothionate is the most effective compound, and its inhibitory effect is greater than that of Hinosan. All compounds have less oral insecticidal activity than salithion against *P. americana*. They are less toxic to male rats than salithion, and are not phytotoxic. For all compounds the HFAChE - housefly is more inhibited than the ChE - blood.

The rate of alkali hydrolysis is increased as the pH value increases from 7.7 to 11.85; the compounds containing the disubstituted amido groups are extremely resistant to hydrolysis compared to other compounds having the monosubstituted amido groups.

The biological activities and other data justify further examination of these phosphorothionates as potential pesticides.