EVALUATION OF THE TOXICITY OF O, O—DIETHYL-THIONO PHOSPHORIC ACID O [QUINOXALYL (2)] -ESTER (SANDOZ INSECTICIDE-6538) TO INSECT PESTS

BY

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THESIS

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C E R T I F I C A T E

This is to certify that the thesis herewith submitted contains the results of bonafide research work carried out by Shri. P. Gopinathan Nair. under my supervision. No part of the work embodied in this thesis has been submitted earlier for the award of any degree.

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C O N T E N T S

INTRODUCTION

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Insecticidal organophosphates form such an integral part of modern crop protection, that it is practically inconceivable to do without them. The popularity and versatility of these compounds as insecticides during the past two decades have inspired organic chemists to synthesise more and varied types of this class of chemicals. This dedicated endeavour has led to the discovery of many compounds with varying properties and combinations of properties.

The credit of developing organophosphatic pesticides is entirely that of Dr. Gerhard Schredar and his associates in Germany. Dr. Schradar discovered that insecticidal properties could always be expected for compounds with the general formula,

$$\begin{matrix} & & O\ (S) \\ R_1 & \searrow & \| \\ & & P\text{-"acyl"} \\ R_2 & \nearrow & \end{matrix}$$

where R_1 and R_2 stood for alkyl radicals and 'acyl' denoted the radical of an inorganic or organic acid.

To have effective insecticidal property, the compound should have besides a doubly bound oxygen or sulphur atom, two identical or different phosphorus bound radicals and the radicals of an inorganic or organic acid. This finding paved the way for the development of insecticidally active phosphorus compounds, a field that had hardly been explored before. In the first few years, a large number of compounds of astonishingly high insecticidal activity and mammalian toxicity were produced. The subsequent efforts were aimed at separating the insecticidal activity from high mammalian toxicity and to produce such substances which possessed useful insecticidal properties and could be applied without any hazards to human beings. Consequently a large range of chemicals with insecticidal, nematocidal, fungicidal and weed killing properties were synthesized.

A land mark in this venture, was the discovery of parathion (E.605) by Dr. Schrader in 1944, which soon gained a pride of place among insecticides. The molecule of parathion was modified in different ways by Schrader and other research workers in many other laboratories, with the object of relating structure with activity of this group of compounds. "O,O-diethyl-thionophosphoric acid-O (quinoxalyl-(2))-ester" is a new chemical synthesized in this family of insecticides. It is at present designated under the code name "Sandoz Insecticide 6538".

The technical material of this insecticide is a colourless crystaline solid, slightly soluble in water (22 mg/litre at 20°C), well soluble in organic solvents like methyl and ethyl alcohol, ethyl ether, acetone, ketones and aromatic hydrocarbons and slightly soluble in petroleum ether. The acute oral mammalian toxicity, in terms of L.D. 50, is reported to be approximately 30-40 mg/kg in white rats, while this value of parathion is 3 to 6 mg/kg. The acute dermal toxicity of the material, in terms of L.D. 50, is reported to be 300-400 mg/kg in white rats.

The object of the present studies is to determine the insecticidal effectiveness of this new chemical against the usual common insect pests of the region and its persistence on plant surface. In these studies relative toxicity of this chemical to twelve different insect pests and its relative residual toxicity to four species of crop pests have been ascertained taking ethyl parathion as the standard and employing the bioassay technique.

A review of literature on the bioassay of organophosphorus insecticides, is also presented.

REVIEW OF LITERATURE

REVIEW OF LITERATURE

The earliest instance of bioassay appears to be that of the detection of rotenoids by Takie et al (1930) using Misgurnus anguillicaudatus as test insect. Much work has been done in this line subsequently using different methods, for various purposes; such as determination of the amount of insecticide on or in plants or animal tissues, determination of the residues of insecticides in plants and plant products, screening of chemicals for their insecticidal properties, determination of the relative toxicity of various insecticides and measuring the susceptibility of insect populations.

A large volume of literature has accumulated on the bioassay of insecticides and the present review is restricted to those works on the study of the relative toxicity of organophosphorus insecticides and their persistence on plants.

Bioassay of relative toxicity of organophosphorus insecticides

Magee and Gaines (1950) found that 5 per cent dust of 3677 (0,0, diethyl 0-2-chloro-4-nitrophenyl thiophosphate) at 25 lb per acre gave 74.5 per cent mortality of nymphs of the squash bug, Anasa tritis on cotton whereas parathion at the same rate gave only 59.4 per cent kill. Dusts containing 1 per cent 3700 (S-tert-butyl mercapto methyl 0-0-bis (2-chloro-ethyl) dithiophosphate), 3677 (0,0, diethylo-2-chloro-4-nitrophenyl thiophosphate), 3741 (S-carbamyl methyl 0,0-diethyl dithiophosphate) and parathion gave 98.3, 95.2, 89 and 94 per cent kill of Aphis gossypii on cotton leaves. Dusts containing 1 per cent of 3677 (0,0-diethyl 0-2-chloro-4-nitrophenyl thiophosphate) and parathion on cotton leaves gave 99 per cent kill of Septanychus sp.

Gaines et al (1950), observed that the order of decreasing toxicity of the compounds against Tetranychid mites and Aphis gossypii on cotton were tetra ethyl pyrophosphate (T.E.P.P.), Parathion, diethoxy thiophosphoric acid ester of 4-methyl

7-hydroxy coumarin, a mixture of parathion and its methyl analogue, tetra ethyl dithionopyrophosphate, mercurated pentaethyl triphosphate and Octamethyl pyrophosphoramide (Schradan).

Pradhan and Satpathy (1953) observed that in the case of the adults of Oxycaroenus laetus, released on dry films of insecticides in petridishes, the LC 50 of parathion was 0.0008215 per cent, as against 0.02680 per cent of p-p' DDT used as standard. In the case of Rhophalosiphum pseudobrassicae, directly sprayed under the Potter's tower the LC.50 of parathion was 0.000376 per cent, while that of p-p' DDT was 0.01644 per cent.

Smith et al (1956) in tests on the contact toxicity of parathion and E.P.N. on plum curculio. Conotrachelus nenuphar (H bst) showed that in adults wetted with water suspensions of the insecticides, the median lethal concentrations were 14 and 32 parts per million respectively, as against 4000 parts per million in case of methoxychlor.

Harries and Matsumori (1956) in tests using adults of cucumber beetle, Acalymma vittata (F) and

1 per cent dusts of insecticides observed that after 24 hours of contact, the mortality percentages were 100 for parathion, 94 for E.P.N. (O-ethyl O-p-nitrophenyl phosphonothioate), 80 for malathion and 81 for N.P.D. (Tetra-n-propyldithionate). In the case of Diabortica undecimpunctata howardi (Barber), tested in the same method, malathion gave 95 per cent kill, while other chemicals gave 100 per cent kill.

Stringer (1956) in his studies on the toxicities of organophosphorus compounds to adult males of Locusta migratoria migratoreoides, applied as acetone solutions topically or as injection into the body cavity as aqueous suspensions found that paraoxon (diethyl-p-nitrophenyl phosphate) was significantly more toxic than the rest; its L.D.50 being 0.4 microgram and 0.3 microgram per locust for topical application and injection respectively. The L.D.50 for topical application for other compounds were parathion, 1 to 1.5 microgram, O-p-nitrophenyl phosphorothioate 34.34 microgram E.P.N. 2.24 microgram and malathion 28.74 microgram per locust.

Gast et al (1956) in laboratory tests using insecticides applied topically to the sixth instar larvae of Heliothes zea (Boddie) and Heliothes virescens (F), found that L.D.50 values as microgram per gram body weight were 4.8 for both species for shell OS-2046 (dimethyl-2-methoxy carbonyl-1-methyl-vinyl, phosphate),40 and 54 for Bayer 17147 (0,0-dimethyl S-(4-oxo-benzotriazine-3-methyl) phosphorodithioate). 30 and 60 for Bayer L.13/59 (dimethyl 2,2, 2-trichloro-1-hydroxy ethyl phosphonate) and 130 and 160 for malathion while those for DDT were 3000 and 6500.

Pradhan et al (1956) found that L.C.50 values of parathion, systox, diazinon and malathion, sprayed on nymphs of Drosicha stebbingi. Guenc were respectively 36, 6, 3 and 0.169 times as much as that of p-p' DDT.

Pradhan et al (1957) in studies on the relative toxicity of some organic insecticides sprayed on the larvae of Euproctis lunata (Walker) found the L.C.50s to be 0.05218 for diazinon and 0.81230 for malathion, while that of p-p' DDT was 0.4604. Diazinion and malathion were thus 8.9 and 0.6 times as toxic as p-p' DDT. In studies based on the dry film technic, the L.C.50 values, were found to be 0.03645 for

Diazinon and 1.04200 for malathion, while that of p-p' DDT was 0.29730. Diazinon and malathion were found to be 8.2 times and 0.3 times as toxic as p-p' DDT.

Pradhan <u>et al</u> (1957), in their further studies on the relative toxicity of organo-phosphorus insecticides to <u>Lepaphis erysimi</u> (Kalt) observed that the LD 50 values were 0.00314 for systox, 0.00388 for parathion, 0.00437 for malathion, 0.01556 for H.E.T.P. and 0.03273 for pestox.

Pradhan <u>et al</u> (1958) in studies using the dry film technique found that in the case of <u>Cylas formicarius</u> the L.C. 50s were 0.00108 for parathion, 0.00126 for diazinon, 0.00222 for systox, 0.01147 for malathion while that of p-p' DDT was 1.24000. The relative toxicities of parathion, diazinon, systox and malathion were thus 1153.5, 985.7, 559.3 and 108.4 respectively as compared to that of DDT. In the case <u>Myllocerus undecimpunctatus</u> the L.C.50s were found to be 0.02911 for malathion, 0.03162 for parathion, 0.10960 for systox, 0.11750 for diazinon and 0.05649 for p-p' DDT. The relative toxicities of malathion, parathion, systox and diazinon were being respectively 1.940, 1.786, 0.515 and 0.355 taking that of p-p' DDT being equal to 1.

Pradhan et al (1958) assessed the relative toxicity of some insecticides to Aulacophora foveicollis (Lucas), by the dry film method and by the direct spraying method. Under the dry film method L.C. 50s were found to be 0.003148 for parathion 0.006683 for diazinon, 0.2415 for malathion and 0.1879 for p-p' DDT. Parathion, diazinon and malathion were respectively 60, 28 and 0.8 times as toxic as p-p' DDT. In the direct spraying method the L.C. 50s were 0.00697 for parathion and 0.05540 for p-p' DDT. Parathion was found to be 7.9 times as toxic as p-p' DDT.

Pradhan et al (1959) studying the relative toxicities of different insecticides to 6 ± 2 days old adults of Locusta migratoria, under laboratory conditions found, that the L.C. 50s were 0.005585 for parathion, 0.007852 for methyl parathion, 0.01266 for T.E.P.P., 0.06792 for diazinon, 0.07079 for systox, 0.08710 for H.E.T.P. and 0.1340 for malathion, while that of p-p' DDT taken as standard was 0.6109. Ethyl parathion, methyl parathion, T.E.P.P., diazinon, H.E.T.P., systox and malathion were found to be respectively 109.4, 77.8, 48.2, 9.0, 7.0, 8.6 and 4.6 times as toxic as p-p' DDT.

Jotwani et al (1960) studying the relative toxicity of different insecticides to the larvae of Prodenia litura (Fabricius) under laboratory condition, found that the L.C. 50s were 0.008091 for parathion, 0.03908 for malathion, 0.09506 for diazinon, while that of p-p' DDT taken as standard was 0.01626. Parathion was 2 times as toxic as p-p' DDT, while diazinon and malathion were found to be inferior to p-p' DDT.

Shi et al (1960) found that parathion was 84.1 times as toxic as p-p' DDT to adults of Tribolium castaneum, the L.C. 50 for DDT was 0.7784 per cent.

Pradhan et al (1960) found that methyl parathion and malathion were 39.72 and 8.65 times, respectively, as toxic as p-p' DDT to grubs of Hypera variabelis.

Shi et al (1960) studying the relative toxicity of insecticides to the grubs of Epilachna viginetiocto-punctata, found that the L.C. 50s were 0.00287 for parathion, 0.02340 for diazinon, 0.3388 for malathion and 0.03941 for phosdrin, while that of p-p' DDT, taken as standard was 0.21010. Parathion, diazinon, malathion and phosdrin were respectively 73.2056, 8.9786, 6.2013 and 5.3311 times as toxic as p-p' DDT.

Sarup _et al_ (1960) studying the relative toxicity of insecticides to _Aphis craccivora_ infesting cowpea, under laboratory conditions found that the L.C. 50s were 0.0001274 for phosdrin, 0.0007293 for parathion and 0.0008670 for malathion, while that of p-p' DDT taken as standard was 0.02100. Based on the L.C. 50s phosdrin, parathion and malathion were found to be respectively 164.8, 28.8 and 24.2 times as toxic as p-p' DDT.

Jotwani _et al_ (1960) studying the relative toxicity of some insecticides to the coccinellid predator _Stethorus pauperculus_ (Weise), found that the L.C. 50s were 0.5102×10^{-6} for phosdrin, 0.2375×10^{-5} for thimet, 0.2467×10^{-4} for malathion, 0.2657×10^{-4} for parathion, 0.2802×10^{-3} for gusathion, 0.3197×10^{-3} for Rogor and 0.5474×10^{-3} for thiodan, while that of p-p' DDT was 0.2253×10^{-1}. It was found that phosdrin, thimet, malathion, parathion, Rogor and thiodan were respectively 44159, 9486, 913.3, 847.9, 70.5 and 41.4 times as toxic as p-p' DDT.

Rattan lal _et al_ (1960) assessing the relative toxicity of some insecticides to the sugarcane mites

Schizotetranychus andropogoni (Hirst), under field conditions, found that the L.C. 50s were 0.0000929 for parathion, 0.0003581 for phorate, 0.001062 for thiemeton, 0.001445 for diazinon, 0.008954 for phosdrin and 0.01026 for malathion.

Trehan *et al* (1961) studying the relative contact toxicity of some insecticides to the red cotton bug, *Dysdercus cingulatus* (F) under laboratory conditions found that parathion was 1.6 times as toxic as DDT, based on their L.C. 50s.

Rathan Lal *et al* (1961) studying the relative toxicity of parathion dust, to different stage of the nymphs and adults of *Locusta migratoria* (Linnaeus) found that the L.C. 50s of parathion were 0.0290 for first stage hoppers, 0.0394 for second stage hoppers, 0.0682 for third stage hoppers, 0.0703 for fourth stage hoppers, 0.0745 for fifth stage hopper and 0.0700 for the adults.

Jotwani *et al* (1962) studying the efficacy of different insecticides as stomach poisons to *Locusta migratoria* (Linnaeus), using the sandwitch feeding method, found that parathion and systox were 45.19 and 5.07 times, respectively as toxic as p-p' DDT.

Jotwani *et al* (1962) in their study of the comparative toxicity of some insecticides to the adults of *Epilachna viginctioctopunctata* under laboratory conditions, found that the L.C. 50s were 0.002098 for parathion, 0.003082 for phosdrin and 0.018500 for malathion, while that of p-p' DDT, taken as standard was 0.1805. Parathion, phosdrin and malathion were 86.034, 58.566 and 0.979 times as toxic as p-p' DDT.

Shashikanta *et al* (1963) evaluating the toxicity of some insecticides to the Pigmite, *Eotetranychus hirsti* (Pritchard & Bales) under laboratory conditions, found that the L.C. 50 values were 0.000363 for phosphamidon 0.000377 for parathion, 0.000549 for dimethoate 0.000737 for thiometon and 0.000812 for diazinon.

Chang and Li (1964) in a laboratory test on the effect of trichlorofon dust against the oriental army worm, *Pseudaletia* (Leucania) *separata* (Walker) found that the L.C. 50s were 0.5, 1 and 2.5 per cent for the second, third and fifth instar larvae, respectively, when the larvae were dusted directly and 0.25, 0.5 and 1 respectively, when the seedlings were dusted and larvae of the second, third and fifth instar released on them.

Mac Cuaig and Yeates (1964) studying the toxicities of few insecticides, by topical application to the first instar nymphs of the desert locust, Schistocerca gregaria (Forsk) found that the mean L.D. 50s and L.D. 99s in micrograms per gram body weight were 0.43 and 1.51 for parathion, 4.22 and 10.3 for diazinon and 7.3 and 39 for BHC.

Sarup et al (1964) in testing the effect of pesticides against sawflower aphid, Dactynotus carthami (HRL), by direct spraying upon the insects taken in petridishes, under laboratory conditions, found that the L.C. 50s were 0.0001936 for phorate, 0.0004015 for phosphamidon, 0.0007409 for mevinphos 0.001442 for parathion, 0.001528 for malathion, 0.00204 for diazinon while it was 0.008523 for gamma BHC taken as standard. It was found that phorate, phosphamidon, mevinphos, parathion, malathion and diazinon were respectively 44.0, 21.2, 11.5, 5.9, 5.6 and 4.2 times as toxic as gamma BHC.

Metcalf and Frederickson (1965) found that the L.D. 50s of parathion and isopropyl parathion (O,O-diisopropyl-O-p nitrophenyl phosphorothioate) to Dacus dorsalis by topical application, under laboratory conditions were 1.2 and 3.5 microgram per gram body weight respectively, while those for Opius longicaudatus and Opius persulcatus, parasites of Dacus dorsalis were 1-2 and 100 microgram respectively.

Johnson (1965) studying the relative toxicity of some synthetic organic insecticides to the banana aphid, Pentalonia nigronervosa, under laboratory conditions, found that parathion was 8.9 times as toxic as DDT.

Herne and Chant (1965) studying the relative toxicity of kelthane and parathion to the predaceous mite, Phytoseiulus persimilis (Athias Henriot) and its prey Tetranychus urticae (Koch), under laboratory conditions, found that the L.C. 50s for Tetranychus urticae and Phytoseiulus persimilis were 0.051 and 0.29 per cent respectively, in the case of dicofol (kelthane) and 0.050 and 0.0044 per cent in the case of parathion.

Srivastava and Kaul (1965) studying the comparative toxicity of some insecticides to the full grown larvae of Amsacta moorii (Butler), under laboratory conditions, found that the L.C. 50s were 0.0097 for parathion 0.0135 for folithion and 0.129 for BHC. Parathion and folithion were 13.256 and 9.855 times as toxic as BHC.

Nigam et al (1965) studying the susceptibility of rice weevil, Sitophilus oryzae (L), by the impregnated filter paper method, under laboratory conditions, found that malathion and diazinon were respectively 12.923 and 1.445 times as toxic as DDT, whereas T.E.P.P., H.E.T.P. and pestox were progressively less toxic than DDT.

Shashi kanta et al (1965) studying the comparative toxicity of some insecticides to the Jamun leaf minor, Acrocercops phaeospora, by spraying the upper and lower surfaces of infected leaves, under laboratory conditions, found that the L.C. 50s were 0.000238 for parathion, 0.002094 for phosphamidon, 0.006699 for diazinon, 0.01884 for malathion while that of lindane taken as standard, was 0.005998.

Jotwani and Prakash sarup (1966) studying the relative toxicities of different pesticides to the adults of singhra beetle, Galerucella birmanica (Jacoby) under laboratory conditions, found that the L.C. 50s were 0.002973 for mevinphos, 0.003276 for phosphamidon, 0.003611 for parathion, 0.009757 for diazinon, 0.01363 for systox, 0.083810 for trichlorofon, 0.2485 for dimethoate, 0.7273 for malathion and 0.67850 for p-p' DDT, taken as standard.

Salama et al (1966) found that the L.C. 50s of trichlorofon and malathion as stomach poison to Prodenia litura were 0.05 and 0.132 mg per gram body weight respectively.

Rai et al (1966), studying the relative toxicity of some organophosphorus insecticides, to the mite, Eutetranychus banksi (Mc. Gregor), attacking castor, neem etc. under laboratory conditions, found that parathion, malathion, E.P.N., diazinon, phosphamidon, dimethoate and D.M.C. were respectively 22.86, 12.97, 6.8, 4.72, 0.9, 0.9 and 0.46 as toxic as dicofol (Kelthane).

Tripathi (1966) studying the relative toxicity of some insecticides to the hairy caterpillar, Diacrisia obliqua (Walker). under laboratory conditions, found that the L.C. 50s were 0.0242 for endosulfan, 0.0245 for parathion and 0.04075 for gamma BHC (Lindane).

Sarup et al (1966) in a comparative test of insecticides against apterae of cabbage aphid, Brevicoryne brassicae, under laboratory conditions, found that dimethoate, methyl parathion, phosphomidon, morphothion, carbophenthion, formothion, phorate, parathion, malathion, diazinon and E.P.N. were respectively 1182, 935, 833, 623. 425, 116. 101, 96,96 33 and 15 times as toxic as gamma BHC.

Verma et al (1967) studying the efficacy of different insecticides, to the adults of singhara beetle, Galerucella birmanica, under laboratory conditions found that mevinphos, bidrin, parathion and phosphamidon were respectively 170, 66, 44 and 26 times as toxic as gamma BHC.

Verma and Sehi (1967) found that foliar sprays of 0.03 per cent methyl demeton and 0.035 per cent phosphomidon, killed over 92 per cent of the larvae in the leaves.

Verma and Sandhu (1967) studying the relative efficacy of different insecticides as contact poisons to the larvae of diamond black moth, Plutella maculipennis (Curtis), under laboratory conditions, found that mevinphos, diazinon, malathion, bidrin and phosphomidon were respectively 366, 46, 31, 17 and 6 times as toxic as parathion.

Sarup et al (1967) testing different insecticides as contact poisons against adults of Myzus persicae (Sulz), under laboratory conditions, found that dimethoate, phosphomidon, methyl parathion, parathion, morphothion and malathion were respectively 22.9, 18 1, 12 9 9.3, 6 3 and 1 5 times as toxic as gamma BHC

Teotia and Nigam (1967) studying the relative toxicity of some insecticides as contact poisons to the larvae of Earias fabia (Stoll), using the dry film technic, under laboratory conditions found that the L C 50s were 0 00019744 for malat ion, 0 0002113 for diazinon, 0 0001367 for phosdrin and 0 00039595 for D D V P

Hari et al (1967) in the laboratory evaluation of certain organo phosphorus insecticides against the larvae of the khapra beetle, Trogoderma granarium (Everts), using the topical application of insecticides as acetone solutions under laboratory conditions, found that the L C 50s were 0 00703 for methyl parathion, 0 01132 for Bayer 41831 (0,0-dimethyl 0-(4-nitro-m-tolyl) phosphorothioate), 0.01193 for E P N ,0 01348 for guthion, 0 01742 for Fenthion, 0 01348 for parathion, 0 02622 for dicapthon, 0 02959 for ethyl guthion, 0.04335 for malathion, 0 06266 for Bayer 37289 (0-ethyl, 0-2,4,5, trichlorophenyl ethyl phosphonothioate), 0 06637 for diazinon, 0 0359 for S.D 7438 (Toluene-a-dithiolbis (0-0-dimethyl) phosphoro dithioate), 0 14160 for Dursban, 0 19510 for Stauffer N 2404 (0-isopropyl-0 (2-chloro-4-nitrophenyl) ethyl phosphorothioate), 0 3349 for D D V P , 0.43950 for AB/TE 4-E (0,0,0,0-tetramethyl 0,0 -thiodip-phenylene phosphorothioate) 1 07200 for Dylox, 3 922 for Zytron and 9 37600 for tributyl phosphate

Saini (1967) studying the effectiveness of some organophosphorus insecticides to the adults of mustard aphid, Hyadaphis (Lipaphis) erysimi, under laboratory conditions, found that the L C 50s, in the case of direct spraying under potters tower, were

0 00084 for parathion, 0 00125 for thiometon, 0.0021 for methyl demeton and 0 6045 for diazinon and those in the case when the adult aphids were released on sprayed mustard plants were 0 0038 for mevinphos, 0 0053 for parathion, 0 0074 for methyl demeton, 0 0095 for diazinon and 0.0098 for thiometon

Sarup et al (1967) studying the toxicity of some insecticides to the larvae of Euproctis lunata (Walker), under laboratory conditions, found that the L C 50s were 0 007?5 for mevinphos, 0.01450 for parathion, 0 02877 for E P N , 0 04154 for trichlorofon, 0 1364 for endosulfan, 0 1350 for methyl parathion, 0 6027 for formothion and [illegible] for phosphamidon, while that was 0 3045 for p-p' DDT, taken as the standard.

Tripathi (1967) studying the relative contact toxicity of some insecticides, to the larvae of jute semilooper, Anomis sabulifera (Guen) under laboratory conditions found that the L C 50 were 0 00028 for endosulfan, 0 0012 for ethyl parathion, while that of p-p' DDT was 0 00266

Pritamsingh et al (1968) found that diazinon and azinphos-methyl were respectively 7 and 0.1 times as toxic as oxy-demeton methyl

Singh et al (1968) studying the relative toxicity of some important pesticides to the adults of blister beetle, Mylabris pustulata (Thunb), under laboratory condition, found that the L D 50s were 0 006398 for phosphomidon, 0.020380 for parathion, 0 03539 for formathion, 0 042400 for malathion and 0 171800 for thiodemeton, while that was 0.06459 for p-p' DDT Phosphamidon, parathion, formothion, malathion and thiodemeton were 10 0953, 3 169, 1 825, 1 523 and 0.376 times as toxic as p-p' DDT.

Sarup et al (1969) studying the relative toxicity of different insecticides to the larvae of Pseudaletia seperata (Walker), under laboratory conditions, found that the L C 50s were 0 003352 for methyl parathion, 0 008383 for mevinphos, 0 01124 for E P N , 0 02860 for ethyl parathion 0 06377 for trichlorofon, 0 1171 for diazinon 0.3060 for malathion and 0 5514 for p-p DDT, taken as standard Methyl parathion, mevinphos, E.P N , ethyl parathion, trichlorofon, diazinon and malathion were respectively 164 5, 65 8, 49.1, 19 3, 8 7, 4 7 and 1 6 times as toxic as p-p' DDT.

Teotia and Upadhyaya (1969) studying the relative toxicity of some important insecticides to the larvae of

0.001828 for formathion and 0.005198 for trichlorofon while it was 0.004094 for p-p' DDT, taken as standard.

Sarup et al (1969) in testing of different pesticides against adults of sugarcane leaf hopper Pyrilla perpusilla (Walker), under laboratory conditions found that the L.C. 50s were 0.00002746 for methyl parathion, 0.00003945 for ethyl parathion, 0.0002456 for malathion, 0.0003073 for azinphos ethyl carbophenthion, 0.0009822 for dimethoate, 0.001095 for fenitrothion, 0 001601 for phosphamidon, 0.002061 for formothion, 0.002156 for morphothion, 0.0022240 for disulfaton, 0.002803 for fenthion and 0.015680 for trichlorofon while it was 0.002803 for p-p' DDT.

Bogawat et al (1969) while studying the susceptibility of two species of pumpkin beetles, to some insecticides, under laboratory conditions found that the L.D. 50 value of malathion to Aulacophora foveicollis and to Aulacophora stripenis were found to be 0.281910 and 0.086257 respectively.

Sarup et al (1969) studying the toxicity of different insecticides to Aphis craccivora, infesting pea crop, under laboratory conditions found that the

L C 50s were 0.00004052 for phorate, 0 00001496 for methyl demeton, 0.00002823 for phosphamidon, 0 00003955 for dimethoate, 0.0007150 for parathion, 0 00008849 for methyl parathion, 0.00009712 for E.P N , 0 0003438 for malathion, 0.0004048 for fenitrothion, 0 0004816 for azinphos methyl, 0 0005505 for diazinon, 0 000624 for formathion, while that of p-p' DDT taken as standard was 0.02511

Bioassay of residues of organophosphorus insecticides on plant surfaces

The conception of residual toxicity and its utilisation to control insects was first put forth by Potter (1938) He from his studies, on the control of *Plodia interpunctella* (Hb) and *Ephestia elutella* (Hb) concluded that it was desirable to spray warehouses not only for directly killing the insects during treatment, but also to deposit a protective film on the exposed surfaces, so that the moths which emerge, subsequent to spray might get a fatal dose, when they settle on that film

The work of Todd (1938) seems to be the first in this kind of experiments studying the persistence of insecticidal residues on plant surfaces He studied the persistence of derris on bean foliage and found that under field conditions it did not give protection against the Mexican beetle, beyond 7 days of exposure in open places, but in shaded bean plants, it persisted for a period of two weeks.

Dickson (1944) published a short note on the technique for evaluating the residual toxicity of organic insecticides on plant surfaces. In his studies he sprayed potted bean seedlings with a known amount of toxicant per unit area and on the treated leaf, ten mites were confined to a definite area for 48 hours by means of a sticky barrier at various intervals afterwards and mortality recorded.

Hoskins (1949) in studying the danger of contamination of food stuffs of vegetable and animal origin with insecticidal chemicals, found that parathion residues disappeared rapidly and all dried and processed fruits were free from it. Residues exceeding 1 ppm, after a few days were found only on grapes and olives and they rapidly decreased thereafter.

Hopkin et al (1952) from their studies on the persistence of insecticide residues on forage crops, found that in case of contact insecticides, increase in leaf area resulted in a decrease in the insecticide deposit per unit area of leaf, rather than a decrease in the total quantity of insecticides.

Carman (1952) in laboratory tests to elucidate the factors controlling the re-issuance or vapourisation of parathion existing as extra cuticular or sub-cuticular residues on field sprayed oranges, using housefly adults as test insects, found that a current of air passing over the sprayed oranges and directed through a cage containing the adult houseflies, produced no mortality.

Smith et al (1956) in studying the persistence effect of some insecticides on plum leaves, using the adults of plum curculio, Conotrachelus nenuphar (Hbst) as test insect, found that parathion, weather most rapidly, only one per cent of the original deposit being left after 14 days while DDT showed 20 per cent of the original deposit after 14 days.

Jotwani and Girish (1963) in an experiment in which wheat plants sprayed with emulsion of parathion at 0 0625, 0.094 and 0.125 lb of active ingredient per acre and the sprayed leaves cut periodically and fed to first stage hoppers of <u>Locusta migratoria</u> found that after 4 days the loss of toxicity were 81.9, 77.2 and 59.3 per cent respectively. Toxicity of all the three doses practically lost after 8 days, when treated against the first stage hoppers.

Desmoras (1963) studying the persistence of the residues of vamidothion in the fruits of apple, sprayed with vamidothion at 0.5 lb per 100 gallons using <u>Daphnia pulex</u>, found that the residue of the insecticide in the fruits were 1 ppm after 41 days

Williams (1963) found that sprays of methyl demeton, dimethoate, and phosphamidon at concentrations of 0.09, 0.06 and 0.04 per cent respectively, applied in June, 1961 at 60 gallons per acre gave satisfactory control and significantly reduced the population of <u>Aphis fabae</u> (Scoh), on tick beans for upto 14 days.

Pramanik (1963) in experiments to determine the persistence of residues of parathion on the leaf of sugarcane, found that residues on the sugarcane leaf, formed by 0.05 to 1 per cent sprays of parathion, gave complete mortality of newly hatched larvae of <u>Chilotraea infuscatellus</u> (Snellen), exposed for

15 minutes on the sprayed leaves, but lost all effectiveness 2 days after.

Rattan Lal and Dhall (1965) in studying the persistence of insecticidal spray residues on bhindi leaves against the first instar larvae of Earias fabia (Stoll) found that sprays of 0 095-0 38 per cent malathion and 0 0125 - 0 05 per cent parathion gave 94 to 100 per cent mortality after an hour, but the deposits gradually lost toxicity Parathion lost toxicity completely within 3 days and malathion within 7 days.

Cox (1966) in laboratory investigations on the effectiveness of some insecticides applied as sprays to the foliage of grapevines, against the red banded leaf roller, Argyrotaenia velutinana (Wlk) found that high initial mortality of adults was given by deposit of parathion, azinphos-methyl (Guthion), fenitrothion and NIA 9203 (0,0-dimethyl-S(2-oxo-3-benzoxazalinyl) methyl phosphorothioate) but persistence was poor. Residues of parathion and azinphos-methyl were effective against second instar larvae one day after treatment, but lost toxicity after 5 days.

Peretz *et al* (1966) in their trials in the control of the mediteranian fruit fly, *Ceratitis capitata* (Wied) found that fenthion 0 05 per cent was the most effective against adults and against larvae within the fruits, giving 90-100 per cent mortality of flies, confined in the laboratory for 24 hours with apricots upto 11 days and on peaches upto 9 days after these had been sprayed and 80-100 per cent mortality of those confined with guavas upto 7 days after spraying. Dimethoate at 0 04 per cent and phosphamidon at 0.05 per cent were less effective than fenthion against the adults, but almost equally effective against the larvae.

Liopold *et al* (1967) studying the disappearance of parathion residues from braccoli treated in the field with emulsion sprays at 0.5 and 0 8 lb per acre, by subjecting samples taken from 0 to 7 days from the time of application, to gas-liquid chromatography, spectrophotometry and bioassay with *Drosophila melanogaster* (Mg), found that the results from all the three methods showed similar trends and fair agreement and the half life for parathion on braccoli was found to be 3.3 days.

Pritam Singh and Rattan Lal (1967) assessing the persistence of parathion residues on tomato fruits sprayed in the field, with 0.05 per cent and 0.1 per cent emulsions, during summer, using Bracon brevicornis as the test insect, found that 4 days after spraying the residues were reduced by 99.8 per cent and 99.9 per cent respectively.

Teotia and Singh (1969) during laboratory assessment of the toxicity of field-weathered deposits of some insecticides on mustard leaves, using the larvae of mustard sawfly, Athalia proxima (Klug), have found that with diazinon 0 03 per cent, malathion 0.05 per cent, parathion 0.03 per cent and phosphamidon 0 03 per cent, 100 per cent mortality was obtained with fresh deposits, with all the four compounds, while the deposits of malathion, showed 50 per cent reduction of toxicity on the third day and became ineffective on the fifteenth day, those of parathion, phosphamidon and diazinon continued to remain highly effective upto 3 days after spraying with a mortality of 96.3 per cent in all cases 15 days after application, the deposit of diazinon also become wholy ineffective, with an average mortality of 1 2 per cent only while deposit of parathion and phosphamidon showed 63 4 and 33 3 per cent average mortalities respectively. At the higher concentrations diazinon (0.065 per cent), parathion (0.065 per cent), malathion (0 1 per cent) and phosphamidon (0 065 per cent) the percentage reduction of toxicity after 1 day, 3 days, 7 days and 15 days were respectively 0, 0, 0 and 73 5 for diazinon, 0, 0, 0 and 20 0 for parathion, 0, 6 7, 46 6 and 80.7 for malathion and 0, 0, 0 and 0 for phosphamidon.

Kalode <u>et al</u> (1969) studying the persistence of insecticidal residues on rice plant against <u>Leptocorisa varicornis</u> (Fabricius), found that the relative residual toxicity of 0 05 per cent emulsions sprayed on 40 days old potted plants of Taichung Native-1, and measured at intervals of 2, 24 and 48 hours after spraying, in terms of P T indexes (products of period and average of the residual toxicities for the period) were 196.2 for fenthion, 177.8 for phosphamidon, 106 for endosulfan, 87 8 for E P N., 87.2 for parathion, 73 6 for diazinon and 73 4 for malathion, while it was 48 only for gammaxene

Dewan <u>et al</u> (1969) studying the loss of malathion residues on developing pods of cowpea, found that the residues, developed as a result of a 0 3 per cent spray of malathion, lost rapidly. There was only 2 04 ppm after one day, 1.03 ppm 2 days after and no residues from 7th days onwards.

Israel *et al* (1969) studying the persistence of insecticidal residues on rice plant, against newly hatched larvae of *Tryporyza incertulas*, found that the relative residual toxicity of 0 1 per cent emulsions sprayed on potted plants of Taichung Native-1 and measured at intervals of 1 3 and 4 days after spraying in terms of P.T. indexes were 173 2 for fenitrothion 308.4 for phenthoate, 300 0 for parathion, 112 4 for formothion and 290 8 for phosphamidon.

MATERIALS AND METHODS

MATERIAL AND METHODS

MATERIAL

Insecticides

Sandoz Insecticide 6538: A new insecticide supplied by Sandoz of Switzerland was used in the present studies. The insecticide was obtained as an emulsifiable concentrate containing 25 per cent of the active ingredient - O,O-diethyl-thionophosphoric acid-O-(quinoxalyl-(2))-ester

Parathion: A hundred per cent technical grade of ethyl parathion supplied by M/s. Bayer (India) Ltd , Bombay was used as the standard.

Emulsifier

Triton x 100 supplied by M/s. Indophil Chemicals, Bombay was used as emulsifier in the preparation of parathion emulsions.

Benzene

Benzene supplied by M/s. Quality Products, Bombay was used as a solvent in the preparation of emulsion from parathion.

Equipments used

Potters spraying tower

Hand operated atomizer

Glass wares used

These included pippettes, measuring cylinders, glass bottles, petridishes, glass troughs, glass chimminies, specimen tubes and earthen pots.

Test insects

Spodoptera littoralis (Prodenia litura Fabricius)
(Noctuidae Lepidoptera)

The caterpillars required for the studies were collected from banana plants in the College Farm and reared in the laboratory on banana leaves for few days Caterpillars measuring between 2 25 and 2 50 cm length were selected and used for the experiment.

Diacrisia obliqua Walker (Arctiidae Lepidoptera)

The larvae were collected in their early stages from *Clerodendron* plants in the College Farm and reared in the laboratory on groundnut leaves Caterpillars measuring between 1 25 and 1.50 cm long were used for the experiments

Spodoptera mauritia Boisd (Noctuidae Lepidoptera)

The caterpillars required for the studies were reared in the laboratory on paddy leaves, from egg masses collected from paddy seedlings in the Agricultural College Farm Caterpillars measuring between 1 6 and 2 0 cm long were used for the experiments

Nymphula depunctalis Guen (Pyraustidae: Lepidoptera)

The larvae were collected from the infected paddy crop in the Agricultural College Farm The larvae with their cases thus collected from the field were directly used in the bioassay experiments.

Aphis craccivora Koch (Aphididae Hemiptera)

The aphids required for the experiments were collected from *Glyricidia maculata* which is heavily infested by the aphid Apterous adults alone were used in the experiments

<u>Cnaphalocrocis</u> <u>medinalis</u> Guen (Pyralidae Lepidoptera)

The caterpillars required for the studies were collected from the paddy crop in the Agricultural College Farm and used as such Fairly grown up caterpillars were used for the experiments

<u>Tribolium</u> <u>castaneum</u> Herbst (Tenebrionidae Coleoptera)

The adult beetles required for the studies were reared in the laboratory on wheat flour in glass bottles. The adult beetles that have emerged upto the 45th day after releasing of the parents in the wheat flour, were collected and used for the experiments

<u>Pericallia</u> <u>ricini</u> Fabricius (Arctiidae Lepidoptera)

The caterpillars required for these studies were reared in the laboratory on banana leaves Caterpillars ranging between 1 5 and 1 8 cm in length were used for these experiments

Epilachna implicata Muls (Coccinellidae Coleoptera)

The grubs and adults required for the experiments were reared in the laboratory on bittergourd leaves from eggs or first instar grubs, collected from bittergourd plants in the Agricultural College Farm Grubs measuring 0 8 cm long and adults of 2 to 4 days old were used in the experiments

Cylas formicarius Fabricius (Curculionidae: Coleoptera)

The adult weevils required for the experiments were reared in the laboratory on sweet potato tubers. 2 to 5 days old adults were used in the experiments.

Corcyra cephalonica Stainton (Phycitidae Lepidoptera)

The larvae required for the studies were reared in the laboratory on wheat flour 12 days old (including the egg stage) larvae were used for the experiments

METHODS

Preparation of the insecticide formulations

Both the insecticides were used as emulsions, prepared from the technical grade in the case of parathion and from the emulsifiable concentrate in the case of Sandoz Insecticide 6538 Fourteen graded concentrations ranging from 0 000039 to 0 32 per cent of each insecticide were used in the experiment. In the case of parathion, its solution in benzene was prepared first, from which lower concentrations of emulsions were obtained by mixing with water containing 0 625 per cent of the emulsifier triton x 100 The proportions of the solution, emulsifier and water in the final formulations were so adjusted that the percentages of benzene and emulsifier in all dilutions were kept constant at 5 per cent and 0 625 per cent respectively In the case of Sandoz Insecticide 6538 the emulsifiable concentrate was diluted with water to give the required concentration of emulsions Details of proportions of the different constituents of each insecticide are given in the following tables.

Sandoz Insecticide 6538

Insecticide concentrate	Water added (in ml)	Concentration of emulsion (in percentage)	
1 gram 25% E C.	77.125	0.32	(A)
10 ml A	10.00	0.16	(B)
10 ml B	10.00	0.08	(C)
10 ml C	10.00	0.04	(D)
10 ml D	10.00	0.02	(E)
10 ml E	10.00	0.01	(F)
10 ml F	10.00	0.005	(G)
10 ml G	10.00	0.0025	(H)
10 ml H	10.00	0.00125	(I)
10 ml I	10.00	0.000625	(J)
10 ml J	10.00	0.0003125	(K)
10 ml K	10.00	0.00015625	(L)
10 ml L	10.00	0.0000781	(M)
10 ml M	10.00	0.000039	(N)

Parathion

Stock solutions

1 gram of parathion technical + 14 625 ml benzene =

= 6 4 per cent solution (S_1)

Insecticide concentrate	Benzene added (in ml)	Resulting solution (per cent)	
2 ml S_1	2	3 2	(S_2)
2 ml S_2	2	1 6	(S_3)
2 ml S_3	2	0.8	(S_4)
2 ml S_4	2	0 4	(S_5)
2 ml S_5	2	0 2	(S_6)
2 ml S_6	2	0 1	(S_7)
2 ml S_7	2	0 05	(S_8)
2 ml S_8	2	0 025	(S_9)
2 ml S_9	2	0 0125	(S_{10})
2 ml S_{10}	2	0 00625	(S_{11})
2 ml S_{11}	2	0 003125	(S_{12})
2 ml S_{12}	2	0 0015625	(S_{13})
2 ml S_{13}	2	0 00078125	(S_{14})

<u>Emulsions</u> Emulsions were prepared from the above solutions by adding emulsifying water as per details given in the following table

Insecticide solution	Emulsifying water added (ml)	Resulting emulsion (per cent)	
1 ml S_1	19	0 32	(A)
1 ml S_2	19	0 16	(B)
1 ml S_3	19	0 08	(C)
1 ml S_4	19	0 04	(D)
1 ml S_5	19	0 02	(E)
1 ml S_6	19	0 01	(F)
1 ml S_7	19	0 005	(G)
1 ml S_8	19	0 0025	(H)
1 ml S_9	19	0 00125	(I)
1 ml S_{10}	19	0 000625	(J)
1 ml S_{11}	19	0 0003125	(K)
1 ml S_{12}	19	0 00015625	(L)
1 ml S_{13}	19	0 0000781	(M)
1 ml S_{14}	19	0 000039	(N)

The emulsions used for the study of the persistence of residues on plants were of different concentrations in some cases and were prepared as follows:-

0 02 per cent and 0 04 per cent emulsions were prepared in the same way as given above

Sandoz Insecticide 6538

0 3 gram of 25% E C + 24 7 ml water	= 0.3% emulsion	(A)
1 ml A + 9 ml water	= 0 03% emulsion	(B)
0 4 gram 25% E C + 24 6 ml water	= 0.4% emulsion	(C)
1 ml C + 99 ml water	= 0.004% emulsion	(D)

Parathion

0 2 gram of parathion technical + 33 13 ml benzene	= 0 6% solution (S_1)
1 ml S_1 + 19 ml E W	= 0 03% emulsion (A)
1 ml S_1 + 9 ml benzene	= 0 06% solution(S_2)
1 ml S_2 + 19 ml E W	= 0 003% emulsion (B)

Collection and rearing of test insects

Spodoptera littoralis (= Prodenia litura, Fabricius)

Early stage caterpillars, which are by habit gregarious, were collected from banana leaves and reared in the laboratory on tender banana leaves in clean glass troughs The caterpillars were daily transferred to clean fresh troughs and fresh leaves given as food

Diacrisia obliqua Walker

The tiny caterpillars found in large gregarious groups on Clerodendron plants were collected and reared in clean troughs on groundnut leaves

Spodoptera mauritia Boisd

Egg masses collected from paddy seedlings were kept in clean chimnies The hatched out larvae were fed for 2 days in the chimney itself, giving leaves of paddy seedlings On the third day the larvae were transferred to clean glass troughs and thereafter reared in glass troughs, giving leaves of paddy seedlings as food

Tribolium castaneum Herbst

The adults required for the study were reared in the laboratory in wheat flour. Glass bottles (7 cm x 17 cm size) were half filled with wheat flour and adult beetles were released in the wheat flour, at the rate of 15 per bottle The top of the bottles were covered with white cotton cloth, held in position by means of rubber bands On the 45th day, the adult beetles which have emerged were collected by seiving the contents in the bottles through a 60 mesh seive

Pericallia ricini Fabricius

The caterpillars required were reared in the laboratory on banana leaves Few grown up caterpillars obtained from a banana plant in the College farm were reared in glass chimneys on tender unopened banana leaves, till they pupated The emerging adults were given 5 per cent sugar solution in watch glass as food. The female moths laid eggs from the 3rd day after emergence The eggs laid were collected and kept in clean glass chimneys The larvae were fed with tender banana leaves cut into pieces. Later the caterpillars were reared in glass trough on tender banana leaves

Epilachna implicata Muls

The grubs and adults, required for the studies were reared in the laboratory on bittergourd leaves. Egg masses or first instar grubs collected from bittergourd plants were reared in glass trough on bittergourd leaves.

For collecting adults, the pupae were daily collected from the rearing troughs and kept in separate glass trough The adults which emerged were given bittergourd leaves as feed

Cylas formicarius Fabricius

The beetles were reared on sweet potato tuber in glass troughs The weevils collected from the field were put on the tubers and the troughs kept closed with musline cloth The emerging beetles were used for the experiments

Corcyra cephalonica Stainton

The larvae required for the experiments were reared, in the laboratory on wheat flour. Adult moths reared in the laboratory were released in glass troughs containing wheat flour to about 2 cm thickness and covered with white cotton cloth The moths were collected back and removed on the next day. This was to ensure that all the larvae which developed in the trough were of the same age and brood.

Determination of dosage mortality relations between the insecticides and the different test insects

In these studies the test insects were taken in petridishes and sprayed directly under a Potter's spraying tower. One ml of the emulsion was used for each spraying and the spraying was done at a pressure of 25 lb per square inch. Fifteen minutes after spraying, the sprayed test insects were transferred to clean petridishes or tubes with or without food as the case may be The containers were kept in the laboratory under laboratory conditions and the mortality data recorded 24 hours after treatment.

In the case of the test insect *Nymphula depunctalis* Guen 22 days old paddy seedlings (I R 8 variety) were planted in glass bottles (7 x 17 cm) at the rate of 2 seedlings per bottle Ten days after planting, the plants in each bottle were sprayed with

3 cc of the insecticide emulsion concerned, with a hand operated atomizer Twenty minutes after the spraying, by which time the spray fluid had dried up, the larvae of Nymphula depunctalis were released along with the cases, on the paddy seedlings at the rate of 10 larvae per seedling The plants in each bottle was then covered by a glass chimney, the top of which being closed with a muslin cloth The bottles containing the plants were kept in the open The mortality of the caterpillars were noted 24 hours after releasing them on the sprayed plants

Determination of the persistence of insecticidal residues on plants

These experiments were done in potted plants The required number of potted plants of each crop were grown under identical conditions. Three potted plants of each crop were sprayed with the insecticide emulsion. The dosage of the insecticide in the emulsion was fixed based on the L D 90 values for the concerned test insect The sprays were applied using a hand operated atomizer to the point of slight run-off The potted plants for each treatment and control were selected at random The sprayed plants were kept in the open For assessment of the toxicities of both fresh and field weathered deposits of the two insecticides, 3 leaves of uniform size, from each plant were collected at specified intervals after treatment The leaves collected from each plant were placed separately in clean petridishes and the concerned test insects exposed to them The petridishes containing the test insects and leaves were kept in the laboratory for 24 hours, after which the mortality of the insects were recorded.

In the case of the larvae of Cnaphalocrocis medinalis Guen, paddy seedlings of 20 days old were transplanted in glass bottles and fifteen days after transplanting, the plants in the bottles, selected at random, were sprayed with the concerned insecticide with a hand operated atomizer to the point of slight run-off All the sprayed plants in the bottles were kept in the open Larvae of Cnaphalocrocis medinalis were released on the plants at different intervals following the insecticidal application After releasing the larvae, the plants were covered with glass chimneys, the top of which were covered by muslin cloth The bottles containing the plants and larvae covered by chimneys were kept in the laboratory for 24 hours and mortality count of the larvae taken at the end of that period.

The relative persistence of the residues of the two insecticides was assessed by calculating the 'P.T' value, as elaborated by Pradhan (1967), in which the product (PT) of the average residual toxicity (T) and the period (P) for which the residual toxicity could be studied, are taken as a measure of the relative residual toxicity.

RESULTS

DETAILS OF EXPERIMENTS AND RESULTS

Determination of the toxicity of Sandoz Insecticide 6538 to crop pests in comparison with that of parathion

Concentration-mortality relations between parathion and Sandoz Insecticide 6538 and twelve species of crop pests were determined by direct application of the graded concentrations of the insecticides or by releasing the test insects upon plants sprayed with graded concentrations of the insecticides Details of these experiments and their results are presented below

Experiment 1

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and *Spodoptera littoralis* larvae

Details of experiment

Concentration of insecticides The concentration of the two insecticides used were 0 04, 0 02, 0 01, 0 005, 0 0025 and 0 00125 per cent

Number of insects in each replication: 10

Number of replication	3
Control	Caterpillars contained in petridishes were sprayed with water
Date of spraying:	20-12-1969
Temperature during experiment:	Maximum 32°C Minimum 31°C
Humidity during experiment:	Maximum 85 Minimum 58

<u>Procedure</u>: Preparation of the dilutions of insecticides and their application and assessment of results were done as described under 'Material and methods The caterpillars after spraying were transferred to clean petridishes and fed with tender banana leaves, cut into pieces.

<u>Results</u>: Results are presented in Table 1 and Fig 1 The results of analysis of the data are as follows -

	Parathion	Sandoz Insecticide 6538
Regression equation	y = 1 567x - 0 104	y = 2 6018x - 1 861
Chi-square	7 957	15 42 (Significant)
Heterogenity coefficient	1 989	5 104
L D 50	0 01807	0 004335
Fiducial limits: m_1	0 01087	0 00236
m_2	0 03007	0 00796
Relative toxicity taking that of parathion as equal to one	1	4 17

Table 1

Mortality of caterpillars of Spodoptera littoralis, when sprayed with emulsions of parathion and Sandoz Insecticide 6538 in different concentrations

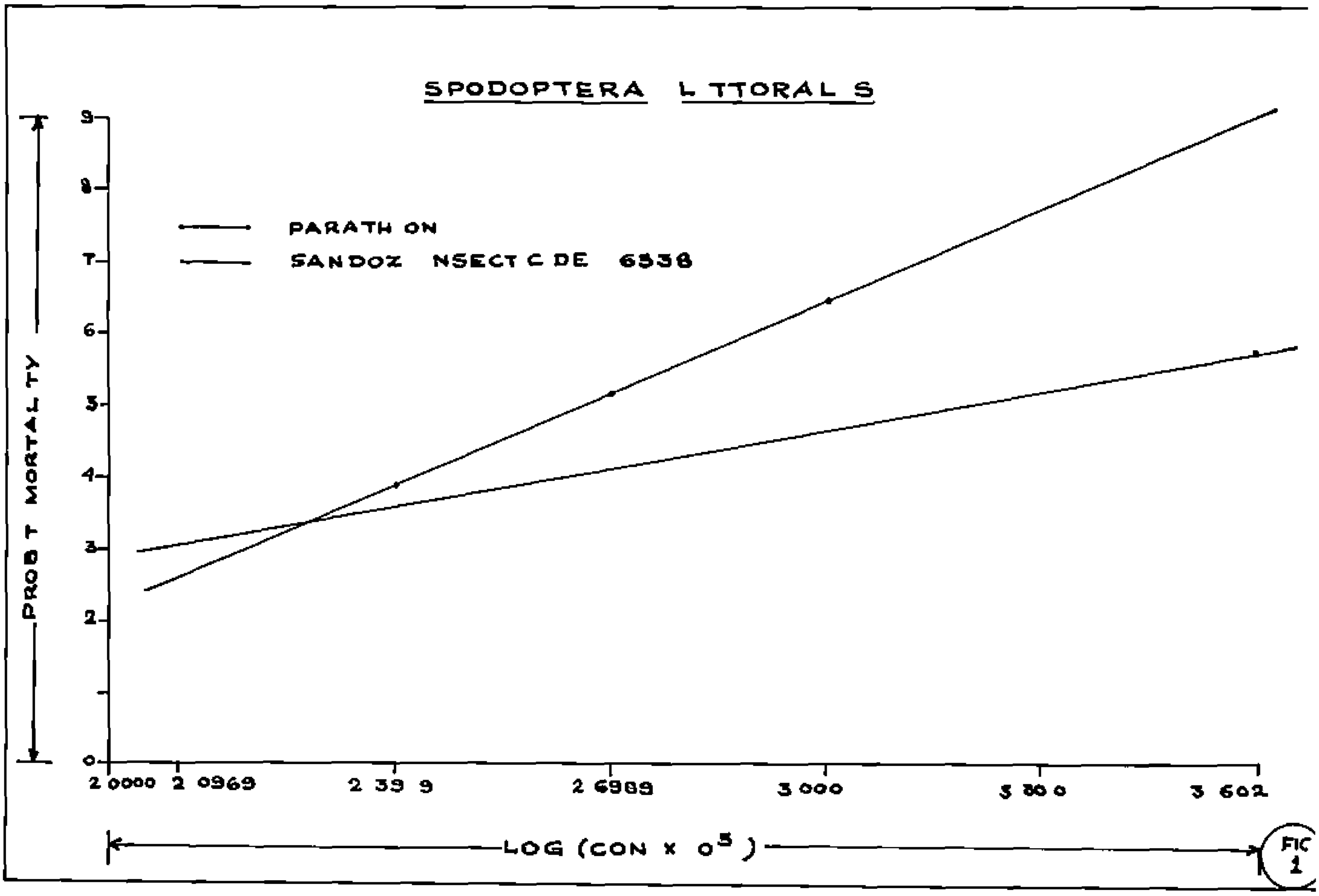
Concentration of the insecticides (%)	Percentage mortality in 24 hours	
	Parathion	Sandoz Insecticide 6538
0.04	76 67	100.00
0 02	60 00	96 67
0 01	16.67	93 33
0 005	13 33	56 67
0 0025	13.33	13 33
0 00125	6 67	6 67
Control	0	0

Fig 1

Log concentration - Probit Mortality relationship between parathion and Sandoz Insecticide 6538 and larvae of Spodoptera littoralis

Fig 2

Log concentration - Probit Mortality relationship between parathion and Sandoz Insecticide 6538 and larvae of Diacrisia obliqua


SPODOPTERA L TTORAL S
PARATH ON
SANDOZ NSECT C DE 6538
PROB T MORTAL TY
9
8
7
6
5
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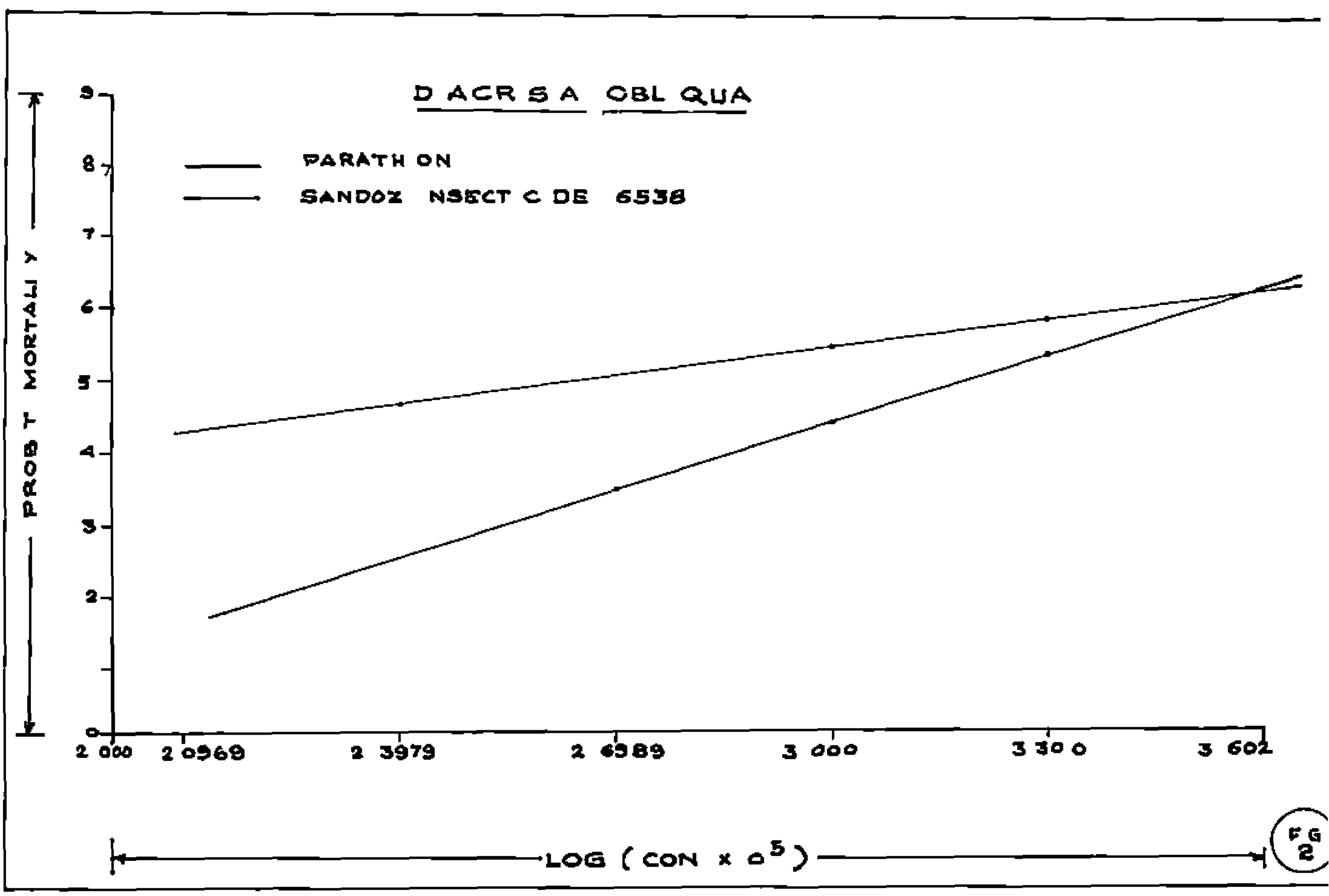
0
2 0000
2 0969
2 39 9
2 6989
3 000
3 300
3 602
LOG (CON x 0⁵)
FIG 1


D ACR S A OBL QUA
PARATH ON
SANDOZ NSECT C DE 6538
PROB T MORTALI Y
9
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0
2 000
2 0969
2 3979
2 6989
3 000
3 300
3 602
LOG (CON x 0⁵)
F G 2

It will be seen that Sandoz Insecticide 6538 is relatively more toxic to the caterpillars of *Spodoptera littoralis* than parathion Thus based on L D 50 values Sandoz Insecticide 6538 is found to be 4 17 times more toxic than parathion Judging from the relative slopes of the ld-p lines the Sandoz Insecticide 6538 appears to have increased responses to increases in the doses

Experiment 2

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and *Diacrisia obliqua* larvae

Details of experiment:

Date of spraying	29-12-1969
Temperature during experiment:	Maximum 30°C Minimum 28 5°C
Humidity during experiment:	Maximum: 93 Minimum: 66

Procedure: The caterpillars transferred to clean petri-dishes, after spraying were not supplied with leaves for food.

Rest of the details as in experiment 1

Results: Results are represented in Table 2 and Fig 2

The results of the analysis of the data are as follows

	Parathion	Sandoz Insecticide 6538
Regression equation	y = 3 3994x - 5 769	y = 1 703x + 0 417
Chi-square	0 51	7 81
Heterogenity coefficient	0 26	1 952
L D 50	0 01472	0 00492
Fiducial limits m_1	0 01341	0 00331
m_2	0 01627	0 00727
Relative toxicity taking that of parathion is equal to one	1	2 99

It will be seen that the Sandoz Insecticide 6538 is relatively more toxic to *Diacrisia obliqua* larvae than parathion Based on L D 50 values Sandoz Insecticide 6538 is found to be 2 99 times more toxic than parathion Judging from the relative slopes of the ld-p lines Sandoz Insecticide 6538, appears to have lesser responses to increases in the doses, than that of parathion.

Experiment 3

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and *Spodoptera mauritia* larvae

Details of experiment As in experiment 2

Table 3

Mortality of *Spodoptera mauritia* larvae when sprayed with emulsions of parathion and Sandoz Insecticide 6538, in different concentrations

Concentration of the insecticides (%)	Percentage mortality in 24 hours	
	Parathion	Sandoz Insecticide 6538
0 04	100 00	100 00
0.02	73 33	100 00
0 01	33 33	86 67
0 005	16 67	50 00
0.0025	13 33	23 33
0 00125	0	10 00
Control	0	0

Table 2

Mortality of caterpillars of *Diacrisia obliqua* when sprayed with emulsions of parathion and Sandoz Insecticide 6538 in different concentrations

Concentration of the insecticides (%)	Percentage mortality in 24 hours	
	Parathion	Sandoz Insecticide 6538
0 04	96 67	93 33
0 02	63 33	80 00
0.01	26 67	70 00
0 005	6 67	66 67
0 0025	0	36 67
0 00125	0	3 33
Control	0	0

Results: Results are represented in Table 3 and Fig 3

The results of analysis of the data are as follows -

	Parathion	Sandoz Insecticide 6538
Regression equation	y = 1 641x - 0.224	y = 2 343x - 1 220
Chi-square	12.86(Significant)	7 23
Heterogenity coefficient	6 43	3 615
L D 50	0 01525	0 004515
Fiducial limits m_1	0 004892	0 002838
m_2	0.04757	0 007162
Relative toxicity taking that of parathion is equal to one	1	3 377

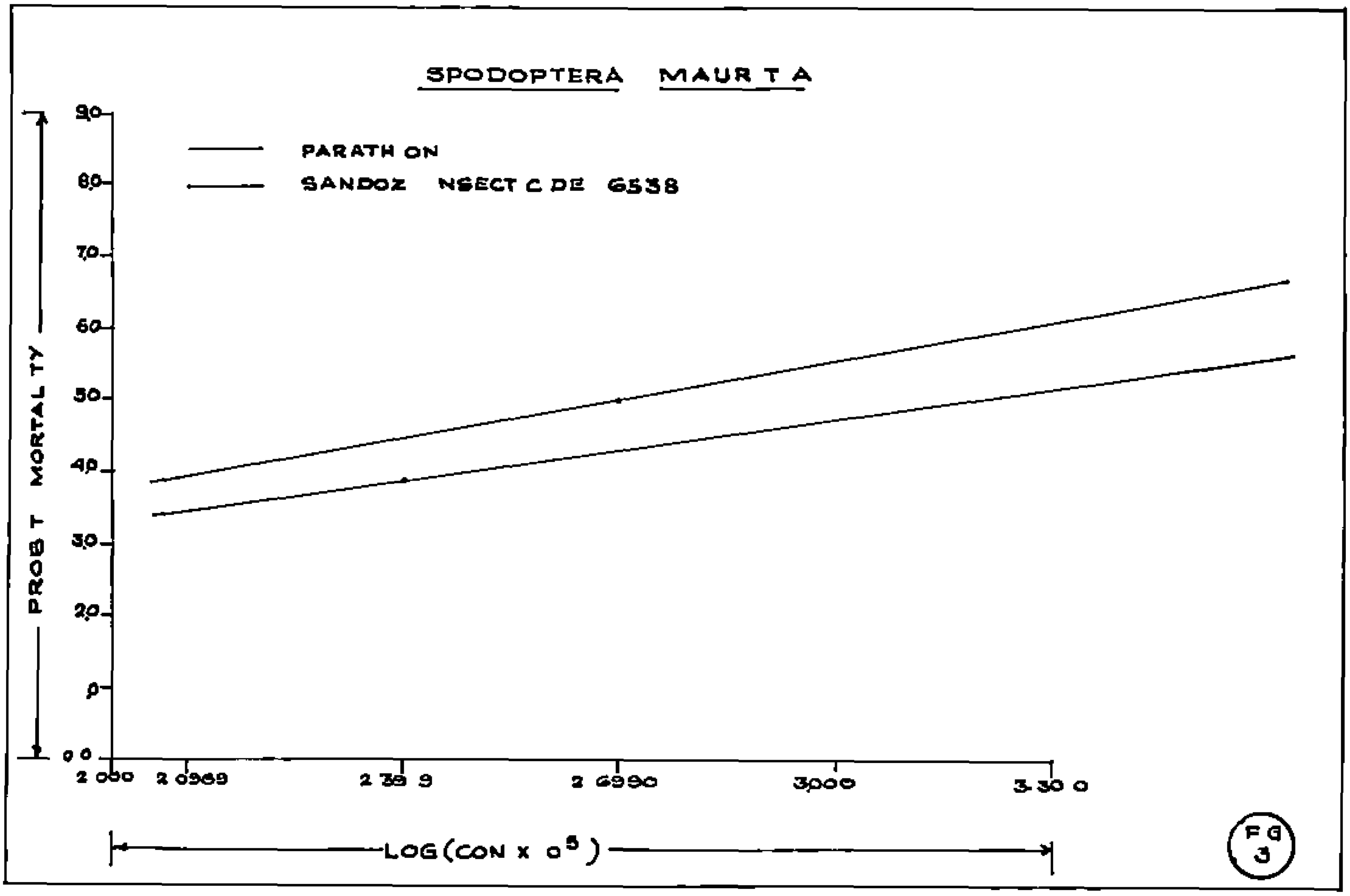
It will be seen that Sandoz Insecticide 6538 is relatively more toxic to the caterpillars of <u>Spodoptera mauritia</u> than parathion Further Sandoz Insecticide is found to be 3 377 times more toxic than parathion The ld-p lines tend to be parallel indicating that the caterpillars manifests similar responses to increasing doses of the two insecticides

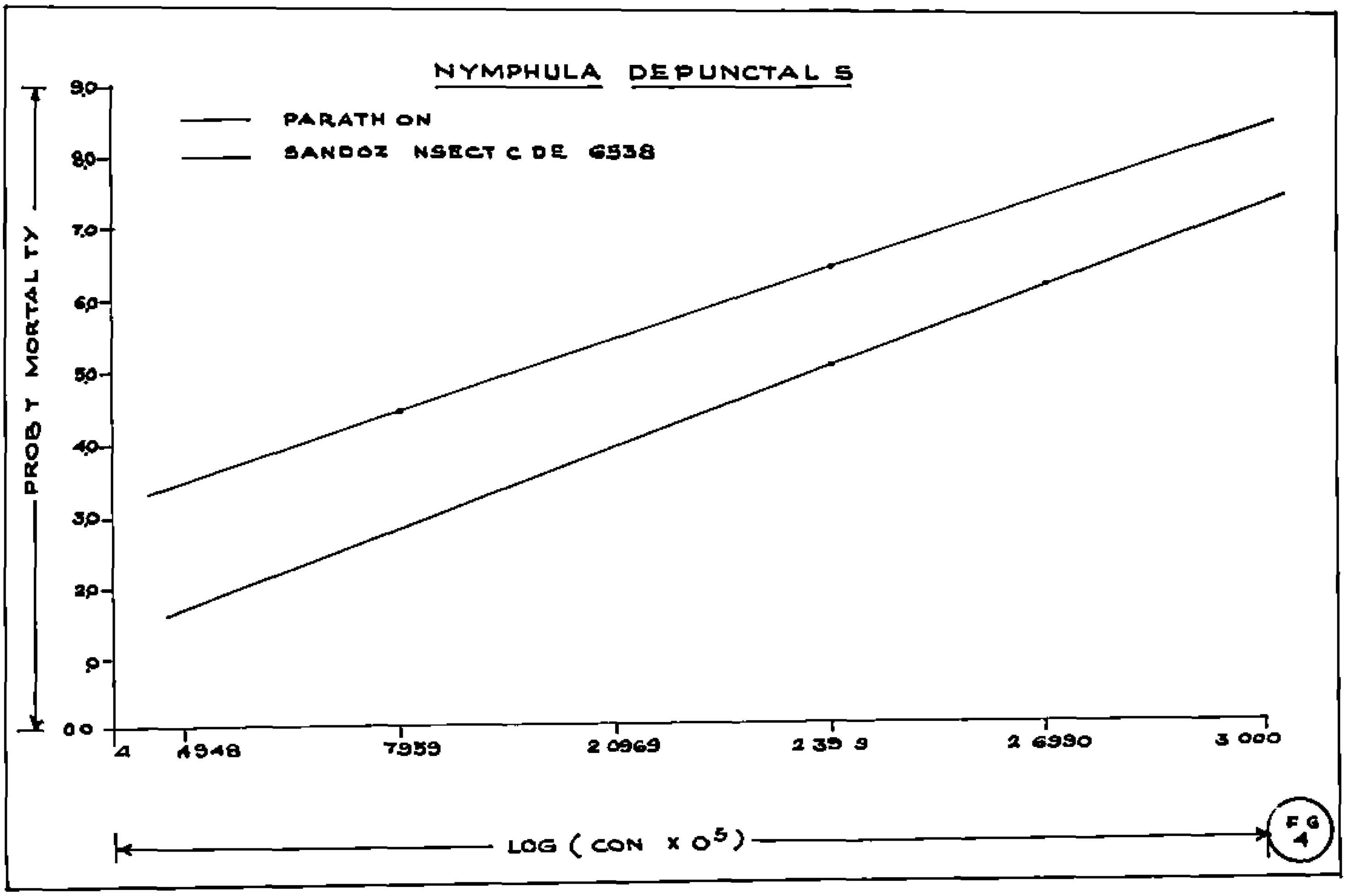
Fig 3

Log Concentration - Probit Mortality relationship between parathion and Sandoz Insecticide 6538 and larvae of *Spodoptera mauritia*

Fig 4

Log Concentration - Probit Mortality relationship between parathion and Sandoz Insecticide 6538 and larvae of *Nymphula depunctalis*


SPODOPTERA MAUR T A
PARATH ON
SANDOZ NSECT C DE 6538
PROB T MORTAL TY
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0.0
2 000
2 0969
2 39 9
2 6990
3.000
3 30 0
LOG (CON X 0^5)
F G 3


NYMPHULA DEPUNCTAL S
PARATH ON
SANDOZ NSECT C DE 6538
PROB T MORTAL TY
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0.0
4
4948
7959
2 0969
2 39 9
2 6990
3 000
LOG (CON X 0^5)
F G 4

Experiment 4

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and *Nymphula depunctalis* larvae

Details of experiment:

Concentration of insecticides The concentrations of the two insecticides used were 0.02, 0 01, 0 005, 0 0025, 0 00125, 0 000625 and 0 0003125 per cent

Control: Paddy plants sprayed with water

Date of spraying:	9-1-1970	
Temperature during experiment	Maximum	31°C
	Minimum	30 5°C
Humidity during experiment:	Maximum	95
	Minimum	67

Procedure As described in detail under "Material and Methods"

Rest of the details as in experiment 1

Results: Results are represented in Table 4 and Fig 4

The results of analysis of the data are as follows:-

Table 4

Mortality of caterpillars of *Nymphula depunctalis* when released on paddy plants sprayed with parathion and Sandoz Insecticide 6538 in different concentrations

Concentration of the insecticides (%)	Percentage mortality in 24 hours*	
	Parathion	Sandoz Insecticides 6538
0.02	100.00	100.00
0.01	100.00	96.30
0.005	96.30	88.69
0.0025	92.59	51.86
0.00125	74.08	7.41
0.000625	29.63	3.33
0.0003125	11.11	0
Control	10.00	10.00

* All percentages except cent per cent and that of control, corrected by applying Abott's formula

		Parathion	Sandoz insecticide 6538
Regression equation		y = 2 8302x - 0 447	y = 3 939x - 4 608
Chi-square		2 42	4 29
Heterogenity coefficient		0 807	1 43
L D 50		0 000840[illegible]	0 002527
Fiducial limits	m_1	0 000448	0 001370
	m_2	0 001576	0 004669
Relative toxicity taking that of parathion is equal to one		1	0 333

Sandoz Insecticide 6538 is seen to be less toxic to *Nymphula depunctalis* larvae than parathion L D 50 values indicate that Sandoz Insecticide 6538 is 0 333 times as toxic as parathion The ld-p lines are nearly parallel showing that the larvae have more or less identical responses to increased doses of the two toxicants

Experiment 5

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and apterous adults of *Aphis craccivora*

Details of experiment

Concentration of insecticides The concentrations of insecticides used were 0 00125, 0 000625, 0 0003125, 0 000156, 0.000078 and 0 000039 per cent

Date of spraying	19-1-1970	
Temperature during experiment:	Maximum:	33^{o}C
	Minimum	32^{o}C
Humidity during experiment	Maximum	90
	Minimum:	67

Procedure: Preparation of dilutions of insecticides and their application and assessment of results were done as described under Methods. The aphids after spraying were transferred to clean petri dishes and fed with tender [illegible]

Results Results are represented in Table 5 and Fig 5 The results of analysis of the data are as follows -

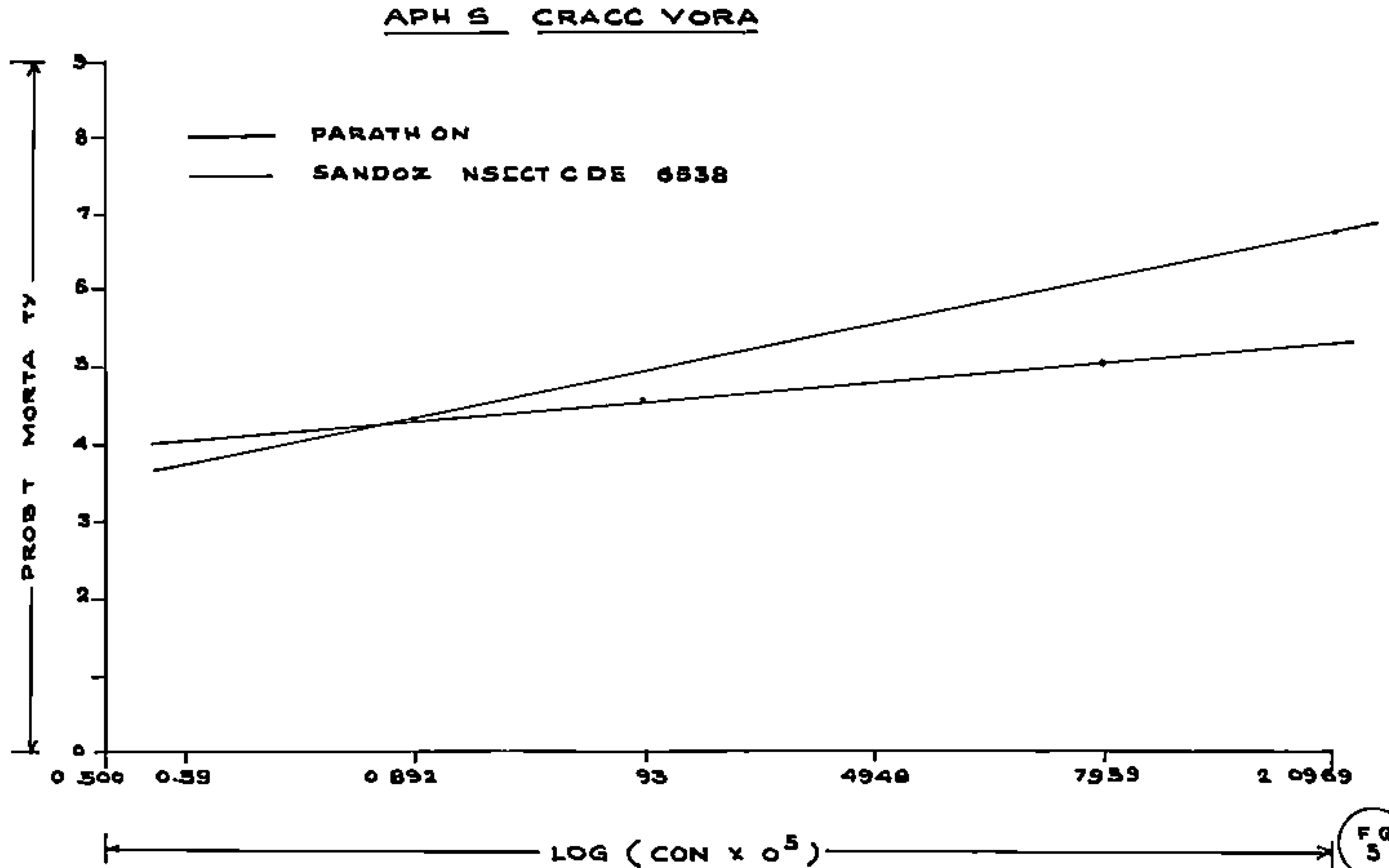
	Parathion	Sandoz Insecticide 6538
Regression equation	y = 1 1508x + 3 0921	y = 2 256x + 2 134
Chi-square	11 83(Significant)	5 64
Heterogenity coefficient:	2 973	1 41
L D 50	0 0004548	0 0001862
Fiducial limits m_1	0 000215	0 0001387
m_2	0 000962	0 0002508
Relative toxicity taking that of parathion is equal to one	1	2 44

Table 5

Mortality of adults of *Aphis craccivora* when sprayed with emulsions of parathion and Sandoz Insecticide 6538 in different concentrations

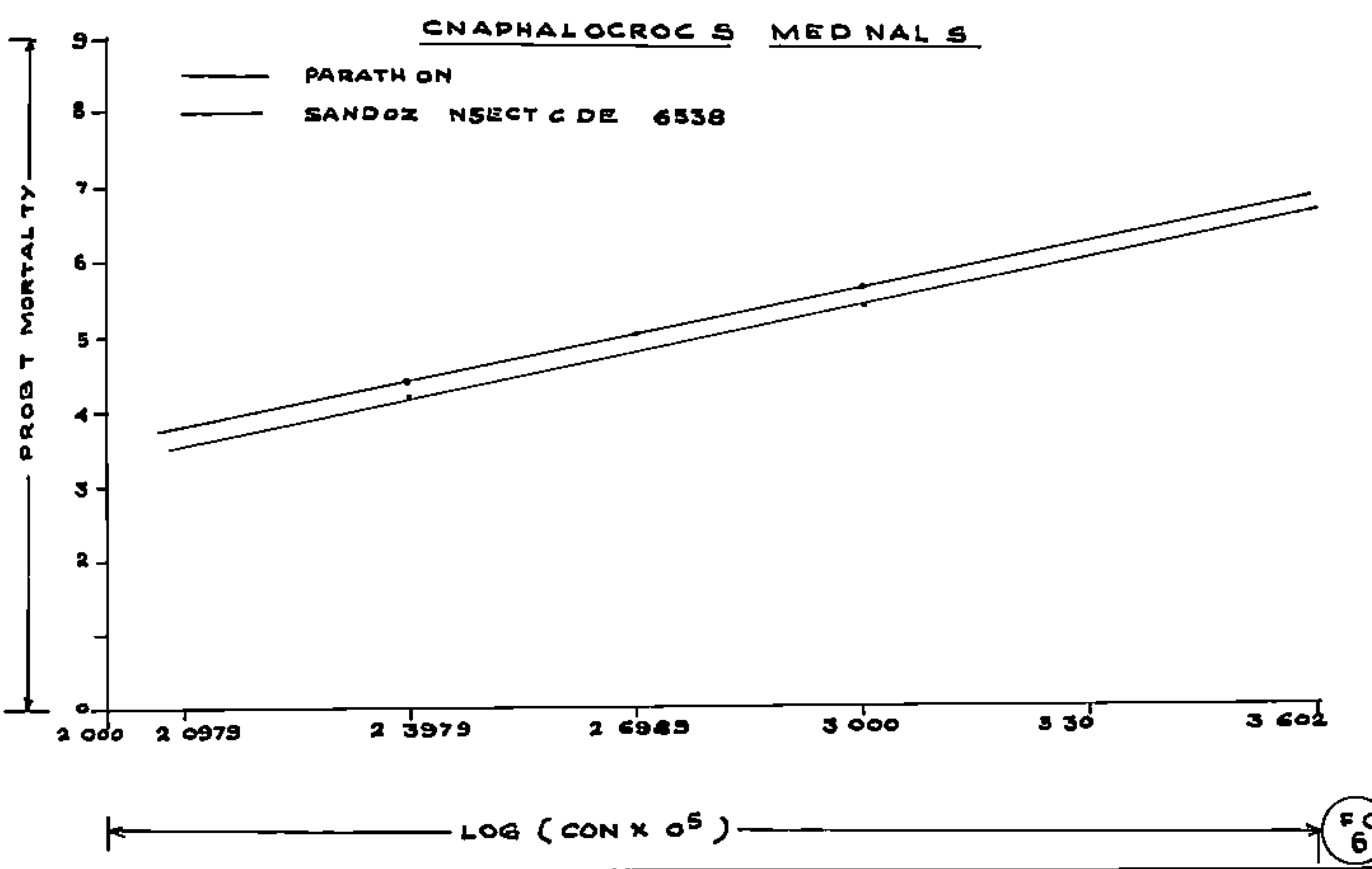
Concentration of the insecticides (%)	Percentage mortality in 24 hours*	
	Parathion	Sandoz Insecticide 6538
0.00125	77 78	96 30
0 000625	51 86	96 30
0 0003125	37 03	59 26
0 000156	33 33	37 03
0 000078	22 22	25 92
0 000039	14 81	0 00
Control	10 00	10 00

* All percentages, except that of control corrected for control mortality applying Abott's formula



APH S CRACC VORA
PARATH ON
SANDOZ NSECT C DE 6838
PROB T MORTA TY
0 500
0.59
0 892
93
4948
7939
2 0969
LOG (CON x 0^5)

F G
5



CNAPHALOCROC S MED NAL S
PARATH ON
SANDOZ NSECT C DE 6538
PROB T MORTAL TY
2 000
2 0979
2 3979
2 6989
3 000
3 30
3 602
LOG (CON x 0^5)

F G
6

It will be seen that Sandoz Insecticide 6538 is relatively more toxic to *Aphis craccivora* than parathion Thus based on L D 50 values Sandoz Insecticide 6538 is found to be 2 44 times more toxic than parathion Judging from the relative slopes of the ld-p lines, Sandoz Insecticide 6538 appears to have slightly more response to increases in dosage than parathion.

Experiment 6

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and *Cnaphalocrocis medinalis* larvae

Details of experiment

Date of experiment:	19-1-1970	
Temperature during experiment	Maximum	33°C
	Minimum:	32°C
Humidity during experiment:	Maximum	90
	Minimum	67

Rest of details as in experiment 2

Results: Results are represented in Table 6 and Fig 6 The results of the analysis of the data are as follows:-

Experiment 7

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and *Tribolium castaneum* adults

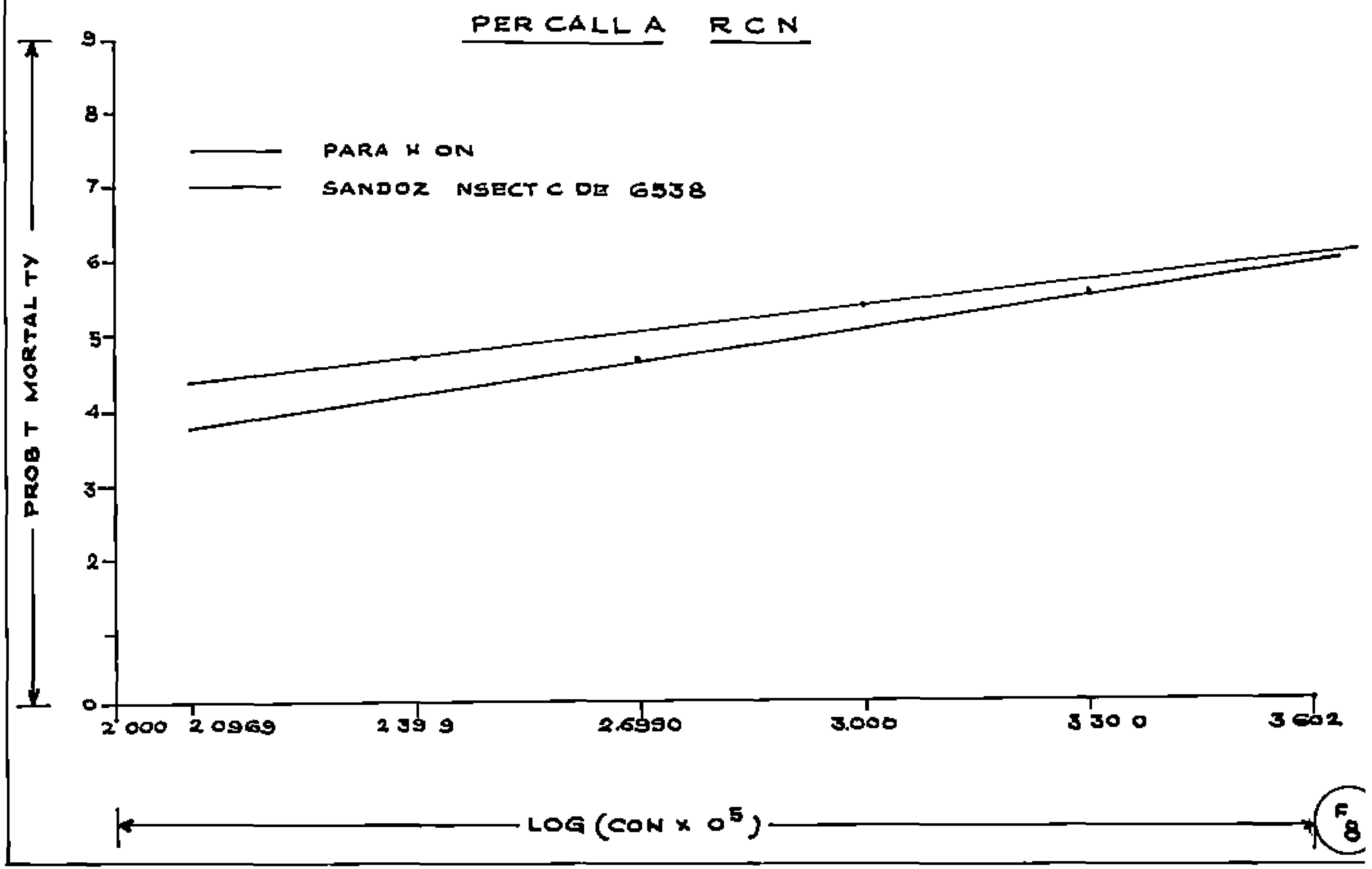
Details of experiment

Concentration of insecticides: The concentrations of the two insecticides used were 0 005, 0 0025, 0 00125, 0 000625, 0 0003125 and 0 00015625 per cent

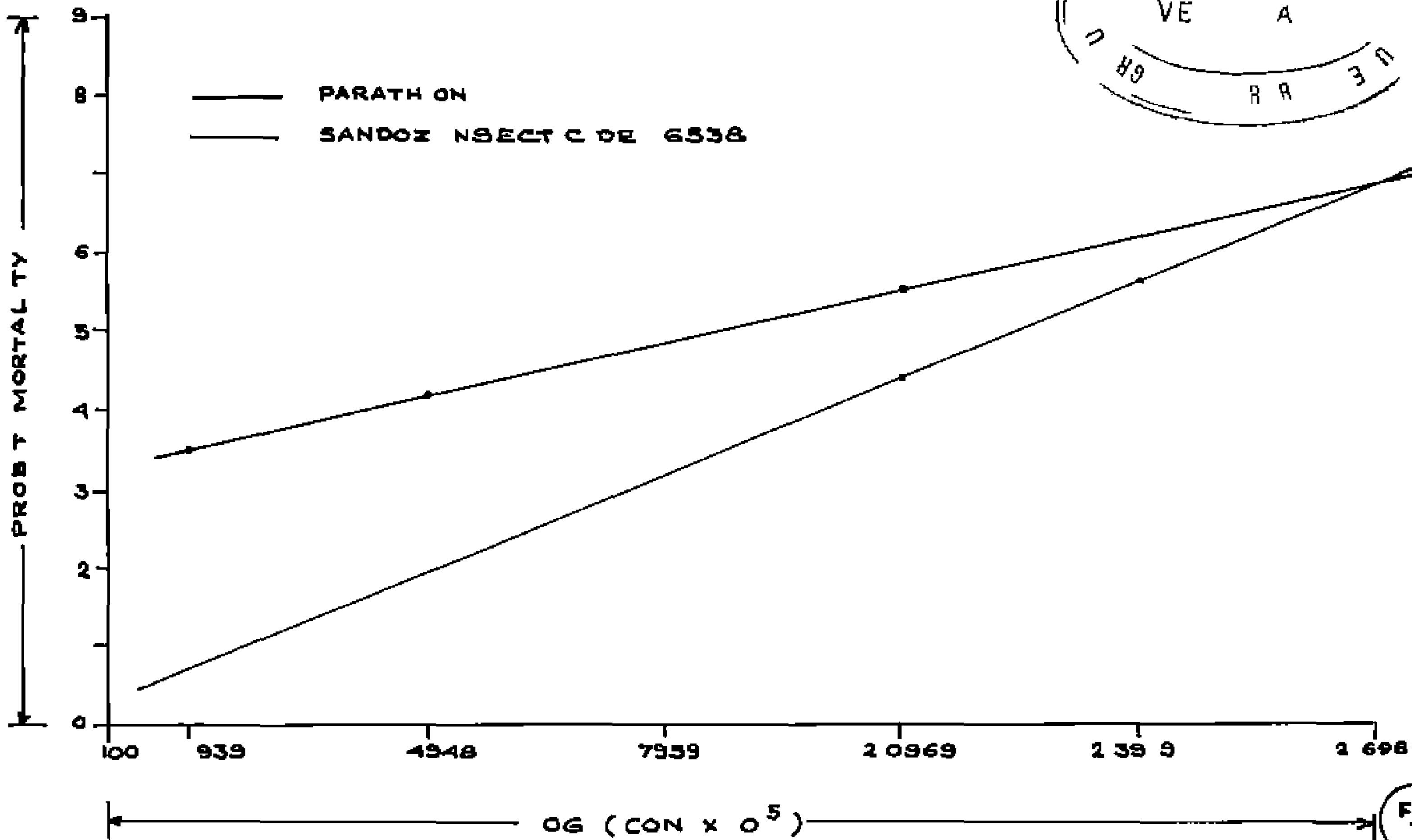
Number of insects in each replication	15	
Date of experiment	19-1-1970	
Temperature during experiment:	Maximum	33°C
	Minimum	32°C
Humidity during experiment	Maximum	90
	Minimum	67

Rest of the details as in experiment 2

Results Results are represented in Table 7 and Fig 7 The results of the analyses of the data are as follows -


PER CALL A R C N
PARA ĸ ON
SANDOZ NSECT C DE G538
PROB T MORTAL TY
9
8
7
6
5
4
3
2
0
2 000
2 0969
2 39 9
2.6990
3.000
3 30 0
3 602
LOG (CON x 0^5)
F 8

TR BOL UM CASTANEUM



F G 7

		Parathion	Sandoz Insecticide 6538
Regression equation:		y - 2 129X + 1 091	y - 3 823X - 3 590
Chi-square		0 85	2 26
Heterogenity coefficient:		0 212	1 13
L D 50		0 0006855	0 001766
Fiducial limits	m_1	0 0006252	0 001679
	m_2	0 0007516	0 001858
Relative toxicity taking that of parathion is equal to one		1 0	0 389

The Sandoz Insecticide 6538, is seen to be relatively less toxic to the adults of *Tribolium casteneum*, than parathion, the former is found to be only 0 389 times as toxic as the latter The response of the insect to increases in doses is higher in Sandoz Insecticide 6538 so much so that at the higher doses they approximate in their toxicity

Experiment 8

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and *Pericallia ricini* larvae

Details of experiment

Date of experiment 20-1-1970

Temperature during experiment: Maximum 33 5°C
Minimum: 32 5°C

Humidity during experiment: Maximum: 95
Minimum 62

Rest of the details as in experiment 2

Results: Results are represented in Table 8 and Fig 8 The results of analysis of the data are as follows:-

	Parathion	Sandoz Insecticide 6538
Regression equation:	y = 1 9934 - 0 927	y = 1 6947X + 0 415
Chi-square	0 67	1 87
Heterogenity coefficient	0 223	0 468
L D 50	0 00942	0 00507
Fiducial limits m_1	0 006516	0 004207
m_2	0 01361	0 00611
Relative toxicity taking that of parathion is equal to one	1	1 857

It will be observed that Sandoz Insecticide 6538 is slightly more toxic to Pericallia ricini caterpillars than parathion, it being 1 857 times more toxic than parathion The ld-p lines are more or less parallel

Table 8

Mortality of caterpillars of *Pericallia ricini* when sprayed with emulsions of parathion and Sandoz Insecticide 6538, in different concentrations

Concentration of the insecticides (%)	Percentage mortality in 24 hours	
	Parathion	Sandoz Insecticide 6538
0.04	93 33	93 33
0.02	70 00	86 67
0.01	46 67	63 33
0.005	36 67	56 67
0.0025	10 00	36 67
0 00125	0 00	6 67
Control	0	0

indicating similar responses to increases in doses of the two insecticides.

Experiment 9

Concentration-mortality relationship between parathion and Sandoz Insecticide 6538 and the grubs of *Epilachna implicata*

<u>Details of experiment</u>

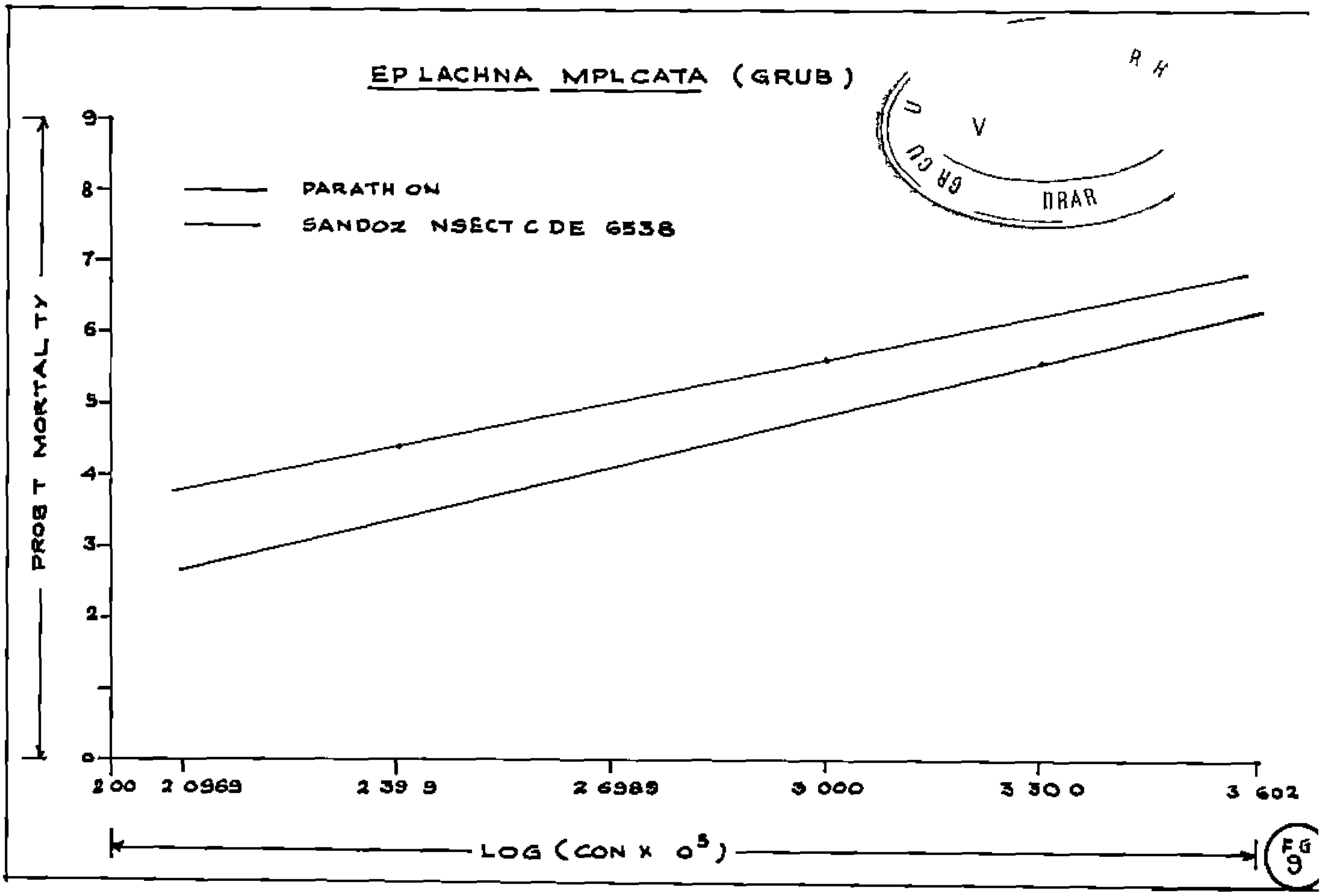
Date of spraying:	24-2-1970
Temperature during experiment:	Maximum 35 5°C Minimum: 32 5°C
Humidity during experiment	Maximum 95 Minimum: 61

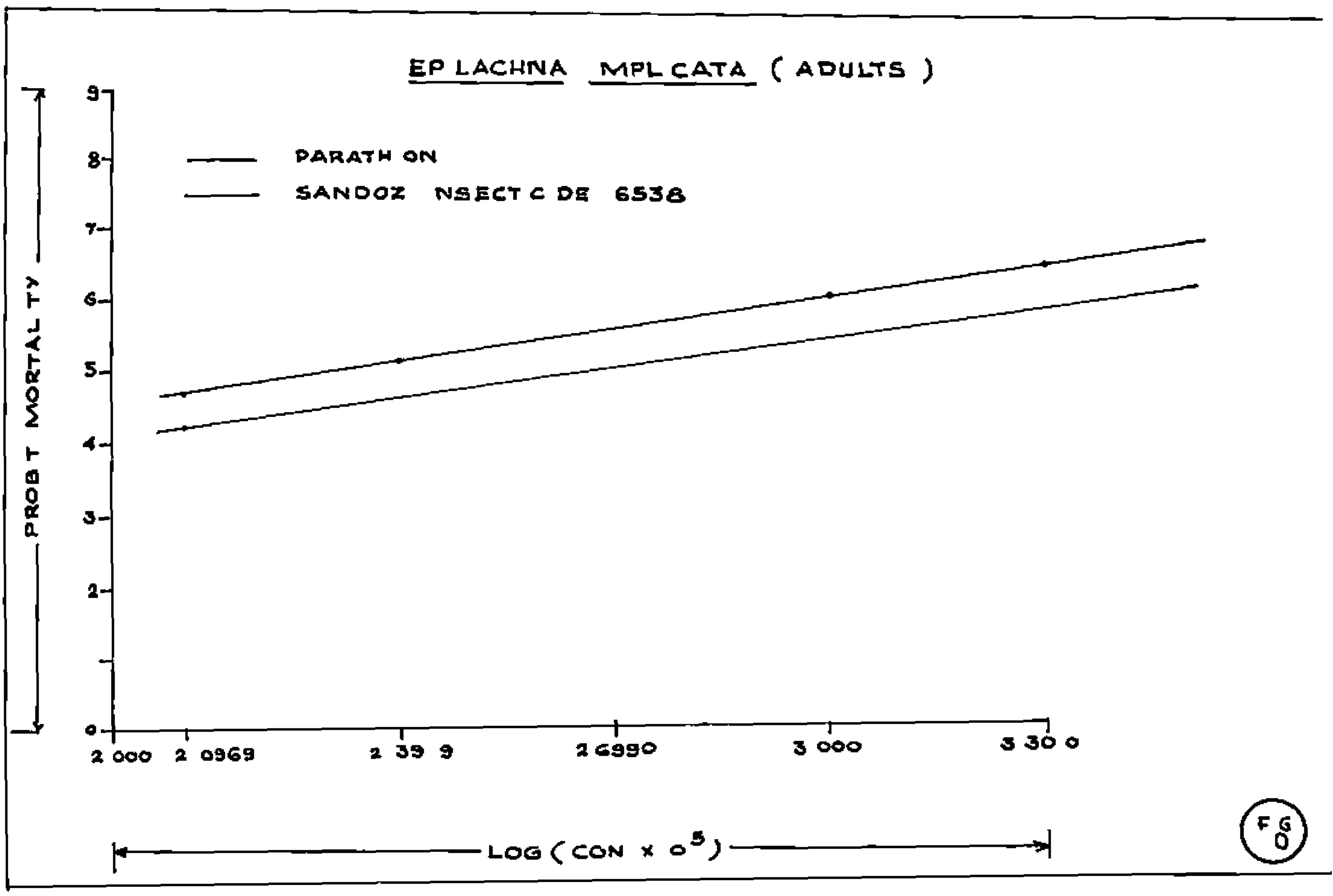
<u>Procedure:</u> Preparation of the dilutions of insecticides and their application and assessment of results were done as described under Methods. The grubs after spraying were transferred to clean petridishes and fed with bittergourd leaves

Rest of the details as in experiment 1

<u>Results:</u> Results are represented in Table 9 and Fig 9

The results of the analysis of the data are as follows -


EP LACHNA MPLCATA (GRUB)
PARATH ON
SANDOZ NSECT C DE 6538
PROB T MORTAL TY
9
8
7
6
5
4
3
2
0
2 00
2 0969
2 39 9
2 6989
3 000
3 30 0
3 602
LOG (CON x 0^5)
F G 9


EP LACHNA MPLCATA (ADULTS)
PARATH ON
SANDOZ NSECT C DE 6538
PROB T MORTAL TY
9
8
7
6
5
4
3
2
0
2 000
2 0969
2 39 9
2 6990
3 000
3 30 0
LOG (CON x 0^5)
F G 0

cuticle which offers an efficient barrier to the free entry of contact toxicants.

The Sandoz Insecticide 6538 under trial is seen to be more toxic than parathion to some important pests such as larvae of *Spodoptera littoralis*, *Spodoptera mauritia*, *Epilachna implicata*, *Pericallia ricini* and adults of *Aphis craccivora*. Its toxicity approaches that of parathion to pests like larvae of *Cnaphalocrocis medinalis*, adults of *Cylas formicarius* and larvae of *Corcyra cephalonica* To insects like adults of *Epilachna implicata* and larvae of *Nymphula depunctalis* parathion is far more toxic than Sandoz Insecticide 6538 (Table 17)

As regards the persistence of toxic residues it is observed that in general both parathion and the Sandoz product behave in the same way The Sandoz Insecticide 6538 loses its residual toxicity completely to *Cylas formicarius* by the 4th day, to *Epilachna implicata* (grubs) and *Cnaphalocrocis medinalis* larvae by the 8th day and to *Diacrisia obliqua* larvae by the 16th day (Tables 13 to 16)

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