ROTHAMSTED RESEARCH

Report for 1981 - Part 1

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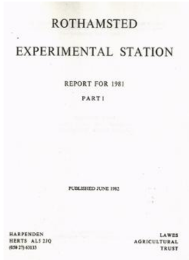

ROTHAMSTED

EXPERIMENTAL STATION

REPORT FOR 1981

PART I

Insecticides and Fungicides Department

M. Elliott

M. Elliott (1982) *Insecticides and Fungicides Department ;* Report For 1981 - Part 1, pp 123 - 145 **- DOI: https://doi.org/10.23637/ERADOC-1-128**

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https://doi.org/10.23637/ERADOC-1-128

Introduction

The Department's role is to study both fundamental and applied aspects of using biologically active compounds to protect crops, and this year developments in our applied research on spray applications are particularly significant.

Some of the disadvantages of conventional hydraulic sprays can be overcome by spinning disc applicators. These permit size and uniformity of drops to be closely controlled and use small volumes of carrier. More recently, electrostatic charging has been shown not only to diminish drift problems associated with the small drops in low volume sprays, but also to improve leaf and stem coverage. Practical systems to exploit these features have been designed here and patented (rights assigned to the National Research Development Corporation) and they will now be produced commercially. Our work shows that, in open canopy crops, biological activity equivalent to that from hydraulic sprays can be obtained with half dosages in one hundredth the volume of carrier. Hand-held and tractor-mounted systems with low power requirements are already in use and aerial application, for which the low volumes of solvent are particularly appropriate, will be evaluated. Because the Rothamsted system can dispense aqueous and non-aqueous formulations equally effectively, a wide range of practical applications can be anticipated. Presentation of this work at the Brighton Crop Protection Conference in November, and elsewhere, stimulated considerable commercial interest and publicity.

Efficient crop protection depends as much on the availability of powerful agrochemicals as on the means to apply them, but in changing economic circumstances a succession of novel compounds is no longer assured. Therefore the full effectiveness of established pesticides must be maintained as long as possible, and a significant proportion of our work still concentrates on principles determining the onset and development of resistance and strategies for countering it.

The incipient resistance to pyrethroids in pig breeding farms near Harpenden continues to provide an exceptional opportunity to observe a developing situation and to establish the parameters needed for a mathematical model to describe it more comprehensively than has been possible in previous comparable studies. The investigation has already indicated an unsuspected link between a male-determining factor and pyrethroid resistance which, if substantiated, is a factor which must be included in future models; the finding emphasises that adequate field work on which to base models is essential. In situations where resistance may lead to failure of chemical control, the work should make possible decisions on the relative efficacies of persistent or non-persistent compounds, with narrower or broader spectra of activity against pests, parasites and predators. An immediate practical conclusion is that very effective control of housefly populations known to have potential for rapid development of strong pyrethroid resistance can be achieved without leading to resistance if non-persistent pyrethroids are used sparingly.

Knowledge of resistance-associated biochemical changes offers the prospect of understanding and overcoming (by chemical modification of structures) some forms of resistance; in this connection differences have been demonstrated between the fatty acid components of phospholipids in the heads of resistant and susceptible houseflies and between the insensitive acetylcholinesterases of resistant British and Danish houseflies. Another approach to the study of resistance is to examine nerve preparations from susceptible and resistant species electrophysiologically, but of many systems (e.g. flight muscles and sensory nerves) investigated, few are sufficiently sensitive to pyrethroids to represent the fatal poisoning process. Promising results have now been obtained with a purely sensory system involving the halteres (flight stabilisers) of Muscid flies (blowflies and houseflies). The preparation will be used to investigate and characterise functional changes associated with mechanisms such as the knockdown resistance (*kdr*) mechanism in houseflies which is widespread and potentially menacing. To provide the essential

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anatomical basis for these neurophysiological studies of the mode of action of insecticides the central nervous systems of the American cockroach, the locust and the housefly are being mapped by histological techniques to identify and describe the functions of the units involved.

Despite laboratory demonstrations of strong resistance in some species of insects to pyrethroids, there are still few fully authenticated cases of failure of control in the field. Pyrethroid use in agriculture (some 20 million ha were estimated to have been treated in 1980) and in veterinary, public health, household, stored grain, garden and horticultural fields and for timber and wool preservation continues to expand. Our chemical studies to correlate potency with structure concentrate particularly on the constitution of active chiral molecules which are still the only source of detailed information about receptor sites.

Studies on resistance to fungicides parallel those on insecticides and similarly aim to provide a framework on which to develop strategies to preserve their effectiveness. Triazole fungicides, particularly triadimenol ('Baytan'), are increasingly important; for instance they permitted some above average barley yields in 1981, despite conditions favouring diseases. Monitoring of resistance levels, however, detected decreased sensitivity to triazoles in barley mildew. Triazole-resistant strains were somewhat more sensitive to ethirimol, an encouraging observation which may be exploitable.

Another group of related projects is concerned with the difficult problems of controlling soil-borne pests and diseases. Approximate but powerful generalisations have been deduced (Chemical Liaison Unit) to permit sufficiently accurate descriptions, solely from chemical structures, of distribution and degradation of pesticides in soil, air, water and organic phases after field application. Significant progress has been made in defining the properties needed by active soil insecticides, using organophosphorus insecticides with a wide range of physical properties, a soil walking insect and soils with a range of organic matter contents; simulation models give increasingly precise predictions of the fate of pesticides in soil. Increased yields of wheat, associated with control of take-all by large doses of suitably applied soil fungicides, were demonstrated for the first time this year.

Compounds that influence invertebrate behaviour (e.g. pheromones) are potentially valuable in crop protection and disease control yet in practice their properties and the specificity of their biological activities often render economic exploitation difficult. The oviposition attractant pheromone of a Culicine mosquito, recently identified in the Department as a novel stable and relatively involatile lactone, promises to be an exception to this generalisation. The range of compounds which interfere with colonisation of plants and virus transmission by aphids has been extended from pyrethroids (which are less active on resistant strains) to non-insecticidal antifeedants such as polygodial and compounds derived from the aphid alarm pheromone which have the important advantage that they influence resistant and susceptible insects similarly. Collaboration with the Plant Pathology Department to exploit these findings in practical control of virus transmission has therefore been expanded.

Insecticides

Relationships between molecular structure and insecticidal activity of pyrethroids. Although the discovery of the extremely active photostable pyrethroids followed a rational course, many subtleties in structure–activity relationships, not suspected earlier, are now apparent. Knowledge of the nature of the receptor is still limited to what can be deduced from the types of molecule that are insecticidal, so progress can only be made by increasing the precision with which the essential chemical and steric characteristics are defined.

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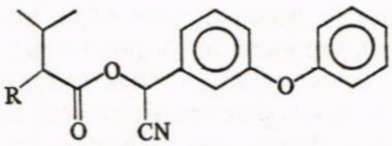
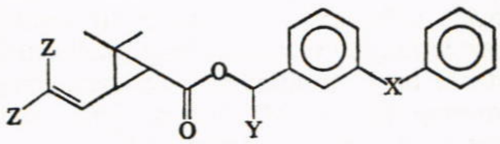
The work this year exemplifies this approach for two separate parts of the pyrethroid molecule.

2-Alkyl- and -alkenyl-3-methylbutyrates. A systematic study of the effect of changing the group R in esters related to fenvalerate (I; R = p-chlorophenyl) has shown that even simple analogues in which R is acyclic may also be insecticidal. In the R = alkyl series, activities were in the order Me ⟨Et⟩ Pr^1; alkenyl groups (R = $-CH{=}CHMe$; $-CH{=}CHEt$; $-CH{=}CHPr$; $-CH{=}CMe_2$; $-CH{=}CCl_2$; $-CH{=}CBr_2$) gave compounds about one-tenth as active as the standard (bioresmethrin) and about one-seventh as active as fenvalerate to houseflies (*Musca domestica*) and mustard beetles (*Phaedon cochleariae*). Over 20 other variations, including polar groups such as $-Br$ and $-CN$, were much less effective.



(I)



(II)

3-Phenyl-X- analogues of 3-phenoxybenzyl esters. Compounds exemplifying 20 further variations of the bridging group X (cf. *Rothamsted Report for 1979*, Part 1, 111) have been synthesised and tested. The most insecticidal apart from those already known (II; X = O, CH_2, C=O) contained X = $-CH{=}CH-$(Z) [but not (E)], $>C{=}CH_2$, or $>C{=}CHMe$. These results help to define more accurately the requirements for the bridging group—in most of the more active compounds, but in few of the less active, the two bonds from this group originate from a common atom at an angle of 100–130°. The striking exception [$-CH{=}CH-$(Z)] must impose a degree of rigidity which brings the essential groups to the most appropriate relative orientation in an alternative way.

Interaction between the groups X and Y in (II) has been studied for a series of esters (Z = Me or Br) with X = O, CH_2, CO, — (i.e. a direct bond) or $>C{=}CH_2$ and Y = H, CN, C≡CH or CH_3. The acids in these esters ((1R) *trans*-chrysanthemic and (1R)*cis*-3-(2,2-dibromovinyl)2,2-dimethylcyclopropanecarboxylic) were both fully resolved, but the alcohols were racemic at the α-centre. The resulting mixture of two diastereomers could be tested directly, because in all such cases examined, activity has been shown to arise almost completely from one of the two isomers, with little or no interference from the other. The results for this wide range of compounds, show that in the phenoxybenzyl series (with X = O) activity is enhanced strongly if the α-substituent is cyano, and weakly if ethynyl. At the other extreme (X = $>C{=}CH_2$) all α-substituents lower activity. The remaining bridging groups examined are intermediate in their response to α-substitution. Previously isolated examples of interactions between groups (which reflect the non-additivity of two separate effects on activity) have been noted, but the present wide-ranging study constitutes the most clear-cut case.

Decomposition of dihalo adducts of pyrethroids. The mixtures (IIIA) and (IIIB) formed by addition of bromine to deltamethrin and cypermethrin respectively act strongly as insecticides. Exposure to either ultraviolet light or to the metabolic processes of an insect induces loss of bromine to form the original insecticide (Ruzo *et al.*, *Pesticide, Biochemistry and Physiology* (1981), **15**, 137, and *Journal of Agricultural and Food Chemistry* (1981), **29**, 702). In addition we have now shown that mixture (IIIA) sprayed on turnip leaves and exposed to sunlight decomposes readily, and that in practice, for

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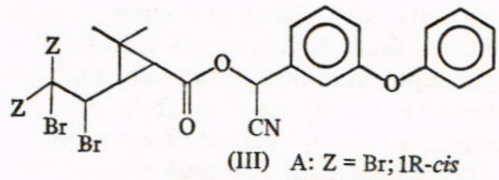

(III) A: Z = Br; 1R-*cis*
B: Z = Cl; all isomers

much of the protective period, there is more deltamethrin present than either component of (IIIA). Much of the insecticidal action of (IIIA) must therefore depend on this process. (Elliott, Janes, Johnson, Khambay and Pulman; biological work: Jenkinson and O'Dell)

Action of insecticides on insect nervous systems

Neuroanatomy of the insect central nervous system. Mapping ventral nerve cord ganglion structure to complement electrophysiological studies of pyrethroid mode of action continued; description of the midline groups of nerve cell bodies (somata) of the mesothoracic ganglion of the cockroach *Periplaneta americana* (L.) was completed. Seven groups of cells were named according to position, and each was characterised by general appearance and position, numbers and sizes of constituent somata, and numbers and pathways of fibre bundles. Groups consist largely of interneurons, with a few efferent, presumed motor, neuron somata in some. Different functional types of neurons do not appear to be strictly segregated in different groups. The somata in the seven groups total 200 or more, and intraganglionic interneurons seem greatly to outnumber interganglionic ones. (Gregory)

Action of pyrethroids on the nervous systems of Muscid flies. To clarify the mode of action of pyrethroids and to identify the functional changes in the insect nervous system associated with the *kdr* mechanism of resistance requires suitable nerve preparations from insects in which the toxicology and genetics of resistance have been studied thoroughly. The adult housefly is most eligible but all the preparations, e.g. flight muscle, sensory nerves, available so far have certain drawbacks. Recently, however, Sandeman and Markl (*Journal of Experimental Biology* (1980) **85**, 43) studied the flight stabilisation system of *Calliphora erythrocephala* (the blowfly) which detects yawing movements of the flying insect and applies appropriate corrections. Their preparation includes the halteres and sensory receptors at their base, the haltere nerve, synapses in the central nervous system (CNS) and the motor innervation of appropriate wing and neck muscles. Containing all the components of a typical reflex and triggered by a readily controlled stimulus (an electromechanical transducer) the preparation is well suited to studying the action of neurotoxicants. We have made recordings with suction electrodes from the wholly sensory haltere nerve (nh) and from the motor axons of the frontal prothoracic nerve (nf) and have shown that similar preparations for the housefly are feasible.

Recordings from nerve preparations investigated with pyrethroids in saline (*in vitro*) or from intact blowflies previously treated with lethal doses of pyrethroids (*in vivo*) showed that both bioresmethrin and (1R)-*trans*-permethrin increased spontaneous activity and then caused repetitive discharges in both nh and nf. *In vitro*, sustained symptoms were observed below 0·33 μM, but higher concentrations soon decreased nerve action potential amplitudes and eventually blocked conduction. Correspondingly, *in vivo*, increased spontaneous nervous activity coinciding with discoordinated movements was followed by depressed nervous activity.

Haltere stimulation normally induces a very phasic response in nh, but in treated preparations *in vivo* and *in vitro*, it caused multiple discharges. In contrast, the response

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in nf (detected adequately only with signal averaging to suppress interference from random activity) rarely showed multiple discharges, a surprising observation suggesting that the CNS conditions the input from nh substantially, and that the motor axons of nf themselves show little repetitive activity resulting from pyrethroid intoxication. Treatment of nh with deltamethrin confirmed earlier observations that α-cyano-3-phenoxybenzyl esters may block axonic conduction without eliciting repetitive activity.

The type and severity of symptoms in the nervous system of blowflies fatally poisoned by bioresmethrin and (1R)-*trans*-permethrin *in vivo* are most closely matched by symptoms produced *in vitro* at concentrations of these toxicants in the range 0·01–0·1 μM. This is close to the concentration (0·12 μM) of radiolabelled 'NRDC 157' (3-phenoxybenzyl (1R)-*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate) found in the haemolymph of fatally poisoned cockroaches (*Rothamsted Report for 1977*, Part 1, 135–136).

These results show that when the synaptic pharmacology of this preparation is fully defined it will be suitable for examining many aspects of the action of neurotoxicants, such as structure-activity relationships of pyrethroids, reversibility of intoxication, temperature coefficients and mechanism of *kdr*. (Burt, Goodchild and Stewart)

Resistance

Resistance of houseflies (*Musca domestica*) on local pig-breeding farms. The following parameters needed for a mathematical model describing the development of resistance to pyrethroids in housefly populations on local pig-breeding farms were examined: (a) in the field, fly production in relation to farm design and animal management, survival rate of adults, dispersal and gene flow, and the response of adult populations to treatments with photostable and photolabile pyrethroids; (b) in the laboratory, the qualitative genetics of resistance to pyrethroids and factors likely to influence the expression of this resistance, as well as the biochemistry of the isolated resistance mechanisms.

Biological parameters of field populations. Monitoring flies twice weekly by visual counts and by sticky traps on nine farms showed that productivity depended on many factors including accessibility of warm buildings in winter, design of animal pens, throughput of piglets and availability of fresh dung for larval breeding. Fly numbers often varied considerably between sites even within individual farms. Mark–release–recapture experiments confirmed the short mean life-spans of both males (2–5 days) and females (4–7 days). Movement into and from buildings and from farm to farm was restricted (2/24 000 recaptured at a farm 1·5 km distant) but was rapid between open sites within farms. To estimate gene flow more directly, a recessive visible mutant marker on autosome 3, brown body (*bwb*), was introduced into a farm population and shown to persist at a frequency of *c.* 10% for at least 2 months.

Response to treatment with pyrethroids. During the fly season (July to October) houseflies on four pig farms with varying potentials for resistance development were controlled either by direct sprays with bioresmethrin (25% emulsifiable concentrate) or with residual treatments of permethrin (5% e.c.). The level of control achieved with each treatment was monitored and compared with changes in tolerance shown by concurrent laboratory assays of F_1 flies with bioresmethrin, permethrin, or natural pyrethrins, applied topically. Changes in the frequency of *kdr* in the treated population were assessed using a discriminating dose of DDT following pre-treatment with FDMC (fluorinated (dichlorophenyl)methyl carbinol). On a farm with a history of strong pyrethroid resistance caused by the excessive use of synergised pyrethrins, control failure was shown

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to be coupled with lower kill in bioassays and a substantial increase in the frequency of *kdr*.

The results confirmed the uneven distribution of strong pyrethroid resistance locally, and the importance of using pyrethroids sparingly where control is still feasible. Long-term control with photostable or photolabile pyrethroids was impossible where excessive use of these materials had led to strong pyrethroid resistance. However, the sparing use of sprays of photolabile pyrethroids such as bioresmethrin successfully controlled even houseflies with a proven potential for strong resistance without detectably increasing it further, because such treatments do not continuously select resistance mechanisms. This demonstrates that pyrethroid resistance can be kept in check with appropriate pyrethroids.

Qualitative genetics of the resistance to pyrethroids and other insecticides. Why selection of some local populations with deltamethrin in the laboratory rapidly produces flies each of which can withstand more than 40 μg of deltamethrin, at least 10 000 $\times$ the LD50 for susceptible flies, is still not clear. Available evidence indicates that this high resistance is partly caused by synergistic interactions between some of the factors which singly confer very weak resistance to pyrethroids. Of the factors isolated so far, only *super-kdr* and to a much smaller extent *kdr* (both on autosome 3) singly confer moderate to strong resistance (*c*. 100-fold) to pyrethroids. Other factors, which singly give barely detectable resistance to pyrethroids, have been localised to autosome 1 and 5 (at least one mechanism each) and autosome 2 (at least two mechanisms). An esterase, controlled by a gene on autosome 2 and detectable by electrophoresis, can be selected directly with trichlorphon or pyrethroids and appears to be closely linked with pyrethroid resistance. When combined genetically with *super-kdr* (selected using a synergised DDT and trichlorphon) the chromosome with this esterase gave the resistance factor (250 $\times$) to be expected if the two mechanisms were multiplicative (*super-kdr* = *c*. 100 $\times$, esterase = 2·3 $\times$), no pyrethroid having been used in the selection process. This demonstrates that the sequential use of insecticides can select, and for pyrethroids probably has selected, resistance mechanisms giving cross-resistance to insecticides even before they have been applied. The role of this esterase in trichlorphon or pyrethroid resistance is not yet fully understood.

A survey of the distribution of the esterase linked with pyrethroid resistance on autosome 2 in European populations showed it to be absent from Denmark, but often present elsewhere (England, Belgium, France and Switzerland). The distribution did not correlate with the presence of resistance to either pyrethroids or trichlorphon. Since resistance to these two groups of insecticides is polyfactorial the presence or absence of the esterase represents genetic variation between different resistant populations.

Analysis of sex-determining mechanisms. Local strains of houseflies, unlike most Danish strains, have unusual mechanisms of sex determination. Crosses of males from local populations with females of standard laboratory stocks yield progeny with very aberrant sex ratios.

Cytological studies of our field strains by Drs P. G. and M. Rubini of the University of Pavia, Italy, confirmed that the typical male-determining Y chromosome is very rare in local populations, suggesting that sex determination must be due principally to autosomal sex determinants or to aberrant sex chromosomes.

Qualitative genetics have shown that two male-determining factors are present in field strains—one on autosome 3 (MIII), the other apparently associated with the X chromosome. Following strong selection with pyrethroids the frequency of MIII in a local field strain increased from 32 to 72%, demonstrating a possible link between MIII and pyrethroid resistance. If substantiated this connection must be included in modelling for resistance.

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Insensitive acetylcholinesterase in British houseflies. The acetylcholinesterase (AChE) from many of the houseflies collected recently in Hertfordshire was relatively insensitive to inhibition by organophosphorus insecticides. This mechanism was homozygous in one sample of flies and its substrate affinity (K_m) and spectrum of insensitivity were compared with a previously identified form of this enzyme from Danish houseflies. The two forms differed (Table 1), particularly in their sensitivity to the chlorinated organophosphorus compounds tetrachlorvinphos and dichlorvos, and by implication to trichlorphon, which acts through conversion to dichlorvos. These latter insecticides have been used extensively to control houseflies on British farms. The great insensitivity to tetrachlorvinphos and the limited solubility of this inhibitor combine to preclude accurate comparisons of kinetic constants. The insensitive AChE from British flies also differed greatly from that from susceptible and Danish flies in having a much greater affinity for the substrate acetylthiocholine, with a K_m of 0·034 mM compared with 0·154 and 0·115 mM for the enzymes from Danish and susceptible flies respectively.

TABLE 1

Factors of insensitivity of AChE from Danish and British houseflies relative to the enzyme from susceptible insects

Insecticide	Danish (strain ar D)	British
Omethoate	11	4
Methyl paraoxon	4	14
Paraoxon	4	12
Malaoxon	18	11
Ethyl malaoxon	10	14
Tetrachlorvinphos	7	>100
Dichlorvos	5	57

Biochemistry of the knock-down resistance (*kdr*) mechanism. Indirect biochemical evidence (last year's *Report*, Part 1, 124), from the transition temperatures in Arrhenius plots of acetylcholinesterase activity, indicated that the *kdr* mechanisms in houseflies were associated with a change in the properties of their phospholipids. The chemical nature of the lipids from the heads of susceptible and *super-kdr* houseflies was therefore examined. The microsomal fractions from the two strains showed no differences in the proportions of the various phospholipid classes, but distinct differences in the proportions of fatty acids (palmitic, palmitoleic, stearic, oleic, linoleic, linolenic) obtained from them by saponification.

The ratio of unsaturated to saturated acids from susceptible flies ($11{\cdot}3 \pm 0{\cdot}6$) was significantly greater than that from *super-kdr* flies ($6{\cdot}3 \pm 0{\cdot}7$) in accordance with the earlier observation that the membranes of the latter undergo a phase transition at 22°C compared with 14°C in susceptible flies. Whether these chemical differences in the lipids influence directly the interaction between membranes and insecticides or whether they do so by affecting the conformation of a target protein in the membrane is not yet clear. (Chiang Chia-liang, Denholm, Devonshire, Farnham, O'Dell, Moores, Sawicki and Willott)

Compounds influencing invertebrate behaviour

Trials with (E)-β-farnesene. (E)-β-Farnesene ((E)-β-F), the major component of the aphid alarm pheromone, conveniently accessible by a new method (last year's *Report*, Part 1, 126), is active in laboratory tests against the economically important species *Myzus persicae*, *Aphis fabae*, *Phorodon humuli*, *Sitobion avenae*, *Rhopalosiphum padi*, *Nasonovia ribis-nigri*, *Metopolophium dirhodum* but not against *Brevicoryne brassicae*,

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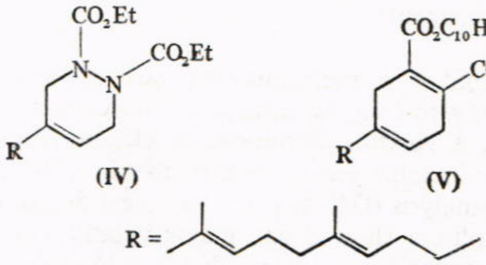
despite the presence of (E)-β-F (< 0·01 ng per aphid) in the cornicle secretion from this species. In field tests attempting to improve the activity of contact pesticides, permethrin alone or pheromone alone decreased numbers of *Aphis fabae* on field beans; when permethrin and pheromone were applied together the effect was greater, but smaller than with treatments with the standard insecticides pirimicarb or demeton-S-methyl. A similar result was obtained with aphids on potato except that pheromone alone had little effect in the field.

Compounds influencing aphid feeding. Twelve derivatives or structural relatives of (E)-β-F (e.g. cycloaddition compounds such as (IV) or (V)) applied to leaf surfaces at 1% a.i. decreased settling by starved apterae of *M. persicae*, whereas (E)-β-F itself did not. At decreased dosages several of the compounds, including benzylgeranyl, were



ineffective but this was not correlated with inability to regenerate (E)-β-F. At 0·1% a.i. only compound (V) (with a higher molecular weight than most of the others) was still active. When applied to the plant 3 days before testing, higher molecular weight compounds were the more effective.

The antifeeding agent polygodial, obtained from marsh pepper (*Polygonum hydropiper*), at 0·1% a.i. also decreased settling by apterae (cf. this report below, and p. 190).

Probing of the surface by apterae as observed under the microscope was apparently not affected by treatment with polygodial. Similarly probing by alatae that had flown for 0·5 h held on suction tubes was unaffected. Therefore further studies to establish the mechanisms of action by these compounds are necessary. Sublethal doses of deltamethrin caused flown alatae to fall off the plant but again did not influence the initial probe. (Dawson, Griffiths, Pickett, Smith and Woodcock)

Chemical interference with virus transmission by *M. persicae*. In laboratory tests, deltamethrin (0·001% a.i.) applied to healthy plants decreased by 86–94% infection with beet yellows virus (BYV) and beet mild yellowing virus (BMYV) by viruliferous S (insecticide-susceptible), R1 (moderately resistant) but not R2 (strongly resistant) apterae. Treatment of BYV-source plants decreased transmission by 95–99% and settling and nymph production by 80–93%, but a concentration of 0·1% a.i. was required to achieve similar effects on R2s.

In flight-chamber experiments, BYV-transmission to treated healthy plants by free-flying alates (R1) was decreased, respectively, 83% by deltamethrin (0·001% a.i.), 59% by pirimicarb (0·03% a.i.) and 29% by demeton-S-methyl (0·09% a.i.).

Repellent and antitransmission effects were demonstrated in the non-insecticidal antifeedant polygodial and in a number of derivatives of the aphid alarm pheromone (cf. previous section). Polygodial (0·1% a.i.) decreased BYV-transmission from treated source plants by 76–86%, settling by 45–53% and nymph production by 83–93%; alarm pheromone derivative (V) (0.1% a.i.) decreased transmission by 38–60%, settling by 44–64% and nymph production by 46–67%. These effects, on apterae, were similar

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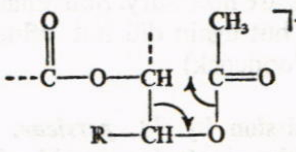
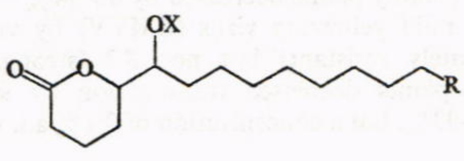
with S, R1 and R2 aphids, unlike those from insecticides (above). (Rice, Sawicki, Stribley and Tuckett, with Gibson, Plant Pathology Department)

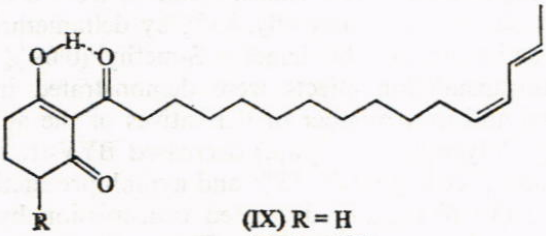
Sex attractants for pea moth. Slow-release formulations of (*E,E*)-8,10-dodecadien-1-yl acetate (*E,E*8,10-12:Ac) are initially much more attractive in the field than those containing (*E*)-10-dodecen-1-yl acetate (*E*10-12:Ac) (*Rothamsted Report for 1976*, Part 1, 125). However, *E,E*8,10-12:Ac in these formulations degrades to inhibitory compound(s) so that lures containing this attractant decline rapidly in activity and thus are unsuitable for practical monitoring of pea moth populations. Formation of these inhibitory compound(s) is prevented by the antioxidant, N-2-octyl-N′-phenyl-p-phenylenediamine, thus providing lures which maintain constant attractiveness for up to 60 days in the field. Such lures, with the more attractive *E,E*8,10-12:Ac, now permit monitoring of small moth populations such as are found in the vining pea crop and at the start of the flight season. (Greenway, with Wall, Entomology Department)

Mosquito pheromone. Mosquitoes of the genus *Culex* are important vectors of disease, particularly *Culex pipiens fatigans* (=*quinquefasciatus*) Wiedemann which transmits the filarial disease elephantiasis. A volatile pheromone is released from droplets that form on apices of eggs of *Culex* and related genera, as they float in rafts on water, and attracts gravid females to oviposit. Analysis (GC–MS) of egg apical droplets from *C.p. fatigans* on a fused silica capillary column showed one major volatile component (0·3 μg per egg raft). Accurate mass determination at low resolution using the data system suggested a long chain methyl-γ- or -δ-lactone with a 5 or 6 acetoxy group giving in the MS source a surprising rearrangement involving migration of the acyl group to the lactone ring (see figure). Identity was confirmed by microchemical methods and synthesis as *erythro*-6-acetoxy-5-hexadecanolide (VI). Minor volatile components were 6-acetoxy-5-tetradecanolide (VII) and 6-hydroxy-5-hexadeconolide (VIII). Synthetic (VI), in dishes of water, at 25 egg raft equivalents, caused five times the number of egg rafts to be laid compared with untreated dishes, similar to the response from an equivalent amount of natural material (*Journal of Medical Entomology* (1979), **16**, 300). (Pickett, with Dr B. R. Laurence, London School of Hygiene and Tropical Medicine)





(VI): X = CH_3CO, R = C_2H_5
(VII): X = CH_3CO, R = H
(VIII): X = H, R = C_2H_5



(IX) R = H
(X) R = OH

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Structure–activity effects in 2-acylcyclohexane-1,3-diones from *Ephestia kuehniella*. The relative activities of the nine 2-acylcyclohexane-1,3-diones from the larval mandibular glands of *E. kuehniella* (last year's *Report*, Part 1, 126) in eliciting oviposition responses from the parasite *Nemeritis canescens* were determined from relative numbers of oviposition movements. The components showed a very wide range (over 100 times) of activity as kairomones. The most active component, 4-hydroxy-2-[(Z,E)-12,14-hexadecadienoyl] cyclohexane-1,3-dione (X) and the next most active (IX) differ only in the hydroxyl group at C-4. The kairomonal activity therefore seems mainly associated with a terminal diene and 4-hydroxy groups in these 2-acylcyclohexane-1,3-diones. (Mudd and Walters, with Dr S. A. Corbet, Cambridge University)

***Dufour's gland components from the parasite* Nemeritis canescens.** After ovipositing into larvae the parasite *N. canescens* marks its host with a pheromone from the Dufour's gland to deter further parasitisation. Volatile components of this gland were shown by GC–MS to contain a mixture of saturated and unsaturated C_{21}, C_{23} and C_{25} hydrocarbons. The unsaturated components were isolated and the configuration and position of double bonds determined from their infrared spectra and ozonolysis products respectively.

Unusual (*Z*)-10-hydrocarbons (tricosene, *c.* 62%; pentacosene, *c.* 1%) and a mixture of (*Z*)-10,9 and 8 heneicosenes (*c.* 1%) were found in the gland together with the saturated hydrocarbons heneicosane (*c.* 20%), tricosane (*c.* 11%), and pentacosane (*c.* 5%). In natural C_{21}, C_{23} and C_{25} alkenes, unsaturation is often at C-9 but very rarely at C-10 and the main component of the gland, (*Z*)-10-tricosene, has not previously been identified. (Mudd and Smith, with Dr R. C. Fisher, University College, London)

Pesticides and beneficial insects

Field poisoning of honeybees. Investigations in 1981 were concentrated on a survey organised by MAFF, to obtain a more precise assessment of the hazard to bees from ground application of insecticides, especially triazophos, to oilseed rape. Triazophos was identified by the MAFF Wildlife Investigation Scheme in bees from 50 apiaries, deduced to represent 27 spray incidents. One further incident probably involved demeton-S-methyl.

Analyses supported by detailed field investigations provided more reliable data than in previous years, and confirmed the pattern of mortalities reported in previous years. The area of oilseed rape increased from 64 000 ha in 1978 to an estimated 124 000 ha in 1981, but ADAS advised that low pest numbers in 1981 made spraying unnecessary unless there was a local history of pest attack. Therefore in a year of high pest incidence, the resulting increase in insecticide application to oilseed rape might cause considerable damage to honeybee colonies.

Investigations of other causes of poisoning showed results similar to previous years. (Smart and Stevenson, with Mr V. A. Cook, MAFF Bee Advisory Unit, and Dr A. R. Hardy, MAFF, Tolworth Laboratory)

Insects on barley. Laboratory assessment of toxicity of pesticides to individual species of beneficial insects provides a basis for studying selectivity, but may not realistically predict effects in the field. Long- and short-term hazards are best assessed by field observation of whole populations despite difficulties involved.

To develop a field method for studying short-term effects of pesticide applications to arable crops, 3·3 and 0·84 ha square plots of spring barley were treated with demeton-S-methyl during flowering in 1980 and 1981 respectively. Insect populations in the plots and the surrounding unsprayed areas were sampled by several techniques, principally the Devac. As expected numbers of cereal aphids and their parasites were greatly lowered

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but the latter started to increase, most slowly near the centre of the plot, 1 week after treatment. Predators were caught in smaller numbers and effects were more difficult to assess but they were probably less affected by the insecticide than the parasites. Further work will compare insecticide treatments, and assess the influence of plot size and aphid abundance. (Smart, Stevenson and Walters)

Control of spring barley pests. A field experiment to study the effects of insecticides on pests of spring barley confirmed last year's result (last year's *Report*, Part 1, 128–129) that insecticidal sprays can increase yields of a late sown crop. In barley sown on 14 April, demeton-S-methyl and omethoate gave 5–8% yield increases when applied on 9 July and 17% increases when applied three times throughout the growing season. Fenitrothion applied on 9 July increased yield by 12%. These effects are believed to be due to the control of dipterous stem borers; the repeated omethoate sprays decreased the damage caused by dipterous larvae, mainly the gout fly, *Chlorops pumilionis*, from 13·2 to 3·9% damaged shoots. (Griffiths, Scott and Woodcock)

Control of *Sitona*. (Griffiths, with Bardner and Fletcher—*see* Entomology Department Report p. 102.)

Soil-borne pests

Control of wheat bulb fly larvae. A further four pyrethroids were tested (cf. last year's *Report*, Part 1, 127) as seed treatments at 2 g a.i. kg^{-1} seed to suppress wheat bulb fly attack. 'Kadethrin' was almost as effective as permethrin but was also adversely affected by deep sowing. Bioneopynamin and cismethrin were phytotoxic and bioallethrin was ineffective. Other materials tested were cloethocarb at 0·4%, carbosulfan at 0·2% and a microencapsulated formulation of ethyl parathion at 0·2%, which all decreased attack. The performance of these materials was not affected by deep sowing, but only ethyl parathion matched the effectiveness of chlorfenvinphos and permethrin. (Griffiths, Scott, Smith and Woodcock)

Behaviour of pesticides in soil

Biological activity of insecticides in soil. The toxicities to vestigial winged *Drosophila melanogaster* of six organophosphorus insecticides (carbophenothion, chlorfenvinphos, dimethoate, phorate, tetrachlorvinphos and thionazin), with a wide range of physical properties, were measured by topical application, after uptake from a glass surface, after uptake from soils and by fumigant action above soils. Eight soils with organic matter content in the range 0·5–57% were used. Results of bioassays in each soil were related to insecticide water solubility, vapour pressure, soil adsorption coefficient and octanol–water, air–water and air–wet soil partition coefficients, leading to recognition of suitable values for efficient uptake of lethal doses from soil. (Buxton, Farnham and Nicholls)

Leaching in the field. The movement and persistence of atrazine and metribuzin in a sandy loam soil after application in spring was simulated using two models. That of Leistra (last year's *Report*, Part 1, 129), using measured values of soil hydraulic properties, underestimated herbicide mobility in soil and overestimated speed of drying of the deeper soil layers. A second and simpler model (CALF) simulating water and herbicide movement using mobile and immobile water categories accurately predicted soil water contents but tended to underestimate herbicide movement just after applications and overestimate

https://doi.org/10.23637/ERADOC-1-128

it later. Predictions of degradation rates in the field from laboratory data were satisfactory for atrazine but not for metribuzin.

The movement and degradation of simazine in soil at Rothamsted was studied as part of a collaborative experiment organised by the European Weed Research Society. Calculations indicated that immediately after application nearly 90% of simazine (water solubility 3·5 μg ml^{-1} at 20°C) was undissolved. Simulations, using a suitably adapted CALF model, agreed closely with measurements until a period of heavy rainfall towards the end of the experiment when the amount of undissolved chemical approached zero; simazine behaviour then became difficult to simulate because it was very sensitive to the value of water solubility chosen.

Water solubility itself is probably only a factor limiting behaviour for the few relatively polar pesticides having small water solubilities. (Nicholls, with Dr A. Walker, National Vegetable Research Station (atrazine and metribuzin); Nicholls and Briggs, Chemical Liaison Unit (simazine)).

Systemic transport of pesticides in plants

Continuing the project (last year's *Report*, Part 1, 129) to establish the relationship between the physical and chemical properties of a compound and its ability to move through the plant in the phloem, the behaviour of more compounds was examined in the *Ricinus communis* test system. In this technique radiolabelled test compounds in buffer are perfused for 1 h through the hollow petiole of a leaf actively exporting assimilate. Radioactivity in the exudate from a cut in the stem below the leaf was monitored for several hours. The series of compounds examined showed a range of behaviours, from compounds loaded and translocated at least as readily as sucrose (methionine, 3-phenoxypropionic acid, phenyl hydrogen malonate) through an intermediate class (3-indolylacetic acid, phenylalanine) to those appearing well after the pulse for sucrose with a much broader peak (maleic hydrazide, phenoxyacetic acid, 3-amino-1,2,4-triazole and 2,4-dichlorophenoxyacetic acid). (Burrell, Butcher, Chamberlain and White)

Electrically charged spray application systems

Design. These spray systems continue to attract considerable commercial interest. The design of the APE 80 spray head has been modified, allowing rapid changing of the liquid jets, and calibration of flow rates. Field trials with the latest experimental hand-held units in the USA on both cotton and soybean crops established that applications of water-based formulations are possible in high ambient temperatures, because the accelerated passage of charged drops diminishes evaporation.

Both u.v. tracers and active chemicals were applied at 4 litres ha^{-1} using three or more tractor-mounted units attached to a conventional spray boom. Analyses consistently showed a greatly enhanced total deposition, mostly on stems and abaxial surfaces of upper leaves, while spray penetration was restricted to the upper 25 cm of the crop when the canopy was dense. With an open canopy, stem and abaxial leaf surface deposition was achieved almost to soil level, whilst a much smaller volume of spray reached the soil.

Improvements being investigated, such as liquid flow control, tank isolation and an atomiser suitable for increased flow rates, should permit application from higher ground speed vehicles and, possibly, from aircraft. (Arnold and Pye)

Field trials. Field experiments in 1981 were designed to measure chemical deposition and biological effectiveness of sprays applied by tractor-mounted electrostatic apparatus

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of the APE 80 type. The tests compared electrostatically charged sprays applied at 4 litres ha^{-1} with a conventional hydraulic sprayer delivering 400 litres ha^{-1}.

On an open row crop (field beans at an early stage of growth) the electrostatic sprayer deposited two to three times more dimethoate than the hydraulic sprayer; dimethoate or permethrin applied at half doses controlled the pea and bean weevil (*Sitona lineatus*) to the same extent as hydraulic sprays applied at the full dose of insecticide. Increased deposits of pesticide were also achieved by microencapsulated permethrin applied electrostatically.

Deposition of demeton-S-methyl on the top 10 cm of field beans at a later growth stage (90 cm tall) was also improved by electrostatically charged sprays, so increasing activity against bean aphids. However, charging did not enhance the biological effectiveness of sprays of the non-systemic insecticide permethrin, possibly because these failed to penetrate rolled terminal leaves harbouring aphids.

With sprays in calm conditions on spring barley the dense canopy collected similar amounts of chemical whether applied electrostatically or hydraulically. Failures of penetration with the non-systemic fungicide ditalimfos applied electrostatically caused poor control of barley mildew but the systemic fungicide tridemorph was active when applied by both spray methods, as judged by mildew scores of the leaves and by final yield.

These results suggest that electrostatic sprays may not be suitable for situations which require penetration of dense crops by non-systemic materials. When systemic materials are used or the crop has an open canopy, or the pest is mobile, use of electrostatic sprays allows amounts of pesticide to be decreased to one-half and volumes of carrier to be decreased 100-fold without loss of biological activity. (Arnold, Cayley, Etheridge, Griffiths, Phillips, Pye and Scott)

Formulation

Microencapsulation. Further microcapsules with polyurea walls were prepared as formulations of permethrin (for electrostatic CDA spraying of field beans against *Sitona* weevil), methiocarb (as a molluscicide), pirimicarb (as an aphicide), and amyl acetate (for bee pheromone trials). (Etheridge and Phillips)

Bird repellents

Evaluation of the activity of various formulations of compounds considered to be bird repellents continued (cf. last year's *Report*, Part 1, 130–131). Bud damage of plum trees (47% in the control) was reduced somewhat by fentin hydroxide w.p. applied at three concentrations: as a high volume spray with 5% 'Acronal 4D' as sticker (damage 46–24%), and significantly by 1,8,9-trihydroxyanthracene, applied as an aqueous emulsion (27% damage) or as a solution in quinoline+vegetable oil (22% damage) using a spinning disc. (Etheridge and Phillips, with Dr D. A. Kendall and Dr B. D. Smith, Long Ashton Research Station)

Insect species reared

Homoptera	*Aphis fabae* Scop.;
	Lipaphis erysimi (Kltb.);
	Metapolophium dirhodum (Wlk.);
	Myzus persicae (Sulz.) (Susceptible and several resistant strains);
	Rhopalosiphum padi (L.);
	Sitobion avenae (F.).
Coleoptera	*Phaedon cochleariae* (F.).

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Dictyoptera	*Periplaneta americana* (L.).	
Diptera	*Calliphora erythrocephala* (Meig.);	
	Delia antiqua (Meig.);	
	Drosophila melanogaster Meig.	(Vestigial wing strain);
	Musca domestica L.	
	Strains:	wild-type susceptible;
		ac: ar; bwb; ocra-called 608, multimarker susceptible.
		SKA-diazinon selected, very resistant to many organophosphorus insecticides.
		Several derived from the dimethoate resistant 49r$_2$b, resistant to dimethoate and other organophosphorus insecticides.
		290BIO, a substrain of the dimethoate/bioresmethrin resistant 290rb derived by selection with bioresmethrin.
		Several derived from 290BIO each resistant to pyrethroids and DDT.
		NPR-pyrethrum extract selected.
		538ge-*kdr* knock-down resistant.
		IPSWICH pyrethroid-resistant. Several derived from IPSWICH resistant to pyrethroids.
Hymenoptera	*Aphidius matricariae* (Haliday);	
	Venturia canescens (Grav.).	
Lepidoptera	*Ephestia kuehniella* Zeller;	
	Plutella xylostella (L).	
Neuroptera	*Chrysopa carnea* Steph.	
also Mollusca	*Deroceras reticulatum* (Muller).	

Fungal diseases and fungicides

Clubroot disease: the host–parasite relationship. Earlier suggestions that the clubroot symptoms are caused by an excessive production of the auxin precursor 3-indolylacetonitrile (IAN) from 3-indolylmethylglucosinolate (IMG) have been criticised on the grounds that this is unlikely at the natural pH (5–6) of brassica tissues. However, a detailed *in vitro* study using [methylene-^{14}C]-IMG has shown that myrosinase (thioglucosidase 3.2.3.1) can convert IMG to IAN over the pH range 4–6.

Spectrophotofluorimetric estimations of small concentrations of IMG ($\geqslant 0 \cdot 1$ nM) and IAN ($\geqslant 0 \cdot 2$ nM) have been developed. Rapid estimation of these compounds will assist in breeding varieties of *Brassica campestris* low in the indoles, and therefore possibly less susceptible to clubroot; this is being explored. (Butcher, Chamberlain and Searle)

Control of soil-borne disease by foliar sprays. Earlier glasshouse work showed that foliar sprays of the downward translocated compound 3,5-D (the 3,5-analogue of 2,4-D), or of other analogues of 3,5-D, greatly decreased the severity of potato common scab, caused by soil-borne *Streptomyces scabies*.

Glasshouse tests of analogues against scab. In further glasshouse tests (conditions as described in last year's *Report*, Part 1, 133) the following analogues were as effective as 3,5-D in suppressing scab, did not decrease yield but, like 3,5-D, slightly increased tuber number and distortion: 3-chloro-5-bromo-, 3-chloro-5-iodo- and 3-bromo-5-iodophenoxyacetic acids. With the exception of MCPA, which decreased scab slightly, all other analogues tested were ineffective: unsubstituted phenoxyacetic acid, 2-chloro-4-methyl-, 2- and 4-hydroxy-3,5-dichloro-, 3,5-difluoro- and pentafluorophenoxyacetic acids; the isopropyl ester of 3,5-di(trifluoromethyl)-phenoxyacetic acid; *m*-trifluoromethyl-*trans*-cinnamic acid; 3-[3,5-di(trifluoromethyl)phenyl]propionic acid; and 3,5-dichloro-DL-phenylalanine. A difficulty with these tests, using the very early cv. Maris Bard, was that the periods of root development (preferably in moist soil) and of infection (preferably in dry soil) overlapped more than usual; this led to unusual variations in scab incidence,

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and in the preventative action of 3,5-D sprays. In late-tuberising cultivars (e.g. Majestic, Arran Banner), results were much less erratic.

Field trials. At Woburn, plants (cv. Maris Piper) were sprayed once or several times between 7 and 28 June with phenoxyacetic acids at 0·23–0·9 mM (0·05–0·2 g litre^{-1} for 3,5-D) and 1400 litres ha^{-1}. The largest decrease in scab from 3,5-D (four sprays at 0·45 mM or 0·1 g litre^{-1}) was about 50%, but this was accompanied by significant decreases in yield and tuber size. This effect on scab was similar to that in earlier trials, but by contrast was not significant because of an exceptionally large coefficient of variation in the scab figures. Sprays of 3,5-di(trifluoromethyl) phenoxy acetic acid, which was as effective as 3,5-D in glasshouse tests (*see* last year's *Report*, Part 1, 133) had only a slight effect on scab, but did not affect yield or tuber size.

In a similar trial, with 3,5-D only on cv. Desirée at Gleadthorpe EHF (for which we thank Mr J. H. Hawkins, ADAS, Shardlow), the maximum decrease in scab (37%: significant at $P < 0·05$) was given by three sprays at 0·45 mM; yield and tuber size were not affected.

Mode of action of 3,5-D. The following results were obtained in experiments on potato tuber discs *in vitro*.

Several substituted phenoxyacetic acids, besides 3,5-D, are known to decrease scab severity as foliage sprays; each of these acids inhibited browning of tuber discs, during ageing, to some extent. However, the two effects were not correlated; inhibition of disc-browning was not a reliable guide to antiscab action.

Inhibition of disc-browning was reversed by coumaric acid, ferulic acid and tyrosine, but not by phenylalanine or cinnamic acid. Studies on the metabolism of [U-^{14}C] phenylalanine showed that 3,5-D decreased its absorption and decreased still further metabolism to ethanol-insoluble compounds and soluble phenolics. The inhibition was not paralleled by a similar decrease in metabolism of [U-^{14}C] sucrose to $^{14}CO_2$. Analysis of soluble phenolic compounds synthesised from [U-^{14}C] phenylalanine showed that 3,5-D decreased synthesis of coumaric and ferulic acids more than of cinnamic acid. Assay of extractable phenylalanine ammonia lyase and cinnamate-4-hydroxylase showed that 3,5-D caused a lag in synthesis of these enzymes during ageing.

One of the effects of 3,5-D in tuber tissue is therefore to inhibit scab lesion development by suppressing the increase in phenolic biosynthesis which normally follows infection. (Burrell, Chamberlain, Dawson and McIntosh)

Fungicides for soil-borne wheat diseases. Glasshouse experiments confirmed that localised inoculum of take-all is most harmful if placed near newly emerging roots, and that control by benomyl fungicide is most effective near the site of primary infection. To prevent early injury, and to act against later infection via the crown region, benomyl should therefore be placed near the seed and the crown respectively. In an attempt to apply this conclusion in long-term outdoor pot experiments, benomyl was applied in seed pellets. The rate used (20 g kg^{-1} seed) would have been phytotoxic if unpelleted, and although persisting longer than an unpelleted treatment (4 g kg^{-1}) still did not control take-all for the whole season (November to July) probably because the fungicide was too localised to prevent later infection. However, as reported previously (last year's *Report*, Part 1, 133) carbendazim formulated in polyurea-walled microcapsules and mixed into soil in pots outdoors persisted well enough to give a considerable degree of protection throughout the growing season.

Field plots of winter wheat were treated in October and April as previously (last year's *Report*, Part 1, 133). Take-all was suppressed up to July by benomyl (20 kg ha^{-1}) applied

https://doi.org/10.23637/ERADOC-1-128

in April and nuarimol (2·2 kg ha^{-1}) applied in October. These treatments and nuarimol in April also suppressed sharp eyespot. The April benomyl treatment significantly increased yield. Foliar diseases were not affected.

Last year's field experiment site was resown and sampled to detect residual effects. Take-all infection was less in the nuarimol-treated plots (4·4 kg ha^{-1} in October 1979 and April 1980), and these and April-treated benomyl plots (20 kg ha^{-1}) gave greater yields than the untreated plots. (Bateman)

The CALF model (see above) was used to simulate the distribution in soils of benomyl, carbendazim and iprodione following applications as soil drenches with and without surfactants in pot experiments. The results correlated well with disease control observed (see last year's *Report*, Part 1, 133). (Bateman and Nicholls)

Seed treatment and *Rhynchosporium* in winter barley Seed of cv. Maris Otter, infected or uninfected with *R. secalis*, was drilled at Rothamsted and Long Ashton on sites free from trash-borne inoculum to assess the effects of organomercury seed treatment on leaf blotch. The plots were separated by barrier plots of oats or wheat. Leaf disease became visible in March, and all plots were equally infected by April. (Bateman, with Dr V. W. L. Jordan, Long Ashton Research Station)

Mode of action of hydroxypyrimidine fungicides. Continuing last year's work, partially purified adenosine deaminases (ADA-ase) from mildew conidia, infected barley and *Neurospora crassa* (which is not affected by ethirimol) were compared with calf intestine ADA-ase. Those from conidia and infected plants were similar (mol. wt *c.* 300 000) but larger than calf intestine ADA-ase (mol. wt *c.* 60 000). Infected plant ADA-ase was stable for several months at −20°C, whereas the conidial and *N. crassa* enzymes lost activity when stored. Conidial ADA-ase was nore sensitive to ethirimol than was the infected plant enzyme. (Hollomon)

Variation in response of barley pathogens to the fungicide triadimenol. Using laboratory and greenhouse assays already developed (last year's *Report*, Part 1, 134), isolates of barley powdery mildew (*Erysiphe graminis* f.sp. *hordei*), from both treated and untreated crops, showed a range of sensitivity to triadimenol greater than in previous years. For the first time, some isolates infected plants grown from seed treated (with 'Baytan') at commercially recommended rates. This decline in triadimenol sensitivity was apparently associated with more intense use during 1981 of those fungicides which inhibit sterol synthesis. The insensitive isolates were also insensitive to triadimefon, triforine, propiconazole, prochloraz, fenarimol, nuarimol and diclobutrazol, but not to the morpholine fungicides tridemorph and fenpropimorph and, significantly, were *more* sensitive to ethirimol. The frequency of occurrence of this negative cross-insensitivity and its practical value are not yet clear. (Butters and Hollomon)

THE CHEMICAL LIAISON UNIT

Application or distribution of pesticides is an essential part of any control measure and much remains to be done in developing methods which give the most effective patterns of pesticide distribution. An increasing amount of effort is being devoted to determining the performance of various systems of application of pesticides to crops in the field and in store, with emphasis on comparison of the patterns of distribution achieved by conventional and electrostatic sprayers. The subsequent behaviour of a chemical is equally important and investigations to relate chemical structure with movement of chemicals in soils and crops promise to eliminate some of the trial and

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error from the selection of pesticides with appropriate properties for specific problems.

Since its formation the Unit has been involved in collaborative investigations on the control of nematodes and fungal diseases attacking potatoes. Practical control of nematodes has been achieved with fairly mobile nematicides distributed to depth in soil. Control of 'seed-borne' fungal diseases requires other strategies; seed treatments are useful but the chemicals are immobilised on the tuber skin and systemic fungicides applied to the growing plant tend to move away from the points of fungal attack so further investigations to overcome these difficulties are in progress. These practical control problems illustrate the importance of distribution and the subsequent redistribution of chemicals in pest control. These problems are now recognised and unifying concepts are developing but it will be necessary to continue to tailor investigations to the solution of specific problems, to measure residues and to check achievements of methods of application, not only for experimental purposes but also on a commercial scale.

Collaborative work continues with the Unit providing chemical expertise for a variety of topics ranging from the fatty acid composition of worms to assessment of the efficiency of seed-dressing and pesticide residues in crops. Major projects are listed at the end.

Uptake and movement of chemicals in plants

Root application. Further work on the uptake of oximecarbamates and phenylureas by barley plants from nutrient solution has reinforced previous conclusions (*Rothamsted Report for 1976*, Part 1, 184). The accumulation of non-ionised chemicals by roots is ascribed to two processes: (i) partitioning of chemicals on to lipophilic root solids; (ii) uptake into the aqueous phase of roots contained in the free space and within the cells. The partitioning process dominates for lipophilic chemicals, giving concentrations in roots much larger than the external aqueous concentration, and occurs to a comparable extent both with the roots of intact plants and with the solids obtained by maceration of frozen roots. For polar chemicals, which partition only weakly on to root solids, the second process accounts for a lower limiting concentration of chemical in the roots of about 0·8 of the external solution concentration. Translocation from roots to shoots is a passive process and is maximal for chemicals of moderate lipophilicity having octan-1-ol/water partition coefficients in the range 50–100. Results in the literature for the root uptake and translocation of a wide range of non-ionised pesticides in several plant species generally agree well with the above conclusions.

The limited translocation of both the more polar and more lipophilic chemicals cannot be explained in terms of a series of simple partitions in the root. When transferred to a solution of chemical, the roots of intact plants rapidly absorb chemical, coming to equilibrium within a few hours. Subsequently neither the root concentration nor the rate of translocation change and the translocation of lipophilic chemicals is therefore not limited by further adsorption by the root. Presumably the translocation of polar and lipophilic chemicals is limited by penetration of membrane barriers to the transpiration stream. (Briggs, Bromilow and Evans)

Foliar application. When it was observed that the proportions of chlormequat chloride taken into leaves increased with the concentration applied to wheat and barley leaves (*Rothamsted Report for 1978*, Part 1, 150), a simplified test system was developed and used to confirm these results and investigate the effects of other chemicals. A standard amount of ^{14}C-chlormequat chloride in aqueous acetone (10 μl) containing the test chemical was applied to the second leaf of wheat or barley seedlings. After 2 days the amounts of ^{14}C-chlormequat chloride which could be washed from the leaf surface or extracted from

https://doi.org/10.23637/ERADOC-1-128

its tip were measured. Some substances changed the amounts of chlormequat chloride remaining on the leaf surface or moving to the tip of the treated leaf. Amines, both quarternary ammonium compounds closely related to chlormequat (choline, glycine betaine) and others, such as tetramethylammonium chloride, trimethylphenylammonium chloride, mepiquat and butylamine, were equally effective in increasing penetration and movement of chlormequat to the tip of treated leaves. Triethanolamine and 8-quinolinol decreased uptake, whilst tetraethylammonium chloride and salts of fatty acids had little effect on uptake but increased the amounts of chlormequat reaching the tips of treated leaves.

The wide range of compounds affecting the behaviour of chlormequat suggested that additives might also influence the behaviour of other compounds. We chose to examine the effects of additives on herbicide action using plant damage as an indicator. Tests were made by applying measured volumes to individual leaves of seedlings using 2,4-D on rape and paraquat on barley, wheat and rape. Some additives increased paraquat damage in all three species mainly by increasing damage to leaves not directly treated; however, more compounds increased damage caused by 2,4-D. Thus choline, glycine betaine and dimethylaminoethanol increased damage caused by both herbicides but butylamine, tributylamine and trimethylphenylammonium chloride increased damage caused by 2,4-D but not by paraquat. The ammonium and sodium salts of some fatty acids diminished leaf damage by both herbicides.

Although the mechanisms by which other solutes affect uptake and movement of chemicals in plants are not known these effects were observed with a wide range of ionic chemicals, indicating a general phenomenon, which could be exploited to modify the behaviour of pesticides applied to crops, speeding or slowing uptake and movement to achieve desired biological effects. (Lord, with Wheeler, Botany Department)

Other projects

Collaborative work reported in other sections of the *Rothamsted Report:*

Entomology Department

Cayley, with Edwards—fatty acids in worms as potential fish foods.
Bromilow, with Bardner—phorate residues in peas.

Insecticides Department

Briggs, with Nicholls—modelling of simazine movement in soils.
Cayley, with Arnold—foliar spraying techniques.

Nematology Department

Bromilow, with Whitehead—incorporation of nematicides in soil.

Plant Pathology Department

Cayley, with Hide—effect of chemicals on wound healing and disease.
Cayley, with Rawlinson—control of oilseed rape diseases.

Staff of the Department and the Chemical Liaison Unit

M. Elliott, N. F. Janes and D. A. Pulman received the Mullard Award of the Royal Society for their development of synthetic pyrethroid insecticides. The award was instituted in 1967 by a gift from Mullard Limited and is made annually for an outstanding

https://doi.org/10.23637/ERADOC-1-128

contribution to the advancement of science or technology directly promoting prosperity in the United Kingdom. R. L. Elliott was awarded a Doctorate of Philosophy by the University of Oxford.

Chiang Chia-liang returned to the Shanghai Institute of Entomology, Academia Sinica, after studying the biochemistry of insect resistance to insecticides for 2 years. Mlle Sylvie Jusseaume worked for 6 months as part of her degree training in the University of Rennes, France.

Amal M. Abdalla returned to the Sudan and S. Nwokocha to Nigeria after completing training in the Chemical Liaison Unit supported, respectively, by the International Atomic Energy Authority and the Inter-University Council.

Ritta Jhala left to marry and was replaced by A. R. L. Tuckett. Pamela C. Willott resigned and Valerie J. Church was appointed in her place; Sarah J. Bozzard was appointed to the NRDC-supported post vacated by Valerie Church. D. R. S. Gilmour was appointed (NRDC post). Rosemary Manlove resigned from the Chemical Liaison Unit.

In February R. M. Sawicki contributed a paper to the Royal Society Discussion on Crop Protection Chemicals and in March he participated in the 'Journées d'études et d'informations sur les pucerons des cultures' in Paris at the invitation of the Association de Coordination Technique Agricole; he also visited the School of Agriculture of the University of Rennes at the invitation of the Institut National de Récherche Agronomique to discuss insecticide resistance in aphids; A. D. Rice discussed resistance to *Myzus persicae* at a meeting of the Institut International de Recherches Betteravières: Pests and Disease Group, Denmark, in September. In June, M. Elliott was invited by Rhône Poulenc Agrochimie, France, to discuss synthetic pyrethroids.

J. A. Pickett, supported by the Royal Society and the Chinese Ministry of Agriculture, lectured on 'Gas chromatography, mass spectrometry and behaviour controlling chemicals' to Agricultural Institutes and the Chinese Academy of Sciences Institute in China. He also presented a paper on 'Controlling aphid behaviour' at the International Symposium on Chemicals Acting on Insect Behaviour in Paris (November) funded by ARC. In February A. J. Arnold visited Ciba-Geigy in Switzerland to discuss electrostatic sprayers and in July with B. J. Pye evaluated electrostatic spraying of cotton and soybeans at the University of Arkansas, USA. Arnold and Pye also attended the 4th International Conference on Electrostatics at The Hague. D. W. Hollomon attended a meeting in August on Resistance to Fungicides in Plant Pathogens on the 75th anniversary of the founding of the Phytopathology Department at Wageningen and A. H. McIntosh lectured on 'A new possibility for prevention of common scab' at the 8th Triennial Conference of the European Association for Potato Research in Munich in September. A. R. Greenway visited Dr R. Bournoville, Institut National de Recherche Agronomique, Lusignan, France, with C. Wall, Entomology Department, on behalf of EEC Plant Protection Programme to discuss attractant monitoring systems for pea and lucerne moths. J. H. Stevenson, Lesley E. Smart and J. H. H. Walters represented the Department at a meeting of the International Organisation for Biological Control Working Group: Pesticides and Beneficial Arthropods here in October.

Members of the Department discussed exhibits on the pyrethroid insecticides on the occasions of the ARC Golden Jubilee soirée at the Royal Society, of the Royal Show at the National Agricultural Centre, Stoneleigh, and of the Centenary Conference of the Society of Chemical Industry in March–April.

Twelve members of the Department and two of the Chemical Liaison Unit contributed to the British Crop Protection Conference on Pests and Diseases at Brighton in November (*see* list of publications).

https://doi.org/10.23637/ERADOC-1-128

INSECTICIDES AND FUNGICIDES DEPARTMENT

Publications

General Papers

1 Butcher, D. N., Firmin, J. L. & Searle, L. M. (1980) The role of tissue culture in the study of crown-gall tumorigenesis. In: *Tissue culture methods for plant pathologists.* Ed. D. S. Ingram & J. P. Helgeson. Oxford: Blackwell Scientific Publications, pp. 203–208.

2 Denholm, A. I. (1981) Present trends and future needs in modelling for the management of insecticide resistance. *Proceedings 1981 British Crop Protection Conference—Pests and Diseases* **3,** 847–855.

3 Devonshire, A. L. & Farnham, A. W. (1981) The nature and impact of insecticide resistance. *The Plantsman* **3,** 14–19.

4 Sawicki, R. M. (1981) Problems in countering resistance. *Philosophical Transactions of the Royal Society London B* **295,** 143–151.

Research Papers

5 Arnold, A. J. & Pye, B. J. (1981) Electrostatic spraying of crops. *Proceedings 1981 British Crop Protection Conference—Pests and Diseases* **2,** 661–666.

6 Bateman, G. L. (1981) Effects of soil application of benomyl against take-all (*Gaeumannomyces graminis*) and footrot diseases of wheat. *Zeitschrift für Pflanzenkrankheiten und Pflanzenschutz* **88,** 249–255.

7 Bright, S. W. J., Lea, P. J., Kueh, J. S. H., Woodcock, C., Hollomon, D. W. & Scott, G. C. (1982) Proline content does not influence pest and disease susceptibility of barley. *Nature, London* **295,** 592–593.

8 Burrell, M. M. (1981) The mode of action of ethionine foliar sprays against potato common scab (*Streptomyces scabies*). *Physiological Plant Pathology* **18,** 369–378.

9 Burrell, M. M. & (Brunt, P.) (1981) Preparation of green plant material for liquid scintillation counting. *Annals of Botany* **48,** 395–397.

10 Chamberlain, K. & (Carter, G. A.) (1980) The fungitoxicity of substituted 2-phenylbenzofurans. *Pesticide Science* **11,** 526–532.

11 Chamberlain, K. & (Carter, G. A.) (1981) Fungitoxicity of hydroxy- and methoxy-substituted phenyl- and naphthyl-benzofurans, phenylbenzo(*b*)thiophenes and phenylindoles. *Pesticide Science* **12,** 539–547.

12 Chiang Chia-liang & Devonshire, A. L. (1982) Changes in membrane phospholipids, identified by Arrhenius plots of acetylcholinesterase, associated with pyrethroid resistance (kdr) in houseflies. *Pesticide Science* **13,** 156–161.

13 Elliott, M., Farnham, A. W., Janes, N. F. & Khambay, B. P. S. (1981) The pyrethrins and related compounds. Part XXV. Synthesis and insecticidal activity of conformationally restrained compounds related to 3-phenoxybenzyl esters. *Pesticide Science* **12,** 503–508.

14 Free, J. B., Ferguson, A. W. & Pickett, J. A. (1981) Evaluation of the various components of the Nasonov pheromone used by clustering honeybees. *Physiological Entomology* **6,** 263–268.

15 Free, J. B., Pickett, J. A., Ferguson, A. W. & Smith, M. C. (1981) Synthetic pheromones to attract honeybee (*Apis mellifera*) swarms. *Journal of Agricultural Science, Cambridge* **97,** 427–431.

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16 GREENWAY, A. R., (DAVIS, S. A.) & SMITH, M. C. (1981) Analysis of field-weathered lures containing (E)-10-dodecen-1-yl acetate, a sex attractant for the pea moth, *Cydia nigricana* (F.). *Journal of Chemical Ecology* **7**, 1049–1056.

17 GREENWAY, A. R., SMART, LESLEY, E., SIMPSON, J., SMITH, M. C. & STEVENSON, J. H. (1981) Detection of starvation as the cause of death in honeybees, from thoracic glucose levels. *Journal of Apicultural Research* **20**, 180–183.

18 GRIFFITHS, D. C., ARNOLD, A. J., CAYLEY, G., ETHERIDGE, P., PHILLIPS, F. T., PYE, B. & SCOTT, G. C. (1981) Biological effectiveness of spinning disc electrostatic sprayers. *Proceedings 1981 British Crop Protection Conference—Pests and Diseases* **2**, 667–672.

19 HOLLOMON, D. W. (1981) Genetic control of ethirimol resistance in a natural population of *Erysiphe graminis* f.sp. *hordei*. *Phytopathology* **71**, 536–540.

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24 MUDD, A. (1981) Novel 2-acylcyclohexane-1,3-diones in the mandibular glands of Lepidopteran larvae. Kairomones of *Ephestia kuehniella* (Zeller). *Journal of the Chemical Society: Perkin Transactions I*, 2357–2362.

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29 SCOTT, G. C. (1981) Experimental seed treatments for the control of wheat bulb fly and slugs. *Proceedings 1981 British Crop Protection Conference—Pests and Diseases* **2**, 441–448.

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31 WALL, C. & GREENWAY, A. R. (1981) An effective lure for use in pheromone traps for monitoring pea moth, *Cydia nigricana* (F.). *Plant Pathology* **30**, 73–76.

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32 WALL, C., STURGEON, D. M., GREENWAY, A. R. & PERRY, J. N. (1981) Contamination of vegetation with synthetic sex attractant released from traps for the pea moth, *Cydia nigricana*. *Entomologia experimentalis et Applicata* **30**, 111–115.

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CHEMICAL LIAISON UNIT

GENERAL PAPER

34 BRIGGS, G. G. (1981) Relationships between chemical structure and the behaviour and fate of pesticides. *Proceedings 1981 British Crop Protection Conference—Pests and Diseases* **3**, 701–710.

RESEARCH PAPERS

35 BRIGGS, G. G. (1981) Theoretical and experimental relationships between soil adsorption, octanol–water coefficients, water solubilities, bioconcentration factors, and the parachor. *Journal of Agricultural and Food Chemistry* **29**, 1050–1059.

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