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## Report for 1979 - Part 1

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### Insecticides and Fungicides Department

**M. Elliott**

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### Introduction

Investigating how best to use organic compounds to protect economically important crops from insect pests and fungal diseases is a very important aspect of our work, much of which is therefore necessarily related to themes of the Seventh Report, on Agriculture and Pollution, of the Royal Commission on Environmental Pollution, published in September, 1979.

The Commission recognises the crucial role of pesticides in the dramatic increases in agricultural productivity during the last few decades and that at present they are essential to maintain crop yields and keep down costs of agricultural products, and in the field of public health, to control insects transmitting diseases. The concern of the Commission is not with whether pesticides should be used: it is that they should be used wisely with a balanced assessment of risks and benefits, a philosophy completely in harmony with the Departmental programme. The ideal pesticide would affect only the pest and break down into harmless constituents after achieving its purpose. Many of the current insecticides are too persistent or unduly toxic to mammals and beneficial insect species. Nevertheless the sustained multidisciplinary project in the department to establish principles by which improved insecticides and fungicides might be developed has demonstrated, in the synthetic pyrethroids, an approach to the compounds specified by the Commission. These insecticides are stable enough on leaves in sunlight to protect agricultural crops and because they are so active, are used at very low application rates (for some compounds, down to 1–50 g ha<sup>-1</sup>), so diminishing the risk of environmental pollution. Further, they are broken down readily by esterases and oxidases in mammals and soil microorganisms. They have a more favourable balance of properties than many earlier insecticides and in recent applications, because of their low mammalian toxicity, have been shown to be suitable for immediate pre-harvest treatment of vegetable crops (celery, tomatoes, cabbages, lettuce, potatoes, etc.). The present commercial pyrethroids are still insufficiently selective between pests and predators but the broad range of structures now recognised in the group, all with generally favourable characteristics, indicate that further improved compounds, some selective, can be found.

Significant progress can now also be recorded in another comprehensive project to establish fundamental principles for developing improved crop protection compounds, in which the factors determining the downward mobility of exogenous compounds sprayed onto plant leaves are studied. We previously reported that the growth regulator daminozide and the non-protein amino acid ethionine act in this way against potato common scab. However, the necessary concentrations were high (2–10 g litre<sup>-1</sup>). We now describe an alternative range of simple compounds (growth retardants) active at much lower concentration (0.1–0.2 g litre<sup>-1</sup>), a promising lead for future developments.

Having concluded that, for the foreseeable future, pesticides will be essential for food production and in public health, the Commission considers very serious the potential growth of resistance to pesticides and recommends intensified work to develop strategies to delay the onset of resistance as long as possible. Much of the Department's work is already so oriented with detailed investigations of the mechanisms by which organisms become resistant and of the genetics and dynamics of pest populations; a recent generous grant from the Leverhulme Trust has enabled us to appoint a population geneticist to strengthen this effort. Clarification from fundamental studies is illustrated by our demonstration that strains of *Myzus persicae* react to pressure from insecticides by producing more of the enzyme responsible for insecticide detoxification, individuals having up to 64 copies of the necessary gene. In parallel work on plant diseases, we have shown that the action of hydroxypyrimidine fungicides against powdery mildew on barley involves



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interference with the essential function of adenosine deaminase in salvaging purines during primary infection.

We have been disturbed to find several resistant populations of houseflies and more resistant variants of the peach potato aphid in regions where they were previously rare or absent. In practical field work, we have exterminated complete populations of pyrethroid-resistant houseflies from pig farms by exploiting the low mammalian toxicity of bioresmethrin-synergist mixtures, which allow operators to apply concentrations high enough to kill even very strongly resistant adults, and so stop breeding. However, the surrounding populations of insects which re-infested the farm were already resistant.

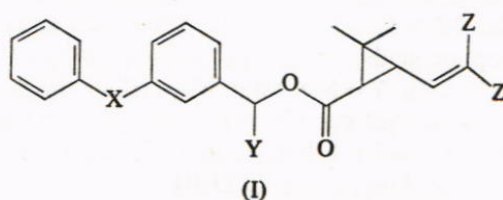
A further section of the Royal Commission's report comments on the scope for improving the efficiency with which pesticides are used—in some cases more than one million times more pesticide is applied than is needed to kill the pest directly. Controlled droplet application might be significantly more efficient. We are developing electrostatically charged spray systems which control droplet size directly and increase deposits on the undersides of leaves.

Although the Commission expects that compounds affecting pest behaviour will have little economic significance before the end of the century, we maintain a broad programme, largely in collaboration with the Entomology Department, to establish potentially important applications within our field of interest of techniques exploiting such compounds; the value of such approaches is confirmed by the commercial success of our development of sex attractant lures for the pea moth. The possibility of using alarm pheromones to increase mobility of aphids and thereby enhance contact with insecticides is being investigated. A practicable synthesis of one of the pheromones from the larval mandibular gland of *Epehstia kuehniella*, reported last year, will enable us to establish the broader significance for pest control of compounds with this novel structure.

### Insecticides

#### Relationships between molecular structure and insecticidal activity of pyrethroids

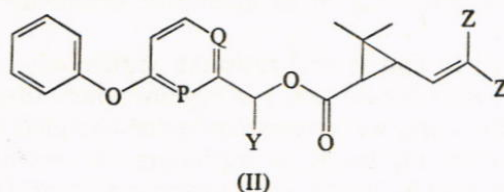
*3-Benzoyl-, 3-benzyl and other analogues of 3-phenoxybenzyl esters.* Previous work established that pyrethroid-like activity is retained with various bridging groups (X) in substituted benzyl esters (I). The effect of varying X in new combinations in which Y and Z are also changed has now been examined.



The compounds with X=O, as in the photostable pyrethroids now being developed commercially, are most active. However, other sterically equivalent groups (CH<sub>2</sub> and C=O) consistently confer some activity (1–30% of the optimum) to both houseflies and mustard beetles. Further, compounds with X=C=O knocked down houseflies more strongly. These results indicate that the requirements for the group X, like those for many other parts of the pyrethroid molecule, are primarily steric rather than chemical, and that varying X gives insecticides with different combinations of properties. Bulkier groups (X=N.COCH<sub>3</sub>, CH<sub>2</sub>O or CHCN) do not fulfil the requirements, presumably because their size and stereochemical characteristics interfere with the ability of the molecule to fit at the site of action.

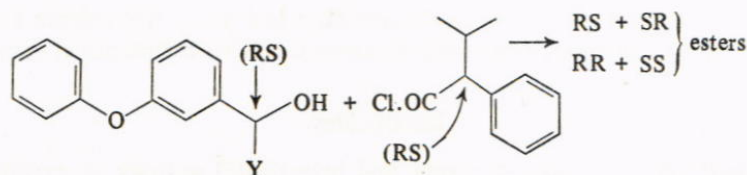


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**Phenoxy-pyridylmethyl esters.** The effects of isosteric replacements have also been investigated in the A ring of 3-phenoxybenzyl esters (II; P=Q=CH) with contrasting results. Two series of pyridines (II; P=CH, Q=N and P=N, Q=CH) were synthesised via rearrangements of the corresponding 2-methylpyridine N-oxides (cf. G. R. Clemo *et al.*, *Journal of the Chemical Society* (1954), 2693). Of the two series, one (with P=N) is about as active as the benzenoid compound, but the other (with Q=N) is almost completely inactive. The change (N for CH) is unlikely to induce severe conformational changes in the free molecule, so presumably some disadvantageous additional binding to the basic centre is possible, but only in the less active series. Much of this work was done in 1974, but for commercial reasons could not be reported then.

**Stereoselectivity in formation of pyrethroidal esters.** A racemic acid chloride reacting with a racemic alcohol will not give exactly a 50/50 mixture of the two diastereomeric pairs of esters, since interaction between the two chiral centres leads to different rates of formation.



An analogue of fenvalerate (Y=Me) prepared by the usual method, showed a large diastereomer imbalance (69:31) due to this effect, the first recorded instance for pyrethroids, so further compounds were synthesised to analyse the influential factors.

The results (details: *Pesticide Science* (1980), in press) show that as Y was changed, imbalance fell in the order Me > Et > Pr<sup>i</sup>, and the effect was more marked with the acid shown than with cyclopropane acids, important for the activity of their esters. Separation of isomers in the example with Y=Me established that the less insecticidal ester is formed preferentially. It has not yet been possible to exploit the effect in a commercially important ester. (Chemical work: Elliott, Janes, Johnson, Khambay and Pulman; biological work: Farnham, Jenkinson and O'Dell)

**Action of insecticides on insect nervous systems**

**Action of pyrethroids in vivo.** The technique described in last year's *Report* (Part 1, 130) for recording action potentials from nerve 5 in the metathoracic legs of living cockroaches (*Periplaneta americana* (L.)) by fine wire electrodes implanted at the trochanter was used to examine the action of pyrethroids *in vivo*.

Thirty minutes after a just lethal dose (3 µg) of bioresmethrin was applied topically to the metathoracic sternites of electrode-implanted cockroaches, small spike repetitive activity (presumably from sensory axons) increased, accompanied by volleys of larger amplitude (presumably motor) spikes as behavioural incoordination developed. After 3-5 h, damped oscillations with flexing of the femur appeared, similar to those observed



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by Narahashi (*Journal of Cellular and Comparative Physiology* (1962), **59**, 61) in cockroach giant interneurons treated with allethrin. Motor activity ceased rather suddenly about 6 h after treatment, but some sensory activity continued up to 12 h. On cutting nerve 5 within the body cavity, the number of large spikes diminished, but, surprisingly, amputation of the leg below the trochanter changed the frequency of large and small spikes only slightly. Hyperactivity persisted in the nervous systems of paralysed cockroaches, confirming other workers' observations.

The repetitive activity caused by bioresmethrin may therefore arise partly from the sensory axons themselves, and not from regions of spike initiation alone. Similarly, some abnormal motor activity apparently arises in motor axons. Further work may establish whether the abnormal motor activity is caused by intoxication of the central nervous system, or of motor axons, or is a response to abnormal sensory input. (Burt)

**Activity of carbinol analogues of DDT in houseflies.** Studies of the action of FDMC (bis(*p*-chlorophenyl)trifluoromethylcarbinol) and dicofol on housefly nervous systems were continued to try to explain the absence of resistance to these carbinol analogues of DDT in DDT-resistant houseflies.

When the action of the carbinols on 'flight-motor' preparations of adult, susceptible houseflies (Miller & Kennedy, *Pesticide Biochemistry and Physiology* (1972), **2**, 206) and on peripheral nerves in the body-cavities of susceptible third instar housefly larvae was compared with that of DDT, different patterns of abnormal nervous activity were observed, suggesting that the action of carbinols may indeed differ from that of DDT. (Goodchild)

**Knock-down resistance in houseflies.** Two neurophysiological techniques were investigated for identifying *kdr* in pyrethroid resistant houseflies. In the first, endogenous trains of pulses from the surface of the eye through a conducting gel electrode were recorded before and after applying bioresmethrin topically to a physically restrained fly. For the second technique, the influence of bioresmethrin on the exposed thoracic ganglia of susceptible and resistant flies was assayed by monitoring nervous activity through a tungsten electrode in the anchored left hind leg. In eight different strains of housefly, susceptible or with various combinations of *kdr* and other resistance mechanisms, the first technique showed no differences that could be correlated with the presence or absence of *kdr*, but preliminary results with the second indicated that it could be developed to diagnose the presence of *kdr* in individual flies although the mode of action of *kdr* remains obscure. (Farnham, with Dr. E. Shipp, Dr. C. J. Orton and Mrs. R. Gunning, University of New South Wales, Australia)

**Neuroanatomy of the insect central nervous system.** This work complements electrophysiological studies of the mode of action of pyrethroids (see above), for the full interpretation of which mapping of the ganglionic structure is essential, because to study effects on individual neurons or groups of neurons, their position, relationships and pathways must be known.

The neuron cell bodies (somata) of the mesothoracic ganglion in the cockroach *Periplaneta americana* (L.) and their nerve fibre pathways were described further. More details of the seven unpaired median groups (*Rothamsted Report for 1976*, Part 1, 165) were obtained, particularly of the courses of the fibres of the posterior median group which are associated with the complex supramedian commissure. The fibre bundles from each cell group follow different courses and some form components of the transverse commissural tracts that join the ganglion halves across the midline. These are some of the



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most complex regions in the ganglion and unravelling of their structure continues. (Gregory)

**Neuroanatomical technique: improved synthetic fixatives for Bodian silver staining.** Continuing to investigate how varying the composition of Bouin fixatives modifies their performance (*Rothamsted Report for 1976*, Part 1, 175), fixatives with no formaldehyde were found to result in neurons staining without affecting adjacent glial cells, and with 25% ethanol: 5% acetic acid, to impregnate hymenopteran (honeybee) nerve tissue well, although this was previously considered resistant. A new, shortened Bodian technique exploits the more intense staining obtainable after these fixatives. Nerve tissue fixed in the 25:5 mixture with or without additional ethyl acetate (last year's *Report*, Part 1, 146) and with or without formaldehyde according to the glial staining desired, needed only one overnight impregnation in the silver-protein protargol and a shorter distilled water rinse. When developer sodium sulphite concentration was adjusted to suit tissue characteristics and section thickness, even thinner (10  $\mu\text{m}$ ) sections were stained satisfactorily. (Gregory)

### Resistant houseflies

**The distribution of resistant housefly populations.** Field populations of houseflies were collected from seven farms (predominantly pig-houses) within 6 miles of Rothamsted where various control agents (e.g. iodofenphos, pyrethroids and sticky paper) had been used. Adult flies reared from the samples were assayed against the standard susceptible Cooper strain with six pyrethroids, two organochlorine insecticides and five organophosphates. Despite variation in sizes of original samples (20 to 400), geographical distribution and previous history of control methods, there were no significant differences between any of the populations including one described last year (last year's *Report*, Part 1, 133) whose resistance level had been little affected by subsequent chemical control. All strains differed genetically from earlier strains now maintained at Rothamsted and all resisted tetrachlorvinphos, malathion, trichlorphon, DDT and dieldrin strongly and pyrethroids weakly. These unexpected results indicate a local distribution of uniformly resistant populations and emphasise the need for sampling from more distant sites. (Farnham and O'Dell)

**Attempted extermination of pyrethroid-resistant houseflies by frequent application of lethal doses.** When arthropods have developed resistance to one group of pesticides control has usually been attempted with alternative effective compounds, but this has sometimes led to pests resistant to almost all suitable control agents. Extermination of isolated infestations with doses great enough to kill even the more resistant individuals has seldom been feasible, because neither operator nor mammals in the vicinity could tolerate the high concentration of pesticide necessary. However, pyrethroid resistant houseflies detected on animal (pig-breeding) farms in Southern England (last year's *Report*, Part 1, 137) provided a suitable opportunity to test the feasibility of this procedure with pyrethroids of low mammalian toxicity. Houseflies moderately ( $\times 5$ – $\times 15$ , near Ipswich) or strongly ( $\times 100$ – $\times 1000$ , near Harpenden) resistant to pyrethroids were sprayed repeatedly with 'Reslin 10' (piperonyl butoxide, bioresmethrin 1:1) to kill all adults and thereby interrupt the breeding cycle. After 6 weeks the farms remained free of adults for the rest of the cold season and were recolonised only in the late spring. However, the new arrivals were also resistant; but only to the extent later found common in Southern England (see Farnham report above). (Sawicki, with Mr. G. T. Bills, ADAS, Ipswich, and Dr. P. R. Chadwick, Wellcome Foundations, Berkhamsted)



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***Insensitive acetylcholinesterase in resistant houseflies.*** The modified acetylcholinesterase in some strains of houseflies that resist organophosphate insecticides is not only less sensitive to inhibition, but is only approximately half as active as normal in hydrolysing the natural substrate. This result could arise from the presence of less enzyme or from its diminished efficiency.

Therefore, the catalytic centre activities (CCA) of the susceptible and resistant forms were compared by irreversible phosphorylation with  $^3\text{H}$  di-isopropylphosphorofluoridate (DFP), followed by measurements of both residual enzyme activity and amount of bound inhibitor. A correction for non-specifically bound DFP was made from control incubations containing excess acetylcholine to protect specifically the acetylcholinesterase. The CCAs were,  $1.36 \times 10^5$  and  $0.69 \times 10^5$  mol acetylthiocholine hydrolysed per minute per mol of normal and insensitive enzyme respectively. Thus both types of fly have the same amount of enzyme, but the mutant form is less efficient.

From these CCAs, and the rate of acetylthiocholine hydrolysis by homogenates of individual houseflies, each fly is estimated to have 0.42 pmol ( $2.5 \times 10^{11}$  molecules) of enzyme. Since the LD50s of most organophosphates to susceptible houseflies are from 0.03–1.0 nmol, only 0.04–1.2% of this is required to inhibit all the acetylcholinesterase, and in a fly surviving this dose, 99% or more is eliminated by metabolism and excretion. In resistant flies LD50s may be 100-fold larger, so that as little as one part in  $10^5$  need bind to the acetylcholinesterase to kill the insect. (Devonshire and Moores)

***Pyrethroid synergism.*** Earlier work (*Rothamsted Report for 1977*, Part 1, 137) on the influence of the time interval between applying synergists and pyrethroids on toxicities to susceptible houseflies was broadened to include strains with either the knock-down resistance factor *kdr* (R.F. 10) or the delayed penetration factor, *pen* (R.F. 1.2). All strains were most affected when the insecticide (either S-bioallethrin or 1R,*trans*-tetramethrin) was applied 1–3 h after 1  $\mu\text{g}$  of either propyl 2-propynyl phenylphosphonate (PPP) (the more effective synergist) or piperonyl butoxide (pb). At peak activity each additive synergised either pyrethroid equally against each strain.

When the synergist was applied before either pyrethroid, the rates of decline in the degrees of synergism as the time interval between treatments increased were broadly similar in all strains, but the decline started earlier (after *c.* 3 h) in the susceptible and *pen* strains than in *kdr* (after *c.* 8 h). The rates of decline of synergism when either synergist was applied after the pyrethroids to susceptible or *kdr* flies were similar, suggesting comparable rates of loss of activity of pyrethroids in both strains.

*Pen* flies showed the greatest differences. With the combination of either pyrethroid and pb, the decline in synergism was much slower whichever compound was applied first. When PPP was applied after the pyrethroid there was also a slowing in the decline in synergism, but not when PPP was applied first. These results show pyrethroid synergism to be a complex phenomenon, probably involving many stages of poisoning rather than a simple inhibition of one degradation pathway. (Farnham and O'Dell)

### Resistant aphids

**Resistance in field populations of *Myzus persicae*.** Aphids with  $R_2$  or even stronger resistance were detected in 32 of 108 samples of field populations received, particularly from those collected near glasshouses, and for the first time a number of sites in East Anglia. This is a disturbing development, for this very resistant variant was endemic only in Western Scotland.

Previous variants with 32 or 64 times more E-4 esterase than the susceptible form readily reverted towards the S variant, but a clone of *M. persicae* with 32 times more E-4



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has now remained stable for 10 months of laboratory rearing free from insecticide. Comparable stability of this mechanism in field populations would produce levels of resistance difficult to overcome.

**Effect of ethiofencarb on beet yellows virus (BYV) transmission in sugar beet by two resistant variants of *Myzus persicae*.** Although some carbamate aphicides were very effective even against the R<sub>2</sub> variant (*Rothamsted Report for 1977*, Part 1, 138) any delay in killing might allow sufficient time for BYV to be transmitted. This possibility was examined in field experiments.

Plots of sugar beet containing a few plants infected with BYV were sprayed with ethiofencarb one day before R<sub>1</sub> or R<sub>2</sub> aphids were released. Although the number of aphids was considerably decreased by the insecticide, which was more effective against R<sub>1</sub> than R<sub>2</sub> aphids, the percentage of BYV in all plots was approximately the same as in the control plots that received no spray.

This surprising result suggests that the proportion of plants infected may sometimes depend less on the number of aphids present rather than on their mobility, which may be enhanced by insecticidal treatment.

**Survey of field populations of cereal aphids.** Insecticides are now used extensively to control cereal aphids, and to establish their baseline susceptibility, we surveyed field populations with the help of G. J. W. Dean and H. Loxdale (Entomology Department) and Mr. K. George (MAFF, Plant Pathology Laboratory).

Dip tests (*Rothamsted Report for 1975*, Part 1, 158) established the discriminating doses of demeton-S-methyl and pirimicarb for *Sitobion avenae*, *Rhopalosiphum padi* and *Metopolophium dirhodum*. There was no indication of resistance to these insecticides. In contrast to *M. persicae* there were considerable differences in the electrophoretic pattern of the carboxylesterases in many populations of these three species of cereal aphids. (Devonshire, Jhala, Moores, Rice, Sawicki and Stribley)

### Compounds influencing invertebrate behaviour

A number of fundamental studies in our wide ranging programme have now reached the stage where progress requires field examination. Further difficulties and complications must be overcome, but even minor successes here may be significant in developing processes suitable for agriculture. Some of these studies continue in collaboration with the Entomology Department, in whose report part of the work is therefore described.

**Aphid alarm pheromones.** (E)- $\beta$ -farnesene, the main component of the alarm pheromone of many aphid species, is conveniently prepared, impure but active, from commercially available nerolidol (last year's *Report*, Part 1, 136). The impurities are isomeric  $\alpha$ -farnesenes which have been shown to act as internal antioxidants; therefore impure (E)- $\beta$ -farnesene may be more suitable than purified material in practice.

The possibility of using the pheromone to increase mobility of aphids and thereby enhance contact with an insecticide was investigated. In preliminary work, numbers of aphids in colonies of *Myzus persicae* on small Chinese cabbage plants diminished by  $38 \pm 6\%$  when sprayed with 0.05% permethrin and by  $92 \pm 3\%$  when insecticide was immediately preceded by treatment with pheromone. This initial promise is being pursued with work on other aphid species and by attempting to develop a field application. If resistance to the present range of systemic aphicides continues to spread, application with a pheromone could extend the range of useful pesticides. (Griffiths, Pickett, C. Smith and Woodcock)



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**Diamond-back moth.** (Z)-11-Hexadecenal and (Z)-11-hexadecenyl acetate reported (Tamaki, Y. *et al.*, *Applied Entomology and Zoology* (1977), **12**, 208–210) to comprise the sex attractant pheromone of female diamond-back moth *Plutella xylostella* were synthesised, and also (Z)-9-tetradecenyl formate, a structural mimic of the aldehyde. Of a number of arrangements investigated, one using 10 µg of the pheromonal components in a polythene tube was most suitable for monitoring and was successfully employed in Oecos Delta traps, catching most moths towards the end of July at coastal sites and in early August at inland sites. (Dawson and Pickett, with Macaulay, Entomology Department, and Mr. P. F. Parmenter, Bird's Eye Foods Ltd.)

**Honeybee pheromones.** The enzyme system postulated to maintain appropriate relative proportions of components in the Nasonov pheromone during scenting (last year's *Report*, Part 1, 136) was not extracted into buffer by ultrasonic treatment, nor with detergents; it remained in the solid precipitate, possibly bound to glandular membranes. Aerial oxidation of the Nasonov pheromone components, (E)-citral and geraniol was shown to yield substantial amounts of epoxides which were not produced during enzymic oxidation by excised Nasonov glands. (Dawson, Pickett and H. Smith, with Williams, Entomology Department)

**Pheromones of *Ephestia kuehniella* (Zeller).** Last year two novel biologically active compounds (2-oleylcyclohexane-1,3-dione and the related 4-hydroxy compound) of a type hitherto unknown in animals were identified in the larval mandibular gland of *E. kuehniella* (last year's *Report*, Part 1, 137). After examining a number of routes, the simpler of the two compounds was eventually synthesised as a yellow oil (20% yield after HPLC purification) by boron trifluoride catalysed C-acylation of cyclohexane-1,3-dione with oleic anhydride. The structure of the product was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR, IR, UV and mass spectral analysis; it elicited an oviposition response from the larval parasite *Venturia canescens* (Grav.). (Mudd)

**Sex attractant lures for pea moth.** Chemical analyses of field-weathered rubber lures containing (E)-10-dodecen-1-yl acetate (E10) reported last year (Part 1, 138) indicated that an initial dose of 3 mg should be constantly attractive for at least the 3 months required to span the season for monitoring. This was confirmed in field tests.

Other field tests with compounds related to the pea moth attractants have shown (Z)- and (E)-8-dodecen-1-yl acetate and (E,E)-8,10-dodecadien-1-ol (all at inhibitor: attractant ratios of 1:10) diminished attractiveness of both E10 and (E,E)-8,10-dodecadien-1-yl acetate (E8, E10) whilst (Z)- and (E)-9-dodecen-1-yl acetate (1:10 and 1:1), (Z)-10-dodecen-1-yl acetate (1:1) and (E)-10-dodecen-1-ol (1:1) inhibited only E10.

Biologically active sex pheromone was obtained either by vacuum distillation of extracts of female abdominal tips or from volatiles collected by entrainment of air over 'calling' females. Single ion monitoring of important ions by GC-MS on two capillary columns showed that E8,E10 (c. 0.1 ng per tip) was present and this was confirmed by other chromatographic and biological evidence. Neither E10 nor (E,E)-8,10-dodecen-1-ol, which are also pea moth attractants, could be detected in extracts or in condensates. (Greenway, with Wall, Entomology Department)

### Pesticides and beneficial insects

**Field poisoning of honeybees.** Examination of poisoned honeybees submitted to the Department continued (last year's *Report*, Part 1, 134). Evidence of insecticide poisoning was found in 97 samples of which 36 involved triazophos residues and 46 other anti-



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cholinesterase insecticides. Aerial application of triazophos on oilseed rape was prohibited in 1979, but 27 samples were poisoned by ground treatment, of which 17 contained triazophos; further measures to protect honeybees from this insecticide are therefore essential. Regrettably also 19 poisonings of honeybees by aphicides applied to field beans and five to cereals were recorded, despite recommended safe procedures. HCH was found in 12 samples of bees and dieldrin in three, despite the diminished use of organochlorine insecticides reported. (Smart and Stevenson)

### Soil-borne pests

**Seed treatments against wheat bulb fly larvae.** Seed treatments against wheat bulb fly were tested at two sites in 1978–79. Quinalphos (a previously untested diethyl organophosphorus insecticide) was phytotoxic. Extracts of *Polygonum hydropiper* and *Capsicum annuum*, plants with repellent properties, had only small effects on attack by larvae. Permethrin–ethion mixtures and all formulations of permethrin applied at 0.1% a.i. to weight of seed gave excellent protection against insect attack and permethrin was effective at both sites at 1/4 or even 1/8 of this dose when applied with the synergist piperonyl butoxide. (Griffiths, Scott, C. Smith and Woodcock)

**Seed treatments against slugs in cereals.** During the last 3 years 13 ‘repellents’ and 35 ‘pesticides’ have been tested in the laboratory as seed treatments to repel or kill slugs (*Deroceras reticulatum*). The ‘repellents’ investigated have a bitter or burning taste to man or repel insects or birds, but none prevented slugs feeding on treated wheat seeds.

Of the pesticides, thiocarbonyl killed most slugs but is too toxic to birds and mammals for commercial use. Methiocarb killed more than half the slugs, but other carbamates, organophosphates, organochlorines, pyrethroids and inorganics had little or no effect; the molluscicides metaldehyde and trifenmorph were also ineffective.

Two groups of pesticides protected seeds but did not kill slugs. These were ioxynil and other phenolic compounds which uncouple oxidative phosphorylation, and ‘SAN 155’ and ‘SAN 329’, related to nereistoxin. These active compounds adversely affect germination, so related non-phytotoxic compounds are being sought. (Griffiths, Pickett and Scott)

### Behaviour of pesticides in soil

**Leaching in the field.** Results from the comprehensive experiment reported last year (Part 1, 143) in collaboration with the Weed Research Organisation and the ARC Letcombe Laboratory were analysed. In Begbroke sandy loam soil about 50% of <sup>36</sup>Cl-percolated below 30 cm in 3 months and 90% in 6 months. Leaching was slightly greater from cultivated than from uncultivated plots. In contrast, on well structured Compton Beauchamp clay leaching did not differ significantly on cultivated and uncultivated plots and more than 60% of the chloride remained within the top 30 cm after 6 months, nearly all at the surface. These results are consistent with observations first made by Lawes, Gilbert and Warrington which later found expression in the mobile and immobile water categories used by Addiscott (last year’s *Report*, Part 1, 288). In Begbroke soil the mode of the distribution profile for the herbicide fluometuron moved 2.5 cm from the soil surface in 6 months but very little in Compton Beauchamp clay. This may be attributed to three effects, adsorption (Freundlich coefficients 0.77 and 2.4 for the two sites), retention within the well developed aggregates at Compton Beauchamp and upward movement as the soil dried during summer.

Soil particle movement, shown by <sup>144</sup>Ce (which is irreversibly bound to soil particles), was appreciable at both sites. Cultivation produced no differences but there was more



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penetration at Compton Beauchamp than at Begbroke. At Compton Beauchamp  $^{144}\text{Ce}$  moved as much as fluometuron, implying that redistribution of solutes in association with small particles though small in absolute terms, may be significant, compared with movement of dissolved material. The immobility in the field of fluometuron (which is not strongly adsorbed) raises doubt about the value of laboratory leaching experiments required by some registration authorities. (Graham-Bryce and Nicholls with Dr. R. Hance, Weed Research Organisation and Mr. D. Hill, ARC Letcombe Laboratory)

**Pesticide soil adsorption-desorption hysteresis.** Irreversible effects, classed as hysteresis, may produce non-coincident adsorption and desorption isotherms in pesticide soil slurry experiments. Isotherms were measured on nine soils using  $^{14}\text{C}$  labelled fluometuron and fitted by linear regression to the Freundlich isotherm  $S = KC^{1/N}$  where  $S$  = solute adsorbed ( $\mu\text{g/g}$  of soil),  $K$  and  $N$  are constants and  $C$  = solution concentration at equilibrium ( $\mu\text{g ml}^{-1}$ ).

In all soils the desorption isotherm curve lay above the adsorption curve. Hysteresis may be defined quantitatively as the area between the two isotherm curves, in the interval,  $C = 0-10$ , expressed as a fraction of the area under the adsorption line on the same interval. Thus  $H$  indicates hysteresis as a proportion of the total adsorption. The mean value of  $H$  for the four soils with organic carbon content in the range 0.5–2.4% was  $0.265 \pm 0.110$  and for the five soils in the range 2.5–33%,  $0.110 \pm 0.071$ . In the soils with most organic matter adsorption of fluometuron is almost completely reversible but in those with least organic matter and most leaching, hysteresis is significant and must be considered in models simulating the behaviour of pesticides in soil. Biological availability will depend on the size of the hysteresis effect which limits the ability of the soil to release adsorbed pesticide when the soil solution concentration falls. (Nicholls)

### Foliar sprays

**Electrostatically charged spray application systems.** Laboratory studies on the direct charging of aqueous sprays formed by spinning disc atomisers showed the effect of charge on the distribution of the spray. Charged rotary atomisers form an inner annulus of drops, and the droplet density within this area is directly related to the applied voltage. This pattern of distribution can be further modified by varying the height of the atomiser above the target.

In further trials on field beans, results with a medium volume hydraulic sprayer delivering 340 litres  $\text{ha}^{-1}$  were compared with directly charged and uncharged rotary atomisers at 15.5 litres  $\text{ha}^{-1}$ . To determine the effect of conductivity on charge and spray drop deposition, two formulations with a resistivity ratio of 3:1 were compared. In all cases the charged high resistivity sprays significantly increased deposits on the underside of both upper and lower leaves. A *Sitona* leaf-notch count 18 days after spraying confirmed the chemical analyses, showing leaves least affected to be those treated by the charged sprays.

The more favourable charge to mass ratios attainable with smaller drops is limited in aqueous formulations by volatility of the solvent, so oil-based sprays are being investigated. Preliminary results with a specially developed sprayhead and high resistivity formulations ( $> 10^6 \text{ ohm cm}^{-1}$ ) give much greater spray deposition than attained with water-based preparations. (Arnold and Pye)

**Controlled drop application: placement and drift spraying.** Controlled drop sprays at low volume were again compared with conventional hydraulic sprays at medium volume, using powdery mildew on barley as the test organism. However, because of the very low



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disease incidence (8%) recorded on the lower leaves of untreated plots, differences on treated plots were not significant. This work, and further investigations of drift spraying (last year's *Report*, Part 1, 145) continues. (Arnold, Etheridge, Phillips and Pye)

### Apparatus

**Equipment for mass pollination of coconuts.** The fluid-bed dryer developed in the Department for the mass pollination of coconuts programme in Jamaica is now in commercial production. (Arnold and Pye)

### Bird repellents

**Effect of formulation on the persistence of deposits.** In the continuing collaboration with Long Ashton Research Station (last year's *Report*, Part 1, 145) to evaluate various formulations of the experimental acaricide 'PP 199' (2'-chloro-2,4-dinitro-5', 6-di(trifluoromethyl)diphenylamine, ICI Plant Protection Ltd.) and of fentin acetate wettable powder as bird repellents, the Rothamsted 5% a.i. microencapsulated formulation of 'PP 199' (using acetophenone as internal phase solvent and polyurea walls) was significantly better than all other treatments on plum trees, with 1% bud damage by birds compared with 26% damage in controls after 80 days. (Etheridge and Phillips, with Dr. D. A. Kendall and Dr. B. D. Smith, Long Ashton Research Station)

### Insect species reared:

|             |   |   |
|-------------|---|---|
| Homoptera   | <i>Aphis fabae</i> (Scop);<br><i>Megoura viciae</i> (Buckt.);<br><i>Metapolophium dirhodum</i> (Wlk.);<br><i>Myzus persicae</i> (Sulz.)                 | (Susceptible and several resistant strains);  |
|             | <i>Rhopalosiphum padi</i> (L.);<br><i>Sitobion avenae</i> (F.).   |   |
| Coleoptera  | <i>Phaedon cochleariae</i> (F.)   |   |
| Dictyoptera | <i>Periplaneta americana</i> (L.)   |   |
| Diptera     | <i>Delia antiqua</i> (Meig.);<br><i>Drosophila melanogaster</i> (Meig.)   | (Vestigial wing strain);  |
|             | <i>Lucilia cuprina</i> (L.);<br><i>Musca domestica</i> (L.)   |   |
|             | Strains:  | wild-type susceptible;<br><i>ac</i> ; <i>ar</i> ; <i>bwb</i> ; <i>ocra</i> —called 608, multi-marker susceptible.<br>SKA-diazinon selected, very resistant to many organophosphorus insecticides.<br>Several derived from SKA, resistant to organophosphorus insecticides or DDT.<br>Several derived from the dimethoate resistant 49r <sub>2</sub> b, resistant to dimethoate and other organophosphorus insecticides.<br>290BIO, a substrain of the dimethoate/bioresmethrin resistant 290rb derived by selection with bioresmethrin.<br>Several derived from 290BIO each resistant to pyrethroids and DDT.<br>NPR-pyrethrum extract selected.<br>538ge- <i>kdr</i> knock-down resistant.<br>IPSWICH pyrethroid-resistant. Several derived from IPSWICH resistant to pyrethroids. |
| Hymenoptera | <i>Acromyrmex octospinosus</i> (Reich.);<br><i>Aphidius matricariae</i> (Haliday);<br><i>Atta cephalotes</i> (L.);<br><i>Venturia canescens</i> (Grav.) |   |
| Lepidoptera | <i>Ephestia kuehniella</i> (Zeller);<br><i>Plutella xylostella</i> (L.)   |   |
| also        |   |   |
| Mollusca    | <i>Deroceras reticulatum</i> (Muller)   |   |



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**Technique for rearing onion fly.** A technique for rearing onion fly (*Delia antiqua*) has been established. The larvae will be used in the bioassay of soil insecticides and suitable methods are being investigated. (Farnham and Walters)

### Fungal diseases and fungicides

**The host-parasite relationship of clubroot disease.** The overgrowth symptoms of clubroot disease (*Plasmodiophora brassicae* Woron) are associated with production of excess of the growth hormone 3-indolylacetonitrile (IAN) (Butcher *et al. Physiological Plant Pathology* (1974) 4, 127). This could be produced by degradation of 3-indolylmethylglucosinolate (IMG) by myrosinase or directly from 3-indolylacetaldoxime, an intermediate on the pathway to IMG. To evaluate these alternatives <sup>14</sup>C-tryptophan, a precursor of IMG, was applied to infected tissue. Both IMG and IAN then incorporated <sup>14</sup>C after 5 min, but whether IMG is labelled before IAN and is therefore its precursor has not yet been established.

Electronmicrographs of cells containing fungal plasmodia show varying degrees of cytoplasmic disorganisation, consistent with an earlier suggestion that the pathogen interferes with the indole metabolism of the host by disrupting cellular organisation. (Bailey, Butcher, Chamberlain and Searle)

**Control of soil-borne diseases by foliar sprays.** Previous work showed that foliar sprays of some growth regulators (GA<sub>3</sub>, daminozide and flurecols) decreased the incidence of potato common scab or clubroot of cabbage.

Many other regulators were ineffective; these included the translocated herbicide, 2,4-D. However, more recent experiments showed that its 3,5-isomer (3,5-D), a weak growth retardant, had an outstanding effect against scab. In the glasshouse, single foliar sprays of 0.2 g litre<sup>-1</sup> decreased scab incidence by about 90%; yields were slightly decreased and the number of tubers per plant slightly increased. Related acids were less effective, in the sequence 3,5-dichloro- > 2,3,4,5-tetrachloro- > 2,3,5,6-tetrachloro- > 2,3,5-trichloro- > 3,4,5-trichlorophenoxyacetic acid. All the other chloro- and all the mono-methyl- and dimethylphenoxyacetic acids were ineffective. Thus the 3,5-dichlorophenoxy structure seemed to be necessary, but need not be attached to an acetic acid residue; comparable effects on scab were found in the series 3,5-dichlorophenoxyacetamide > 3,5-dichlorophenoxydiethylacetamide > 3,5-dichlorophenoxyethylamine. In field trials, single sprays of 3,5-D at 0.1–0.2 g litre<sup>-1</sup> decreased scab by 45–50%; yields and tuber numbers were not affected by the lower concentration.

In *in vitro* tests against *Streptomyces scabies* (the organism causing scab) the ED<sub>50</sub>s of all the dichloro- and dimethylphenoxyacetic acids lay in the range 50–100 µg ml<sup>-1</sup>; 3,5-D was thus no more fungitoxic than close analogues which did not affect the disease *in vivo*. After application to potato foliage, 3,5-D moved rapidly to other parts of the plants. Its concentration in tubers remained unchanged for at least a week after application, despite tuber growth, but was only one-twentieth of the EC<sub>50</sub> to *S. scabies* in culture. The evidence suggests that 3,5-D did not affect scab by systemic action against *S. scabies*, but by altering the host response to infection.

In glasshouse tests against clubroot of cabbage, the effects of 3,5-D and its analogues were smaller than on scab, but the same structural need was evident, 3,5-D being the most effective analogue tested. (Bateman, Burrell, Chamberlain, Dawson, McIntosh, with Macfarlane, Plant Pathology Department)

**Fungicides for soil-borne diseases of wheat.** The systematic search for effective fungicides for the take-all pathogen continued (last year's *Report*, Part 1, 140). In pot tests drench



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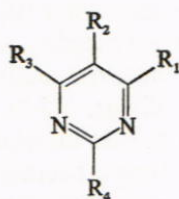
treatments with the compounds examined previously were effective against inoculum placed near the seed when sown 1.5 cm deep, but failed when sown 5 cm deep. Outdoors, soil drenching in November diminished the severity of take-all in April but not in June. Although other pathogens (eyespot and brown footrot (*Fusarium culmorum*)) were comparably susceptible to fungicides *in vitro*, they were less well controlled in soil-mix pot tests.

Persistence of the fungicide, important for the control of diseases such as take-all which can infect throughout the growing season, was investigated by bioassay against *F. culmorum* (Rothamsted Report for 1977, Part 1, 152). Benomyl persisted for up to 8 weeks in sand or sand-loam, but for a shorter time in soils with more organic matter. Of the possible slow release formulations examined, gelatin pieces and polyurea-coated microcapsules, respectively, prolonged the availability of thiabendazole and benomyl.

In field plots treated with benomyl at 35 kg ha<sup>-1</sup> as previously, bioassay showed gelatin formulations to persist until July, but powder treatment was not detected by May. Treatments lessened attack by brown footrot (mainly *Fusarium nivale*) (take-all attack was slight this season), gelatin having little advantage over benomyl powder. (Bateman)

**Mode of action of hydroxypyrimidine fungicides.** In last year's Report (Part 1, 141) ethirimol (2-ethylamino-4-hydroxy-5-*n*-butyl-6-methylpyrimidine; 'Milstem') was shown to non-competitively inhibit adenosine deaminase (ADA-ase, E.C. 3.5.4.4.) from barley powdery mildew (*Erysiphe graminis*) conidia. In further studies ethirimol was found to inhibit most strongly at pH 7.8 ( $K_I 9.0 \times 10^{-6}M$ ). ADA-ase from four other mildews was also inhibited but not the corresponding enzyme from 11 unrelated organisms including fungi, insects and mammals. These results are consistent with the *in vivo* specificity of the fungicide which controls only powdery mildews, is not phytotoxic and has low mammalian toxicity.

By monitoring the deamination of <sup>3</sup>H-adenosine to <sup>3</sup>H-inosine little ADA-ase activity was detected in extracts of healthy 10-day-old barley leaves (cv. Proctor), but activity had increased three- to four-fold 24–30 hours after these leaves were inoculated with mildew conidia. Kinetic experiments suggested that this enzyme differed from that in conidia, for it was less sensitive to ethirimol ( $K_I 3.6 \times 10^{-4}M$ ). ADA-ase did not increase when leaves grown from ethirimol treated seed were inoculated with a mildew strain unable to grow in these plants. The increase in ADA-ase activity on infection of barley by mildew was confirmed by experiments with whole plants where conversion of both <sup>3</sup>H-adenine and <sup>3</sup>H-adenosine to <sup>3</sup>H-inosine increased rapidly as infection progressed.



Formula III

The influence of structural variation in this series of hydroxypyrimidines (Formula III) was examined in three bioassays; two measured effects on different stages of mildew development, but included possibly unconnected effects on uptake and movement within the host plant, and the third measured effects on the pathogen alone. Tables 1 and 2 show results relative to those obtained with dimethirimol. In general, analogues less effective than dimethirimol as ADA-ase inhibitors were also poorer fungicides. Variations



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TABLE 1

Effect of 2-dimethylaminopyrimidines on ADA-ase and mildew growth

| R <sub>1</sub>   | R <sub>2</sub>                    | R <sub>3</sub>  | ADA-ase inhibition | Bioassay               |               |                 |
|------------------|-----------------------------------|-----------------|--------------------|------------------------|---------------|-----------------|
|                  |                                   |                 |                    | Appressorial formation | Colony length | <i>In vitro</i> |
| OH               | C <sub>4</sub> H <sub>9</sub>     | CH <sub>3</sub> | 1                  | 1                      | 1             | 1               |
| OH               | H                                 | CH <sub>3</sub> | —                  | —                      | —             | —               |
| OH               | CH <sub>3</sub>                   | CH <sub>3</sub> | —                  | —                      | —             | —               |
| OH               | CH(CH <sub>3</sub> ) <sub>2</sub> | CH <sub>3</sub> | —                  | —                      | —             | —               |
| OH               | C <sub>6</sub> H <sub>13</sub>    | CH <sub>3</sub> | 18.5               | 21                     | 6             | 520             |
| OH               | C <sub>4</sub> H <sub>9</sub>     | H               | 15.5               | 49                     | —             | 800             |
| OH               | H                                 | H               | —                  | —                      | —             | —               |
| Cl               | C <sub>4</sub> H <sub>9</sub>     | CH <sub>3</sub> | —                  | 10                     | 0.1           | 9.5             |
| OCH <sub>3</sub> | C <sub>4</sub> H <sub>9</sub>     | CH <sub>3</sub> | —                  | 753                    | 0.6           | 753             |

Activities are expressed relative to dimethirimol. K<sub>1</sub> for ADA-ase = 5.4 × 10<sup>-4</sup>M; ED50 appressorial formation = 1.2 × 10<sup>-6</sup>M; colony length = 5.4 × 10<sup>-4</sup>M; *in vitro* = 1.5 × 10<sup>-7</sup>M. — = no effect. R<sub>4</sub> = NMe<sub>2</sub> (in formula III) in all compounds examined.

TABLE 2

Effect of 4-hydroxy-5-n-butyl-6-methylpyrimidines on ADA-ase and mildew growth

| R <sub>4</sub>                                  | Partition coefficient* | ADA-ase inhibition | Bioassay               |               |                 |
|---|------------------------|--------------------|------------------------|---------------|-----------------|
|   |                        |                    | Appressorial formation | Colony length | <i>In vitro</i> |
| H   | 1.38                   | 0.02               | 172                    | 0.3           | 1187            |
| NH <sub>2</sub>                                 | 1.50                   | 0.5                | 300                    | 2.6           | 167             |
| OH  | 1.26                   | 5.1                | 408                    | —             | —               |
| SH  | 1.81                   | 18.5               | —                      | —             | —               |
| NHCH <sub>3</sub>                               | 1.64                   | 0.6                | 4.5                    | 6.5           | 6               |
| NHC <sub>2</sub> H <sub>5</sub> (Ethirimol)     | 2.21                   | 0.02               | 1.0                    | 0.06          | 0.7             |
| N(CH <sub>3</sub> ) <sub>2</sub> (Dimethirimol) | 1.93                   | 1.0                | 1.0                    | 1.0           | 1               |

\*(octanol: water log<sub>10</sub>)

— = no effect. Activities are expressed relative to dimethirimol.

of groups R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> all affected inhibition of both ADA-ase and mildew, usually detrimentally. By contrast, variations at R<sub>4</sub> often increased their effectiveness towards ADA-ase, yet some analogues were largely inactive when assayed *in vitro* or against appressorial formation. This poor performance against mildew of good ADA-ase inhibitors cannot be explained by variations in mobilities through membranes, because differences in partition coefficients were small.

Several adenine analogues (but not the corresponding nucleosides) inhibited both appressorial formation and ADA-ase. However, unlike hydroxypyrimidines, inhibition was competitive, and less specific. Some analogues also inhibited ADA-ase from *Penicillium* sp. and the growth of this organism.

The correlations established between susceptibility of ADA-ase to inhibition by hydroxypyrimidines and susceptibility of the whole organism suggest that these fungicides interfere with the vital function of ADA-ase in salvaging purines during primary infection of barley. However, inhibition of ADA-ase seems unlikely to be their sole site of action, and additional effects may be more important later in development. Adenine analogues produce a different range of effects and may influence mildew development by interfering at the active centre of ADA-ase. (Chamberlain and Hollomon)



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### Other projects

In addition to work already noted, collaboration as follows is recorded in other sections of the Rothamsted Report.

#### Entomology Department:

Etheridge and Goodchild with E. D. M. Macaulay: Monitoring for pea moth.

Griffiths with R. Bardner and K. E. Fletcher: Control of *Sitona* on beans.

Pickett with J. B. Free: Honeybee pheromones.

Pickett with I. H. Williams: Honeybee Nasonov pheromone.

#### Statistics Department:

Greenway with J. N. Perry and C. Wall (Entomology): Design of field experiments with insect sex attractants.

### THE CHEMICAL LIAISON UNIT

An increasing number of requests to help select the most appropriate pesticide for a particular application is being received. This often involves knowing, or predicting, the fate and behaviour of compounds after application. The principles determining availability in various environments are progressively well established, so more attention is now being directed to studying their degradation.

Routine assessments of pesticides and their residues and development of appropriate analytical methods to support research projects throughout the Station continued.

### Fate of pesticides in soil

**Leaching and degradation of aldicarb sulphone in soil.** In association with work described earlier (Graham-Bryce and Nicholls) leaching of the toxic metabolite of aldicarb, a polar sulphone, was investigated in the well-structured clay at Compton Beauchamp. The sulphone ( $N^{14}CH_3$ ) incorporated in the top 5 cm of soil was leached in the first weeks, and later moved towards the surface when water lost by evaporation exceeded rainfall. After 3 months only 13% of the sulphone remained unchanged; no metabolites were detected. The compound moved more in Woburn sandy loam, which, with less organic matter (*Rothamsted Report for 1977, Part 1, 155*) sorbed the compound only weakly. (Bromilow and Freeman)

**Uptake of pesticides into earthworms.** Further results supported the concept (*Rothamsted Report for 1974, Part 1, 158*) that the distribution at equilibrium of a compound between earthworm solids and water is related to the octanol-water distribution by a log-log relationship similar to that between soil organic matter and water, and other bio-accumulations. Thence it may be predicted that all lipophilic compounds will be similarly distributed between soil and worms. However, in soil, equilibrium is approached only after several weeks and metabolism may restrict accumulation.

Greater proportions of less strongly sorbed, more hydrophilic compounds remain in solution in soil water, so that equilibrium may more generally be approached, especially in waterlogged soils. However, worm cuticles are not equally permeable to all compounds; aldicarb sulphoxide is neither absorbed nor readily excreted, so that it may accumulate in worms which absorb aldicarb and rapidly metabolise it to the toxic sulphoxide or to non-toxic hydrolysis products. This explains the deaths of earthworms and their bird predators in waterlogged areas treated with aldicarb. (Briggs, Fitchett and Lord)



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### Microbial studies

**Nitrification.** *Nitrosomonas* and *Nitrosolobus* spp., autotrophic nitrifying bacteria, and nitrite oxidising autotrophs were detected in five of six Canadian soils which remain frozen for several months. Of three ammonia-oxidising isolates, two grew at 2–3°C. Nitrification is therefore possible at near zero temperatures. (Walker, with J. Ashworth (Soils and Plant Nutrition Department) and Dr. M. Nyborg, Plant Industry Division of Alberta Agriculture)

**Microbial degradation of pesticides.** The enhanced degradation of diazinon in soil induced by repeated applications (last year's *Report*, Part 1, 149) was gradually diminished by repeated wetting and drying, but the activity was restored in the presence of diazinon. Frequent freezing and thawing of soil had little effect. A *Flavobacterium* sp. isolated from the soil also resisted drying, chloroform and pasteurisation and degraded diazinon stoichiometrically. The cultured organism in neutral phosphate buffer also degraded parathion, but none of a range of organophosphorus insecticides in soil. (Forrest, Lord and Walker)

**Moulding of hay.** Treatment of damp hay with propionic acid or ammonium bispropionate may not prevent moulding of untreated plugs of hay inserted in the bulk (last year's *Report*, Part 1, 208), from which, in laboratory investigations infection spreads. Several members of the *Aspergillus glaucus* group were isolated which, in culture, tolerate and metabolise concentrations of propionate up to 1%, although 0.2% inhibits the growth of most hay fungi. These isolates, like those of *Paecilomyces varioti*, also degrade other fatty acids, shorter or branched compounds faster than those with longer or unbranched chains. Several fungicides including 8-hydroxyquinoline, 'Sisthane' and imazalil prevent the degradation of propionate in culture (1 µg ml<sup>-1</sup>) but adsorption onto hay renders the dose for controlling moulding impractically great. (Cayley and Lord, with Lacey, Plant Pathology)

**Analysis.** Procedures for two imidazole fungicides, imazalil and prochloraz, promising for controlling potato storage fungi, were developed. Imazalil is extracted from macerated potatoes with alkaline methanol, partitioned between hexane and acid, extracted from the neutralised aqueous layer and analysed by GLC (electron capture). Prochloraz is extracted with acetone and partitioned between hexane and acid; the acid layer is analysed directly by HPLC (UV detector) on a reverse phase ODS column. Even after 6 months, neither fungicide penetrated appreciably beyond the tuber skin. (Cayley and Tillotson)

### Other projects

Cayley investigated fungicides for potato tuber pathogens with Hide (Plant Pathology) and Bromilow, incorporation of nematicides into soil with Whitehead (Nematology)

### Staff of the Department and the Chemical Liaison Unit

In August 1979, I. J. Graham-Bryce, Head of the Department since 1972, left to become Director of the East Malling Research Station and M. Elliott was appointed to succeed him.

M. Elliott was elected a Fellow of the Royal Society of London and Lesley E. Smart was awarded a first class honours degree in the University of London. M. Elliott and



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N. F. Janes received Individual Merit Promotions to, respectively, Deputy Chief Scientific Officer and Senior Principal Scientific Officer for their work on synthetic pyrethroids.

Mrs. I. J. Covell, Mrs. C. M. Porter and I. Glenister left the Department. Sadly Mrs. Covell died in December after only a few months of retirement. K. A. Jeffs left the Department in October to become Station Safety Officer. Chiang Chia-liang of the Shanghai Institute of Entomology, Academic Sinica, came to spend 2 years in the Department working on the biochemistry of insecticide resistance. Thomas Rausch of the Betriebseinheit Botanik, Fachbereich Biologie de Johann Wolfgang Goethe Universität, Frankfurt, West Germany worked for 3 months on clubroot disease. Paul B. Hughes of the Biological and Chemical Research Institute, Rydalmere, N.S.W., Australia started 1 year's study leave on the biochemistry of organophosphate resistance in the sheep blowfly.

M. Elliott contributed to a Gordon Research Conference on Agricultural Science in California in January, to an American Chemical Society symposium in Washington in August and to the National Parasitology conference in Mexico in November. With I. J. Graham-Bryce, he helped to organise a symposium on the Chemistry of the Pyrethroids at Oxford in July at which he and N. F. Janes delivered papers. I. J. Graham-Bryce and P. E. Burt helped to organise the Neurotox '79 conference at York in September and P. E. Burt and A. L. Devonshire lectured there. I. J. Graham-Bryce was a Chairman at both conferences and with P. H. Nicholls gave a paper at the British Society of Soil Science Autumn Meeting.

J. Majchrzak, the Plant Protection Institute, Posnan, Poland, A. Ventosa of the Department of Microbiology, Granada, Spain and M. S. Chanda of the Bio-organic Division, Bhabha Atomic Research Centre, Bombay, India, spent short periods in the Chemical Liaison Unit in January, June and October, respectively.

J. A. Pickett spoke at a conference on the Chemistry of Insects in Sweden and with A. R. Greenway and A. Mudd took part in the OILB Group Meeting on Integrated Control in Switzerland. A. L. Devonshire, D. C. Griffiths, J. H. Stevenson, L. E. Smart and A. J. Arnold were authors of papers presented at the 1979 British Crop Protection Conference in Brighton. A. J. Arnold gave a paper at a meeting of the Society of Chemical Industry and J. H. Stevenson visited Vienna in October to attend an IOBC/WPRS Working Group and a related symposium.

F. T. Phillips and P. Etheridge visited Guyana on behalf of FAO to advise on the leaf-cutting ant baiting campaign and then Barbados to advise the West Indies Central Sugar Cane Breeding Station on spray application and insecticides.

R. H. Bromilow returned from a visit to the Radioisotopes Centre, Biological Institute, São Paulo, Brazil, which K. A. Lord visited briefly to continue collaboration. G. R. Cayley attended the 4th IUPAC Symposium on Mycotoxins and Phytotoxins in Lausanne and N. Walker lectured to the Oceanography Institute of the University of Kiel, Germany

### Publications

#### GENERAL PAPERS

- 1 ARNOLD, A. J. (1979) Field trials comparing charged and uncharged spraying systems. *Proceedings 1979 British Crop Protection Conference—Pests and Diseases*, 289–293.
- 2 BARDNER, R., FLETCHER, K. E. & GRIFFITHS, D. C. (1979) Problems in the control of the pea and bean weevil (*Sitona lineatus*). *Proceedings 1979 British Crop Protection Conference—Pests and Diseases*, 223–229.



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- 3 BURT, P. E. (1979) The effects of neurotoxicants on the nervous systems of intact insects. *Insect neurobiology and pesticide action (Proceedings of Neurotox 1979 Conference)*. London: Society of Chemical Industry, pp. 407–414.
- 4 DEVONSHIRE, A. L. (1979) Insecticide resistance caused by insensitivity of acetylcholinesterase to inhibition. *Insect neurobiology and pesticide action (Proceedings of Neurotox 1979 Conference)*. London: Society of Chemical Industry, pp. 473–480.
- 5 ELLIOTT, M. (1979) Progress in the design of insecticides. *Chemistry and Industry* 757–768.
- 6 ELLIOTT, M. & JANES, N. F. (1978) Synthetic pyrethroids—A new class of insecticides. *Chemical Society Reviews* 7, 473–505.
- 7 ELLIOTT, M., JANES, N. F. & PULMAN, D. A. (1978) Historique du developpement de la decamethrine. *Phytiatrie-Phytopharmacie* 27, 99–106.
- 8 GRAHAM-BRYCE, I. J., HOLLOMON, D. W. & LEWIS, T. (1979) Pest and disease control in cereals: A research viewpoint. *Journal of the Royal Agricultural Society of England* 14, 131–139.
- 9 GREGORY, G. E. (1980) Permanent staining of tracheae with trypan blue. In: *Experimental entomology*, Vol. 2, *Neuroanatomical techniques*. Ed. N. J. Strausfeld and T. A. Miller. New York: Springer-Verlag, Chapter 2, pp. 15–19.
- 10 GREGORY, G. E. (1980) The Bodian protargol technique. In: *Experimental entomology* Vol. 2, *Neuroanatomical techniques*. Ed. N. J. Strausfeld and T. A. Miller. New York: Springer-Verlag, Chapter 6, pp. 75–95.
- 11 GREGORY, G. E. (1980) Simple axonal filling of neurons with Procion yellow. In: *Experimental entomology*, Vol. 2, *Neuroanatomical techniques*. Ed. N. J. Strausfeld and T. A. Miller. New York: Springer-Verlag, Chapter 13, pp. 283–290.
- 12 GRIFFITHS, D. C. & STEVENSON, J. H. (1979) Synthetic pyrethroids in horticulture. *The Plantsman* 1, 106–111.
- 13 HOLLOMON, D. W. (1979) Specificity of ethirimol in relation to inhibition of the enzyme adenosine deaminase. *Proceedings 1979 British Crop Protection Conference—Pests and Diseases* 251–256.
- 14 PHILLIPS, F. T. (1979) Measuring weathering losses of insecticide deposits on plant surfaces. *Journal of Nuclear Agriculture and Biology* 9, 33–38.
- 15 PICKETT, J. A. (1979) Behaviour controlling chemicals. *Education in Chemistry* March, 44–47.
- 16 SAWICKI, R. M. (1979) Resistance to pesticides I. Resistance of insects to insecticides. *SPAN* 22, 50–52.
- 17 STEVENSON, J. H., SMART, L. E. & (WALKER, J.) (1979) Oil seed rape and honeybee poisoning—1978, 1979. *Proceedings 1979 British Crop Protection Conference—Pests and Diseases* 117–120.

## RESEARCH PAPERS

- 18 BATEMAN, G. L. (1979) Relationships between *Fusarium nivale* and other microorganisms on seed of wheat and barley. *Transactions of the British Mycological Society* 72, 245–249.



## ROTHAMSTED REPORT FOR 1979, PART 1

- 19 (COXON, D., DAVIES, A. M. C., FENWICK, G. R., SELF, R., FIRMIN, J. L., LIPKIN, D.) & JANES, N. F. (1980) Agropine, an unusual amino-acid derivative from crown gall tumours. *Tetrahedron Letters* **21**, 495–498.
- 20 DEVONSHIRE, A. L. & SAWICKI, R. M. (1979) Insecticide-resistant *Myzus persicae* as an example of evolution by gene duplication. *Nature, London* **280**, 140–141
- 21 FERGUSON, A. W., FREE, J. B., PICKETT, J. A. & WINDER, M. (1979) Techniques used to study honeybee (*Apis mellifera* L.) pheromones involved in clustering and the effect of Nasonov and queen pheromones. *Physiological Entomology* **4**, 339–344.
- 22 GRAHAM-BRYCE, I. J., NICHOLLS, P. H. & (WILLIAMS, I. H.) (1980) Performance and uptake of some carbendazim-producing fungicides applied as seed treatments to spring barley, in relation to their physicochemical properties. *Pesticide Science* **11**, 1–8.
- 23 HOLLOMON, D. W. (1979) Evidence that ethirimol may interfere with adenine metabolism during primary infection of barley powdery mildew. *Pesticide Biochemistry and Physiology*, **10**, 181–189.
- 24 MCINTOSH, A. H. (1979) Decreased common scab incidence after foliar sprays of daminozide. *Potato Research* **22**, 361–363.
- 25 MCINTOSH, A. H. & BATEMAN, G. L. (1979) Effects of foliar sprays of daminozide on the incidence of potato common scab. *Annals of Applied Biology* **92**, 29–38.
- 26 MUDD, A. & BATEMAN, G. L. (1979) Rates of growth of the food fungus of the leaf-cutting ant *Atta cephalotes* (L.) (Hymenoptera: Formicidae) on different substrates gathered by the ants. *Bulletin of Entomological Research* **69**, 141–148.
- 27 PHILLIPS, F. T., ETHERIDGE, P. & MARTIN, A. P. (1979) Further laboratory and field evaluations of experimental baits to control leaf-cutting ants (Hymenoptera: Formicidae) in Brazil. *Bulletin of Entomological Research* **69**, 309–316.
- 28 PICKETT, J. A. & GRIFFITHS, D. C. (1980) Composition of aphid alarm pheromones. *Journal of Chemical Ecology* **6**, 349–360.
- 29 PICKETT, J. A. & STEPHENSON, J. W. (1979) Plant volatiles and components influencing behaviour of the field slug, *Deroceras reticulatum* (Müll.). *Journal of Chemical Ecology* **6**, 435–444.
- 30 PICKETT, J. A., WILLIAMS, I. H., MARTIN, A. P. & SMITH, M. C. (1980) The Nasonov pheromone of the honey bee, *Apis mellifera* L. (Hymenoptera, Apidae) Part I. Chemical characterisation. *Journal of Chemical Ecology* **6**, 425–434.
- 31 SAWICKI, R. M., DEVONSHIRE, A. L., PAYNE, R. W. & PETZING, S. M. (1980) Stability of insecticide-resistance in the peach-potato aphid *Myzus persicae* (Sulzer). *Pesticide Science* **11**, 33–42.
- 32 SAWICKI, R. M. & RICE, A. D. (1978) Response of susceptible and resistant peach-potato aphid, *Myzus persicae* (Sulz.) to insecticides in leaf-dip bioassays. *Pesticide Science* **9**, 513–516.
- 33 WALTERS, J. (& OSBORNE, D. J.) (1979) Ethylene and auxin-induced cell growth in relation to auxin transport and metabolism and ethylene production in the semi-aquatic plant, *Regnellidium diphyllum*. *Planta* **146**, 309–317.

## CHEMICAL LIAISON UNIT

### RESEARCH PAPERS

- 34 BROMILOW, R. H. & LORD, K. A. (1979) Distribution of nematicides in soil and its influence on control of cyst-nematodes (*Globodera* and *Heterodera* spp.). *Annals of Applied Biology* **92**, 93–104.



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- 35 (CARAZO, E.), LORD, K. A. & (FLORES RUEGG, E.) (1979) The sorption of carbaryl on soils determined by spectrophotometric and radiometric techniques. *Turrialba* **29**, 159-162.
- 36 CAYLEY, G. R., HIDE, G. A., LORD, K. A., AUSTIN, D. J. & DAVIES, A. R. (1979) Control of potato storage diseases with formulations of thiabendazole. *Potato Research* **22**, 177-190.
- 37 WALKER, N. & (WICKRAMASINGHE, K. N.) (1979) Nitrification and autotrophic nitrifying bacteria in acid tea soils. *Soil Biology and Biochemistry* **11**, 231-236.
- 38 WHITEHEAD, A. G., BROMILOW, R. H., TITE, D. J., FINCH, P. H., FRASER, J. E. & FRENCH, E. M. (1979) Incorporation of granular nematicides in soil to control pea cyst-nematode, *Heterodera goettingiana*. *Annals of Applied Biology* **92**, 81-91.