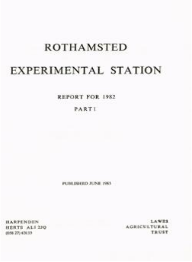
Report for 1982 - Part 1



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Insecticides and Fungicides Department

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Introduction

In the past year the programme of work in the Department as described (*Rothamsted Report for 1980*, Part 1, 120; last year's *Report*, Part 1, 124) continued without major changes in emphasis.

Some particularly promising results were obtained in our project concerned with compounds that influence invertebrate behaviour. Of the numerous compounds now identified with such activity, most are too volatile and unstable in air and light to be deployed effectively in the field. To overcome these limitations less volatile, light sensitive derivatives (propheromones) of some typical pheromonal compounds were investigated; amongst other encouraging results, an acetal of the aldehyde component of the sex pheromone of the diamondback moth (a worldwide pest of vegetables) was more efficient in lures than the compound itself, because adequate concentrations of the parent compound were generated over a longer period. Attempting to exploit the same principle again, derivatives of the aphid alarm pheromone, (*E*)-β-farnesene, were synthesized, anticipating that they would also break down to release the parent compounds as required. However, although actually too stable under field conditions these Diels–Alder adducts were themselves unexpectedly active, and after optimization by structural variation now constitute a new series of compounds which decrease aphid colonization and inhibit transmission of non-persistent viruses. Again, addition of the aphid alarm pheromone itself to appropriately applied sprays of permethrin increased kill of *Myzus persicae*. In collaboration with the Plant Pathology Department, the same pheromone was shown to be present in sufficient concentrations in the exudate from the wild potato species (*Solanum berthaultii*) to repel aphids. This discovery suggests the challenging possibility of breeding plants with aphid repellent characteristics. Another surprising finding, the significance of which is unclear at present, was that two clones of aphids very resistant to organophosphorus pesticides have a greatly diminished sensitivity to their alarm pheromone. These diverse approaches to insect, especially aphid, control from a chemical basis complement a range of studies on aphid behaviour and restriction of virus transmission in collaboration with the Entomology and Plant Pathology Departments.

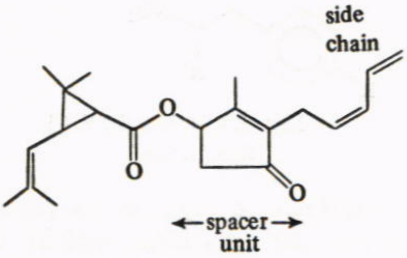
A wide range of investigations to overcome the serious consequences of insect resistance to insecticides continued. Of greatest practical significance was the confirmation that housefly populations with a proven potential for strong resistance to pyrethroids can be controlled satisfactorily with intermittent sprays of non-persistent pyrethroids. The very strong resistance to pyrethroids in houseflies, which can exceed 50 000 fold under selection pressure in the laboratory, is polyfactorial. It involves up to seven factors of which three appear to be located on autosome 2, the others being on autosomes 1, 3 and 5. Because some of the factors are specific only to certain pyrethroids, there is a wide range of resistance levels amongst this class of compounds.

Synthetic pyrethroid insecticides become more important year by year in crop protection and disease vector control worldwide. The total value of sales of the compounds (resmethrin, bioresmethrin, permethrin, cypermethrin and deltamethrin) originated at Rothamsted is now in the region of £500 million. Significant progress has been made in expanding the range of structural features within which insecticidal activity is retained and increased, thanks to the efforts of up to 20 industrial and non-industrial research groups, including that at Rothamsted, throughout the world. Subtle structural variations have been shown greatly to influence potency either generally or against particular species of insects or mites and a range of pyrethroids with activities optimized for particular applications (improved acaricidal activity, diminished fish toxicity, rapid knockdown activity, etc.) are therefore now practicable. Our work continues to define the chemical and steric characteristics essential for activity in this group of compounds, with particular attention recently to the requirements for activity in the soil. This emphasis extends to pyrethroids concepts already applied in the Department and Chemical Liaison Unit to other groups of pesticides. Many aspects of behaviour in the environment can be related to physical properties such as partition coefficients which can either be measured directly or calculated from molecular structure and collections of appropriate constants. Essential characteristics for soil activity (see paper I) are physical properties which can maintain sufficient concentrations of toxicants in the air phase of the soil, adequate insecticidal activities and stability against soil microorganisms; these are possessed by only a few pyrethroids, which are however significant, because the range of compounds at present available to control soil pests is inadequate.

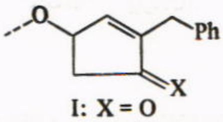
Further field trials with the electrostatic spraying systems designed here have demonstrated the flexibility of the equipment. A wide range of standard formulations have been applied effectively to various crops; fluid metering pumps now give more accurate delivery and atomization of viscous materials, particularly with the larger 'Jumbo' spray heads. Equipment with this recent development can be operated in the charged or uncharged mode and is designed for attachment to standard tractor booms or low ground pressure vehicles. Recent trials on cotton in the USA showed that tilting the trajectory of the 'Jumbo' unit with respect to the crop improves penetration into the crop canopy. The shorter transit time of small aqueous spray drops given an electrostatic charge is an especial advantage in conditions conducive to losses by evaporation.

Insecticides

Relationships between molecular structure and insecticidal activity of pyrethroids. The chemical and steric characteristics essential for activity in pyrethroids (cf. the prototype, pyrethrin I, below) have been more closely defined for two further regions of the molecule, by synthesizing and testing compounds containing alternative cyclic spacer units, or side-chains with oxime-ether groups.



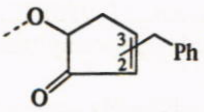
Pyrethrin 1



I: X = O
II: X = H_2

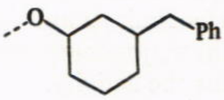
III: at C-3
IV: at C-2
V: at C-1

VI



VII: at C-2
VIII: at C-3

IX: $n = 0$ or 1
$m = 1$ or 2



X

Cyclic spacer units to replace cyclopentenonyl. Discovery of the activity of benzylnorthrin (which contains unit I) (*Rothamsted Report for 1970*, Part 1, 170) indicated (i) that benzyl in the side-chain could simulate penta-2,4-dienyl and (ii) that the methyl group on the C_5 ring in pyrethrin I was not important for activity. By examining a wide range of spacer units (II–X) all directly related to that in benzylnorthrin, further conclusions can now be drawn: (a) The carbonyl group is also not essential, since a compound based on II is active. (b) Omitting the double bond as well (III) or moving it (VI) lowers activity only slightly. (c) Reorientation of the double bond and carbonyl group in the ring (VII, VIII) produces structures more remote from the active form since potency is much lowered. (d) The change from 1,3 substitution (III) to 1,2(IV) or 1,1(V) removes activity completely. (e) Extension by inserting CH_2 groups in either bond of the spacer unit to give (IX) is detrimental whereas shortening the benzyl to phenyl does not destroy activity in all cases. (f) A larger ring (X) which is non-planar is inappropriate, since this analogue is inactive.

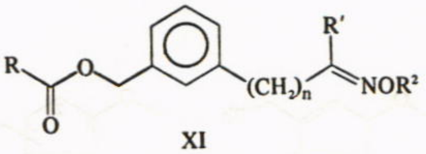
These results confirm that both the distance apart and the relative orientation of the substituents are crucial to activity so that the possible arrangements of the important bonds on the spacer unit are severely restricted. However within these limits, there is considerable flexibility with regard to the chemical nature of the unit.

Oximino-alkyl substituted compounds. Earlier results showed that the isobutenyl ($-CH{=}CMe_2$) side-chain in the acid portion of the molecule could successfully be replaced by oximino-alkyl ($-CH{=}NOAlk$); similar replacement of the unsaturation in the alcohol side chain had not been investigated.

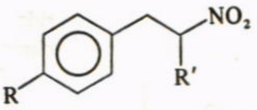
These side-chains have now been shown to be effective on *m*-substituted benzyl, *p*-substituted benzyl, 5-substituted-2-furylmethyl, and 5-substituted-3-furylmethyl, but not on 2,6-substituted pyridylmethyl spacer units.

In the *m*-substituted benzyl series (XI), examined in greatest detail, the side chains with n=0 and 1 were about equally effective. Compounds with R′ other than hydrogen (CH_3, $CH_2CH{=}NOCH_3$, $CH{=}CH_2$, CH_2CH_3, $C{\equiv}C{-}CH_3$, i.e. derivatives of ketones) were almost completely inactive. Elaboration of R^2 tended to decrease activity in the order: methyl > ethyl > allyl and propargyl > benzyl.

All such oxime ethers can exist in *E* or *Z* forms, and separations were therefore attempted. In some cases, the products were labile and reverted to *E*/*Z* mixtures, but where individual components could be tested, *E* isomers were consistently more active than *Z*.



XI



XII: R = H, Me, Br, F, Cl
R′ = H, Me

β-Phenylnitroethanes. A recent paper (Iwuala, Osisiogu & Agbakwaru *Journal of Economic Entomology* (1981) **74,** 249) indicates that the insecticidal activity of the extract of *Dennettia tripetala*, a Nigerian shrub, is as great as that of diazinon to several species, and therefore much higher than for many other natural insecticides. Agbakwaru, Ugochukwu and Osisiogu (*Nigerian Journal of Science* (1978) **12,** 494) have shown that the major component of the extract (80%, identified as β-phenylnitroethane) is responsible for the activity.

We have synthesized this compound (XII, R=R′=H) and a series of analogues by the method of Bachmann and Maleski (*Journal of Organic Chemistry* (1972) **37,** 2810). In our tests against houseflies and mustard beetles, the parent compound alone showed any measurable activity by topical application, and this was very low and only to the latter species. (Chemical work: Elliott, Janes, Johnson, Khambay and Pulman; Biological work: Farnham, Gilmour and Robertson)

Action of insecticides on insect nervous systems

Neuroanatomy of the insect central nervous system. Studies of ventral nerve cord ganglion structure, complementing electrophysiological investigations of pyrethroid mode of action, continued with an examination of the gross neuroanatomy of the pro- and metathoracic ganglia of the cockroach *Periplaneta americana* (L.). Their basic organization was found to be similar to that of the mesothoracic ganglion (Gregory, *Philosophical Transactions of the Royal Society of London* B (1974) **267**, 421–465), but that of the metathoracic ganglion was complicated by the presence of the first abdominal ganglion united with it posteriorly. Nine paired longitudinal nerve fibre tracts could be identified running through each ganglion, between anterior and posterior interganglionic connectives, with six dorsal and four ventral transverse commissural tracts connecting the halves of each neuromere, though in the first abdominal ganglion these commissures were reduced. Four characteristically shaped vertical or oblique tracts, the T-tract, C-tract, I-tract and ring tract, were clearly recognizable in the pro- and metathoracic neuromeres. A significant improvement in the technique for trypan blue filling of tracheae of the ganglia (Gregory (1980) in *Neuroanatomical Techniques*, ed. N. J. Strausfeld & T. A. Miller. New York: Springer-Verlag, 15–19), which provide useful landmarks for describing neuroanatomy, can be achieved by extending the periods of evacuation (from 30 to 120 min) and of staining (from 15 to 45 min). (Gregory)

Pharmacology of the frontal prothoracic nerve preparations of Muscid flies. In tests to facilitate the use of the frontal prothoracic nerve preparation for toxicological studies (last year's *Report*, Part 1, 127), evidence was obtained that, in the blowfly, the synaptic connections between the sensory neurones of the haltere nerve and the motor neurones of the frontal prothoracic nerve are cholinergic, though some results were atypical. Thus, all compounds were effective only at high concentrations (perhaps because all were applied without desheathing the thoracic ganglion) and although both nicotine (0·1 mM) and paraxon (0·01 mM), which act post-synaptically, blocked conduction, block was not, as expected, preceded by bursts of nerve impulses associated with depolarization. Acetylcholine (0·01 mM) caused spontaneous bursts and intermittent block, but was not potentiated by the cholinesterase inhibitor physostigmine, which by itself (0·1 mM) had no effect. Partial reversible block followed application of low calcium and high magnesium salines (which act pre-synaptically).

Action of pyrethroids on the nervous system of Muscid flies. Continued experiments with haltere nerve preparations (last year's *Report*, Part 1, 127) indicated that such nerves from resistant (*super-kdr*) houseflies were about ten times less susceptible to the pyrethroids bioresmethrin, (1R)-*trans*-permethrin and deltamethrin than were nerves from a susceptible (Coopers') strain. When treated *in vitro* with solutions or suspensions (0·01 μM to 0·01 mM) of the toxicants for up to 2 h, all haltere nerves, whether from blowflies, susceptible houseflies or resistant houseflies, showed similar symptoms except that repetitive activity following treatment with bioresmethrin and (1R)-*trans*-permethrin was less intense in housefly than in blowfly nerves. Little repetitive activity followed treatment with deltamethrin, confirming earlier reports that the mode of action of α-cyano-3-phenoxybenzyl esters may differ from that of other pyrethroids.

As haltere nerves from the resistant houseflies had increased in resistance to the pyrethroids tested by only ten times while the resistance of intact insects was greater by 60 times (bioresmethrin), 100 times ((1R)-*trans*-permethrin) or 300 times (deltamethrin), and as *super-kdr* is known to be associated with the nervous system only, these results appear in conflict. If the neurones tested in the haltere nerve preparation reflect the sensitivity of the most susceptible critical sites within the nervous system, the discrepancy must arise elsewhere within the insect and could be associated with the pharmacokinetics of toxicant transport from cuticle to nervous system. Alternatively the neurones tested may have increased in resistance less than other neurones constituting more critical sites of action.

When the condition of haltere nerves from susceptible and resistant houseflies treated externally 30 min–24 h previously with LD95s of the pyrethroids used in the *in vitro* tests was examined, the intensity of the symptoms of intoxication was similar in preparations from both susceptible and resistant insects. This suggests that the concentrations of pyrethroids in the haemolymph of susceptible and resistant flies resemble the *in vitro* concentrations required to cause abnormal symptoms and are in the same ratio (times ten), evidence that the discrepancy between the external and internal factor of resistance is associated with the pharmocokinetics of toxicant transport. (Burt and Goodchild)

Resistance

Resistance of houseflies (*Musca domestica*) on local pig-breeding farms. Following last year's observations that sprays of non-persistent pyrethroids applied intermittently do not elicit resistance over extended periods, the possibilities of exploiting this principle in controlling a fly population with proven potential for strong resistance to pyrethroids was examined. In the laboratory, isolation of factors of resistance to pyrethroids from strongly resistant local strains, and study of their properties continued. Progress was also made in defining some parameters affecting this development of resistance for incorporation in a mathematical model on which strategies delaying or preventing resistance will be based.

Long term control with bioresmethrin of houseflies with strong pyrethroid resistance potential. The strong potential for rapid development of resistance to photostable pyrethroids by houseflies on a farm was detected when permethrin used residually at the recommended rate failed to control the flies within 3 weeks of its first application, and a second treatment 4 weeks after the first was also ineffective. Subsequently, flies were controlled for 10 months with sticky fly papers until the pyrethroid tolerance of the flies had reverted to its original level.

Between June 1981 and May 1982 two flat-deck houses and the farrowing house were sprayed with an aqueous formulation of bioresmethrin, occasionally supplemented by the farmer with synergized photolabile pyrethroids.

Housefly samples from the treated areas were collected approximately monthly and laboratory reared F_1 progenies were tested for response to pyrethrins with and without piperonyl butoxide, bioresmethrin and permethrin. The results of these bioassays confirmed the efficacy of the bioresmethrin in the pig houses. Throughout 11 months, treatments did not increase the tolerance level of the treated fly populations to pyrethroids; this provided for the first time unequivocal proof of the possibility of avoiding resistance even in populations of insects with a strong insecticide-resistance potential.

Dispersal and gene flow in a housefly population. The movements and distributions of houseflies between closely sited pig-breeding units on a farm were again investigated by mass-release-recapture and by introducing a visible mutant marker gene *bwb* (brown body) into the local fly population (cf. last year's *Report*, Part 1, 128). Of 2600 marked flies released in an enclosed farrowing house in July only 38 were recaptured up to 5 days later at 23 trap sites in open areas of the farm, and none in traps in two enclosed flat deck houses 15 m from the release site.

Of 4000 marked flies released in August at two outdoor sites on the same farm, 375 were recaptured in open buildings, 3 in the farrowing house, and none in the flat-deck. As found last year, very few adult flies enter enclosed buildings. In late spring flies leave warm buildings to recolonize the farm and outlying areas where they survive only during the warm part of the year, and do not return.

This conclusion is confirmed by the spread of *bwb* on the farm. F_1 males heterozygous for this gene were released in one of two adjacent flat decks on three occasions between January and March 1982. Progeny of single pair crosses of *bwb*-marked flies sampled at this site in May showed that 10% of the flat-deck population was heterozygous for this gene. By August 7% of the flies in the flat deck and 5% of outdoor flies were heterozygous for *bwb*. Thus adults of the outdoor population came from the resident over-wintering populations of the flat-deck.

Qualitative genetics of resistance to pyrethroids in local houseflies. The isolation and characterization of factors of pyrethroid resistance (R factors) on individual autosomes of strongly pyrethroid-resistant housefly strains caught on local farms proved very difficult, because singly all R factors other than *super-kdr* on autosome 3 are barely detectable by bioassay. These factors show however not only specificity towards different pyrethroids but also interactions producing strong resistance.

The factor on autosome 1 confers weak resistance to bioresmethrin but none to permethrin. Of the 3 factors on autosome 2 one confers resistance to bioresmethrin but not to deltamethrin, another the opposite. The factor on autosome 5 which is inhibited by piperonyl butoxide (like *py-ses* of Danish strains) confers resistance to bioresmethrin (unlike *py-ses*).

The extremely strong interactions between R factors were demonstrated by the consistent failure to obtain homozygosity for R factors on autosome 2 and 3 when strains with R factors on these autosomes were crossed. Even selection with 60 μg deltamethrin/female or 40 μg deltamethrin/male (corresponding to resistance levels exceeding 50 000 at 20°C) followed by holding temperatures of 10°C failed to select a strain homozygous for pyrethroid resistance on autosomes 2 and 3.

The biochemistry of insecticide resistance in *Myzus persicae*. Studies of the enzyme kinetics and binding of radiolabelled paraoxon and di-isopropyl phosphorofluoridate indicated that insectticide-resistant *M. persicae* have a large amount of carboxylesterase E4 that inactivates insecticidal esters by both sequestering and hydrolysis. Resistance to organophosphorus insecticides involves both mechanisms, carbamate resistance mainly sequestering.

Gel filtration and SDS electrophoresis showed the enzyme to be a single polypeptide mol. wt 65 000. From this and an earlier determination of the molar amount of E4 in very resistant aphids, approximately 3% of their total protein must comprise this one enzyme. Therefore the E4 protein was readily apparent in homogenates of resistant, but not of susceptible, aphids when electrophoresis gels were stained for protein, confirming earlier indirect evidence for enhanced production of this particular protein by resistant insects.

Recently an Italian variant of *M. persicae* with an increased amount of esterase was identified. However the properties of this enzyme differed slightly from those of E4. The mol. wt is 66 000, and it hydrolyses naphth-1-yl acetate and organophosphorus insecticides, though not carbamates, about 50% faster than E4. Although total esterase assays with naphth-1-yl acetate adequately characterize organophosphorus resistance in this variant, they slightly overestimate the degree of resistance to carbamates. (Church, Denholm, Devonshire, Farnham, Moores, O'Dell and Sawicki)

Compounds influencing invertebrate behaviour

Trials with (*E*)-β-farnesene. Previously two separate formulations were necessary for application of the aphid alarm pheromone, (*E*)-β-farnesene, with a pesticide, but, by incorporating pentane as a propellant and using the spinning disc electrostatic system small quantities of pesticide and pheromone can now be dispensed simultaneously. Addition of the pheromone to permethrin (equiv. to 2 g ha^{-1}) improved kill of *Myzus persicae* on abaxial leaf surfaces from 12 to 76% and to bendiocarb (equiv. to 40 g ha^{-1}) from 43 to 96%. However, further development will be necessary because the large proportion of pentane in the formulation was inconvenient and control erratic.

The response of aphids to (*E*)-β-farnesene depends on the vapour concentration. Thus at saturation (60 $\mu g\, l^{-1}$) only 42% *Myzus persicae* responded whilst at 1·2 $\mu g\, l^{-1}$ the response was 83%, and *Lipaphis erysimi*, previously considered unresponsive to (*E*)-β-farnesene, was even more sensitive to concentration. In our tests only 10% of *L. erysimi* responded to pheromone at saturation, but analysis confirmed that (*E*)-β-farnesene was the main volatile component of the cornicle secretion of this species and by decreasing the concentration of synthetic pheromone to 1·2 $\mu g\, l^{-1}$ a response of 85% was obtained.

In other laboratory tests with *Myzus persicae* and (*E*)-β-farnesene, two clones very resistant to organophosphorus pesticides gave only about 30% of the response by a susceptible or slightly resistant clone. Biological and chemical tests demonstrated that the resistant aphids produced normal amounts of (*E*)-β-farnesene. Such a diminished response to a pheromone appears to be a novel and possibly significant phenomenon.

Compounds influencing aphid feeding. The cycloaddition product of (*E*)-β-farnesene and bis(decyloxycarbonyl)acetylene [XIIId, $R=(CH,)_9CH_3$] was most active in decreasing aphid colonization (last year's *Report*, Part 1, 131). Related compounds were therefore prepared (Table 1).

TABLE 1

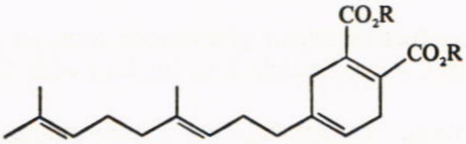
Compound	*R*		*Lowest active concentration* (%)
XIIIa	CH_2CH_3		>0·5
b	$(CH_2)_7CH_3$		0·5
c	$(CH_2)_8CH_3$		0·1
d	$(CH_2)_9CH_3$		0·1
e	$(CH_2)_{10}CH_3$		0·05
f	$(CH_2)_{11}CH_3$		>0·5
g	$(CH_2)_{13}CH_3$		0·5
h	$(CH_2)_{17}CH_3$	(aggregation)	0·5
i	$(CH_2)_8CH{=}CH(CH_2)_7CH_3$		0·5
j	$(CH_2)_9CH{=}CH_2$		>0·5
k	$(CH_2)_5CH{=}CH(CH_2)_3CH_3$		>0·5
l	$CH(CH_3)(CH_2)_8CH_3$		0·5
m	$[(CH_2)_2CH(CH_3)CH_2]_3H$		>0·5
n	$(CH_2)_2CH(CH_3)CH_2[CH_2CH{=}C(CH_3)CH_2]_2H$		>0·5

Where R=n-alkyl (compounds a to h) the C_{11} compound (e) is most active. The C_{18} compound (h) causes aggregation but (*Z*) unsaturation at C_9 (i) restores deterrent activity. Therefore the C_{11} unsaturated compounds (j and k) were prepared but were less active, as was the secondary alkyl C_{11} compound (l). The saturated (m) and partially saturated (n) farnesyl compounds were also less active.

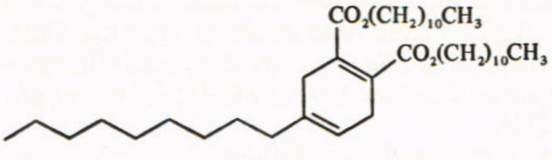
Interference by fatty acids with aphid colonization is maximal at chain lengths between C_8 and C_{13} (*Rothamsted Report for 1977*, Part 2, 145) (cf. R in structure XIII). On hydrolysis compounds XIII would give alcohols corresponding in chain length to these fatty acids, so a range of alcohols was tested. Decan-1-ol prevented settling but only at levels too high to explain the activity of compound (XIIId) in terms of hydrolysis.

Compounds related to series XIII but with modifications to the homogeranyl group, e.g. replacement with $(CH_2)_8CH_3$ (compound XIV) are less active than compounds containing the pheromone moiety.

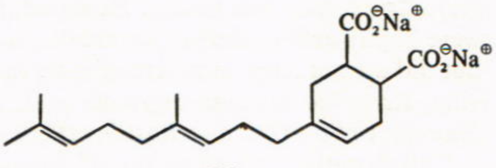
The structures described above are highly lipophilic and have no systemic activity.



XIII



XIV



XV

However hydrolysis of the anhydride derived from the pheromone and maleic anhydride gives the dicarboxylic acid salt (XV) which is systemically active at 0·05% via the leaf petiole, and at 0·1% via the soil.

Racemic polygodial, synthesized from β-cyclocitral, interferes with aphid colonization at 0·02% and therefore shows an activity about half that of the natural (−) isomer (last year's *Report*, Part 1, 131).

In tests described last year (*ibid.*) which measure effects on settling, nymph production and transmission of beet yellows-virus, the cyclic derivatives of (*E*)-β-farnesene (XIII) showed generally moderate activity, the most effective against transmission being compounds c, g and m. (Briggs, Dawson, Griffiths, Pickett, Smith, Stribley, Rice and Woodcock)

Effects of chemicals on dispersal of *M. persicae* and virus transmission. Fuller examination of the initial, excitatory effect of the pyrethroid deltamethrin reported earlier (*Rothamsted Report for 1980*, Part 1, 125) showed that unrestrained aphids placed on treated (0·001% a.i.) leaves quickly dispersed by walking or flying, R_1 (moderately resistant) aphids leaving within *c.* 5 min and R_2s (strongly resistant) within *c.* 10 min. In contrast, the carbamate pirimicarb (0·03% a.i.) and the organophosphate demeton-S-methyl (0·05% a.i.) induce secretion of alarm pheromone, stimulating much later dispersal (15–60 min).

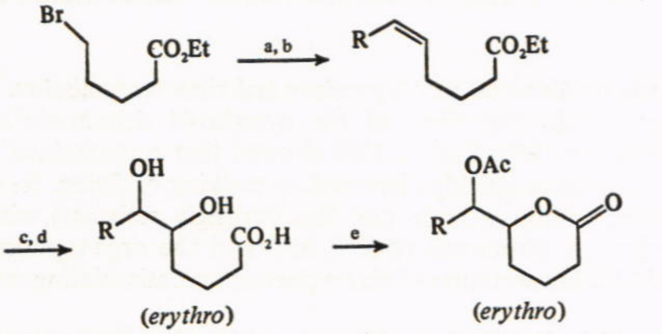
The extent to which disturbed viruliferous aphids then transmitted virus depended on factors such as the strength of dispersal, the degree of incapacitation, and the persistence of the virus. Thus, most R_1 aphids (but fewer R_2s) leaving deltamethrin-treated plants became incapacitated and transmission of even the non-persistent potato virus Y was considerably suppressed for the less resistant strain. However, R_1s dispersed by demeton-S-methyl remained active long enough to transmit the semi-persistent beet yellows virus (BYV) to untreated, but not to demeton-S-methyl-treated, beet seedlings. With R_2s, the time spent feeding and thus the amount of insecticide picked up on the source was influenced by the presence of S nymphs in the colony, which, by early release of alarm pheromone, triggered dispersal. Consequently, such R_2s were less incapacitated and could transmit BYV even to organophosphate-treated seedlings. These observations are important for virus disease control as has been discussed (Rice, Gibson & Sawicki, in press).

The increased efficacy of permethrin reported when used in the presence of alarm pheromone (Griffiths & Pickett, *Entomologia experimentalis et applicata* **27**, 199 (1980)) and the potentiation between deltamethrin and other insecticides may therefore both be due to the dispersive effect of alarm pheromone increasing contact between aphid and pyrethroid. (Gooding, Rice, Sawicki and Stribley with Gibson, Plant Pathology)

Sex attractants for pea moth. In Britain, four closely related compounds, (*E*,*E*)-8,10-dodecadien-1-ol, (*E*,*E*)-8,10-dodecadienal, (*E*)-10-dodecen-1-yl acetate (*E*10-12:Ac) and the natural female sex pheromone, (*E*,*E*)-8,10-dodecadien-1-yl acetate (*E*,*E*8,10–12:Ac) attract male pea moths. However, in Europe, although formulations of *E*10–12:Ac were highly active, similar formulations of *E*,*E*8,10–12:Ac were unattractive to pea moth but did attract large numbers of male lucerne moths (*Cydia medicagenis* Kuzn.) (Bournoville, *Revue de Zoologie Agricole et de Pathologie Végétale* (1979) **78,** 41; Horak *et al.*, *Sbornik Urtiz—Ochrana Rostlin* (1980) **16,** 213).

Collaborative investigation of these conflicting results in Britain and France has indicated that the cause is associated with the more rapid loss of activity of the French formulation, and the weaker inhibitory effect of the decomposition products to *C. medicagenis*. Greenway, with Wall, Entomology Department, and Dr R. Bournoville and Dr J. Einhorn, INRA, France)

Mosquito pheromone. *Erythro*-6-acetoxy-5-hexadecanolide (XVIIa), the mosquito oviposition attractant pheromone (last year's *Report*, Part 1, 132), was prepared as the racemic mixture in gram quantities (over all yield 5%, see Fig. 1) for field trials and commercial evaluation. Recrystallization from ethanol of *erythro*-5,6-dihydroxyhexadecanoic acid (XVIa) removed traces of *threo* isomer generated from the *trans* impurity of the Wittig reaction.



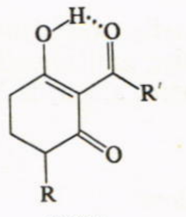
XVI

XVII a: R = $CH_3(CH_2)_9$-
b: R = $CH_3(CH_2)_5$-

FIG. 1. Synthesis of mosquito pheromone
a, pyridine *N*-oxide; b, $CH_3(CH_2)_9CH{=}PPh_3$ (BuLi); c, $OH^{\ominus}$; d, $KMnO_4$; e, Ac_2O.

The more volatile pheromone analogue *erythro*-6-acetoxy-5-dodecanolide (XVIIb) was also prepared but was not active in preliminary trials. (Pickett and Wickenden with Dr B. R. Laurence, London School of Hygiene and Tropical Medicine)

Further 2-acylcyclohexane-1,3-diones from *Ephestia kuehniella*. *E. kuehniella* larvae deposit their mandibular gland secretions on their food substrate, their silk and upon themselves. Therefore, whole cultures of *E. kuehniella* were extracted to provide larger quantities (50–500 mg) of the active compounds identified in the mandibular gland secretions (*Rothamsted Report for 1980*, Part 1, 126 and *1981*, Part 1, 133) for a range of pheromonal (oviposition deficiency, larval repellency) and other bioassays. Six new natural β-triketones, some with acyl side chains that do not correspond with known unsaturated fatty acids, were separated on silver loaded ion exchange columns and identified. The figure (XVIII) summarizes the structures of the compounds isolated (Mudd)

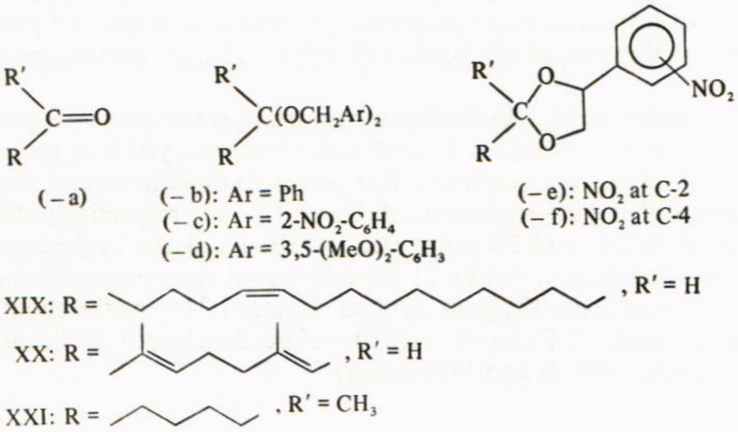

XVIII

R=H(1, 2, 3, 4, 5, 6 and 7)
or OH(8, 9, 10, 11, 12, 13, 14, 15 and 16)
R′=(*Z*, *E*)-11,13-pentadecadienyl (1, 8)
or (*Z*)-10-pentadecenyl (2, 9)
or (*Z*)-8-pentadecenyl (3, 10)
or (*Z*)-6-pentadecenyl (4, 11)
or (*E*)-13-pentadecenyl (5, 12)
or (*Z*, *Z*)-8,11-heptadecadienyl (6, 13)
or (*Z*)-8-heptadecenyl (7, 16)
or (*Z*, *Z*)-6,8-heptadecadienyl (15)
or (*E*, *Z*) or (*Z*, *E*)-6,8-heptadecadienyl (14)

Oviposition deterrent from the Dufour's gland of the parasite *Nemeritis canescens*. Preliminary results showed that, of the alkanes and alkenes present in the gland (last year's *Report*, Part 1, 133), the most active oviposition deterrent was heneicosane.

The major component (*Z*)-10-tricosene had no apparent effect on the behaviour of *Nemeritis*, so this oily substance may function as a lubricant for the passage of eggs down the ovipositor or as a carrier for the active heneicosane, a solid (m.p. 40°C) at room temperature. (Mudd with Dr R. C. Fisher, University College, London)

Propheromones: Release of pheromonal carbonyl compounds in light. Many pheromones are volatile and unstable in air and light, and therefore must be continually released for a sustained influence on an insect population. This might be achieved with more stable, less volatile, synthetic derivatives of the pheromones that would decompose steadily to the parent compounds under field conditions.



(– a)

(– b): Ar = Ph
(– c): Ar = 2-NO$_2$-C$_6$H$_4$
(– d): Ar = 3,5-(MeO)$_2$-C$_6$H$_3$

(– e): NO$_2$ at C-2
(– f): NO$_2$ at C-4

Light sensitive derivatives of three typical pheromonal carbonyl compounds were examined: (*Z*)-11-hexadecenal, (XIXa) (attractant, diamondback moth sex pheromone); (*E*)-citral (XXa) (attractant, honey bee Nasonov pheromone); 2-heptanone, (XXIa) (alarm releaser and repellent, honey bee mandibular gland pheromone). Adducts (b) to (f) were prepared from the three carbonyl compounds and their photo-release was investigated. Recoveries of (*Z*)-11-hexadecenal (XIXa) after irradiation of adducts with u.v. at 350 nm for 24 h in hexane were: XIXe, 96·7%; XIXc, 81·7%; XIXd, 18·8%; XIXb and XIXf, none detected. The other carbonyl compounds (*E*)-citral and 2-heptanone were recovered in similar relative proportions from the respective adducts. Aqueous solvents did not markedly influence recoveries. Under simulated sunlight in the laboratory, release of carbonyl compounds from adducts (e) and (c) was slower than under u.v. although still faster from (e) than from (c). The wide range of stabilities for the five types of adducts described here indicates that propheromones of this type with very varied release rates can be obtained; even compounds (d) and (f) may prove useful for very slow field release rates.

In preliminary biological tests, propheromonal activity was demonstrated: lures containing adducts XIXd and XIXc were highly attractive to diamondback moths and persisted longer in the field than lures containing the parent aldehyde XIXa. (Liu and Pickett with Macaulay, Entomology Department)

Pesticides and insect populations

Beneficial insects on barley. A potentially important factor in determining the balance between insect pests (e.g. aphids) and their parasites in populations recovering in fields of arable crops following spraying is the probability that the early stages of the parasites will survive. Such knowledge guides selection of the most beneficial pesticides and formulations. For example, laboratory assay by topical application to *Aphidius matricariae* (a parasite of *Myzus persicae*, not of cereal aphids) of demeton-S-methyl gave LD50 values of 0·018 μg per insect and for the larvae developing in mummified dead aphids of 0·7 μg. If the susceptibilities of the two stages of cereal aphid parasites differ similarly (×350) they may be protected as mummies from insecticide application to emerge unharmed later. This would help explain the results obtained on the 3·3 ha plot in 1980 (last year's *Report*, Part 1, 133) where numbers of cereal aphids and their parasites were greatly lowered following treatment with demeton-S-methyl; one week after treatment aphid numbers were still low, but parasites were increasing.

Comparison of insect populations in the treated plots and in unsprayed areas is particularly revealing. In a repeat trial in 1981 on a 0·84 ha plot, parasites did not resurge, but background counts made throughout the growing season showed parasite numbers had been falling at the time of application (2 July). (Smart, Stevenson and Walters)

Control of spring barley pests. Indications from trials in two previous years that sprays of insecticides (demeton-S-methyl and omethoate) increased yields of spring barley sown from mid-April onwards were confirmed this year with omethoate and fenitrothion, one or three treatments giving improvements of 6–8 or 13–14% respectively. Few aphids and thrips (at most 50 aphids and 70 thrips per 100 shoots at the beginning of July) were present in the growing season, but by 21 June dipterous stem borers (larvae of *Oscinella* spp. and *Chlorops pumilionis*, the gout fly) had damaged 34% of the shoots in untreated plots. The higher yields (7·7 t ha^{-1}) were therefore considered to be associated with control of these pests. (Scott and Woodcock)

Behaviour of pesticides in soil

Biological activity of insecticides in soil. The toxicities to the corn root worm, *Diabrotica balteata*, of six organophosphorus insecticides tested previously against *Drosophila melanogaster* (last year's *Report*, Part 1, 134) were measured after uptake from five soils with different organic carbon contents. Thionazin and phorate, which had previously shown fumigant action, were consistently about 100 times more active than the non-fumigants tetrachlorvinphos, carbophenothion, chlorfenvinphos or dimethoate of which the potency decreased with increasing soil organic carbon content. These results indicate that physical properties favouring partitioning into the soil-air phase are important for efficient action in the soil. (Buxton, Farnham and Nicholls)

Leaching in the field. The suggestion that simazine moved less than predicted in soil because it is sometimes partly undissolved (last year's *Report*, Part 1, 135) was examined by comparing the movement of simazine (soil adsorption coefficient 0·89 ml g^{-1}, water solubility 3·5 mg l^{-1}) and monuron (0.65, 230), in winter. Monuron, much the more soluble, penetrated significantly deeper than simazine. The effect of pH on the adsorption and mobility of chlorsulfuron, a very active herbicide, was measured by chromatography on thin layers of soils taken from the long term liming experiment on Sawyers field. Adsorption decreased and mobility increased at higher pH values because chlorsulfuron behaved as a weak acid, the anion being less strongly adsorbed than the unionized molecule. Therefore chlorsulfuron might be significantly leached in light soils of high pH in winter. (Nicholls, with Briggs and Evans, Chemical Liaison Unit)

The influence of weather on herbicide behaviour in soils. The movement and degradation of the herbicides propyzamide and chlortoluron following spring and autumn application respectively were simulated, using weather data for the years 1974–81; the results were compared with information from the Pesticide Residues Section of the MAFF-ADAS Regional Agricultural Science Service for these and other herbicides. Large differences in degradation, after spring applications, were simulated for different seasons but for moderately strongly adsorbed herbicides the extent of degradation after autumn applications differed little from year to year; however the effect of movement was more significant. Risk of damage to following crops or failure to control weeds may be predicted by simulation of degradation alone for spring application but knowledge of the extent of movement is necessary for autumn forecasts. In the future such simulations may provide a numerical basis for advice to farmers where soil analyses are not available. (Buxton and Nicholls)

Simulation models. Simulations of pesticide behaviour in soil often predict too much downward movement. This may be because insufficient account is taken of the rates of diffusion into and from soil aggregates. The rates of diffusion of chloride ion, tritiated water and the herbicide 2,4-D, into and from aggregates of different sizes in the range 2–12 mm, were measured in the laboratory. The results were compared with simulations using a model developed by Addiscott (last year's *Report*, Part 1, 265) to describe solute diffusion in soil aggregates and clods. It is hoped that this model will eventually be incorporated as a sub-routine to improve present models which simulate movement and degradation. (Nicholls and Wickenden with Addiscott, Soils and Plant Nutrition)

Systemic transport of pesticides in plants

The system for assessing the phloem mobility of foliar applied compounds using *Ricinus communis* (last year's *Report*, Part 1, 135) was improved to give more reliable quantitative data by using [^{3}H] sucrose as a standard. Phloem translocation factors (PTF) were then defined as

$$\mathrm{PTF} = \frac{([^{14}\mathrm{C}]\text{ compound in exudate in 6 h}) \times ([^{3}\mathrm{H}]\text{ sucrose in treatment solution})}{([^{3}\mathrm{H}]\text{ sucrose in exudate in 6 h}) \times ([^{14}\mathrm{C}]\text{ compound in treatment solution})}$$

The following PTF values (means of 2 or 3 experiments) were obtained: triadimefon, 0·03; 2-(1-naphthoxy)ethanol, <0·05; oxamyl, 0·25; amitrole, 0·35; phenylalanine, 0·40; phenoxyacetic acid, 0·81; sucrose, 1·00; maleic hydrazide, 1·61; 2,4-D, 1·64; 4-(1-naphthoxy)butyric acid, 2·91; IAA, 3·03; 3-(1-naphthoxy)propionic acid, 3·38; 1-naphthoxyacetic acid, 4·75; 3,5-D, 6·65; 3-phenoxypropionic acid, 8·70; methionine, 11·30; phenyl hydrogen malonate, 18·95.

All three (1-naphthoxy)alkylcarboxylic acids, but not the corresponding naphthoxyethanol, are readily translocated. Significantly, the latter compound has a similar partition coefficient to 1-naphthoxyacetic acid, so factors additional to polarity must influence PTF. (Burrell, Butcher, Chamberlain and White)

Electrically charged spray application systems

Design. The hand-held APE 80 system (last year's *Report*, Part 1, 135) was further improved by incorporating a rechargeable battery and adding spray deflector electrodes, which lessen the risk of operator contamination even with a shorter handle. Further, a pumped liquid supply now enables the hand held unit to be used at various angles, so that a wide range of formulations can be applied to both horizontal and vertical surfaces at rates below 15 ml min^{-1}.

A larger 'Jumbo' spray head has been designed and patented. This uses the standard commercial micromax rotor inverted and modified to accept a pumped central liquid supply, designed so that check valves or jets are unnecessary. Because the liquid is pumped to the centre of the disc, distribution to the main cone is uniform and viscous formulations can be dispensed without blocking or changes in flow. The feed tube almost touches the surface so that the spray head can be tilted without seriously affecting dropsize or liquid distribution.

Field trials. In 1982 the performance of tractor mounted electrostatic sprayers of the APE 80 and 'Jumbo' type were compared with hydraulic sprayers against pests or diseases of winter and spring wheat and barley, dry-harvested peas, swedes, oilseed rape, Brussels sprouts and sugar beet. The tractor mounted 'Jumbo' unit with a swath width of 1·3 m and increased flow rates permitted higher ground speed to be used. All tests were with standard commercially available aqueous formulations. Plant samples were analysed for pesticide deposits and the results compared with assessments of biological effectiveness.

In the trial on peas the chemical and biological data matched closely, the increased deposits of permethrin on flowers and pods obtained with the electrostatic system being associated with decreased attack by pea moth. In several crops increased pesticide deposits achieved by the electrostatic spray system resulted in only slightly better or similar pest control but only in three of the 11 trials was control with electrostatics inferior to that obtained by the hydraulic system. In one of these, with swede mildew, the poorer results were associated with insufficient penetration of electrostatically applied fungicide to the lower leaves of the plant, which therefore acted as a continual source of inoculum.

The improvement in pest control with electrostatic machinery is therefore not always proportional to the increase in chemical deposition. However, coupled with the other advantages of the electrostatic system (smaller spray volumes requiring less time to re-fill spray tanks, lower ground pressures, diminished drift and soil contamination) the new equipment is attractive. There are also some opportunities, which need further study, to decrease rates of active ingredient without loss of biological effect. Penetration of the spray into the canopy of some crops is at present a limiting factor with charged spray heads, and methods to overcome this, including electrostatic deflection, disc orientation and air assistance are being developed.

The ability of these charged spray heads to atomize a wide range of both oil- and water-based formulations continues to create much interest from industry and other research units. (Arnold, Cayley, Dunne, Etheridge, Griffiths, Phillips, Pye, Scott and Woodcock)

INSECTICIDES AND FUNGICIDES DEPARTMENT

Bird repellents

Evaluation of various potential bird repellents continued. Oil formulations of both deltamethrin and 1,8,9-trihydroxyanthracene, and aqueous suspensions of methiocarb wettable powder ('Mesurol') and microencapsulated methiocarb were sprayed with an APE 80 electrostatic sprayer on plum trees.

Analysis by GLC of the residues remaining on the twigs in the two methiocarb treatments again showed the value of microcapsules in increasing persistence throughout the critical weathering period, January–March. After 1, 40 or 80 days, the deposits of a.i. remaining were 296, 35 or 5 mg m^{-2} for the wettable powder, and 410, 281 or 25 mg m^{-2} for the microcapsules.

Using only four trees per treatment, assessments showed less bud damage by birds in trihydroxyanthracene or deltamethrin treatments compared with the methiocarb treatments and the untreated trees. (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.);	
	Metopolophium dirhodum (Wlk.);	
	Myzus persicae (Sulz.)	(Susceptible and several resistant strains);
	Rhopalosiphum padi (L.);	
	Sitobion avenae (F.);	
Coleoptera	*Diabrotica balteata* LeConte;	
	Phaedon cochleariae (F.).	
Dictyoptera	*Periplaneta americana* (L.).	
Diptera	*Calliphora erythrocephala* (Meig.);	
	Drosophila melanogaster Meig.	(Vestigial wing strain);
	Musca domestica L.	
	Strains:	wild-type susceptible; *ac*; *ar*; *bwb*; *ocra*-called 608, multimarker susceptible; Several field strains resistant to pyrethroids and DDT; Several derived genetically from field strains resistant to pyrethroids; NPR-pyrethrum extract selected; 538*ge-kdr*.
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. The role of indole glucosinolates in the development of clubroot symptoms is becoming more firmly established. The cations

Fe^{2+}, Fe^{3+}, Cu^{+}, Cu^{2+}, but not Mn^{2+} (200 μM) were shown to enhance *in vitro* formation of 3-indolylacetonitrile (IAN) from 3-indolymethylglucosinolate (IMG) by myrosinase at pH 4. The effects at pH 5·5 and 7 are similar, but less pronounced.

Brassicas low in IAN might be less susceptible to clubroot (last year's *Report*, Part 1, 137). A disruptive selection programme to breed a population of *Brassica campestris* spp. *oleifera* with low levels of IAN has therefore started. A component of the variation in the population has been shown to be genetic in origin; this is an essential prerequisite for achieving low IAN content (with Dr H. Toxopeus, Foundation for Agricultural Plant Breeding, Wageningen).

Having established that indole glucosinolates are involved in auxin-based control of growth, the effects of various growth retardants and anti-auxins on control of the disease were investigated. The compounds were applied directly to the roots. Most were ineffective, but sodium 1-naphthoxyacetate (5 mM) decreased the incidence and size (by 50%) of clubs. (Butcher, Chamberlain and Searle)

Control of soil-borne diseases by foliar sprays

Foliar sprays against potato scab. Investigations continued, based on the earlier discovery that, in the glasshouse, foliar sprays of 3,5-dichlorophenoxyacetic acid (3,5-D) or of some of its analogues decreased the severity of potato common scab, caused by soil-borne *Streptomyces scabies*. About 70 analogues of 3,5-D have now been examined (as described in *Rothamsted Report for 1980*, Part 1, 133). The main general findings were as follows: 3,5-D proved to be one of the very few active compounds; the others were 3,5-disubstituted phenoxyacetic acids in which one or both of the substituents was Br-, Cl- or CF_3-, *viz.* 3,5-dibromo-, 3-bromo-5-chloro-, 3-bromo-5-iodo-, 3-chloro-5-iodo- and 3,5-di(trifluoromethyl)phenoxyacetic acids. To these must be added 2,3,4,5-tetrachlorophenoxyacetic acid and two compounds which are probably converted to 3,5-D in the plants: 3,5-dichlorophenoxyacetamide and 4-(3,5-dichlorophenoxy)butanoic acid. Almost all other changes in structure decreased or destroyed activity: (i) replacing the acid group in 3,5-D by less polar groups (as in 3,5-dichlorophenoxyacetone, 3,5-dichlorophenoxyethanol and 3,5-dichloroanisole); (ii) methylating the 2-position in the acid group (as in (±)-2-(3,5-dichlorophenoxy)propionic acid and 2-(3,5-dichlorophenoxy)-2-methylpropionic acid); (iii) replacing the oxygen bridge (as in 3,5-dichlorophenylthioacetic acid, 3,5-dichlorophenyliminoacetic acid and 3-(3,5-dichlorophenyl) propionic acid); (iv) changing the number and positions of the chloro- ring substituents (as in 3-chlorophenoxyacetic acid, the isomers of 3,5-D and, with the exception of 2,3,4,5-tetrachlorophenoxyacetic acid, further ring chlorination up to pentachlorophenoxyacetic acid); (v) adding hydroxy groups to the ring (as in 2- and 4-hydroxy-3,5-dichlorophenoxyacetic acid); (vi) replacing the 3- and 5-chloro- substituents by other pairs (as in 3,5-difluoro-, 3,5-diiodo-, 3,5-dimethyl- and 3,5-dimethoxyphenoxyacetic acid, and in phenoxyacetic acid itself). Thus the structural requirements for anti-scab action are much stricter than those for auxin action.

Scab severity was decreased to about half, with no effect on yield, by foliar sprays of 3,6-dichloropicolinic acid ($P<0{\cdot}001$ in three tests at 0·05 mM or 0·01 g l^{-1}) or 4-amino-1,2,4-triazole ($P<0{\cdot}01$ in two tests at 60 mM or 5 g l^{-1}). However, analogues of these compounds (4,6-dichloropicolinic acid; and 1,2,4-triazole, amitrole, 3-mercapto-, 3-amino-5-mercapto-, 3-amino-5-methylthio- and 3,5-diamino-1,2,4-triazoles), at the highest rates that did not damage the foliage, were inactive.

The following phenolic compounds, some of which were reported elsewhere to have downward moving systemic effects against nematodes on tomato roots, were inactive against scab at 5 mM: catechol, guaiacol, veratrole, 4-methylcatechol, salicylic acid and caffeic acid.

Mode of action of 3,5-D against common scab. Experiments with discs of potato tuber confirmed previous results that 3,5-D inhibited metabolism of L-[U-^{14}C] phenylalanine to phenolic acids, but stimulated that of [side-chain 3-^{14}C] cinnamic acid. No evidence for a direct effect of 3,5-D on phenylalanine ammonia lyase or cinnamate-4-hydroxylase (the first two enzymes involved in the formation of phenolic acids from phenylalanine) was obtained. This supports the conclusion (last year's *Report*, Part 1, 138) that 3,5-D delays the synthesis of these enzymes.

Changes in enzyme activity in untreated discs could be correlated with the measured flux of carbon from ^{14}C phenylalanine into phenolic acids but not in 3,5-D treated tissue. Therefore 3,5-D alters both the coarse and fine control of phenolic acid biosynthesis and appears to decrease scab because it alters tuber phenolic metabolism to suppress the symptoms of the disease. Other pathways of metabolism in the tuber must be involved in preventing invasion by *S. scabies*.

Aphanomyces root rot of peas. A pot bioassay to test foliar sprays of compounds for pea root disease control is being developed, using fenaminosulf drench as a standard, effective treatment. Plants are grown in sterile sand inoculated with *A. euteiches*. Although 3,5-D suppressed symptoms in one test, none of the compounds tested controlled the disease consistently. (Bateman, Burrell, Chamberlain, Dawson and McIntosh)

Fungicides for soil-borne wheat diseases. In establishing the best site of application for a soil fungicide to control take-all, nuarimol was shown to be effective only when placed near to and above the inoculum in an outdoor pot experiment, similar to previous tests with benomyl. This suggests that eradicant action close to the sites of the most damaging primary infections is important and that systemic activity was not occurring.

In a field experiment an attempt was made to incorporate nuarimol (2·2 kg ha^{-1}) at different depths by pre-drilling cultivations. Ploughed-in nuarimol was ineffective against take-all, and sharp eyespot increased. Both deep and shallow rotary harrowing suppressed take-all and sharp eyespot slightly, consistent with previous conclusions that soil-applied fungicides are most effective when placed in the region of crown formation. Despite different levels of take-all and patchy occurrence of whiteheads, the different treatments gave similar yields.

Take-all bioassays in pots compared the ability of a number of surfactants to increase penetration of soil by fungicide drenches. Differences between surfactants applied with benomyl, nuarimol and guazatine were found, and several combinations were as effective against deep inoculum (6·5 cm) as was the fungicide alone against shallow inoculum (2·0 cm). Guazatine (an effective fungicide *in vitro*) was active against root disease only when plants were grown in sand.

Last year's field experiment was resown and sampled to detect residual effects. Benomyl-treated plots (20 kg ha^{-1}) had slightly more take-all than untreated plots, but nuarimol (2 kg ha^{-1}) had no residual effects and yields were not affected. (Bateman)

Sensitivity of barley powdery mildew to fungicides. Continued monitoring of mildew isolates collected in 1981 confirmed the decline in sensitivity to triadimenol (last year's *Report*, Part 1, 139) but no further change has been observed so far in isolates collected during 1982. No active mildew was obtained from crops sprayed with fenpropemorph ('Corbel', 'Mistral') used extensively on spring barley, especially in Scotland. Cross-sensitivity did not change significantly and the pattern remains much as reported last year.

Characterization of virulence genes and fungicide sensitivity showed that triadimenol sensitivity was linked with host plant resistance. Virulence on varieties with the Mla$_6$ resistance gene (Midas, Carnival) is associated with reduced sensitivity, whereas isolates able to infect varieties with $Mla_{4/7}$ (Keg, Ark Royal, Triumph) or Ml_v (Lofa Abed, Atem) are more sensitive to the fungicide. These observations should support development of strategies for using fungicides to minimize the risk of resistance.

Two such strategies were examined in a field experiment with both autumn (Maris Otter) and spring (Golden Promise) sown barley. Sequential treatment with the same group of fungicides ('Baytan', a.i. triadimenol+fuberidazole; 'Tilt' a.i. propiconazole) was compared to alternated fungicides from different groups ('Baytan' and 'Corbel'). Particular attention was paid to the performance of 'Baytan' on the spring sown crop. 'Baytan' initially controlled mildew well on Golden Promise but, 8 weeks after sowing, was no longer effective and yields were not increased. Mildew was, however, extremely severe during May and early June. Treatment of adjacent winter barley with 'Baytan' and 'Tilt' did not affect the performance of 'Baytan' on spring sown plots. Treatments of winter barley with 'Corbel', however, improved the performance of 'Baytan' treated Golden Promise, and significant yield increases were achieved. None of these effects could be related to differences in sensitivity of mildew to triadimenol although overall mildew was less sensitive to this fungicide during 1982 than the previous year.

'Tilt' and 'Corbel' controlled mildew on Maris Otter, but the effects of 'Corbel' persisted longer. Leaf scald, *Rhynchosporium secalis* was severe during early spring, and was controlled by 'Baytan' or 'Tilt' but not by 'Corbel'. Only 'Baytan' increased yield of winter barley. (Butters, Clark and Hollomon)

Mechanism of lowered sensitivity to triadimenol in barley powdery mildew. Resistance to sterol synthesis inhibiting fungicides may result from diminished uptake [Waard and Nistelrooy, *Pesticide biochemistry and physiology* (1979) **10,** 219–29). To examine if such mechanisms might explain differences in the sensitivity of barley powdery mildew to one of these fungicides, triadimenol, techniques were developed to measure the specific uptake of [^{14}C] triadimenol by the pathogen from its host. Because differences in triadimenol uptake might simply reflect general changes in uptake, absorption of [^{3}H] adenosine and [^{3}H] methionine was also examined. Radioisotopes were taken up through cut ends of detached, infected, barley leaves and were soon detected in the surface mycelium which was removed using nail varnish. Analysis of this layer showed that adenosine and methionine were metabolized to RNA and protein respectively, and that this metabolism was not inhibited by triadimenol at concentrations affecting mildew development. Triadimenol was recovered largely unaltered from the mildew. Experiments with several mildew isolates suggest that diminished uptake of triadimenol may not be associated with lowered sensitivity to this fungicide. (Burrell, Butters, Chamberlain and Hollomon)

THE CHEMICAL LIAISON UNIT

Introduction

An essential part of the Unit's contribution to collaborative projects continues to be the development of sensitive methods for the assay of pesticides, tracer chemicals and natural products. With the increased interest in vapour movement of pesticides following reports of damage by herbicidal phenoxyacetic acid esters and the movement of triadimefon between experimental plots we have started work on the volatilization of pesticides and pheromones from inert surfaces and plants.

Work continues on the evaluation of the equipment for the application of pesticides in the field and on to stored products and on the subsequent fate and behaviour of the chemicals used.

Uptake and movement of chemicals in plants

Previous studies on the uptake from nutrient solution of non-ionized chemicals by plants (*Rothamsted Report for 1981*, Part I, 140) have shown that the accumulation of phenylureas and oximecarbamates by plant roots and their translocation to shoots are determined by chemical polarity. Relationships have now been established (Pesticide Science (1982) **13,** 495–504) that enable Root Concentration Factors (RCF) and Transpiration Stream Concentration Factors (TSCF) to be calculated from polarities, assessed using octan-l-ol/water partition coefficients (K_{ow}).

Using a similar experimental system, the distribution of chemicals within barley shoots following uptake by roots was investigated. Shoots were divided into sections: concentrations in the basal and central section reached a constant maximum value, this being rapidly attained for polar chemicals but more slowly for lipophilic chemicals with $K_{ow} > 1000$. Only small amounts of chemical reached the upper shoot leaves until this maximum concentration in the lower shoot was reached.

Accumulation in the lower shoot sections arises by partition of chemical between the plant tissue and the xylem transpiration stream. This partition process is analogous to that previously observed for roots and is ascribed to two processes, sorption by the shoot solids, which increased with increasing lipophilicity of chemicals, and equilibration of the tissue water. The maximum concentration in the lower shoot could be calculated from this partition and the TSCF of the compounds. The ratio of concentration in the lower shoot or stem to that in the nutrient solution around the roots was estimated to reach a maximum value for chemicals with $K_{ow} \sim 10\,000$, the stronger sorption of more lipophilic chemicals to the shoot solids being outweighed by the rapid decrease in TSCF. (Briggs, Bromilow, Evans and Williams)

Catalysis of oxamyl degradation by ferrous ion

Smelt *et al.* (personal communication) reported that oxamyl and methomyl were very rapidly degraded ($t_{1/2} < 5$ h) in anaerobic soils, whereas the breakdown of aldoxycarb (aldicarb sulphone) was slower but still more rapid than under aerobic conditions. The possibility that ferrous and manganous ions, produced in anaerobic soils at concentrations of up to 250 and 30 μg g^{-1} respectively, were catalysing the reactions was investigated.

Oxamyl was rapidly degraded ($t_{1/2} = 9$ h) in deoxygenated water at 30°C containing 250 μg ml^{-1} ferrous ion, whilst manganous ions at the same concentration had no effect. The breakdown products of oxamyl from the reaction with ferrous ion were N,N-dimethyl-l-cyanoformamide and methanethiol (with, presumably carbon dioxide and methylamine), in contrast to the water reaction which yielded methyl N-hydroxy-N′, N′-dimethyl-l-thiooxamidate. Incubating the latter with ferrous ions did not yield either N,N-dimethyl-l-cyanoformamide or methanethiol, and so it is not an intermediate in the ferrous ion-catalysed reaction. The water reaction was very sensitive to pH, the half-life changing from more than 1000 h at pH 5·65 to 39 h at pH 7·66, whilst the rate of the ferrous ion catalysed reaction was essentially constant over this pH range. (Briggs, Bromilow and Williams).

Application of fungicides to potato tubers

In collaboration with the Potato Marketing Board at Sutton Bridge Experimental Station, the performance of various sprayers in applying fungicides to tubers during store loading was compared.

No sprayer achieved the theoretical application rate but usually about 50% of the applied dose was retained by the tubers. When sprays were applied over a roller table some large tubers did not roll, giving uneven distributions of fungicide on the surfaces. Applying fungicide by hydraulic sprayers in 1 or 2 l water t^{-1} tubers may lead to smearing of the deposits on the tuber surface and redistribution of applied chemical, partly overcoming poor initial distribution.

One applicator relied on sponge rollers to redistribute fungicides over the tuber surface and remove excess liquid but distribution of fungicide over the tuber surface depends on tuber shape and hence variety, and tubers with deep sunken eyes may be inadequately protected. Controlled droplet application of concentrated fungicide formulations may overcome problems of excess wetting of potatoes and give more uniform deposits of fungicide over the tuber surface but inadequate deposits in wounds may lead to ineffective disease control.

During all spraying operations much fungicide was absorbed on to soil adhering to tubers and to store loading elevators and conveyors. (Cayley, Dunne and Vojvodic)

Production of *Alternaria* toxins on wheat grains and agar

An HPLC analysis of *Alternaria* toxins was developed using fluorescence and electrochemical detectors to measure the toxins after separation on a 25 cm 10 μm ODS column with 70% methanol, and 30% 0·2M ammonium acetate, at pH 6, as the mobile phase. The fluorescence detector, with excitation at 315 nm and with a 430 nm emission cut-off filter is most sensitive for altenuene [AE] while the electrochemical detector with an oxidation potential of +0·9 V is more sensitive for alternariol [AOH] (0·1 μg kg^{-1}) and alternariol monomethylether [AME] (0·2 μg kg^{-1}).

Isolates of *A. alternata* grown for 3 weeks at 15°, 25° and 30°C on wheat extract agar modified with glycerol to give water activities (a_w) of 0·95 and 0·98 usually produced twice as much AME as AOH and only traces of AE. However at 15°C and 0·95 a_w the concentration of AOH was three times that of AME. In all cases lowering the water activity decreased the amounts of toxins produced.

Toxin production on whole wheat grains was much less than that on agar at the same temperature and water activity. After 3 weeks storage at 25°C, 0·98 a_w the concentrations of toxins were in the order AME > AOH > AE but at 15°C, 0·98 a_w the order was changed to AOH > AME > AE. Toxin production decreased by about 90% when a_w was lowered lowered from 0·98 to 0·95 and decreased further at a_w 0·9.

The moisture content of wheat grain in the field is about 70% (equivalent to $a_w = 1·0$), 10 to 20 days after anthesis when the grain is watery to milky ripe. At this time the plant is particularly susceptible to attack by *A. alternata* and conditions may be suitable for toxin production. Toxins are unlikely to be produced in store under good conditions (low a_w and low temperature) but if grain is harvested after heavy rainfall late in the growing season, *A. alternata* then may develop rapidly in store with toxin production. (Cayley, Clegg, Dunne, Lacey, Magan)

Other projects

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

Insecticides Department

Cayley, with *Arnold et al.*—electrostatically charged spray application systems.

Nematology Department

Bromilow, and Williams—chemical control of stem nematode.

Plant Pathology Department

Cayley, with Hide—control of storage diseases with fungicides.

INSECTICIDES AND FUNGICIDES DEPARTMENT

Staff of the Department and the Chemical Liaison Unit

K. A. Lord retired in April after 40 years in the Department at Rothamsted, the final 10 as first Head of the Chemical Liaison Unit; Lord was closely involved in establishing the Unit and its research programme. Throughout his career at Rothamsted Lord contributed significantly to many aspects of the work of the Department on the behaviour and action of pesticides. G. R. Cayley, already a member of the Unit, was appointed to succeed him.

In November Roussel Uclaf honoured Rothamsted by the public presentation here of the English edition of their scientific monograph on the pyrethroid deltamethrin. M. Elliott was invited to Paris for a ceremony in connection with the French edition.

Jean C. White was awarded the B.A. Degree of the Open University. Bernadette S. M. Buxton obtained a Higher Technical Certificate in applied biology. Sylvie Jusseaume, having finished her degree training in the University of Rennes, France, returned to the Department to work for the Ph.D. Degree in the University of London. She was recently awarded the 'Prix de la fondation Xavier Bernard' of the French Academy of Agriculture. R. Rigitano joined the Chemical Liaison Unit for 3 years from the Escola Superior de Agricultura de Lavras, Brazil to study for a Ph.D.

Liu Xun returned to the Institute of Zoology, Peking after working for 2 years with the Department's group studying insect behaviour controlling compounds. In October we welcomed Margaret M. Blight and L. J. Wadhams to join this group from the Unit of Invertebrate Chemistry and Physiology at the University of Sussex and Lynda A. Scudder was appointed to work with the group.

M. M. Burrell transferred to the Biochemistry Department to work on the mechanism of resistance of potatoes to potato virus Y.

At the end of his contract R. L. Elliott resigned from the post supported by NRDC for work on synthetic pyrethroids and A. Baydar was appointed to succeed him. Sarah J. Bozzard resigned from another NRDC funded post and Valerie J. Church succeeded her. Lindsay E. Cooper was appointed to a temporary post. Stephanie C. Jenkinson resigned and was replaced by A. J. Robertson.

A. R. L. Tuckett left and was replaced by A. R. Gooding. Janice S. Clark was appointed to a post supported by ICI for work on control of powdery mildew on cereals. P. Vojvodic resigned from the Chemical Liaison Unit and was succeeded in the post supported by the Potato Marketing Board by M. Batchelor. M. Williams and P. J. Hulme were appointed. Dr D. E. Clegg from Griffith Unit, Queensland spent 4 months in CLU working on the use of electrochemical detectors for HPLC. Chen Qui Fang joined CLU for a period of 2 years from Zhejieng Academy of Agricultural Sciences, Hangzhou, China to work on the behaviour of pesticides in the environment.

In March M. Elliott contributed to a Symposium in Paris on 'Research and Industry: a Community?' and in November, with support from the British Council gave an invited plenary lecture to the Arab Society for Plant Protection at its first meeting in the University of Jordan, Amman. A. L. Devonshire, M. Elliott, J. A. Pickett and R. M. Sawicki attended the Fifth International Congress of Pesticide Chemistry in Kyoto, Japan, the last by invitation of the main organizing committee. Devonshire discussed 'The biochemistry of insecticide resistance in the peach-potato aphid, *Myzus persicae*'. M. Elliott helped organize a symposium on 'Recent developments in the synthesis of pesticides and growth regulators', lectured on the 'Present status and future aspects of pyrethroids' and was chairman of a session on pyrethroids. He took part in the celebration of the centennial of pyrethrum in Japan which was honoured by the presence of Professor Ryo Yamamoto, aged 92. After the conference Elliott gave seminars to various agrochemical organizations. Pickett discussed 'Compounds derived from the aphid alarm pheromone of potential use in controlling colonization' and after the Congress had discussions and gave seminars at academic and industrial research organizations. Pickett also visited Hong Kong to discuss diamond-back moth control and other insect problems at the Department of Agriculture and Fisheries; in March he had been invited by Hoechst to visit Frankfurt to discuss behaviour controlling compounds.

In September Sawicki was invited to be Chairman at a meeting of the Second European Congress of Entomology, Kiel, 1982 and to lecture on 'Recent advances in the study of resistance to pyrethroids in the housefly (*Musca domestica*) in the field and laboratory in the United Kingdom'. He also lectured on resistance to pyrethroids to the 'Comité pour les Applications des Insecticides dans les Locaux et la Protection des Denrées Alimentaires' (CILDA) in May; Elliott was nominated as Président d'Honneur du CILDA in October 1982.

A. J. Arnold lectured on electrostatic spraying equipment at the American Society for Agricultural Engineering, Madison, Wisconsin, in June and to the European Plant Protection Organization in Budapest in October. With B. J. Pye he took part in trials of Rothamsted electrostatic spraying equipment in the University of Ohio and at Wooster

In July P. Etheridge attended an intensive course on Microencapsulation in Amsterdam. J. H. Stevenson attended a Symposium in Stuttgart in September of the International Commission for Bee Botany on Harmonization of Methods for Testing the Toxicity of Pesticides to Bees.

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