THE IMPORTANCE OF TUBER DISEASES.

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The importance of potato tuber diseases can be judged only against knowledge of the crop as a whole. Official statistics for the period 1955 to 1965 show that although potatoes occupied a smaller area than wheat or barley they were equal in value (table 1).

Table 1.

Mean acreage and value of potato and other crops in the U.K. 1955 - 1965

	Area (acres x 10^3)	Output (£ x 10^6)
Total for farm crops	17,925	289
Wheat	2,117	75
Barley	3,580	79
Oats	1,855	10
Potatoes	800	78

In England and Wales about 600,000 acres of potatoes are grown annually, mostly at low elevations and on particularly suitable soils or near large markets. (Table 2). In Scotland and Northern Ireland the acreage is larger proportional to population, because both these countries produce seed tubers for export in addition to ware. In England little certified seed is grown but many farmers plant once-grown seed. According to the Potato Marketing Board Main Crop Survey, 1963, about a third of the crop in England and Wales was planted with once-grown uncertified seed, so the figure of 1% of acreage certified does not represent the use of locally produced seed.

Average yields have increased recently but less with potatoes than with wheat and barley. New varieties of cereals have contributed much to these increases but increases with potatoes must come from other causes for Majestic (bred in 1911) and King Edward (bred in 1899) still account for almost a half and a quarter respectively of the main crop acreage in England and Wales. Most of the increase in potato yields must therefore be attributed to better cultivation, increased use of fertilizers or improved control of pests and diseases. The largest national average yield recorded was 10.2 ton/acre in 1965, but there is considerable annual variation resulting from differences in weather and the incidence of pests and diseases. The best growers of ware now expect their better crops to yield at least twice the national average.

Variable yields make it difficult to stabilize the price and marketing of potatoes. The consumption of potatoes has recently been steady at between 195 to 200 lbs per person per year and as few are used for industrial purposes, such as starch or alcohol manufacture, surpluses are difficult to absorb and necessarily frequent so long as

we aim to grow sufficient potatoes to feed the nation in dry years when yields are small.

Table 2.

Total (T) and maincrop (M) potato acreages and production in 1953/4 to 1962/3.

	England & Wales		Scotland		N. Ireland
	T	M	T	M	T
Acres (x 10^3)	587	487	153	130	105
Produce (tons x 10^3)	4,788	4,218	1,216	1,058	795
Yield (tons/acre)	8.2	8.7	8.0	8.2	7.2 *
% Acreage certified for seed	1	-	54	-	31

* Ware only

Price stability is aided by the Potato Marketing Board offering to buy potatoes as prices fall (780,000 tons in 1965). The costs of this are shared between an acreage levy on producers and Government contributions.

The loss of potatoes from diseases has been estimated with different degree of care, boldness or recklessness (Ordish, 1952, Cox and Large, 1960, U.S.D.A. 1965, Cramer, 1967). It is impossible to check the accuracy of such estimates and quite improbable that they include all the stages at which a delicate vegetatively propagated crop could be affected by diseases. Bibliographic assessments and subjective field assessments are quick and comprehensive, but incapable of proof without objective measurements, which are so laborious and costly that they can seldom be comprehensive or even keep up to date with changing husbandry.

Opportunities for Damage or Loss

The potato crop has a cycle of two phases, one the production of seed tubers the other their use to produce ware. Disease problems can be very different in the two phases. Thus although diseases are usually considered to be always damaging they can have social and economic effects that are locally beneficial. For example, the valuable seed potato trade in Scotland and Northern Ireland depends on the fact that viruses and their aphid vectors are more prevalent elsewhere. However, seed growers now seldom give due thanks to the viruses that provide their livelihood, perhaps because other pests and pathogems occupy so much of their time.

There is no time through the year when the potato is free from risk of disease but there are few quantitative results to show when losses are greatest. Even though the seed crop is thoroughly inspected it is difficult to estimate the contribution of diseases from the published statistics. To ensure the purity of seed crops long breaks between potato crops are prescribed but even so in recent years 7 percent of Scottish fields entered for certification were rejected

because eelworms were present and such further restrictions are costly. From 3 to 10 percent of fields fail the inspection each year and an unknown proportion are down-graded to a lower category than the grower expected. This is now less because of virus diseases than because of rogues, bolters and other factors. After lifting, about 5 percent of Scotch stocks are rejected on the farm until redressed. Either this proportion is too small or the tubers deteriorate rapidly afterwards, because a further 14 percent of the small fraction of the crop inspected later during transit was unsatisfactory. There is no evidence to show what proportion of these rejections were because of diseases.

The seed merchant as middleman gets complaints from both producer and customer. Seed merchants' problems are difficult to analyse, because little information about them is published, so the survey in progress by the Department of Political Economy of Glasgow University is particularly interesting. I am grateful to merchants who have given me information, from which it seems that they receive complaints on approx. 10 percent of stocks. On about half of these they agree to make their customer an allowance but some stocks have to be replaced; few are returned to the producers, and most are re-dressed by the merchant (sometimes with dire consequences!)

I can think of no way in which ware growers or users benefit from tuber diseases. The losses suffered by crops during growth and farm storage are the usual concern of plant pathology and plant protection and I shall return to these in more detail after mentioning the losses during storage. If uniform standards could be agreed it would not be difficult to estimate these losses but at present differences are large. Thus, a recent Potato Marketing Board survey suggests that to meet their Grade 1 standard, it would be necessary to reject about 14 percent for disease blemishes (mostly with common scab) and approximately 5 percent for rots. Twiss and Jones (1965) ignored scab and, using different criteria, estimated the loss from rots at 15 percent. If high standards have to be met, even mild diseases like silver scurf and skin spot decrease value by destroying 'bloom' and increasing water loss that causes withering.

Losses during Growth

Virus, bacterial and fungal diseases may all contribute to losses during growth, so my treatment of each must be very brief.

The success of seed certification has made losses from leaf roll and severe mosaic viruses very small, but the necessary insurance of planting certified (or near-certified) seed still means that these diseases cost the ware grower a great deal each year. However the susceptibility of some new varieties to the soil-borne tobacco rattle virus, and the recent recognition of potato mop top virus, shows that there are still troublesome virus diseases needing to be controlled. It is rare for plant pathologists to control pathogen so thoroughly that it no longer causes loss, but this has happened with paracrinkle virus which was throughout the variety of Kind Edward until Dr. B. Kassanis produced a virus-free clone by apical-meristem culture. This clone was multiplied in Scotland and by 1964 there were 1500 acres entered for certification and this year paracrinkle free clones occupied 84% of the total certified acreage of King Edward. A series of trials at N.I.A.B. centres suggested that the paracrinkle free clone yielded about 8.5 percent more than the average of seven infected clones. This scareely seems a sufficient increase to account for recent increases in the national yield of King Edward, which in 1966,

at 10.8 tons/acre of ware (> 1½ in) exceeded that of Majestic (10.2 tons/acre) for the first time, although previously it usually produced about 0.5 tons/acre less than Majestic.

There is very little information on the losses from bacterial diseases. Although blackleg can be common locally in growing crops, the proportion of infected plants is usually small and most of the damage these bacteria cause probably occurs as soft rots during storage.

Without question, blight remains the most important fungal disease Cox and Large (1960) estimated that 8% of yield was lost through premature defoliation and a further 3% by tuber infection. This conference has previously discussed blight and I do not wish to repeat what was then said, but I think Fig. 1. illustrates how changing the variety and cultural practices require reassessment of losses. Most of the information Cox and Large considered related to the field-and-tuber resistant variety Majestic, planted unchitted and when sprayed infrequently with rather phytotoxic copper compounds. We introduced the variety King Edward in the middle of our series of experiments to study tuber infection, but the results show how changes in variety, seed storage and the number and kind of sprays all had important effects on total yield, the losses from blight and the gain from protective fungicides. Thus even careful disease assessments have only a limited relevance and may be meaningful for only a short time.

Recently gangrene, skinspot and other tuber-borne fungi have caused more complaints from growers than all the other diseases put together. Although their etiology has been much studied, there has little quantitative information about their prevalence or the damage they do. Mr. Hide will describe our recent studies on the distribution of seed tuber diseases and I shall try to summarise the effects of gangrene (Phoma spp), skin spot (Oospora pustulans) and Rhizoctonia (black scurf and stem canker).

At present it is impossible to find stocks free from these diseases, so until we have produced such stocks in quantity, their effect on yield cannot be measured critically. As an interim measure we have taken poor stocks and selected grades of tubers that seem healthy ('clean') and moderately or severely infected by particular pathogens. These selections, when planted in plots of replicated experiments, provide information on yield, quality and disease incidence on the progeny. The results presented are preliminary because the series of experiments is incomplete and only the ungraded yields weighed in the field have so far been analysed from the 1967 experiments.

Other than with wart disease, there has never been a conscientious attempt to free seed potato stocks from fungal pathogens and it still seems to be generally accepted that, because these are ubiquitous they are unavoidable. Perhaps we never shall be able to produce certified fungus-free stocks, but we should not accept defeat before we have tried, and I think that much can be done to improve the health of seed. Certainly all our experiments suggest that 'the cleaner the seed the cleaner the produce'. Table 3 shows this effect and carries a message particularly to seed producers. It is easiest and most effective to begin 'cleaning-up' stocks on plant breeding stations or on farms where 'virus-tested' stocks are grown. Our attempts to do this show promise, but our success is still doubtful and will depend much on finding more effective and safer alternatives to the organo-mercurial fungicides.

Table 3.

Effects of seed tuber disease on diseases of progeny tubers

Pathogen	No. of tests	Seed tuber health 'Clean'	Moderate	Severe
Oospora (% buds infected)	5	34	54	63
Rhizoctonia	2			
Corticium stage (% plants)		4	30	41
Black scurf (% tubers)		18	52	58
Phoma spp (gangrene)	2			
After riddling (% tubers)		1	5	3
" damage (% tubers)		1	10	9

Infection of the seed tuber, or the roots and shoots that develop from them, helps to determine the number and size of the tubers formed and so the proportion of saleable ware. Rhizoctonia and Oospora make stems fewer and prevent some early-formed tubers developing, this means some early formed ones grow too large and that some tubers are formed very late, so at lifting there are many oversize tubers and chats. Gangrene causes sprouts to branch and also multiple sprouting. Too many stems develop and consequently there are many small tubers. Table 4 shows that on average these effects decreased saleable ware by about 2.5 percent when each disease was severe. These effects are

Table 4.

Effect of seed tuber disease on percentage ware (1¾ - 3¼ in) *

Pathogen	No. of tests	Seed tuber health 'Clean'	Moderate	Severe
Oospora	5	93.3	92.0	90.8
Rhizoctonia	4	92.4	91.4	90.2
Phoma	2	95.0	92.7	92.4

* Experiments at Rothamsted 1965-1966

small but, because each works in a different way they can be additive.

Finally we may consider the effects of these diseases on yield. To include mention of the 1967 experiments I must restrict my comments to the total dirty yield (Table 5). Therefore the results quoted are approximate and intended merely to illustrate the order of the differences. The middle column of results compares the differences between 'clean' and severe. Tubers, which when planted showed no live

Table 5.

Effect of seed tuber disease on total yield

Pathogen	No. of tests	Mean percent difference from yield of 'clean' seed tuber health: Moderate	Severe	Unselected
Oospora (Skin spotting)	7	0	-15	-2
(Dead eyes)	2	-7	-48	-1
Rhizoctonia	5	-5	- 7	-2
Gangrene	6	-9	-23	-10

eyes, produced about a 40 percent plant population and a 50 percent yield. Chitting the seed tubers before mid-January, even in the worst infected stocks would prevent this degree of damage and bring losses to no more than that caused by 'skin spotting' (Table 5). The gangrene experiments represented two years; in one there was negligible effect, but in the other about twice as much as shown. Rhizoctonia affected yield least, but its effects were more consistent than with the other pathogens; the greatest losses we have measured (in 1964) have been omitted because they were obtained in an experiment with very small plots. It is not surprising that moderately infected plots had intermediate yields but the small effects of planting unselected whole stocks (most of which had been the cause of complaint) is important.

There is little doubt that these small effects result mainly from the ability of the healthy potato plants in the crop from the unselected stocks to profit from the lack of competition when they were adjacent to gaps or sickly neighbours and so to compensate for the potential losses these implied. To measure the ability to compensate, we have made a series of experiments in which crops of normal health have had 0 to 24 percent of their plants removed from random positions either at emergence and flowering (Fig. 2). Compensation was greater with gapping at emergence than at flowering. Field experiments with potatoes will seldom detect yield differences smaller than about 5 percent and accordingly would not be expected to distinguish significantly between yields from full crops and from crops with fewer than 11 and 7 percent of gaps at emergence or flowering respectively. The ability of severely diseased plants to compensate for absent neighbours would be less than that of healthy plants, so the ability to detect the effect of gaps might be more in diseased crops than in our experiment. Only very bad stocks are likely to exceed the 21 percent of emergence gaps likely to produce a 10 percent decrease in yield.

In conclusion, let me remind you that even this long after the Irish Famine, potato diseases can still have important social as well as economic effects. They increase costs or cause loss at many stages, not only during growth, but as seed, in storage and during usage. They hazard the health of future crops and so their control is especially important in seed production. In this hasty review of our current work, brevity has forced me to present averages, but there is ample evidence that the effects of each disease differ from year to year, and depend on soil type, weather and variety. We need to study the occurrence and causes of these differences so that we can predict the exceptionally large or recurrent losses from which farmers suffer most

and which they remember longest.

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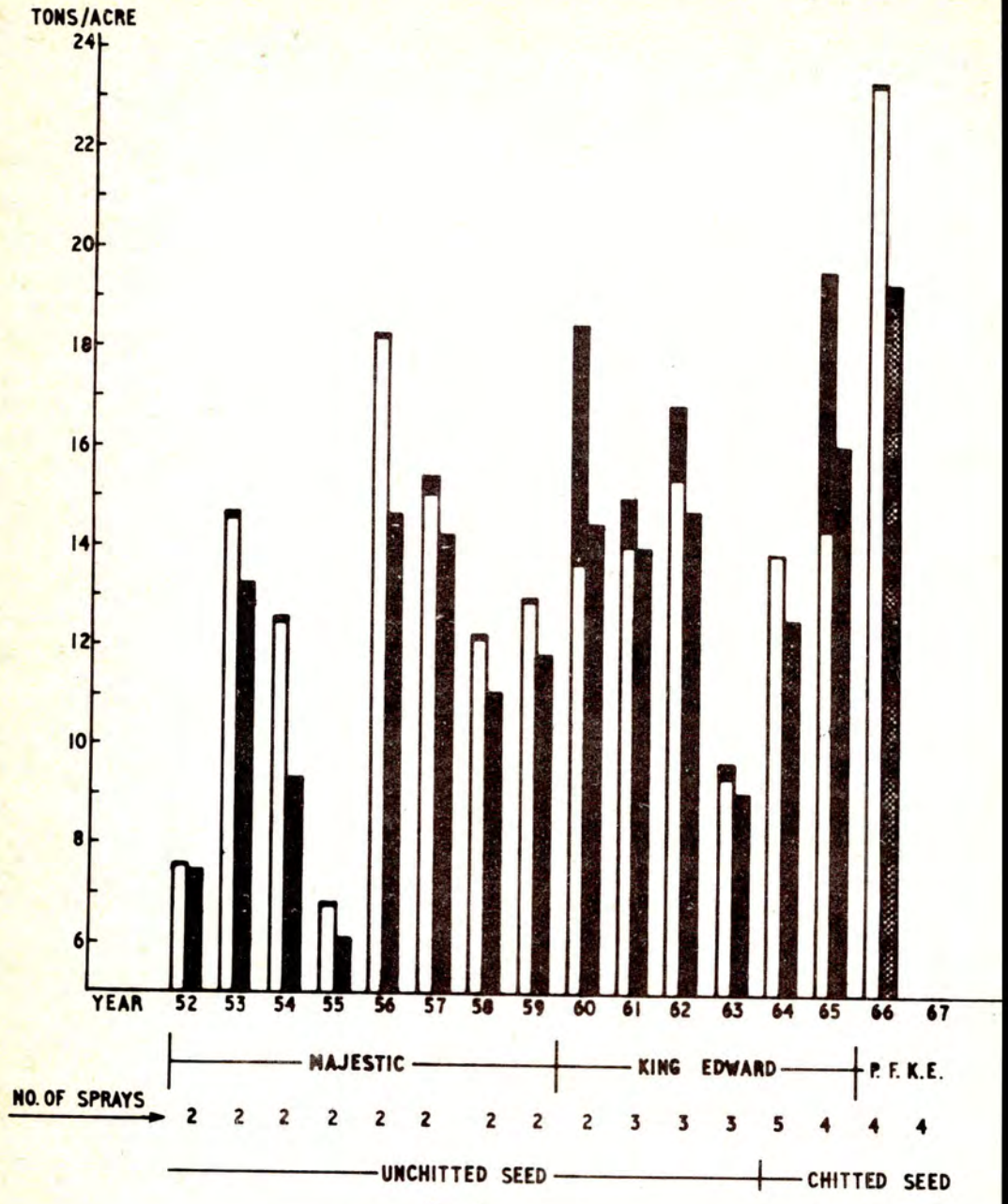
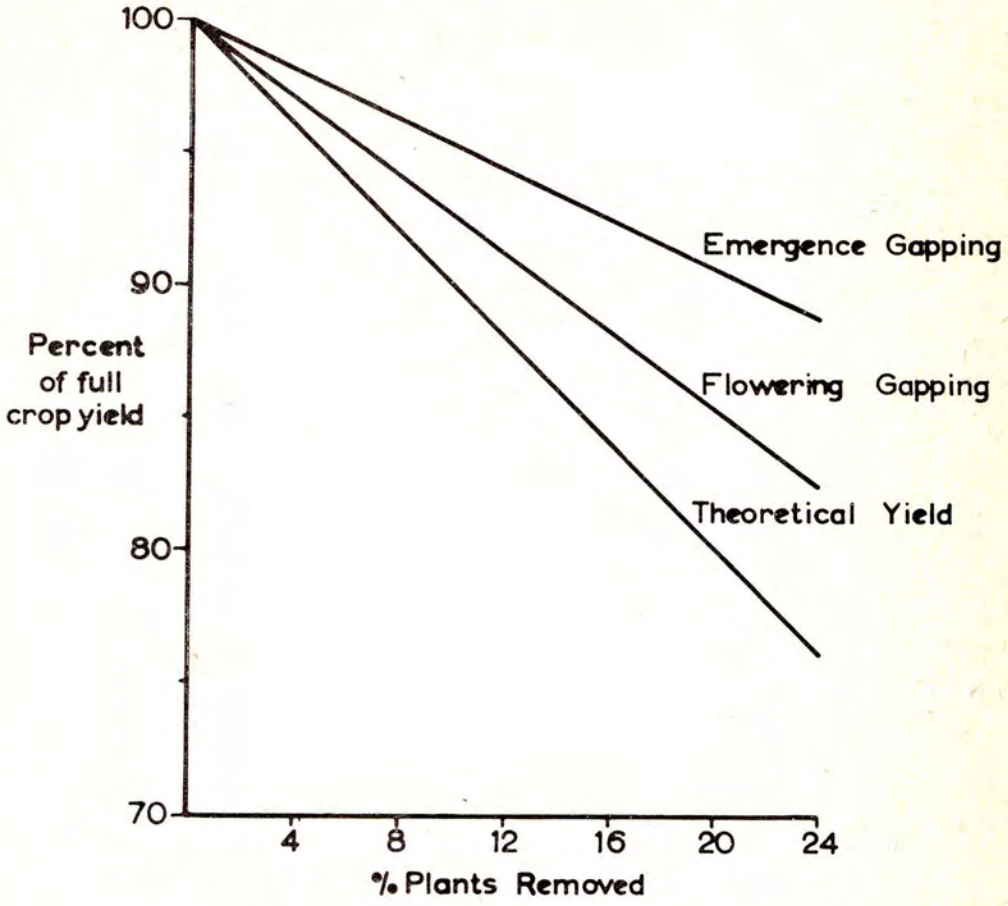


Fig. 1.

Histogram columns indicate the total yields from sprayed (white) and unsprayed (stippled treatments of blight control experiments at Rothamsted. Solid portions indicate weight of infected tubers on treatment burnt-off late. (P.F.K.E. = paracrinkle free King Edward).



Artificial Gapping of Potato Crops
Rothamsted. 1966 & 1967

Fig. 2.

Linear regressions of percent artificial gaps made at emergence and flowering on total yield of experiments at Rothamsted (1966 and 1967) compared with theoretical curve.

SESSION 6A

DISCUSSION

Dr. I. W. Prentice: If atmospheric humidity in storage plays an important part in skin spot development, why does disinfection during storage not effect any control?

Dr. A. E. W. Boyd: We presume that atmospheric humidity affects the superficial layers of tuber cells and encourages the development of latent infection, most of which has already taken place before lifting. Dry conditions, on the other hand, tend to inhibit the further development of the fungus, but we do not really know why. The organo-mercury solution effects a progressively smaller degree of control up to about six weeks after lifting, e.g. to about mid-November, and presumably penetrates the tissues to do this.

Dr. D. C. Graham: We have carried out analyses of tuber tissues disinfected with mercury at lifting, and found evidence of mercury penetration. Up to 80 per cent of this was present in the first millimetre of tissue but 20 to 40 per cent was below this depth. In tubers disinfected about six weeks after lifting, there was practically no penetration of mercury.

Dr. H. H. Glasscock: Silver scurf very frequently accompanies dead eyes. Is there any evidence that dead eyes and excessive silver scurf are associated?

Mr. G. A. Hide: Russian workers record a disorder called "Black skin", which is said to be caused by Oospera pustulans and Helminthosporium atrovirens. In the survey of diseases on seed tubers, we have noted that these two fungi are often associated but condiophores of H. atrovirens are seldom found on bud scales of live or dead eyes, whereas almost all eyes where buds are dead yield condiophores of O. pustulans.

Dr. A. E. W. Boyd: I should like to ask Dr. Hirst what spacing was used in his experiments to determine the effects of blanking upon yield. From our skin spot experiments, it would appear that at the close spacing of 9 inches used for seed production, blanking has more effect on the proportion of ware to seed than on total yield. With wider spacing for ware production, the same degree of blanking should have a greater influence on total yield.

Dr. J. M. Hirst: The spacing we used was 16 inches on 28 inch rows.

Mr. W. T. Cowan: In view of supply and other considerations I am doubtful whether sulphur really has any future as a practical disease control measure, and I wonder whether any other fungicide could achieve the same effect.

Mr. C. L. S. Ryan: Has Dr. Wakerley any experience of the use of parathion granules for symphilid control on potatoes, and has this material any effect on slugs or potato root eelworm?

Does Mr. Caldicott know if phorate has any effect on symphilids and these other two pests?

Mr. J. J. B. Caldicott: Phorate has little activity against symphilids but there is evidence that another organo-phosphorus material, thionazin, is active against this pest.

Phorate has no direct activity against slugs, but since many slugs are secondary feeders or wireworms, slug damage is often reduced following treatment of potatoes with phorate.

Dr. S. B. Wakerley: I have no experience of the use of granular parathion on symphilids or potato root eelworm. We looked at slug damage in the 1966 trials but the level of attack was low and there was no evidence of effective control.

NATURAL CHEMICAL PROTECTION IN PLANTS

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In our preoccupation with diseases and pests, we tend to overlook the fact that, in many plants, susceptibility is the exception and not the rule. Plants clearly can protect themselves, but their ability to do so differs considerably even between cultivars; one apple shoot, for example, may be devastated by mildew and another comparatively unaffected. Most of our information on chemical defensive mechanisms comes from the study of the reactions of plants to attack by fungi. Kuc (1966), reviewing the many factors involved in resistance, points out that a micro-organism on or in a plant tissue is under the influence of a multitude of compounds in its environment. The wax encountered by a fungus or insect alighting on a plant surface is a complex chemical mixture, but even so is much less complex than the protoplasmic contents of the underlying cells. I propose first to examine the possible role of surface structures in defense and then to consider contributions made by the cellular tissue.

SURFACE DEFENSE

The surface wax of plants is composed of long-chain compounds, among which paraffins, esters and acids usually predominate, but in widely differing proportions. Aromatic compounds are sometimes included. Each fraction contains many individual components; the acids may be fatty (saturated and unsaturated), hydroxy-fatty, and triterpenoid. In many tests of the effects of fractions of waxes of plants on their respective fungal pathogens, some of the acidic compounds have shown slight activity, while the non-acidic have had no effect or have even stimulated mycelial growth; the overall effect of the wax, in either direction, is usually slight. The wax, if highly water-repellent and of slight permeability, may contribute to protection by preventing the deposition of water-borne inoculum and by limiting the exudation of nutrients to the surface. These factors do not always operate; many waxes contain sufficient non-hydrophobic components to make them easily wetted and permeable.

The plant wax may play a part in repelling insects. In collaborative work with the Scottish Horticultural Research Institute, we have examined chemical factors involved in the unattractiveness of Rubus phoeniculasius to the raspberry beetle. The flower-buds are exceptionally waxy, and the wax differs in chemical make-up from the waxes of susceptible commercial raspberry varieties. Repellency to the beetle was associated with a particular fraction of the wax, whose detailed composition is being examined. Repulsion of the parasite by the host has been exploited by Lupton (1967) in the breeding of raspberry repellent to the rubus aphid responsible for the spread of virus disease. Way and Murdie (1965) found that a non-glaucous strain of Brussels sprout was more resistant to Brevicoryne brassicae than the normal glaucous, but relatively more attractive to Myzus persicae. They suggested that, among other factors, Brevicoryne may be deterred from the plant after alighting. Furthermore, the glossy strain appears to be more susceptible to white blister (Albugo candida) than the waxy (North and Priestley, 1962). The surface of the non-glaucous leaf differs considerably, both physically and chemically, from that of the glaucous. The glossy brassica leaf is less waxy and less water-repellent, and its wax has a much lower content of paraffins, ketones and esters and a higher content of acidic substances than the wax from the glaucous leaf.

The cuticle of the plant is sometimes regarded as a protective barrier against fungi. For most plants, the value of the cuticle as a mechanical barrier cannot be great (Martin, 1964), but whether it serves as a chemical barrier is uncertain. The cutin of the cuticle is a polyester chiefly of mono-, di- and tri-

hydroxylated fatty acids. Cutinolytic enzymes are produced by some fungi and yeasts. If a fungal infection thread hydrolyses cutin, it may liberate a local concentration of acids of sufficient toxicity to arrest its progress. Whether a fungus such as Venturia degrades cutin in its path is still uncertain; the consensus of opinion at present is that certain saprophytes such as Penicillium spinulosum found on rotting leaves do so but that pathogens do not.

Some cuticles contain appreciable amounts of material of a condensed tannin kind, whose possible role as a chemical barrier is unknown. Free phenolic compounds occur in cuticles only in small amounts and no qualitative or quantitative differences in the compounds have so far been detected in the cuticles of susceptible and resistant varieties. Hulme and Edney (1960) examined phenolic substances in the peel of Cox's Orange Pippin apple in relation to infection by Gloeosporium perennans and concluded that if they play a part in resistance, it must be due to some special individual compound or compounds present in relatively small amount.

In general, it seems that the contribution of the cuticle to protection is of little significance. The cuticles of many plants are extremely fragile and, if anything, contribute to susceptibility by permitting the outward diffusion of nutrients rather than to resistance. The heaviest leaf cuticle that we have so far found, that of an ornamental plant, is readily penetrated by a powdery mildew. The mainstay of chemical defense is clearly located in the cellular tissue.

CELLULAR DEFENSE

Cruickshank (1966) differentiates between natural defense called into play after infection by fungi, and natural protection due to fungitoxic compounds which occur as normal components of the cells. The concept is a useful one, but the boundary between the mechanisms is narrow. At present, information on naturally-occurring protective agents is limited. Many classes of compounds have been isolated from plants but their activities in situ against invading organisms are largely unknown.

Natural defense

Natural defense is embodied in the phytoalexin theory which emerged from the work of Muller and Borger (1940). This postulates that plants produce substances, which inhibit micro-organisms, as a direct response to infection or injury. The substances, named phytoalexins, do not occur preformed in the host cells but arise, by mechanisms not yet understood, from inter-actions between parasites and hosts. Many recent publications support this concept. Examples are pisatin and phaseollin isolated by Cruickshank and Perrin (1960, 1961, 1963) from fungus-infected pea and bean pods. Susceptibility or resistance is linked with the speed of production of the phytoalexin and the sensitivity of the inducing organism to it; pea pathogens, for example, are relatively insensitive to pisatin and non-pathogens are sensitive. The compounds are chromanocoumaranes. The aglycone, named inermin, of the antifungal glycoside trifolirhizin isolated by Hietala (1960) from Trifolium pratense also contains the chromanocoumarane ring nucleus.

Cruickshank thought in terms of the production of a single inhibitor specific to the plant species. Other work indicates that multiple inhibitors may be formed in response to infection. Condon and Kuc (1960, 1962) for example isolated a substituted isocoumarin and chlorogenic acid from carrot tissue inoculated with Ceratocystis fimbriata, a non-pathogen of carrot. Both compounds increased to fungitoxic levels after infection. The isocoumarin inhibits the growth of C. fimbriata but chlorogenic acid does not; its role is against other non-pathogens of carrot. Uritani and his co-workers have shown that roots of sweet potato rotted by C. fimbriata produce a mixture of substances containing reactive furano compounds such as ipomeamarone, the substituted coumarins umbelliferone (7-hydroxycoumarin) and scopoletin (6-methoxy-7-hydroxycoumarin), and phenolic substances including chlorogenic and caffeic acids. The furan derivatives occur in the infected tissue and the phenolic compounds in the adjacent healthy zone. A close correlation exists between the amount of ipomeamarone synthesized in the host and its resistance to the fungus (Uritani and Miyano, 1955; Akazawa and Wada, 1961; Minamikawa et al., 1963).

Natural protection

Protective antifungal agents, not known to be produced in response to infection, have been isolated from plants and identified chemically. 6-Methoxy-2(3) benzoxazolinone was obtained by Virtanen et al., (1957) from cereal plants. The glucoside of a substituted benzoxazinone was shown by Virtanen and Hietala (1960) to occur in wheat; its concentration in the plant has been correlated by Naghy and Shaw (1966) with the level of resistance to rust. The antifungal agent extracted by Koshimizu et al (1961) from barley shoots was identified by Stoessl (1965) as p-coumaroyl-agmatine, and the compound isolated by workers at Wye from broad bean has been shown by Fawcett et al (1965) to be an acetylenic keto-ester.

Members of the Rutaceae, Umbelliferae, Leguminosae and other families contain furocoumarins such as the pimpinellins, isobergapten and sphondin. Extractives of furocoumarin-containing leaves suppress in vitro mycelial growth of fungi at concentrations lower than those of the extractives in the leaves, and furocoumarins appear to contribute to the defense of the citrus lime leaf against Gloeosporium limetticola responsible for the wither-tip disease (Martin et al., 1966a, b). In collaboration with the National Vegetable Research Station we are examining the possible role of furocoumarins in the resistance of parsnip to canker-producing fungi. An extract of a susceptible root stimulated Centrospora and a Phoma sp. but suppressed Itersonilia; a comparable extract of a resistant root suppressed all three. The effects were slight; the furocoumarins at most contribute to, but cannot be the sole cause of, resistance in the root. The leaves of the canker-susceptible variety naturally colonised in the glasshouse supported Aphis fabae but those of the resistant variety had none; the leaves of both varieties were equally infested with the aphid Cavariella theobaldi. The parsnip root contains the insecticidal compound myristicin (5-allyl-1-methoxy-2,3-methylenedioxybenzene (Lichtenstein and Casida, 1963)); this is one example of many insecticidal plant constituents whose contributions to natural defense are unknown.

Many reports, reviewed by Hare (1966), have described the role of phenolic substances and polyphenoloxidase in plant defense against fungi. Fawcett and Spencer (1967) have shown that fungitoxic 4-hydroxy-benzoic and 4-hydroxy-3-methoxy-benzoic acids are formed in the juice of apple fruits following attack by Sclerotinia fructigena.

Often hypersensitivity of the host culminates in resistance to the pathogen. Noveroske et al (1964) found that in an apple leaf resistant to Venturia inaequalis, the cells around the zone of infection collapse, phloridzin (a non-toxic phenolic glycoside) is hydrolysed to the aglycone phloretin, and products of oxidation of this halt the invasion. In a susceptible leaf, the cells do not collapse and phloridzin, although to hand, plays no part.

Unsaturated fatty acids have been associated with resistance. An antimycotic substance, composed chiefly of linoleic and linolenic acids, was obtained by Honkanen and Virtanen (1960) from rye seedlings. Epton (1967) has produced evidence that the resistance of dwarf bean to the halo blight bacterium Pseudomonas phaseolicola is due to the effect on the organism of linoleic and linolenic acids, acting possibly as their hydroperoxides. The acids are released from mono- and di-galactosyl diglycerides by hydrolytic enzyme action on breakdown of the plant tissue. Resistance is associated with a high level of activity of the galactolipid hydrolase.

DISCUSSION

The examples given demonstrate the wide range in structure of the natural defensive chemicals so far uncovered, from the substituted benzoic acids to the chromanocoumaranes. A vast field awaits exploration by the concerted efforts of chemists and biologists; of special interest are the measures used by plants to protect themselves against insects. No definite clues are given by the natural chemicals to molecular structure-toxicity relationships, but it may be noted that the furan nucleus occurs in ipomeamarone, the acetylenic keto-ester and the furocoumarins. Little resemblance is seen between the plant products and the organic

compounds used by man. The natural antifungal agents show broad spectra of activity and moderate toxicity; the synthetics tend to be more specific with greater intrinsic toxicity, but are mostly surface protectants.

Ideally, crop protection practices should supplement the natural defensive mechanisms of plants. The knowledge of these already gained is likely to lead to new concepts in disease control and to efficient materials with systemic action in which interest in the future will largely lie. Van der Kerk (1963) has suggested that the best hopes for further progress in systemic control of fungi lie not in fungicides per se but in compounds which augment the natural resistance of plants by their influence on metabolism. Cruickshank (1966), in a full account of the role of phytoalexins, also suggests that plant diseases in future may be controlled not so much by surface protectants but by chemicals which enter the plants cells and stimulate them to synthesize defensive compounds. Already the fields of growth regulation and pest and disease control have converged. Chlormequat influences blackcurrant parasites and TCA and 2,4-dinitrophenol may induce the formation of ipomeamarone. Heavy metal ions promote phytoalexin formation, and the interesting suggestion has been made that compounds such as the organomercurials, which are known to be absorbed and translocated, may act in part in this way. Further work on the triggering mechanism may lead to the use of new chemicals which, non-toxic in themselves, stimulate the plant's defense. Will this form part of the pattern of crop protection practice of the future? We have discussed various forms of integrated control; Professor Ray Smith has pointed out that this includes making use of the resistant qualities of plants, and Dr Empson has referred to the need for an understanding of plant resistance to pests. A potentially fruitful approach is the integration of our own chemical measures for defense with those of the plant.

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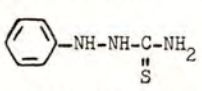
THE ANTIFUNGAL ACTION OF 1-ARYLTHIOSEMICARBAZIDES

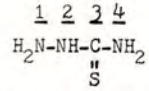
G.J.M. van der Kerk

(Institute for Organic Chemistry T.N.O., Utrecht, the Netherlands)

In 1961 at Utrecht Pluijgers uncovered the remarkable antifungal properties of 1-phenylthiosemicarbazide.



1-phenylthiosemicarbazide



thiosemicarbazide

This compound, which is highly fungitoxic in vitro showed considerable antifungal activity as well when applied to plants, both directly and systemically. Favourable effects were obtained by Dr.A.Tempel (N.V.Philips-Duphar, Weesp, the Netherlands) a.o. with the following plant/parasite combinations: Venturia on apples, Botrytis on lettuce, Phytophthora on potatoes and Cladosporium on cucumber.

Because of its interesting properties we have studied the antifungal action of 1-phenylthiosemicarbazide more thoroughly, and it is my intention today to give an account of this work, which has been carried out at the Institute for Organic Chemistry TNO at Utrecht by Dr.A.Kaars Sijpesteijn and Dr.C.W.Pluijgers.

In my presentation I should like to include a few basic results which I communicated in 1963 at the 5th International Pesticide Congress in London and which were published more extensively in 1966 by Pluijgers and Kaars Sijpesteijn. It was found that within the class of thiosemicarbazides a high structural specificity exists. Elimination or displacement of the phenyl group, or the introduction of further alkyl or aryl groups at any of the nitrogen atoms had an unfavourable effect on the in vitro antifungal activity. Replacement of sulphur by oxygen resulted in complete inactivation. These tendencies are illustrated with a few examples in Tables 1 and 2.

Table 1.

The in vitro antifungal activity of phenyl-substituted thiosemicarbazides

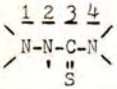
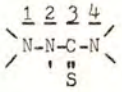
Compound 	Minimum inhibitory concentrations in ppm; glucose agar, pH 6.5			
	B.allii	P.italicum	A.niger	Cl.cucumerinum
thiosemicarbazide	200	100	200	100
1-phenyl	5	1	2	1
2-phenyl	500	500	200	50
4-phenyl	200	200	500	100
1-phenylsemicarbazide	500	500	500	500

Table 1 shows the paramount importance of the placing of the phenyl group and the essential significance of the thiocarbonyl group for activity.

Table 2.

The in vitro antifungal activity of differently-substituted thiosemicarbazides

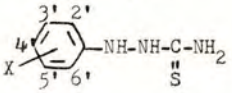
Compound 	Minimum inhibitory concentrations in ppm; glucose agar, pH 6.5			
	B.allii	P.italicum	A.niger	Cl.cucumerinum
1-phenyl	5	1	2	1
1-(α-naphthyl)	5	1	20	5
1-benzyl	500	500	500	200
1-phenyl-4-methyl	20	50	100	10
1-phenyl-4,4-dimethyl	0.5	50	100	5
1-phenyl-4-acetyl	500	500	500	500
1,1-diphenyl	500	500	500	500
1-methyl	200	100	200	200
4-methyl	5	5	500	200
4-allyl	5	10	500	200

From Table 2 it is clear that replacement of phenyl by α-naphthyl in 1-phenylthiosemicarbazide is not connected with a significant drop in activity, contrary to replacement by benzyl. Remarkably, the introduction of one or two methyl groups in the 4-position is much less damaging to general activity than the introduction of the more easily removable acetyl (or benzoyl) group. The presence of a second phenyl group at the 1-position results in almost complete loss of activity.

The only substitutions which occasionally led to increased in vitro activity were those made into the phenyl group of 1-phenylthiosemicarbazide. A few examples are given in Table 3.

Table 3.

The in vitro antifungal activity of ring-substituted 1-phenylthiosemicarbazide

Compound 	Minimum inhibitory concentrations in ppm; glucose agar, pH 6.5			
	B.allii	P.italicum	A-niger	Cl.cucumerinum
4'-methyl	2	2	5	1
4'-methoxy	5	5	20	5
4'-chloro	0.5	0.2	0.5	0.5
4'-nitro	5	5	50	20
2',6'-dichloro	50	2	5	1
2',4',5'-trichloro	20	2	10	1
non-substituted	5	1	2	1

Replacement of the phenyl by the p-chloro phenyl group leads to a two to tenfold increase in antifungal activity. I shall return to these structure-in vitro activity relations in a few moments.

When applied to the roots or to the cotelydons of cucumber plants 1-phenylthiosemicarbazide rendered systemic protection towards post-applicational infection with spores of Cl.cucumerinum. Since the compound can easily be recovered from treated

plants it was supposed that the systemic activity was the direct consequence of its in vitro fungitoxicity and of its capability for being taken up by and translocated within plants. It appeared, however, that the structure-systemic activity relations within this group of compounds are somewhat less transparent than the structure-in vitro activity relations. This is exemplified in Table 4. The systemic activity against Cl.cucumerinum on cucumber was assessed after root application to cucumber seedlings. The compounds were applied in non-phytotoxic concentrations and the degree of protection was assessed as follows: ++ complete protection; + moderate protection; - no protection.

Table 4.

The relation between in vitro fungitoxicity and systemic activity for substituted thiosemicarbazides

Compound	In vitro activity in ppm against Cl.cucumerinum	Systemic activity
$H_2N-NH-\overset{\overset{S}{\|}}{C}-NH_2$	100	+
$C_6H_5NH-NH-\overset{\overset{S}{\|}}{C}-NH_2$	1	++
$C_6H_5CH_2NH-NH-\overset{\overset{S}{\|}}{C}-NH_2$	200	++
$H_2N-\underset{\underset{C_6H_5}{\|}}{N}-\overset{\overset{S}{\|}}{C}-NH_2$	50	++
$(C_6H_5)_2N-NH-\overset{\overset{S}{\|}}{C}-NH_2$	500	-
$C_{10}H_7NH-NH-\overset{\overset{S}{\|}}{C}-NH_2$	5	++

It is evident that there is no simple relationship between the observed in vitro fungitoxicity and systemic activity. Certain compounds which were almost inactive in vitro were as active systemically as 1-phenylthiosemicarbazide. On the other hand, the reverse situation, viz. high in vitro and low systemic activity, has not been encountered. In the further course of this work we have come to the conclusion that the systemic action of certain representatives of this class of compounds depends on other factors than their direct fungitoxicity or their biochemical conversion into fungitoxic metabolites. We are reminded here of the high systemic activity of a closely related type of compounds, phenylthiourea and its phenyl-substituted derivatives, which are neither fungitoxic nor converted in vivo into fungitoxic metabolites (A.Kaars Sijpesteijn and C.W.Pluijgers (1962) and A.Kaars Sijpesteijn and H.D.Sisler (in the press)). At this occasion I shall not deal further with the systemic aspects of the thiosemicarbazides but will discuss in some detail our studies on the observed direct fungitoxic action of 1-phenylthiosemicarbazide (PTS) and its ring-substituted derivatives.

It was found that the in vitro fungitoxicity of PTS is unusually pH-sensitive. The minimum inhibitory concentration for A.niger at pH 6.5 and beyond is 2 ppm; at pH 5.8 this value is 20 ppm and at pH 5.1 200 ppm. Inclusion of 1% of peptone in the glucose medium did not appreciably influence activity.

Warburg experiments showed that respiration of A.niger is slightly inhibited by PTS, but only at concentrations which are well above the minimum growth-inhibitory concentration. Further, it was established that PTS acts fungicidal rather than

fungistatic.

Since PTS is known to be a strongly metal-chelating compound it seemed possible that it might act on fungi by virtue of this capacity, by withdrawing or withholding essential metals from the fungus. Addition of trace amounts of copper, zinc or ferrous sulphates did not, however, influence fungitoxicity. Also the reverse possibility, viz. that PTS might act only after previous chelation with a metal from the medium, could be excluded. Incorporation in the medium of 100 ppm of potassium dibutyldithiocarbamate did not lower the fungitoxicity of PTS, whereas the former is a very effective antagonist of the antifungal action of dimethyldithiocarbamates because of its much stronger copper chelating capacity (A.Kaars Sijpesteijn and M.J.Janssen (1959)).

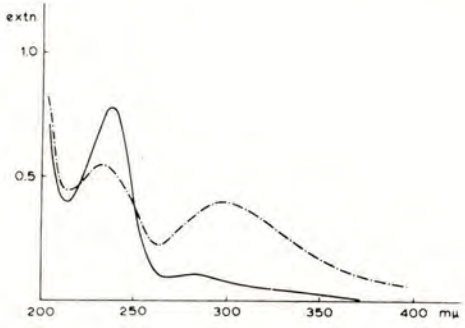
A clue to the mode of action was the apparent relation between in vitro antifungal activity and the occurrence of orange-red discolourations in aqueous solutions of the compounds under consideration.

It was observed that at pH values of 6.5 to 7.0, where PTS exhibits high activity, the nutrient medium slowly turns orange-red, whereas at pH 5.0, where PTS is 100 times less active, the medium remains colourless. The colour change, which is independent of the presence of mould material, does not occur in the absence of oxygen and can be prevented by the simultaneous presence of large amounts of strongly reducing agents, in particular thioglycollic acid. Since also the antifungal action of PTS is antagonized by this reducing agent it was supposed that not PTS itself is the active agent but some oxidation product of it.

The conversion of PTS in aqueous media into the coloured oxidation product at pH 7.0 could easily be followed by means of ultraviolet spectroscopy. The PTS spectrum with its maximum at 239 mμ changes characteristically, a new maximum being formed at 298 mμ. This is illustrated in Fig.1.

Figure 1

The conversion of PTS into its oxidation product at pH 7.0; established spectroscopically

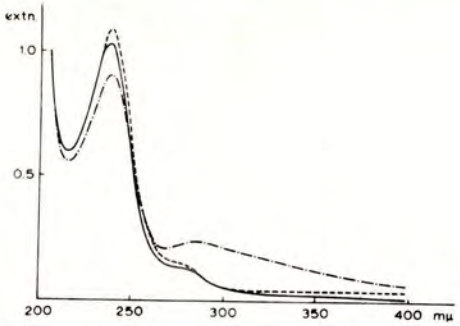


——— 10 ppm PTS, measured directly
-·-·- 10 ppm PTS, measured after shaking 24 h with air. (both uninoculated and inoculated with spores of A.niger; no growth)

On the other hand, at pH 5.0 -at which the in vitro activity of PTS is 100 times less than at pH 7.0- no spectral change takes place, irrespective of whether or not inoculation with A.niger has taken place (Fig.2). At the concentration applied (10 ppm) and at pH 5.0 growth of this mould is not inhibited.

Figure 2

The non-conversion of PTS at pH 5.0; established spectroscopically



——— 10 ppm PTS; measured directly
-·-·- 10 ppm PTS, measured after shaking 48 h with air
----- the same, inoculated at t = 0 with A.niger. No growth inhibition

It was found by Dr.A.Verloop (N.V.Philips-Duphar, Weesp, the Netherlands) that the oxidative conversion of PTS to a compound with the characteristic new spectrum could be strongly accelerated by carrying out the air-oxidation in strongly alkaline solution (4 n NaOH, at -10°C). Under these conditions it was possible to isolate the oxidation product as a pure crystalline red-brown compound. Its composition showed that it had been formed from PTS by the loss of two hydrogen atoms:

$$C_7H_9N_3S \xrightarrow[pH > 6.0]{O_2} C_7H_7N_3S$$

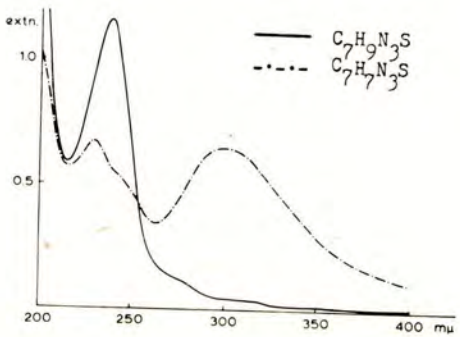
PTS — oxidation product

PTS appeared to be stable in alkaline medium in the absence of oxygen or of oxidizing agents.

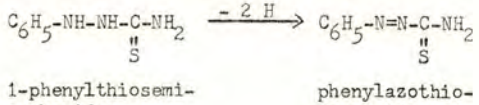
In Fig.3 the spectra of pure PTS and of the pure oxidation product are shown.

Figure 3

The UV-spectra of PTS ($C_7H_9N_3S$) and of its air-oxidation product ($C_7H_7N_3S$) at 10 ppm in 10% ethanol

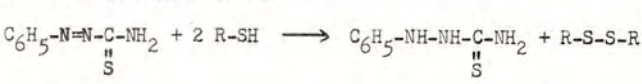


On the basis of the analysis, and of the UV, IR and NMR spectra the oxidation product was supposed to be phenylazothioformamide and this conclusion was confirmed by a different synthesis of this compound.



1-phenylthiosemicarbazide — phenylazothioformamide

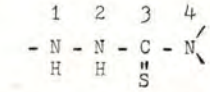
Contrary to PTS itself, phenylazothioformamide is highly fungitoxic both at pH 7.0 and at pH 5.0. Like for PTS its antifungal action is antagonized by adding thioglycollic acid to the culture medium. It appeared that in aqueous solution thioglycollic acid, which is a strongly reducing agent, hydrogenates phenylazothioformamide with formation of PTS:



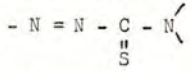
There is no further chemical reaction between PTS and thioglycollic acid.

These observations clearly indicate that in fact PTS is not fungitoxic at all and that its apparent activity under normal growth conditions is entirely based upon its oxidative conversion into phenylazothioformamide, which is the actual fungicide. It is clear also that the low *in vitro* activity of PTS at pH 5.0 is due to its very slow rate of oxidation at this pH. Again, thioglycollic acid is an effective antagonist of PTS because it prevents its oxidation, even at pH 7.0. Or to say it more precisely: thioglycollic acid is in fact only an antagonist of phenylazothioformamide.

These observations provide a rationale for the structure-activity relations shown a few moments ago. Only those substituted thiosemicarbazides were found to be active fungitoxicants *in vitro* which possess the structural element



It is clear that the replacement of the hydrogen atoms at the nitrogens 1 and 2 by organic substituents prevents the formation of the structural element



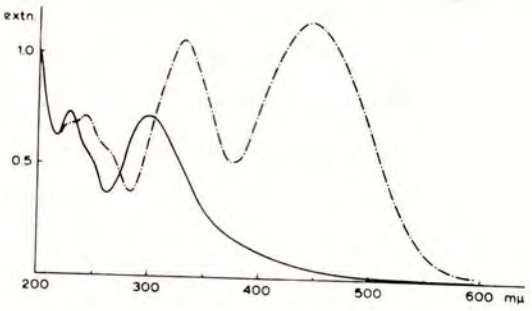
which is considered essential for activity.

We may thus say that the presence of hydrogen at the nitrogen atoms 1 and 2 is a prerequisite for *in vitro* fungitoxicity within this class of compounds. That it is not the *only* condition for activity is evident from the non-activity of 1-benzylthiosemicarbazide and the much lower activities of derivatives carrying substituents at nitrogen atom 4. All "active" thiosemicarbazides exhibited the red discolouration in the culture medium which is characteristic for the azothioformamide structure, whereas the others did not.

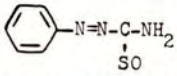
In our attempts to find more suitable chemical systems for the oxidation of PTS we ran into a second oxidation product with high *in vitro* antifungal activity. Upon oxidizing PTS with hydrogen peroxide in aqueous solution we obtained a red crystalline compound, very similar to phenylazothioformamide, but with a rather different ultraviolet spectrum. In Fig.4 the spectra of phenylazothioformamide and of the new oxidation product are shown.

Figure 4

Spectrum of phenylazothioformamide ——
and of the product formed upon oxidation of PTS with H_2O_2 -·-·-

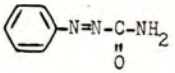


The molecular formula of the new compound is $C_7H_7N_3OS$ and it thus differs from phenylazothioformamide ($C_7H_7N_3S$) by one oxygen atom. Reduction with hydrogen sulphide or thioglycollic acid yielded back the starting material PTS. This observation, in combination with spectroscopic evidence led us to the following structure for the new oxidation product:



phenylazothioformamide-S-oxide

This compound proved to be as active a fungicide as phenylazothioformamide and to have an identical antifungal spectrum. Its action was, again, antagonized by thioglycollic acid. Upon further oxidation with hydrogen peroxide in alkaline solution the compound was transformed into phenylazoformamide:



which is completely devoid of fungicidal activity.

Whereas within this class of compounds the structural requirements for activity seem to have been established fairly well, we are still completely ignorant regarding their biochemical mode of action. At present only negative clues have been established: there is no significant interference with respiration and no specific antagonists -except reducing agents- are known. The interesting practical aspects of this new class of fungicides warrant a complete investigation as well of this aspect of their antifungal action.

Acknowledgment

The author wishes to thank the Board of N.V.Philips-Duphar, Weesp, the Netherlands, for permission to report these results.

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DETERMINATION OF RESIDUES OF BROMOPHOS AND BROMOPHOS-ETHYL

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SUMMARY

Bromophos and Bromophos-ethyl residues can be determined either colorimetrically after saponification and oxidative coupling of the resulting phenol with 4-aminoantipyrin or directly by gas chromatography.

The O-analogues Bromoxon and Bromoxon-ethyl which may be relevant to toxicity can be determined colorimetrically or by thin layer chromatography.

The residues of the O-analogues formed in different crops are on average 1% of the Bromophos residues.

An identification method for residues of Bromophos and Bromophos-ethyl on crops is described.

INTRODUCTION

Bromophos and Bromophos-ethyl are common names for O,O-dimethyl- and O,O-diethyl-o-2,5-dichloro-4-bromophenyl-monothiophosphate

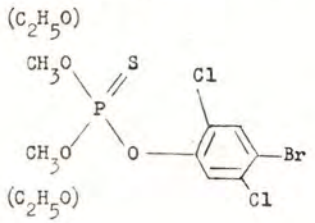

Fig. 1: Bromophos (Bromophos-ethyl)

The first step of the chemical or the biochemical degradation of Bromophos or Bromophos-ethyl can proceed by:

1. saponification of one methoxy or ethoxy group,
2. saponification of the phenoxy group,
3. oxidation of the monothiophosphate to phosphate.

The O-analogues Bromoxon and Bromoxon-ethyl arising from reaction 3 are the only metabolites which may be important for toxicity because they are both strong cholinesterase inhibitors.

The average residue of Bromoxon we found on crops is only about 1% of the residue of Bromophos. The explanation for this low level of the O-analogues can be found in that Bromoxon is generally degraded much faster than Bromophos. For example in blood Bromoxon is degraded about 30 times faster than Bromophos.

In view of the very low content of Bromoxon generally a special determination of this metabolite in the routine analysis of residues is not necessary.

DETERMINATION OF BROMOPHOS AND BROMOPHOS-ETHYL IN CROPS AND ANIMAL TISSUES

1. Extraction

Acetone has been found to be the best and most suitable solvent for the extraction of Bromophos and Bromophos-ethyl from all crops having a low fat content. Crops containing large quantities of fat, such as olives, nuts, etc. and animal tissues are better extracted with acetonitrile or methanol. In view of the volatility of Bromophos and Bromophos-ethyl in steam direct concentration of the extracts is not possible. The acetonitrile, methanol, or acetone extracts are, therefore, diluted with saturated salt solution and the insecticidal compounds extracted with petroleum spirit, b.p. 40 to 60 °C. The petroleum extract, after drying with sodium sulphate, can be evaporated to dryness on a rotating evaporator without loss of the compounds.

2. Purification of the extracts

The petroleum extract is purified using a Florisil column. The Florisil is brought to a definite activity by adjusting the water content to 5%. A mixture of petroleum - benzene 1:1 is used as eluting solvent.

Plant pigments, other interfering substances, and all co-extracted metabolites of Bromophos and Bromophos-ethyl are retained on the column. To achieve good separation the petroleum used must be free of polar impurities which can be removed by chromatography on basic alumina.

3. Colorimetric determination

The eluate from the Florisil column is evaporated to dryness and the Bromophos is saponified with sodium methylate solution.

The resulting 2,5-dichloro-4-bromophenol is oxidatively coupled with 4-aminoantopyrin at pH 7.6 using the method developed by E. I. Emerson and modified by R. Haslinger and W. Struns. The red pyrazolone dye formed is extracted with chloroform and determined at the absorption maximum of 480 mμ. This method of determination is of high specifity: only phenol containing phosphoric acid esters as for example Ronnel or Nemacide can interfere.

Occasionally there was interference in the formation of the dye during residue determinations in crops containing mustard oil such as radish, onions, etc. This interference could be overcome, however, by increasing the amount of potassium ferricyanide solution added. The strongly reducing extracts appear to reduce the oxidant necessary for the formation of the dye, resulting in incomplete dye formation.

4. Gas chromatographic determination

The eluate from the Florisil column can be used directly for gas chromatographic analysis after evaporation and making up to a definite volume with n-hexane.

The following experimental conditions are used:

apparatus:	Varian Aerograph Model 1200
column:	5% SE 30 on Chromosorb W DMCS 60 to 80 mesh; length 1 m; diameter 1/8 inch
detector:	thermoinic detector hydrogen: 9 ml/min air: 170 ml/min
carrier gas:	nitrogen: 20 ml/min
temperatures:	inlet and detector 220 °C column 200 °C.

The detection limit is 0.001 to 0.005 ppm using 100 g crop for the analysis.

5. Results of residue analysis:

Table 1 shows some typical results of residue analysis in crops.

Table 1

Bromophos residues on crops

Crops	Dosage of active ingredient	Days between treatment and sampling 7	14
Apples	0.05%	0.9 ppm	0.5 ppm
Cherries	0.05%	0.07 ppm	0.02 ppm
Lettuce	0.015 g/m^2	0.17 ppm	0.04 ppm
Cauliflower	0.040 g/m^2	0.11 ppm	0.02 ppm

The relatively high residues in apples result from the concentration of the compounds in the wax layer of the apple peel as could be shown by analysing the wax layer, the peel, and the peeled fruits individually.

DETERMINATION OF BROMOXON IN CROPS

The only toxic metabolities of Bromophos and Bromophos-ethyl are the corresponding O-analogues. Bromoxon can be determined as follows:

1. Extraction

The extraction procedure is the same as that of Bromophos.

2. Chromatographic purification

The petroleum extract is evaporated and the residue dissolved in methanol. An equal volume of water is added and the extract chromatographed on a polyamide column using a methanol water mixture 1:1 as eluting solvent. Bromoxon is eluted with the first fraction as shown in Figure 2. The eluate is diluted with saturated salt solution and Bromoxon extracted with petroleum.

3. Colorimetric determination

Bromoxon can be determined colorimetrically after saponification in the same way as Bromophos.

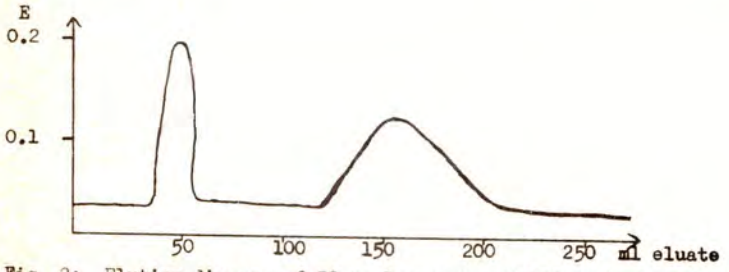

Fig. 2: Elution diagram of 50 µg Bromoxon and 100 µg Bromophos from a polyamid column.

A gas chromatographic determination of Bromoxon is not possible because it is liable to decomposition during chromatography.

4. Semi-quantitative estimation by means of thin layer chromatography

The thin layer chromatographic method of Ali El-Refai and T. L. Hopkins was modified for the semi-quantitative estimation of Bromoxon.

The residue of the petroleum extract is dissolved in n-hexane and 1, 2, and 5 ul of the solution from each sample are spotted on a cellulose plate. Simultaneously 1 ng Bromoxon is spotted as standard for comparison. The plate is impregnated with dimethylformamide and developed with n-hexane. The plate is then sprayed with an enzyme-indicator solution prepared of human serum and bromthymol-blue and, after 20 minutes incubation, sprayed with a substrate solution containing acetylcholin hydrochloride. Bromoxon appears as a blue spot on a yellow-green background. The Bromoxon content is estimated by comparison of the intensity of the spots. The detection limit is 0.02 ppm.

5. Results of Bromoxon determination

For illustration the results of the examination of spinach are shown in Table 2. The average Bromoxon content was about 1% of that of Bromophos. Similar examination of apples showed a Bromoxon content between 0.1 and 1% of the corresponding Bromophos content.

Table 2

Bromophos and Bromoxon residues in spinach

Days between treatment and sampling	ppm Bromophos	ppm Bromoxon
0	8.8	0.08
3	6.6	0.07
5	5.4	0.06
7	3.0	0.04
14	0.3	<0.02

IDENTIFICATION OF BROMOPHOS AND BROMOPHOS-ETHYL RESIDUES

For the purpose of basket and market control it is important to be able to distinguish Bromophos and Bromophos-ethyl from other insecticides.

The method of K. C. Walker and M. Beroza was used as the basis for the identification of Bromophos and Bromophos-ethyl residues. The Rf-values determined by these authors were compared with Rf-values of Bromophos and Bromophos-ethyl obtained under the same conditions, after checking the reproducibility of the given values. Bromophos and Bromophos-ethyl can be detected on thin layer plates with 4-p-nitrobenzylpyridin after the method of A. A. Watts and can be distinguished in this way from all insecticides containing no organically bound phosphorus.

The differences between the Rf values of the phosphoric acid esters shown in Table 3 are too small to distinguish between these insecticides.

A separation of these phosphoric acid esters is possible, however, after saponification and thin layer chromatographic examination of the resulting degradation productions. Table 4 shows the products of saponification of the phosphoric acid esters; the Rf values of the phenols were determined after locating the spots with N-chloro-2,6-dinitro-p-benzoquinoneimin.

Table 3

Rf values of insecticides developed in benzene

Insecticide	Found	Walker et al
Bromophos	0.63	-
Bromophos-ethyl	0.67	-
Ronnel	0.64	-
Nemacide	0.61	0.59
Carbophenothion, Dicapthon, Disyston, EPN, Ethion, Phorate, Phostex		0.52 to 0.65

Table 4

Rf values of phenols

Insecticide	phenol after saponification	Rf value ethanol	Rf value benzene	colour
Bromophos, Bromophos-ethyl	2,5-dichloro-4-bromophenol	0.70	0.35	grey-blue
Ronnel	2,4,5-trichlorophenol	0.68	0.35	grey-blue
Nemacide	2,4-dichlorophenol	0.70	0.43	grey-blue
Carbophenothion	4-chlorothiophenol	0.70	0.83	orange
Dicapthon	2-chloro-4-nitrophenol	0.63	0.09	olive
EPN	4-nitrophenol	0.68	0.05	brown

Bromophos, Bromophos-ethyl, and Ronnel cannot be distinguished from each other using this method. The first two form the same phenol compound; and the differences of Rf values are too small to distinguish 2,5-dichloro-4-bromophenol from 2,4,5-trichlorophenol.

Using gas chromatography, however, with the experimental conditions given above a distinct separation of Bromophos, Bromophos-ethyl, and Ronnel is possible.

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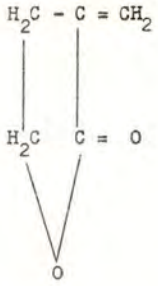
SESSION 6B

DISCUSSION

Professor Van der Kerk: May I tell you of some recent work that has been done in Holland with regard to natural resistance to infection in tulips. Tulip bulbs are normally resistant to rots until two weeks before harvest, after which they become susceptible to fungal infections. At the Bulb Research Institute at Lisse, the compound responsible for this natural resistance has been isolated and it has been

characterized in my laboratory at Utrecht (T.N.O.). The structure is as follows:



The compound is present as a glycoside and we have found that when it disappears from bulbs, they become susceptible.

Dr. C. R. Worthing: Would it be possible to synthesize the precursors of these naturally-occurring substances which impart resistance to attack and feed them to plants to enhance their endogenous production.

Dr. J. T. Martin: We really know very little about the biochemical processes associated with the formation of these substances and until the biochemical pathways have been unravelled it would be impossible to judge whether such a technique would be feasible.

Mr. C. A. Collingwood: Could you comment on the poor results which we got from the use of phorate granules for the control of bean aphid in 1967 and which have been attributed to dry soil conditions in June?

Dr. I. J. Graham-Bryce: I have heard that phorate is not very satisfactory for the control of bean aphid. This is probably attributable to poor uptake which is conitioned by the distribution of the absorbing roots. In potatoes, the granules are placed immediately under the tubers and uptake is quite rapid but in beans the distribution of roots in the soil is quite different and it is possible that absorption is less rapid and consequently systemic control resulting from granular application is not so successful.

Mr. J. F. Newman: I would endorse this. When potato tubers start to grow adventitious roots arise around the base of the growing shoot. In the broad bean, one would expect that the absorption pattern would be different since the bean sends a main root straight down through the soil.

Mr. M. J. Way: It has been our experience that phorate gives longer protection than menazon in potatoes. In Brussels sprouts, however, menazon seems to give the better protection than phorate.

Dr. I. J. Graham-Bryce: I find it difficult to interpret differences between different crops growing in different soils without going into precise details in each case. It is clear nevertheless that the factors controlling entry into the plant may be as important in determining systemic protection as the soil conditions which determine availability.

Mr. C. E. Metcalfe: We have found that the carrier used in the granules is important. Can you tell me what carriers were used in these experiments?

Dr. I. J. Graham-Bryce: Both pumice and Fullers Earth were used as carriers but it is not possible to distinguish differences although I accept that the formulation of granules may be important in determining uptake.

Professor S. H. Crowdy: Can you tell us something about the systemic activity of these fungicides. Were you able to recover them from the tops of treated plants?

Professor van der Kerk: We have recovered P.T.S. from treated plants but not its oxidation products. It would seem that the fungus carries its own "lethal factor" in the form of oxygen and this gives rise to the oxidised compound which is highly toxic.

Dr. A. H. McIntosh: P.T.S. seems to be systemic when applied to foliage or to roots from water culture. Is it systemic in your experience when applied to soil around growing plants? At Rothamsted we have had no success with P.T.S. applied to the soil to control potato blight (Phytophthora infestans).

Professor van der Kerk: Our experiments have all been carried out in water culture but it is reasonable to suppose that P.T.S. will be broken down by soil micro-organisms.

Mr. R. Paquet: How stable are these fungicides?

Professor van der Kerk: They are very unstable.

Mr. C. E. Dyte: Does the sesamex-sensitive factor in the third linkage group give any cross-tolerance of Pyrethroids?

Dr. R. M. Sawicki: No.

Dr. C. R. Worthing: The growth retardants CCC and B-nine are used to produce dwarf pot chrysanthemums. We have examined the effect on populations of Myzus persicae and glasshouse red spider mite (Tetranychus urticae) on chrysanthemums following such treatments. Whilst the results are still being analysed I think it is clear that there is no major effect on the populations of red spider mite. This is not inconsistent with Dr. Smith's suggestion that growth retardants restrict the number of suitable habitats in the host plant which the pest can attack.

INFLUENCE OF FORMULATION ON THE BIOLOGICAL EFFECTIVENESS OF INSECTICIDES

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Summary

A formulation should provide a convenient vehicle to enable a small quantity of pesticide to be distributed uniformly over a large target area and it should present the toxicant to the pest in a way that will optimise its biological efficiency.

The first requirement is met by selecting an appropriate type of formulation for the particular application and examining its physical and chemical properties together with its applicational characteristics. The second requirement can be met by studying the interaction of the toxicant with the environment in which it is to be used. The environments in which insecticides are commonly used include the atmosphere, water, soil and foliage; the interactions which may occur between the toxicant and these environments are listed and discussed briefly.

Examples are given of formulations which have been developed to modify the persistence of a toxicant in each of these important environments. The examples include plastic generators to control the release of dichlorvos vapour into the atmosphere, expanded plastic formulations of 'Abate' (O,O,O′,O′-tetramethyl-O,O′-thiodi-p-phenylene phosphorothioate) for application to water, the use of chlorfenvinphos granules in soil and water-in-oil emulsions of monocrotophos on foliage.

INTRODUCTION

A pesticide formulation should be designed with two requirements in mind. Firstly, it should provide a convenient vehicle by means of which a small quantity of pesticide may be uniformly distributed over a large target area or throughout a large volume of air or water. Secondly, it should provide a means of presenting the toxicant so as to optimise the biological efficiency of the toxicant after application.

The first of these requirements may be met by selecting the most appropriate type of formulation - dust, wettable powder, emulsifiable concentrate, granule, aerosol, bait - for the particular application, examining its ease of manufacture and the physical and chemical properties of the formulation together with its handling, storage and applicational characteristics. Selection of the most appropriate ingredients and extensive laboratory testing of the resulting formulations will take a considerable amount of time and effort, but by this approach it is possible to prepare products which are very good in terms of the first definition given above. However, a formulation which is developed purely on the basis of physical and chemical tests may well not possess optimum biological performance and it is here that the second requirement becomes important.

If the formulation is to provide the best means of presenting the toxicant to the pest, it is necessary to know just what will happen to the toxicant after it has been applied and to know the behaviour of the pest to be controlled. A study is required of the interaction of the toxicant itself with the environment in which it is to be used. These interactions may be physical, chemical, biophysical or biochemical and will, of course, vary with the nature of the environment, with the mode of action and chemical nature of the toxicant and with the life history of the pest. Within the space of a short paper, it is obviously impossible to discuss this enormous field of work in any detail or to delineate the many and varied problems that arise, since these will be specific to a particular toxicant and to a particular type of outlet. What can be done is to consider the more important interactions that may occur in the commonest environments into which pesticides are

placed and briefly to provide examples of the way in which the efficiency of an insecticide may be increased by improving its persistence in the environment to which it is applied.

The environment in which insecticides are used include various combinations of the atmosphere, water, soil and foliage. The complexity of these environments, in terms of their effect on the behaviour of the insecticide, varies considerably.

The Atmosphere

Insecticides are used in the atmosphere as fumigants or space sprays. Space sprays, or aerosols, usually contain non-volatile insecticides and the activity of these is closely related to the drop size of the spray. This is governed by the physical properties of the formulation and the type of atomiser used, as well as by the volatility of the solvents present in the formulation.[1] Assuming that the treatment is carried out in an enclosed space, activity will be lost by the physical processes of sedimentation and impaction of the spray drops and also by decomposition of the toxicant by hydrolysis, oxidation or photochemical action.

For fumigant activity, the vapour pressure of the insecticide must be high enough for a suitable concentration of vapour to be produced in the atmosphere and this concentration must be maintained for a sufficient length of time to kill the insects. In an enclosed space, the desired activity may be lost by adsorption of the vapour on any available solid surface and by chemical decomposition of the toxicant as mentioned previously.

Most insecticides used as fumigants are materials with a relatively high vapour pressure so that the main problem in their use is not one of getting a sufficiently high concentration in the atmosphere but of maintaining a suitable concentration for a time long enough to obtain insect control over the desired period. Consider dichlorvos (I)

$$(CH_3O)_2 - \overset{O}{\overset{\uparrow}{P}} - O - CH = CCl_2$$

(I)

whose saturation concentration in the atmosphere at normal temperature is around 400 µg/litre. This is approximately 10,000 times as much as is needed to kill quite a large range of insects, provided that the concentration can be maintained for the periods of time shown in Table 1.[2]

Table 1

Activity of Vapona* vapour

Species	LT95 at 0.03 Microgrammes per litre
Musca domestica	2.8 hours
Aedes aegypti	1.8 hours
Blatella germanica	5.0 days
Tribolium confusum	3.1 days
Lasioderma serricorne	3.5 days
Sitophilus granaria	7.0 days
Vespula germanica	3.2 hours
Acyrthosiphon pisum	1.8 days
Tetranychus telarius	7.9 days

* 'Vapona' is the Shell trade mark for an insecticide containing a minimum of 93% w dichlorvos.

Unfortunately, dichlorvos vapour is rapidly lost from the atmosphere, as illustrated by curve A, Fig. 1 which shows the decrease in atmospheric concentration in an enclosed chamber following the release of 100 µg/litre of dichlorvos as an aerosol.[2] The situation can be improved greatly by formulating dichlorvos so as to

provide a slow continuous release of insecticide and this may be achieved by using the dichlorvos as a co-plasticiser in a polyvinyl chloride matrix. The formulation consists of 21.4% w Vapona in PVC in the form of a strip 10 in. x 2.5 in. x 0.25 in. thick. This generator is designed to give insect control within 1000 cu. ft. of enclosed or semi-enclosed space for 10 to 15 weeks. The concentration of vapour produced in an enclosed chamber is shown by curves B and C in Fig. 1; the difference between the curves shows the considerable effect that atmospheric moisture has on the availability of dichlorvos since curve B was obtained at a relative humidity of 30% while curve C was obtained at a relative humidity of 70%.[2]

A direct comparison between the performance of the aerosol and slow-release formulations as shown in Fig. 1 is not altogether fair. The initial concentration produced by the aerosol formulation was 100 µg/litre, whereas the plastic strip contained initially about 10 times this quantity; that is, if all the dichlorvos in the plastic strip were released at zero time, it would provide a concentration of 1000 µg/litre.

If it were possible to apply the aerosol to give a concentration of 1000 µg/litre, then curve A would be moved to higher concentrations and longer times. However, even if this ten-fold increase was maintained over the whole decay period, the atmospheric concentration obtained from the aerosol would still fall below that obtained from the generator after 7 - 10 days. In any case, the decay curves shown in Fig. 1 are obtained under the ideal condition of a totally enclosed chamber. When ventilation occurs, the activity of the aerosol fumigant would be rapidly and irreversibly lost, whereas the slow-release generator would still provide a reduced concentration, and when the ventilation was removed (as for example at night) the full atmospheric concentration as shown in Fig. 1 would be re-achieved.

The actual concentration of dichlorvos released shown in Fig. 1 can be modified by minor changes in the formulation or by changing the physical dimensions of the plastic generator. Thus, the level of activity and the persistence of the generator can be varied readily and matched to the requirements of any given outlet.

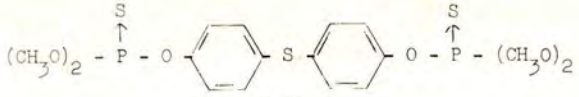
Aqueous environment

In many respects, the application of insecticides to water is analogous to their application in the atmosphere. Water-soluble insecticides are somewhat analogous to fumigants and water-insoluble insecticides are applied as dispersions of emulsions or suspensions which behave similarly to space sprays in the atmosphere.

In addition to these applications to the bulk of the water, there is the possibility of using oils which spread in a thin film over the water surface. The oil can be formulated such that the toxicant remains within this film to control pests which spend some part of their life cycle in the surface layers of the water, or it may be formulated so that the toxicant diffuses out of the film and dissolves in the bulk water phase. In the latter case, the spreading oil may be used to assist in the uniform distribution of the toxicant throughout the water phase or to act as a controlled release generator to modify the persistence of the toxicant.

When toxicants are applied to water, hydrolysis, microbiological degradation and adsorption to solid surfaces such as mud are the most important factors likely to limit biological activity. In addition, if dispersions of solid toxicants are used, sedimentation of the particles may also reduce the activity. It is difficult to modify the adsorption of a toxicant to a mud surface in any practical way, and, in general, this factor must be lived with and taken into consideration in making the decision as to whether to progress an experimental toxicant for a purpose that requires application in an aqueous environment. Both chemical and microbiological decomposition of water-soluble toxicants can be controlled by the use of slow-release formulations which can be developed along similar lines to those described for dichlorvos. Of course, it is essential that the formulation should be so designed that the toxicant cannot be decomposed while it remains within the generator and that it is released at a rate that matches its decomposition and that allows a toxic concentration to be maintained in the water.

An example of such a formulation has been reported recently[3] for Abate (II), a promising new mosquito larvicide (LC_{50} of 0.005 ppm to the larvae of Aedes spp).



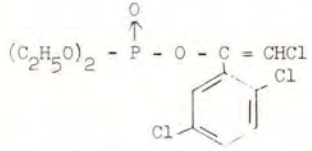
(II)

The problem was to apply this compound to water in a way that would allow a toxic concentration to be maintained for several weeks despite the fact that the toxicant is inactivated through hydrolysis and adsorption. Formulations similar to the Vapona strip containing 5% w toxicant and based on PVC and dibutyl phthalate were tried, but were completely ineffective. The addition of 10% w Triton X-100 doubled the rate of toxicant release from the formulation but still insufficient toxicant was released to be effective. The plastic was then expanded by adding small quantities of ammonium carbonate, citric acid and water as blowing agents and the resulting formulations were highly effective and gave a persistent effect.[3] The expanded plastic was applied in the form of "biscuits", 2 in. diameter blocks, and their only disadvantage was that they had to be weighed down in water.

Soil environment

Soil is a much more complex environment than either air or water and generalisations on the behaviour of toxicants becomes much more difficult and usually meaningless. Nevertheless, one important generalisation that can be made is that adsorption of the toxicant to the surface of the soil will play a dominant role in determining the activity and fate of the toxicant.[4] Adsorption not only influences the proportion of the applied dose of toxicant that is available to kill the pest but it also governs the extent to which the toxicant is leached through the soil and the rate at which the toxicant is decomposed, either chemically or microbiologically. As in the case of the aqueous environment, it is difficult to modify adsorption by means of formulation but formulations that control the release of a toxicant can be used to modify some aspects of soil behaviour.

Rapid degradation of organophosphorus insecticides by soil is frequently a problem where a persistent effect is required. Provided that the kinetics of the toxicant degradation are not zero-order, and provided that the toxicant is prevented from decomposing while it remains within the formulation, a slow-release formulation can have a very beneficial effect on the persistence of an insecticide. The behaviour of chlorfenvinphos (III)



(III)

in soil provides a useful example.

Chlorfenvinphos is a highly active insecticide against the major root-fly pests; it is relatively strongly sorbed by soil and has a good hydrolytic stability. However, in soil it is decomposed microbiologically; the time for half the applied dose to decompose varies considerably between different soils but is usually in the range 3 - 5 weeks. This order of lifetime is likely to be insufficient when the insecticide is applied as a pre-sowing treatment to a crop such as carrots which may need protection over a period of months.

This problem can be overcome by the use of granular formulations designed to provide a slow-release of toxicant. The way in which the release of chlorfenvinphos from granules can be controlled has been described elsewhere.[5] Two granular formulations were selected for field trials; one that released all its toxicant within 2 in. of rain in a standard simulated raining test[6] and one that released only 25% of its toxicant in 2 in. of simulated rain. The performance of these two formulations for the control of carrot fly (Psila rosae) in the U.K. was compared with that of a 50% w/v emulsifiable concentrate of chlorfenvinphos. In an attempt to

reduce the microbial decomposition of chlorfenvinphos, 3% w pentachlorophenol was added to the slow release granule formulation and this formulation was also included in the tests. The trial was started in May when the formulations were applied as broadcast treatments to the soil surface immediately before drilling and the treatments were incorporated to a depth of a few inches. Infestation by carrot root fly was expected to become serious in early August and the trial was assessed in November (after 5 1/2 months). Each treatment was replicated 4 times in a randomised block design and the results are briefly summarised in Table 2.

Table 2.

The use of Birlane* for the control of carrot root fly in the U.K.

Formulation	Application rate (lb/acre)	% un-marketable carrots
50% w/v EC	3	10.4
50% w/v EC	6	7.0
10% w granule (fast release)	4	8.3
10% w granule (slow release)	4	4.3
10% w granule (slow release) (plus PCP)	4	0.5
Control plots		31.4

*Birlane is the Shell Trade Mark for chlorfenvinphos.

These results suggested that the application of slow release granules containing PCP was the most effective treatment, though a statistical analysis showed that this treatment was not significantly different from that due to the slow release without PCP. However, the performance of both the slow release formulations was significantly better ($p<0.01$) than the fast release granules and also more effective than the EC applied at 6 lb/ac.

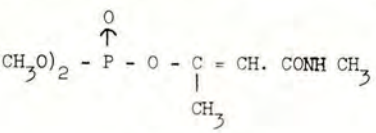
Foliage

Foliage is the most complex environment of all. Insecticides are usually applied to foliage by means of sprays and dusts though granules are also becoming important for the treatment of those crops whose leaves can collect and trap them. The requirements in a foliar deposit depend on whether the insecticide acts through contact or systemic activity and, if the former, on whether or not the pest is mobile. The way in which these requirements may be built into a formulation will vary with the nature of the foliage surface, in particular its wettability and the ease with which the insecticide can penetrate either the plant wax or the cuticle, or both. Also to be taken into account with some insecticides is the safety margin in activity (the difference between an insecticidally active dose and a phytotoxic dose) since this can be increased or decreased considerably by the type of formulation and by the ingredients used in formulations.

The formulation can affect many aspects of spray performance including the drop size of the spray, its evaporation rate and its impaction efficiency, the coverage of the target by spray, the retention of spray liquid on the target, the deposition of insecticide and the physical form of the deposit, and finally the persistence of the deposit. Of all these aspects, persistence of the deposit is the one which most frequently proves to be a problem in the development of any new insecticide. Persistence is either too great, so that unacceptably high residues remain in crops at time of harvest, or too low so that insecticidal activity is lost before satisfactory protection of the crop is achieved. In these days, the latter is more common than the former. The activity of insecticide deposits can be lost in a variety of ways; by physical means such as volatilisation, weathering by wind or rain and by penetration of a contact insecticide into the leaf cuticle, by chemical or photochemical decomposition on the leaf surface, and by biochemical degradation within the leaf or plant. It can be very difficult to establish the causes of lack of persistence of a particular insecticide since frequently it is due to a

combination of many of the above factors. However, it is essential to determine at least the major causes of loss if the problem is to be overcome.

With water-soluble toxicants, it is obvious that the resistance of foliar deposits to rain is likely to be poor. Such is the case with monocrotophos [Azodrin, *(IV)]



cis isomer (IV)

which is highly effective against a wide variety of insects but which is miscible with water. The performance of this compound following rain, when tested against chewing insects, can be improved considerably by formulating it as an invert (water-in-oil) emulsion. The order of improvement is shown in Table 3 which summarises results obtained on the performance of monocrotophos against larvae of the Large White Butterfly (Pieris brassicae). Whole cabbage plants were sprayed in the glasshouse with four dosages of monocrotophos applied in a spray volume equivalent to 10 litres/hectare. Two formulations are compared in Table 3; one is a standard water-miscible concentrate (based on acetone) and the other is an invert emulsion, in which the insecticide was present in the aqueous phase which was then emulsified in xylene, to give a 10:1 ratio of aqueous:oil phases. In addition to the cabbage plants, metal foil targets were also sprayed at the 1% active matter dosage of each formulation, and the targets were analysed chemically to provide a comparison of the actual dosage deposited from each formulation. Shortly after spraying, half of the sprayed plants were exposed to artificial rain for 1 hour, during which time they received the equivalent of 0.83 in. of rain. After the rained plants had dried, they were infested with 10 Pieris larvae, the mortality of which was assessed after a further 24 hours.

Table 3

Rain-fastness of Azodrin formulations.

Formulation	Dosage % a.m. in spray	% kill in 24 hours of Pieris larvae, mean of two replicates			
		Experiment I		Experiment II	
		No Rain	Rain	No Rain	Rain
Water miscible concentrate	3	-	-	-	37
	1*	100	11	100	33
	0.3	55	5	100	11
	0.1	10	0	80	-
Invert emulsion	1*	100	95	-	-
	0.3	95	100	100	100
	0.1	79	67	95	84
	0.03	-	-	85	21

Notes: In Experiment I the rain was applied 1 1/2 hours after spraying.
In Experiment II the rain was applied 1/2 hour after spraying.

* The actual dosage of Azodrin deposited initially, determined chemically in Experiments I and II were 2.11 and 2.59 $\mu g/cm^2$ respectively from the water miscible concentrate and 1.68 and 1.71 $\mu g/cm^2$ from the invert emulsion.

The results clearly show the superior performance of the invert emulsion formulation in terms of rain-resistance. They also indicate that the inherent

* Azodrin is the Shell Trade Mark for monocrotophos.

activity of the initial spray deposit may be greater with the invert than with the conventional formulation.

Conclusions

The biological effectiveness of insecticides is governed by a very large number of factors which vary with the nature of the toxicant, the way in which it is to be applied, and the nature of the pest to be controlled. Many of these factors can be modified by means of formulation, but to do so requires a comprehensive study of the interactions occurring between the toxicant, its environment after application, and the pest. Such a study can be very complex but, by selecting and concentrating on the most important interactions that are likely to ruin the desired biological activity, it is possible to improve the performance of toxicants very considerably by means of formulation. However, in all cases, the formulation must be easy to manufacture, be as cheap as possible, have good storage stability and must always be tailored to the type of application best suited to the various locations where the pest exists.

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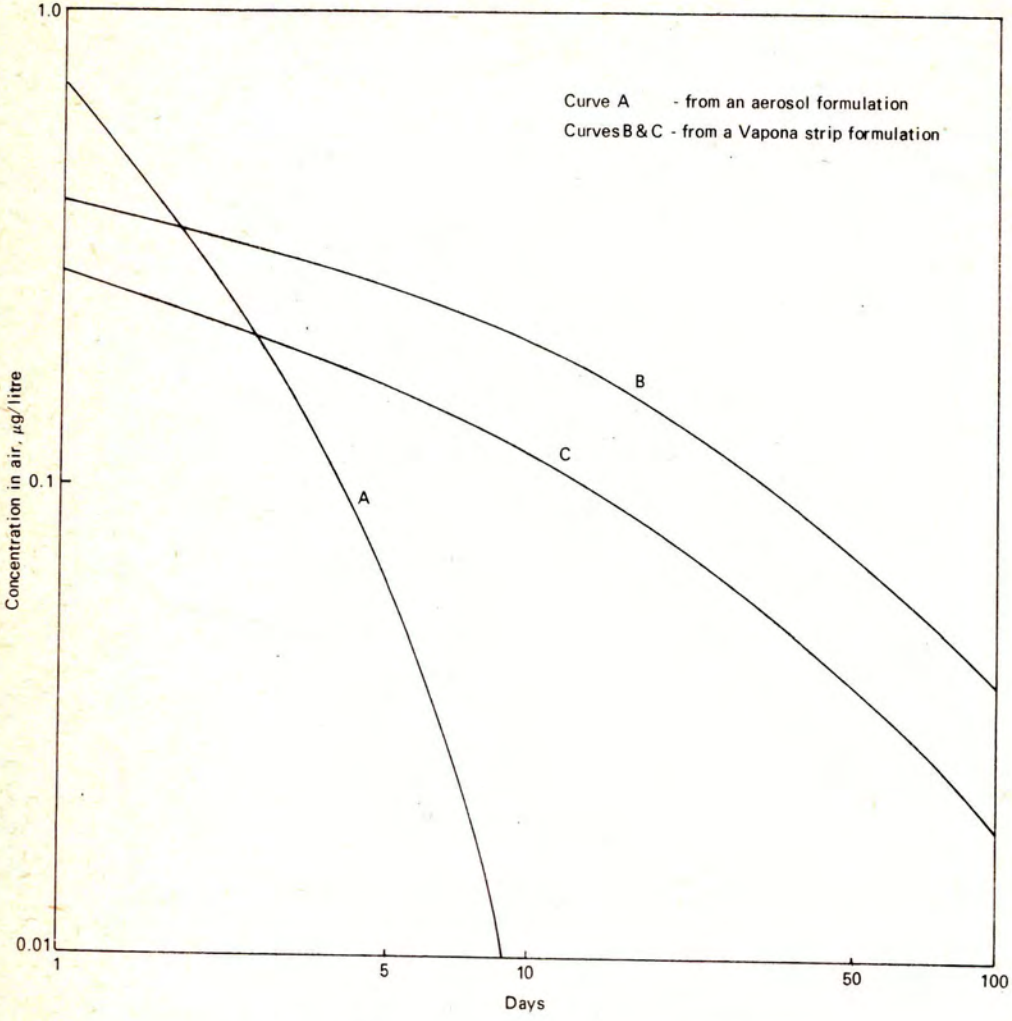

Fig 1 The persistence of Dichlorovos vapour in an enclosed chamber

FUNGICIDES - A DEPOSIT ACCOUNT

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Summary A review is given of the properties affecting the deposits of pesticides on target surfaces. The main properties described are : The application of maximum dose to the target surface, the physical form of the pesticides, the physical properties of the chemical and weathering of the deposit.

To illustrate these properties, the paper describes the effect of different formulations on deposits, volatility and vapour pressure, differences in particle size, effect of surface active agents and rain-washing tests. These tests are described with special reference to drazoxolon.

Early assessment of the properties of formulations is required and the need for liaison between the application specialist, biologist and chemist is stressed.

INTRODUCTION

The experience of being asked to provide a main paper for a Conference such as this, makes one pause, makes one think and makes one try and clarify one's own work and the ideas one has captured from the literature. Three avenues seem to be open - not one of which offers any escape - a review of the literature, a detailed description of experimental work which is novel and of interest to the audience or, the one adopted here, that is, a mixture of the two. As you know crossbreeding and hybridisation have their defects as well as their advantages.

It was pointed out by Potter[1] in the opening remarks of his paper to this Conference in 1963 that it is impossible to review all the factors known to affect the biological efficiency and persistence of insecticides in the time available. This remark must also be used as a cloak when attempting to discuss fungicides, but, out of the multitude of physical and biophysical, chemical and biochemical, biological, applications and other problems involved, the main theme to be developed covers a few simple questions which ought to be asked before, during and after - preferably before and during - a new compound or formulation of a pesticide is being assessed in the field or glasshouse.

The question to be asked is ' Is there the maximum amount of chemical in the best form, at the correct site, at the right time to produce the greatest biological effect '.

Norman[2] in his paper to this Conference in 1965 used as his theme 'No chemical is better than its application' and forecast that chemicals of the future may need a more critical application technique than chemicals of today'.

The application of the maximum dose, is, of course, only one part of this composite and other factors described herein such as physical form, the physical properties of the chemical and weathering have as important roles to play and it may well be, in fact it is proposed here, that the overall best solution can only be resolved by adequate liaison between applicator, biologist, and chemist. Inattention to the factors raised here may well result in the rejection of compounds in field trials - a matter of considerable economic importance to the manufacturer and the community alike.

The machinery will have been designed for a fairly specific job say high volume application to top fruit and if operated properly will perform this function adequately. It may also be that the deficiencies of inadequate cover of the target can be somewhat obviated by e.g. the vapour toxicity Morgan[3] or the solubility of the chemical or systemic activity. It is nevertheless of great importance for assessments to be made of the weight of the chemical on the target at the time the pest arrives, in order to correlate the biological result obtained with the activity of the chemical. A rejection of the chemical, which could result from the lack of it, would be a serious error, yet an extremely small proportion of the papers offered to conferences have any indication of this correlation. Although the machine may perform properly, the nature of the material being sprayed, particularly the physicochemical properties of the liquid has a major effect on the amount retained on the target surface - be it leaf, leaf bud, flower, fruit etc.

The properties of spray fluids

Much has been written on the effect of surface active agents on the initial loading of chemicals in solution or suspension on to leaf surfaces by e.g. Ford & Furmidge [4] and Furmidge [5,6,7,8].

The phenomenon of bounce of droplets from various surfaces has been described by Brunskill [9].

It is however quite possible that the adsorption of the surface active agent on to particles of pesticide and filler in suspension i.e. a reduction in the amount of surface active agent in solution and modification in 'wetting' properties by reaction with other agents may in practice complicate the picture portrayed in these papers.

In the course of the research and development on the fungicide drazoxolon work was carried out to measure the loading on a vine leaf surface. A biological colleague, Mr. R.S. Elias, devised a relatively simple test to measure the maximum loading on this surface, and the resistance of the deposits to rainwashing.

This technique is described in the Appendix 1.

The results from this test can be used to show the difference between various types of formulation, including the effect of wetters, stickers etc. see Figs. 1, 2 & 3. Other similar tests have been described elsewhere e.g. Birchfield & Ovenaga[10], Evans et al.[11]. It is interesting to see Fig. 4 that the use of wetter decreases the effect of rainwashing. This is probably due to an increase of the solubility of drazoxolon in the leaf waxes or a deflocculative effect giving better distribution of small particles.

This technique appears to be most useful for examining certain properties of sprays on chosen leaf surfaces under this condition of application. It was used to examine the deposits of drazoxolon on young vine leaves in the Loire Valley with a fair degree of replication as shown in Table 1. This shows a more than 3 fold difference in loading between the worst to the best formulation.

Table 1

Replicate	ug/cm^2 of drazoxolon on the upper leaf surface		
	Formulation A	B	C
1	8·6	4·1	18·6
2	8·9	4·9	14·1
3	8·9	4·5	15·4
4	10·4	4·6	12·7
5	8·6	4·3	15·0
6	11·2	5·0	13·9
Mean	9·5	4·5	15·0

We may consider at this stage that we have progressed a little way along the path I defined at the beginning of this lecture and are at the stage where we know how to measure the maximum loading on the target surface.

Consideration must now be given to those physical properties of the chemical which affect activity and also, probably the rate of disappearance of the chemical e.g. vapour pressure/volatility, particle size, solubility and weathering. I am not here going to discuss other aspects such as photosensitivity, enzymatic breakdown etc.

Volatility and vapour pressure

Hartley[12] has dealt with some theoretical aspects of the effect of the concentration of vapour from a volatile chemical which may be in the vicinity of an organism. His assumption that it may only be beyond a distance of approx. 10 mm from a leaf surface that wind turbulence greatly reduces vapour concentration does not seem to be borne out by graph of the loss of dieldrin againt time given in Potter's paper[1]. In this paper Potter showed that whereas a change of 100 fold in the size of crystals of dieldrin only altered the loss from a deposit on a glass surface twofold, an increase in the temperature of the ambient air from 20°C to 40°C and in the speed of air from nil to 2·5 m.p.h. reduced the persistence of deposits from about 5 weeks to 4 hr. This condition of temperature and wind could be met under many tropical conditions and the probability of loss of chemical and therefore of biological activity must be a factor of major concern.

The adsorptive nature of the substrate and the reversible desorption may greatly effect the life of a deposit. This effect on building materials has been described by Barlow and Haddaway[13] with reference to insecticides. The mobility of the molecules and therefore the loss by volatilisation may also be modified by 'encapsulation' either deliberate or inadvertent or by the solubilisation of the chemical in the leaf wax. Deliberate encapsulation by film forming agents of solid particles has been known for a very long time and is described for example in Moillet[14].

Inadvertent encapsulation is a trap into which the enthusiastic formulator seeking to improve tenacity and reduce loss by weathering may so easily fall. Although it is not easy to see why two water soluble polymers i.e. PVA and PVB should affect the biological activity of copper differently - as shown by Evans[11], a recent paper by Peries & Dayaratne[15] dramatically shows how fungal hyphae may unrestrictedly grow amongst a deposit of copper particles which have been inadvertently encapsulated and thereby made inactive.

In the case of drazoxolon, which has a partition very much in favour of non-polar solvents, it is suspected that solubility in leaf waxes may be a reason for the lower activity shown against the 'wet' fungal diseases.

The toxicity of drazoxolon in the vapour phase can be demonstrated by for example inverting a beaker, the inside of which has been treated with a formulation of the compound, over a plant infected with cucumber powdery mildew disease is completely eradicated. Similarly a small quantity of the compound, on a cover glass slip, when placed on an infected leaf promotes a circle of inhibition which in the presence of a light wind changes to an ellipse the longer axis being in the direction of the wind.

The vapour pressure of a compound -measured for example- by the Knudsen effusiometer method[16]- is of some help in the assessment of varying activities in a homologous series showing biological activity, but in practice, it is the rate of loss of the chemical from the formulated product, on site, which affects the biological result. The method of Barlow & Haddaway[17] can be modified to use a surface appropriate to the condition of the experiment.

Physical form of the deposit

The effect of surface active agents on droplet bounce and spread have already been mentioned. What have not been considered are the effects caused by such agents, with or without other excipients, on the nature of the deposit left on leaf surfaces. When the machinery specialist is able to report an even coverage of foliage due to the use of an efficient technique no further investigation of the deposit left by these drying droplets is usually carried out. An examination of such deposits shows major differences in the distribution of chemical, in some cases there is a marked concentration in the periphery of the dried deposit. This may result in ring spotting on the crop, or, where vapour phase and solution activity are low, sufficient clear space may be available for fungus spores for example to grow within the confines of the droplet.

The exact cause of this corona effect is not obvious, as it occurs when salts crystallise from solution as well as with suspensions but in the case of drazoxolon reduction in the quantity of surface active agent added, reduces the corona effect giving a more even deposit.

Another phenomenon more well known, is the flocculation of fine particles which also reduces the area covered by the product.

It is a well known fact that in certain circumstances and particularly with fungicides finer particles result in greater biological activity an effect also of marked interest in pharmacology eg. refs 18, 19, 20. The formulator who does not examine the deposit produced on the target may well mislead himself as to the success of his work.

Weathering

The effect of weather - usually considered mainly the effect of rainwashing - is the last factor to be discussed here. Although information is gradually becoming available on this particular aspect, little work appears to be done regarding the effect ot wind which indirectly causes loss of deposit by accelerating the erosive effect of leaves, flexing and rubbing together.

When one tries to define a specification for the velocity, number and size of water droplets to be used in a laboratory rain simulation apparatus there is obviously no standard available. This is not surprising in view of the multitude of variations between the types of precipitation met even in temperate climates. Experimenters have therefore designed their own techniques e.g. refs 10,13,21,22,23 and have shown within the limits of their own experiments, the severity of leaching caused by the application of water sprays.

In the work of Elias, mentioned above, and in Appendix 1 and Fig 3,4, & 5 the effect of rainwashing was examined on a number of formulations of drazoxolon containing various agents. After rainwashing using the technique described in the Appendix 1, for 15 minutes, the amount retained varied from 0 to 86%.

Exposing a further series of discs to 'dew' for 40 hrs produced a loss of deposit of approx. 30% of the initial load. The 'dew' was produced in the super-saturated atmosphere of a humidity cabinet.

It is well known that there may be a factor of times 10 between the dosage of a pesticide required to control pests in the glasshouse and in the field. Someday, someone perhaps, will deal with this in much greater detail than has been done in this lecture. It needs no great arithmetical ability to sum up the results of bad spray application, poor formulation and leaching. It is easy to see that any of these factors will lead to poor biological control and any biological control, if the factors were additive, would be miraculous.

A great deal of work has gone into the preparation of chemical specification such as those issued by the Ministry of Agriculture Fisheries & Food, W.H.O. etc but in biological practice these may be the least important factor in this complex. The simple tests described here give a basis for the early assessment of formulations. A standardisation of such tests to cover the many aspects of pesticide evaluation should be evalued by a group of people experienced in application, the physical chemistry of formulation and the appropriate biological discipline. Until these are available those assessing the biological activity of chemicals in the field should determine the quantity of the chemical on the target they are using to ensure that failure is not due to the simple explanation that there was no chemical available to exert its effect.

The general remarks I have made are primarily associated with work done on a fungicide. They apply equally to the investigation of the activity of herbicides, insecticides and other pesticides no matter which technique is used.

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Appendix 1

Vine leaf - wetting test

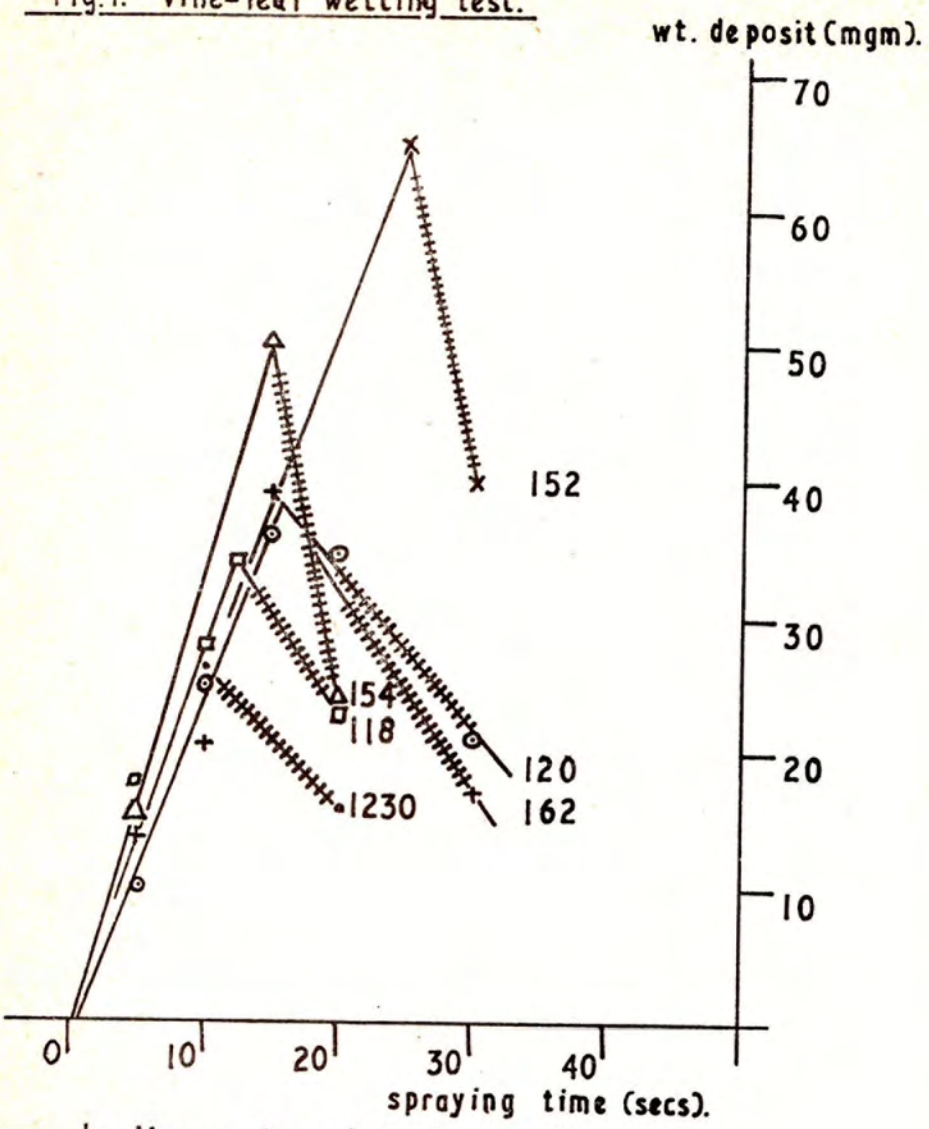
Leaf discs, diameter 22 m.m. were cut from one mature but relatively young leaf taken from vines (var. Black Hamburg) grown in pots in a glasshouse. Each disc was weighed on a B.T.L. 0·5g torsion balance before spraying, then pinned to a cork so that the upper leaf surface was vertical and at right angles to the spray axis. The disc was then sprayed with the appropriate formulation for a known time from a distance of 2'9" using a De Vilbiss Aerograph type M.P. gun at 10 p.s.i. The disc was then reweighed to find the weight of the wet deposit. The maximum weight of spray solution that the disc could retain before run off occurred gave a measure of the wetting properties and retention of the formulation. With this simple test the wetting properties of various formulation can be compared.

Vine leaf - rainfastness test

Vine leaves (var. Black Hamburg) of similar age and about 18 cm long by 14 cm wide were taken from 6 month old plants grown in pots in a glasshouse. The upper surface of each leaf was sprayed from a distance of 18" using a De Vilbiss type M.P. gun at 10 p.s.i. Each leaf was sprayed for 5½ sec. to give an even cover of fine discrete drops without run off . Three leaves were sprayed with 0·3% and 0·15% suspensions of the active ingredient. From these sprayed leaves, discs of 22 m.m. diameter were cut out with a cork borer. Six replicate discs, two from each leaf were set aside to determine the amount of active ingredient present before rainwashing. Twelve discs, 4 from each leaf were used for each rainwashing time. The discs were pinned round the external vertical edge of a 11·5 cm cork boiling ring. These cork rings were put on a turntable each ring rotating on its own axis every 2½ sec., the turntable revolving 8 times per minute. An Aerograph gun was placed at right angles to the discs at a distance of 3'4". Rainwashing was done for times varying between 5 and 80 min. at 40 p.s.i. using tap water.

A product whose rainfastness had been checked in the field and by other tests i.e. 'Perenox' was used to check the severity of the test.

Fig. 1. Vine-leaf wetting test.



——— loading up to point of run-off.

+++++ loss occurring after run-off.

Numbers indicate identity of experiment with Drazoxolon.

Fig.2. The effect of the concentration of wetter (Agral 90) on the retention of a spray "solution" of Drazoxolon on vine-leaf discs.(held vertically).

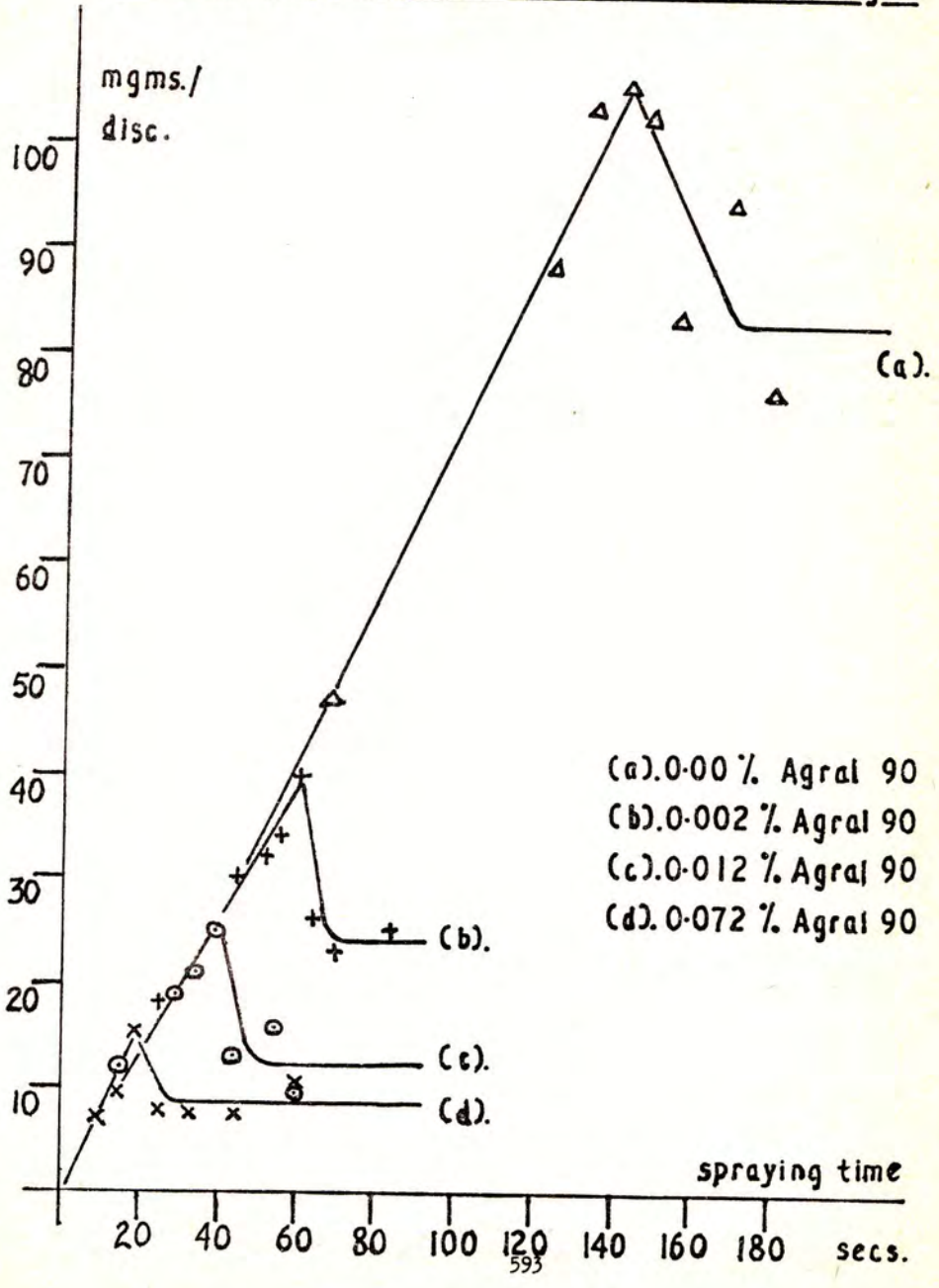
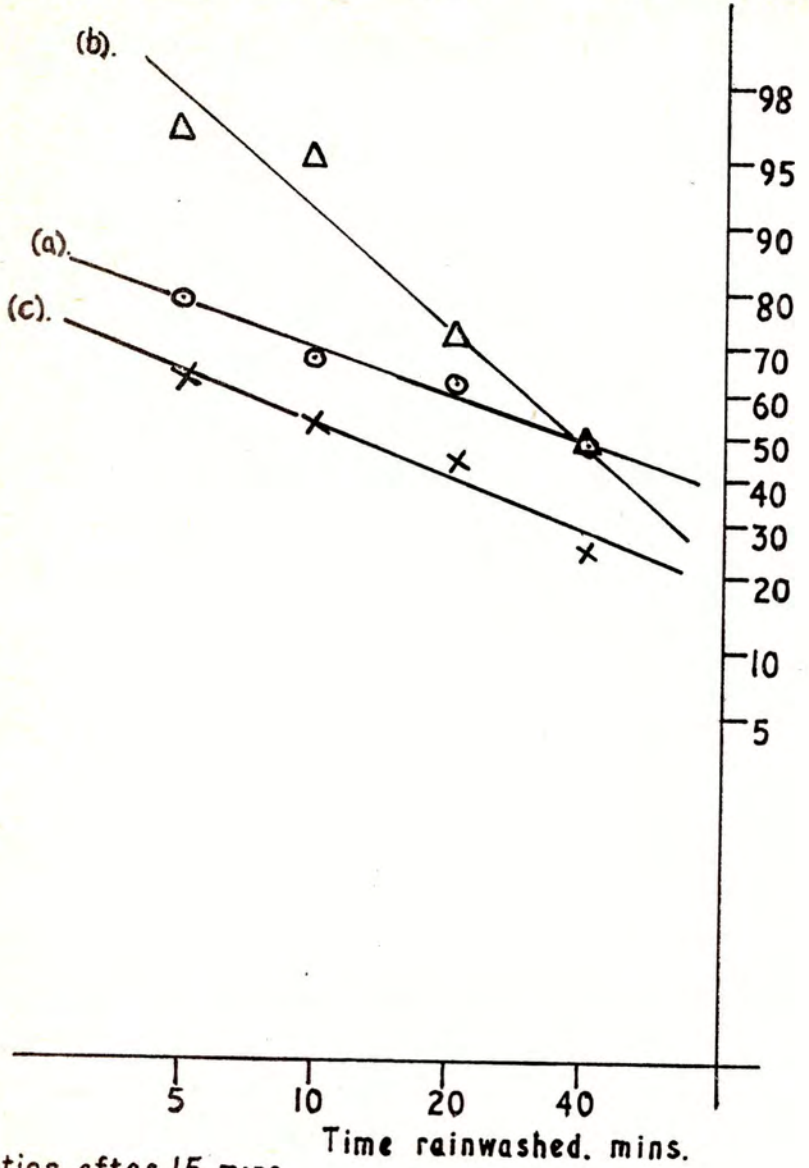


Fig. 3. Rainfastness-test.



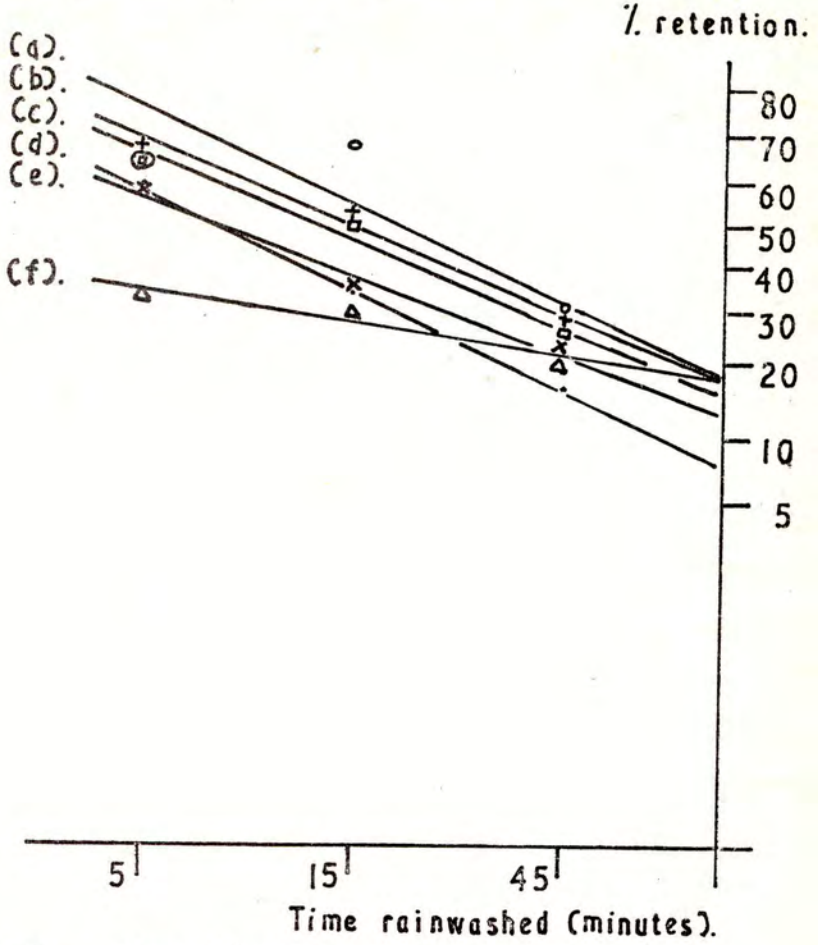
Retention after 15 mins.

(a). Natrosol 250 HR - 82 %.

(b). Natrosol High - 64 %.

(c). Calcium caseinate - 46 %.

Fig.4. Rainfastness-test.



Retention after 15 mins.

With 0·005 % Agral 90

JF 1557- 49 % (a).

JF 1558- 49 % (b).

JF 1481- 49 % (c).

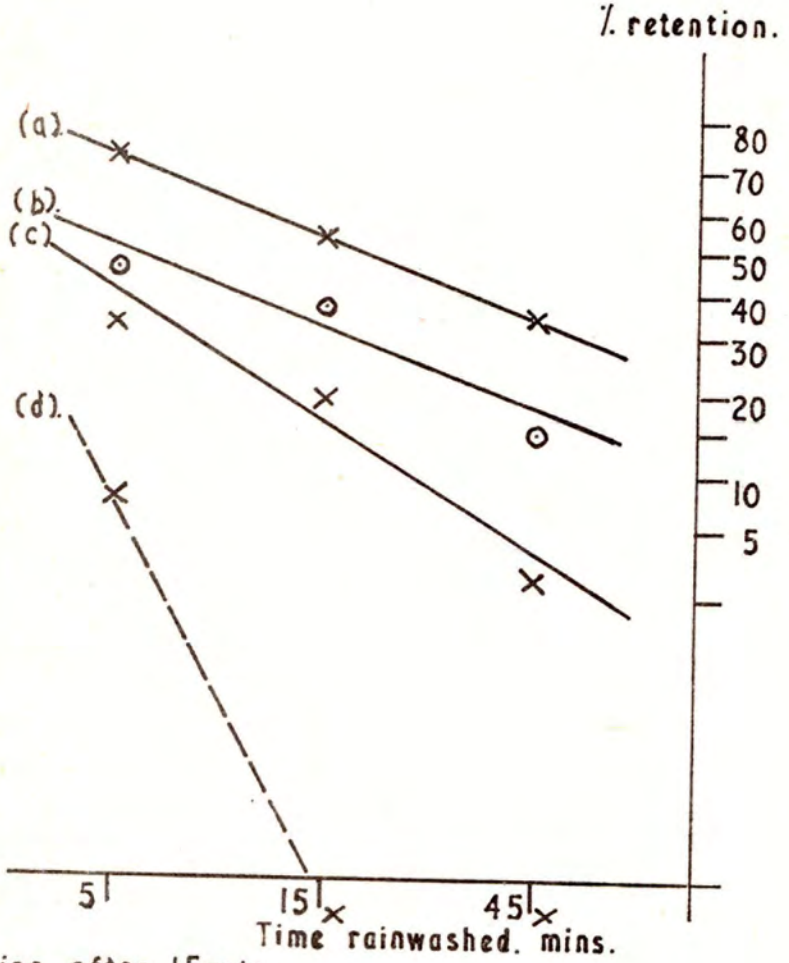
Without Agral 90

JF 1557- 35 % (d).

JF 1481- 35 % (e).

JF 1558- 31 % (f).

Fig. 5. Rainfastness-test.



Retention after 15 mins.

(a). B 642/166 - 56 %.
(b). JF 1230 - 33 %.
(c). B642/152 - 15 %.
(d). JF 1185 - 0 %.

DISCUSSION

Dr. C. R. Worthing: We have had three very good papers on the use of formulations to optimise the performance of a given pesticide. In practice, the N.A.A.S., and we at the Glasshouse Crops Research Institute, are frequently receiving enquiries from growers as to whether they can use a mixture of several pesticides, usually from different manufacturers, in a single application so reducing labour costs. Presumably these optimum formulations are being sabotaged. Has Mr. Winchester, or any of the other experts here, any comment to make on the effect on the formulations and the biological performances of such mixtures, or the use of mixtures in general?

Mr. J. M. Winchester: Within our Company, and I am sure this is the case with other Companies, we ensure that our own products are compatible one with the other, but we do not ensure that our products are compatible with those of other manufacturers primarily because we do not know how other manufacturers may change their formulations from time to time. Although we check the physical compatibility of our own products one with the other, we do not necessarily ensure that, for instance, their retention on plant surfaces had not been modified by this mixing. This is a complicated question because of the differing rates of differing mixtures used by the farmer. This aspect is being considered. The user will undoubtedly hope there will be more emphasis on this problem of incompatibility by manufacturers in order to cover a wide spectrum of pests encountered in any particular outlet. This would mean the development of compatible mixtures of pesticides to cover a whole range of pests. Some consideration should be given to the setting up of some central clearing house to resolve and advise on problems of compatibility.

Dr. H. H. Glasscock: Is much known about the physical dilution of one (or more) pesticide(s) by another when mixed before application?

Mr. J. M. Winchester: There is sometimes synergistic action. In certain circumstances this synergism and potentiation enhances the effect of the mixture. A danger is reduction of persistence of both chemicals if they both happen to be near their optimum retention rate. The farmer is in the most vulnerable position because he may mix compounds containing surfactants which are not compatible.

Mr. P. J. Shipton: Can the speakers comment on the effect of formulation on the effective life of the active ingredient in a compound during a period of storage?

Dr. C. G. L. Furmidge: This is one of the biggest single problems facing formulators, since many of the ingredients used in a formulation can cause chemical decomposition of the toxicant. Any reputable firm will carry out a very stringent series of tests on a formulation they are going to sell. However, it is difficult both to assess what extremes of climatic conditions will be encountered in practice and to carry out tests over a long enough period (which may be several years) to assess stability under ambient conditions. The only way is to conduct accelerated laboratory tests under extreme conditions of temperature, humidity, etc. in excess of those likely to be met with in practice. The physico-chemical properties from these accelerated tests have then to be related to those circumstances which will occur in practice. Any product put on the market by a reputable firm should be perfectly stable for at least one year and usually much longer.

Mr. J. M. Winchester: It is easy to follow the rate of decomposition of the active ingredient, e.g. at accelerated temperatures by, say, thin layer chromatography, to build up some picture of the order of reaction of decomposition of the chemical. In this way, one gets some idea of the stability, in different formulations but forecasting the physical stability of the formulation by using higher temperatures is very difficult. W.H.O. have done work on 75% D.D.T. dispersible powder.

Dr. G. S. Hartley: The decay of dichlorvos concentration in a closed vessel is presumably mainly due to reaction in the absorbed state. One might expect that the nature of the wall surfaces, furnishings etc. and relative humidity would be very important. How constant is the decay rate in practice?

Dr. C. G. L. Furmidge: The decay of dichlorvos vapour is largely decomposition from the absorbed state but may partially be due to chemical hydrolysis or photochemical decomposition in the vapour phase. The nature of the wall surfaces will obviously have an effect on decomposition of the absorbed material but the general shape of the decay curve is similar to that shown in Figure 1 of the paper.

Dr. G. S. Hartley: Mr. Winchester showed us some very striking differences in rain-fastness of a normal wettable powder and very finely ground formulation. What difference of particle size is concerned and is there any other associated difference?

Mr. J. M. Winchester: There is considerable difference between the rain-fastness of a dispersible powder which meets normal W.H.O. specification with an average particle size by the Rigden method of about 30 microns, a fine dispersible powder prepared by micronising with a particle size of about 3 to 4 microns, and a fine suspension with a considerable proportion of the particles below 1 micron, but I cannot give you a complete definition of when small particle size becomes important.

Dr. J. K. Eaton: At present none of the international specifications (e.g. W.H.O.) covering pesticides include clauses directly covering the biological effectiveness of formulated products. Do the speakers feel that such clauses should be included, and, if so, which properties and which tests would they like to see in the specifications?

Dr. C. G. L. Furmidge: The whole purpose of our talk was to point out the difficulties of generalising about formulation behaviour or application behaviour. It follows that there are no tests which one can carry out of a general nature that can be applied to all formulations. Specifications should be based not on the particular type of formulation but should be related to their use in a particular outlet, e.g., a W.H.O. specification for formulations for use in mosquito control, an F.A.O. specification for formulations used in the control of cotton pests. To some extent this is already done but one must consider the biological requirements that must be built into the formulation and this is where specifications fail because they are based entirely on physico-chemical principles. Consider the standard suspensibility tests for wettable powders. A wettable powder may require one form of suspensibility in one outlet and a different suspensibility in another outlet. As we have seen this morning, particle size can have a big effect on weathering and biological activity. Consequently, it may be desirable to develop at least two wettable powder formulations for a given toxicant; in one outlet, a small particle size may be desirable and this would give a product with a high suspensibility but in another outlet, a much larger particle size may be desirable and this would give a product with a lower suspensibility. Therefore there should not be a limiting degree of suspensibility for all products but a minimum degree of suspensibility suitable for the type of outlet. I would make a plea for specifications to be based on outlets and biological performance regardless of type of formulation and then tie physico-chemical tests to biological principles which can be proved in glasshouse or field trials, rather than to rely on physical tests carried out on a particular type of formulation regardless of outlet.

DISCUSSION

Dr. H. C. Gough: Could Mr. Terry say whether the slide he showed on the effect of Phosalone on brassica seed weevil was based on work in the U.K.? In any event could he indicate its value to other pests of brassica seed crops.

Mr. H. J. Terry: The results on seed weevils were in fact obtained from France. We have some encouraging results from U.K. sources with a dose of 10 oz a.i./acre and we are now considering this evidence together with the residue data, with a view to obtaining approval for use on brassica seed crops next year.

Dr. H. H. Glasscock: Has Cufram Z been applied to young hop shoots as they emerge from the rootstocks to reduce downy mildew spikes and also to deal with powdery mildew which occasionally attacks at this stage.

Mr. C. G. Parker: Yes, we have looked at downy mildew treatment of hills, but effects with Streptomycin are in general rather better. Powdery mildew effects have not been examined at this stage.

Dr. M. Cohen: In view of the fact that methods of analysis quoted by Mr. Parker was on disulphide content, is Mr. Parker quite sure that this method gives a real analysis of a mixture of the complexity of Cufram Z?

Mr. C. G. Parker: We agree that the Clarke CS_2 method is not sufficiently accurate, and ancillary techniques of U.V., thin layer chromatography and X-ray methods have been used. However, you are not a chemist, and neither am I, and for full information, I would refer you to our chemist.

Mr. A. Stevenson: The method of determination of crop residues by analysis for CS_2 does not give the complete picture as to the true residues present either from Cufram Z or from the simpler dithiocarbamates zineb and maneb. We are supplementing the CS_2 method by determination of metal residues, ethylene bis-thiuram mono and disulphides, and ethylene thiourea using U.V. thin layer methods.

Mr. R. Gair: Has drazoxolon any acaricidal or aphicidal activity?

Dr. M. J. Geoghegan: No aphicidal effect and little, if any, acaricidal effect.

Dr. S. R. Worthing: I think I can add that drazoxolon is one of the few fungicides that is non-toxic to the predator Phytoseiulus riegeli.

SECRETARY'S REPORT

REPORT OF COUNCIL ACTIVITIES SINCE THE THIRD BRITISH INSECTICIDE AND FUNGICIDE CONFERENCE 1965

MEMBERSHIP OF COUNCIL

President Sir Frederick Bawden

Chairman Mr. F. W. Morris

Treasurer Mr. H. S. Leech

Ministry of Agriculture, Fisheries and Food

Dr. R. de B. Ashworth Dr. H. C. Gough
Dr. H. H. Glasscock Mr. P. N. M. Moore

Department of Agriculture for Scotland

Dr. D. W. Williams

Ministry of Agriculture, Northern Ireland

Professor R. K. McKee

Agricultural Research Council

Dr. D. Rudd Jones Dr. J. T. Martin

Ministry of Overseas Development

Dr. H. S. Hopf

National Farmers' Union

Mr. H. C. Mason (appointment of second representative in abeyance)

Royal Horticultural Society

Mr. K. M. Harris

Institute of Biology

Dr. W. G. Keyworth

Society of Chemical Industry

Dr. J. K. Eaton

Association of British Manufacturers of Agricultural Chemicals

Mr. G. Angell Mr. J. L. Hunt
Dr. V. H. Chambers
Mr. H. C. Mellor

National Association of Agricultural Contractors

Mr. M. B. Dodson
Mr. R. E. Longmate

National Association of Corn and Agricultural Merchants Ltd.

Mr. M. S. Bradford
Mr. G. T. Smith

The Nature Conservancy (Natural Environment Research Council)

Dr. N. W. Moore

Co-opted Members

Mr. A. W. Billitt Dr. H. Martin
Mr. W. F. P. Bishop
Mr. W. A. Williams
Mr. D. J. S. Hartt

Secretary Miss C. M. Simmons

ELECTION OF OFFICERS

The General Meeting of Conference Delegates held on 11th November, 1965 unanimously elected Dr. F. C. Bawden to hold office as President of the Council until the completion of the next Conference.

It is recorded with very great pleasure that a knighthood was conferred on Dr. Bawden in the New Year's Honour List of 1967.

The appointment of the Chairman, Secretary and Honorary Treasurer to hold office for a period of two years was made by Council at the Sixteenth Meeting on 16th December, 1965.

At this meeting, Mr. A. W. Billitt resigned from the office of Chairman which he had held since the foundation of the Council in 1962. Mr. Billitt gave very valuable service to the Council during his period of office and has continued to play an active part as a co-opted member.

Mr. F. W. Morris was elected Chairman and nominated Miss C. M. Simmons to act as Secretary, following the retirement from that office of Mr. W. F. P. Bishop, who had been assisted by Miss M. Polley.

Mr. H. S. Leech was re-elected Treasurer.

REPRESENTATION ON COUNCIL

The changes in representation on the Council are recorded below:

Association of British Manufacturers of Agricultural Chemicals

Mr. G. Angell and Mr. J. L. Hunt have replaced two of the former members, Mr. D. J. S. Hartt and Mr. H. C. Huckle. Mr. Hartt has been co-opted on to the Council, following his retirement.

Royal Horticultural Society

Mr. K. M. Harris was appointed following the resignation of Mr. J. T. Forsyth.

Society of Chemical Industry

Dr. J. K. Eaton replaced Dr. H. Martin, who was co-opted on to the Council when he ceased representative membership.

Ministry of Agriculture, Northern Ireland

Professor R. K. McKee replaced Professor A. E. Muskett who has retired from the Ministry.

National Association of Corn and Agricultural Merchants Ltd.

Mr. M. Taylor resigned from the Council and has been succeeded by Mr. G. T. Smith

National Association of Agricultural Contractors

Mr. M. B. Dodson was nominated following the election of Mr. F. W. Morris to the chair.

National Farmers' Union

Mr. J. R. Macdonald resigned in June 1967 because of ill health. The appointment of his successor has been held in abeyance.

MEETINGS OF COUNCIL

The Council has met eight times during the period of this report. Both the summer meetings have been combined with a visit to a research station and afforded a valuable opportunity for members of Council to meet the scientists engaged in work on the control of pests and diseases and to see some of this work in progress.

The meeting in June 1966 was held at the Agricultural and Horticultural Research Station, Long Ashton by kind invitation of Prof. H. G. H. Kearns. In June 1967, the Council visited Rothamsted Experimental Station as guests of the Director, and President of Council, Sir Frederick Bawden.

COMMITTEES

A full list of the Committees of Council and their membership is given at the end of this report.

AMALGAMATION

In March 1966 the decision was taken to set up a working party jointly with the British Weed Control Council to investigate the desirability and practicability of amalgamation of the two Councils. This working party presented its first report in January 1967. Its findings can be summarised as follows:

(i) that amalgamation is a logical development of the common objectives expressed in the Constitutions of the two Councils and of the considerable degree of collaboration already existing between them;

(ii) that a single Council, by unifying the subject of crop protection and by providing easier communication and closer collaboration between the two fields, would be able to fulfil a more authoritative and effective role in national and international matters;

(iii) that there would be a saving of time and manpower and that the combined incomes of the two Councils would facilitate the employment of paid assistance to relieve the heavy load carried by voluntary workers;

(iv) that there were no major disadvantages to amalgamation which could not be overcome.

The decision in principle to amalgamate was taken, without dissent, at the Twenty-First Meeting of Council on 9th March, 1967. The proposals of the working party on the objectives, membership and structure of a new Council were accepted following the presentation of a second report in June 1967.

The acceptance of this report confirmed the appointment of a Technical Officer to undertake the duties of Secretary to the Conference Programme and the Recommendations Committees of the new Council. The Council is very pleased to report that Mr. A. W. Billitt agreed to accept this appointment when he retired from his company in June 1967.

The working party was re-appointed, with some additional membership, to deal with the process of amalgamation and put forward proposals to a joint meeting of the British Insecticide and Fungicide Council and the British Weed Control Council held on 28th September, 1967.

At this meeting, the Councils agreed to the immediate formation of a British Crop Protection Council and delegated to the Steering Committee the authority to contact the following bodies to invite representation upon the British Crop Protection Council:

Association of Applied Biologists

Association of British Manufacturers of Agricultural Chemicals

Agricultural Research Council

Department of Agriculture and Fisheries for Scotland

Ministry of Agriculture, Fisheries and Food, Headquarters Administration

Ministry of Agriculture, Fisheries and Food, National Agricultural Advisory Service

Ministry of Agriculture, Fisheries and Food, Plant Pathology Laboratory

Ministry of Agriculture Northern Ireland

Ministry of Overseas Development

National Association of Agricultural Contractors

National Association of Corn and Agricultural Merchants

National Farmers' Union

Nature Conservancy (Natural Environment Research Council)

Society of Chemical Industry, Pesticides Group

The British Crop Protection Council, will, in addition, be empowered to co-opt up to five independent members who will be nominated on a personal basis.

Solicitors have been appointed to provide legal advice on setting up the new Council, on the assignment of rights, commitments and assets from the existing Councils to the new body and on their eventual dissolution.

It should be emphasised that the plans for amalgamation are not intended to affect the established pattern of British Conferences on weed, pest and disease control.

BRITISH INSECTICIDE AND FUNGICIDE CONFERENCE

The Third British Insecticide and Fungicide Conference held in November 1965 was attended by 585 delegates. The Council is very pleased to be able to record that 148 of these delegates came from overseas countries.

Following the completion of work on this Conference, new Committees were formed to undertake the arrangements for the Fourth Conference to be held on 21st-23rd November, 1967. The membership of these Committees is given at the end of this report.

A notable innovation at this Conference is the inclusion in the programme of concurrent sessions on specialist subjects, which it is hoped will increase the interest and range of the Conference. The programme includes for the first time, a session on ecological aspects of pesticide usage.

The inclusion of stored products pests was considered by the Council following the suggestion put forward at the General Meeting of Conference Delegates in 1965, but it was agreed that no alteration should be made to the terms of reference, in which such pests are not included.

A random survey will be carried out amongst delegates during the Conference which it is hoped will assist the organisers to improve the facilities afforded to delegates at future conferences.

CONFERENCE PROCEEDINGS

The Proceedings of the Third British Insecticide and Fungicide Conference held in November 1965 were despatched to Conference delegates upon publication. Subsequent sales had brought the total number of copies distributed by 30th September 1967 to 651.

Proceedings of the Third British Insecticide and Fungicide Conference 1965

Available from:

The Secretary
British Insecticide and Fungicide Council
9 Grosvenor Street
London W.1 Price: £3. 0. 0.

Proceedings of the Second British Insecticide and Fungicide Conference 1963

Available from:

The Secretary
British Insecticide and Fungicide Council
9 Grosvenor Street
London W.1 Price: £2. 15. 0.

Proceedings of the First British Insecticide and Fungicide Conference 1961

Available from:

The Secretary
Association of British Manufacturers of Agricultural Chemicals
Alembic House
93 Albert Embankment
London S.E.1 Price: £3. 10. 0.

PESTICIDE MANUAL

The Council has agreed to undertake, with the British Weed Control Council, the publication of a compendium of scientific data on pesticides, under the editorship of Dr. Hubert Martin. The purpose of this venture is to provide an up-to-date source of reference for scientists and workers in this field.

The publication will be available in March 1968 under the title "Pesticide Manual".

INSECTICIDE AND FUNGICIDE HANDBOOK

Second Edition

Published by: Blackwells Scientific
Publications Ltd.
Oxford

Price: £1. 12. 6.

Sales of this edition (published on 9th November, 1965) had reached 2,094 on 31st August, 1967.

Third Edition

The Recommendations Committee has now started work on the Third Edition. This is scheduled for publication in November 1968 when it is anticipated that stocks of the current (second) edition will have been exhausted. The forestry interests have been invited to join the discussions on the content of this edition.

SYMPOSIUM ON THE CONTROL OF WEEDS, PESTS AND DISEASE OF CULTIVATED TURF

The Council collaborated with the British Weed Control Council in organising a one-day symposium on "The Control of Weeds, Pests and Diseases of Cultivated Turf", which was held in London, on Monday, 18th September, 1967.

The programme included papers on the relationship between management practices and the control of weeds, pests and diseases; problems and methods of control; and application techniques.

The three sessions were chaired by the Chairman of the British Weed Control Council and the Presidents of the Institute of Parks and Recreation Administration and the National Association of Groundsmen. The Chairman of the British Insecticide and Fungicide Council summed up.

The Proceedings of the symposium will be published and a limited number of copies will be available for sale.

APPLICATION OF INSECTICIDES AND FUNGICIDES

The Committee set up by Council to establish efficient liaison with the manufacturers of spraying machinery met for the first time in February 1966. The Committee includes in its membership representatives of research, advisers, manufacturers of both chemicals and machines, and the users of insecticides and fungicides. It has consequently provided, in its regular meetings, the means for the constant interchange of information which is one of its main objectives.

The Committee has liaised closely with the Herbicide Application Committee set up by the British Weed Control Council to ensure that, where common problems were concerned, there should be no unnecessary duplication. In its study of application problems, the Committee has consequently not concerned itself in detail with physical and engineering aspects but has concentrated mainly on what may be termed the biological requirements of application to crops. At the same time, the Committee has made a particular investigation of the problems of application to fruit.

At the General Meeting of the Conference Delegates in 1965, it was suggested that a symposium on application should be considered by the Council. This suggestion was referred to the Application Committee and has been kept under review until the Committee felt able to make firm proposals. It is hoped that this is a project which will be progressed under the auspices of the new British Crop Protection Council.

The Council believes that the Application Committee has been of direct value to organisations represented on it and that the industry as a whole may benefit from projects that have been instigated by this or its sister Application Committee. The two Committees are meeting together to produce a joint report which will summarise their discussions and make recommendations for the future.

INTERNATIONAL AGRICULTURAL AVIATION CENTRE

In 1966, the Council agreed to contribute towards the United Kingdom subscription when it appeared that the country's membership of the International Agricultural Aviation Centre might lapse because of lack of support. Half this subscription is paid by the Government, dependent upon the other half being forthcoming from industry. An annual report was asked for to enable the Council to review the continuation of its support.

The Council renewed its contribution in 1967 but at the same time suggested to the Centre additional activities it might undertake. The view was held that support should be maintained while the Centre had an opportunity to provide the kind of service contributors required.

The continuation of United Kingdom membership is, however, once again in the balance and the Government has been consulting with the contributors from industry. The Council has pledged its continued support and would regard with regret the United Kingdom's withdrawal from membership of the Centre.

EDUCATION AND COMMUNICATIONS

The terms of reference of the Education and Communications Committee set up jointly with the British Weed Control Council are to recommend means for the promotion of fuller knowledge in the field of crop protection products by those who are, or are likely to be, involved in their use.

One of the first actions of the Committee was to discuss future courses and their content with the Department of Education and Science. The Department accepted an invitation to be permanently represented on the Committee and, as a result of this close liaison, the Committee has been able to play a constructive part in the planning of regional and local crop protection courses and, in particular, of the National Course for Teachers held at the Essex Institute of Agriculture in 1966.

The Committee has also undertaken a review to establish the extent and scope of all available educational opportunities, literature and visual aids in the field of crop protection.

AGRICULTURAL, HORTICULTURAL AND FORESTRY TRAINING BOARD

The Agricultural, Horticultural and Forestry Training Board was set up by the Ministry of Labour early in 1966. The Council immediately offered all possible help and support to the Board in its work.

C. M. SIMMONS
Secretary

Finance Committee

Mr. D. J. S. Hartt (Chairman)
Mr. H. S. Leech
Mr. H. C. Mason
Mr. F. W. Morris

Trustees

Mr. F. W. Morris
Mr. H. S. Leech
Mr. A. W. Billitt
(vacancy)

Conference Organising Committee

Mr. M. S. Bradford (Chairman)
Mr. W. F. P. Bishop (Secretary)
Mr. A. W. Billitt
Dr. H. H. Glasscock
Mr. H. S. Leech
Mr. F. W. Morris

Conference Programme Committee

Dr. H. H. Glasscock (Chairman)
Dr. H. C. Gough (Vice-Chairman)
Mr. R. Gair (Secretary)
Mr. A. W. Billitt
Dr. A. W. Boyd
Mr. D. J. Higgons
Mr. J. L. Hunt
Dr. N. W. Hussey
Dr. W. G. Keyworth
Mr. E. Lester
Dr. W. Linke
Dr. H. Martin
Dr. N. W. Moore
Mr. F. W. Morris
Dr. D. Price Jones
Dr. D. Rudd Jones
Mr. G. Stell

Recommendations Committee

Dr. H. Martin (Chairman)
Mr. D. J. Higgons (Secretary)
Mr. A. L. Abel (Fisons Pest Control Limited)
Mr. M. S. Bradford, (Chairman, Publications Committee)
Mr. G. H. Brenchley (National Agricultural Advisory Service)
Miss A. V. Brookes (Royal Horticultural Society)
Mr. J. B. Byass (National Institute of Agricultural Engineering)
Mr. G. Culpan (The Murphy Chemical Co. Ltd.)
Dr. R. A. Dunning (Broom's Barn Experimental Station)
Dr. D. W. Empson (National Agricultural Advisory Service)
Mr. R. Gair (National Agricultural Advisory Service)
Mr. K. S. George (Plant Pathology Laboratory, M.A.F.F.)
Dr. H. H. Glasscock (National Agricultural Advisory Service)
Dr. R. Hull (Broom's Barn Experimental Station)
Mr. J. L. Hunt (Shellstar Limited)
Dr. W. G. Keyworth (National Vegetable Research Station)
Mr. B. C. Knight (National Agricultural Advisory Service)
Dr. W. Linke (Baywood Chemicals Limited)
Dr. Joan Moore (Plant Pathology Laboratory, M.A.F.F.)
Mr. B. D. Moreton (National Agricultural Advisory Service)
Mr. W. H. Read
Mr. E. T. Roberts (National Agricultural Advisory Service)
Mr. G. Stell (Plant Pathology Laboratory, M.A.F.F.)
Mr. H. J. Terry (May and Baker Limited)
Mr. D. W. Wright (National Vegetable Research Station)

Publications Committee

Mr. M. S. Bradford (Chairman)
Mr. A. W. Billitt
Mr. D. J. S. Hartt
Mr. H. S. Leech
Mr. H. C. Mason
Mr. F. W. Morris

Application Committee

Mr. J. R. Macdonald (Chairman) (now resigned)
Mr. F. W. Morris (Vice-Chairman)
Mr. J. B. Ryass (Agriculture Research Council)
Dr. N. G. Morgan (Agricultural Research Council)
Mr. A. K. Dorman (Agricultural Engineers' Association Ltd.)
Mr. I. B. Balls (Agricultural Engineers' Association Ltd.)
Mr. P. Wheldon (National Farmers' Union)
Mr. J. Lucas (National Farmers' Union)
Mr. A. E. H. Higgins (Ministry of Overseas Development)
Mr. H. Gould (National Agricultural Advisory Service)
Mr. R. C. Amsden, Mr. D. A. Harris, Mr. J. Stovell — three representatives of A.B.M.A.C.

Joint Education and Communications Committee

Mr. C. V. Dadd (Chairman)
Mr. M. S. Bradford (British Weed Control Council)
Mr. S. A. Evans (British Weed Control Council)
Mr. M. N. Gladstone (British Weed Control Council)
Dr. H. C. Gough (British Insecticide and Fungicide Council)
Mr. D. J. S. Hartt (British Insecticide and Fungicide Council)
Mr. H. C. Mason (British Insecticide and Fungicide Council)
Mr. F. W. Morris (British Insecticide and Fungicide Council)
Dr. T. W. Martin (Department of Education and Science)

MINUTES OF THE GENERAL MEETING OF DELEGATES TO THE FOURTH BRITISH INSECTICIDE AND FUNGICIDE CONFERENCE HELD AT THE HOTEL METROPOLE, BRIGHTON ON THURSDAY, 23RD NOVEMBER, 1967.

Present:	Sir Frederick Bawden	President
	Mr. F. W. Morris	Chairman
	Mr. H. S. Leech	Treasurer
	Miss C. M. Simmons	Secretary

together with about 80 members of the Conference

1. Minutes

The Minutes of the General Meeting of Delegates to the Third British Insecticide and Fungicide Conference held at the Hotel Metropole, Brighton on Thursday, 11th November, 1965 were approved as a true and correct record.

2. Matters arising from the Minutes

There were no matters arising from the Minutes.

3. Report of Activities

A Report covering the activities of Council since the Third British Insecticide and Fungicide Conference 1965 had been circulated to all delegates.

The Chairman drew attention to the proposed amalgamation with the British Weed Control Council and the formation of a new body, the British Crop Protection Council. It was expected that the present pattern of British Conferences would continue, but this would be the last occasion on which the British Insecticide and Fungicide Council would organise this Conference.

Dr. D. Rudd Jones proposed the adoption of the Report of Activities. This was seconded by Mr. H. S. Leech and carried unanimously.

4. Election of President

The Chairman said that when he had introduced the President, Sir Frederick Bawden, at the beginning of the Conference he had said how fortunate Council was to have a 'working' President. He was delighted to be able to tell delegates that Sir Frederick was prepared to offer himself for re-election to serve until such time as the Council should be dissolved.

Mr. M. S. Bradford proposed Sir Frederick Bawden as President. This was seconded by Mr. H. C. Mellor and carried with acclamation.

5. Future Activities

The Chairman reminded delegates that they were entitled to make proposals to Council as to the future activities it should undertake. Although the British Insecticide and Fungicide Council would shortly be dissolved, its work would continue under the new Council. He drew attention to the fact that, resulting from a proposal at the last meeting, the Council had followed up the possibility of holding a conference on application problems, and said that it was hoped two separate events would be held in 1969.

There were no suggestions from delegates for future activities.

6. Any other business

There was no other business.

The Chairman said he wished to record his appreciation of all those companies and organisations who had made it possible for their staff to help not only in the organisation of the Conference but in Council work throughout the year. He also thanked all those people without whose voluntary assistance the Conference could not have been held. He particularly wanted to mention Dr. Glasscock and the Conference Programme Committee, especially the Secretary, Mr. Gair; Mr. Bradford and the Conference Organising Committee; the Session Chairmen and the Secretary to the Council, Miss Simmons.

The Chairman then invited the President, Sir Frederick Bawden, to close the Conference.

CLOSING REMARKS BY THE PRESIDENT

The President thanked delegates for re-electing him. He paid tribute to the Chairman and to all those who had helped to make this Conference, the last to be organised by the British Insecticide and Fungicide Council, such a success, and he looked forward to the same high standard being maintained under the newly-formed British Crop Protection Council.

Sir Frederick said he had been particularly glad that the final paper to be given at the Conference dealt with a new fungicide because, as he had stressed in opening the Conference, he considered the development of an efficient fungicide to be one of the most important requirements at the present time.

Finally, the President thanked delegates for attending and formally declared the Fourth British Insecticide and Fungicide Conference closed.

LIST OF DELEGATES

ABEL, A.L., Fisons Pest Control Ltd., Harston, Cambridge.

ABEL, G.W.P., Baywood Chemicals Ltd., Eastern Way, Bury St. Edmunds, Suffolk.

ADHAM, Dr. M.I., Velsicol International Corporation C.A., P.O. Box 922, Beirut, Lebanon.

AELBERS, E., N.V. Orgachemia, Boseind 2, Bertel, Holland.

ALFONSIN, L.R., Diamond Alkali Ltd., 16 Place Vendome, Paris 1, France.

ALLEN, Dr. H.P., Jealott's Hill Research Station, Bracknell, Berks.

ALLEY, M.O., Shell International Chemical Co., Shell Centre, London S.E.1.

ALLISON, D.A., Mi-Dox Ltd., Smarden, Kent.

ANGELL, G.L., Cyanamid of Great Britain Ltd., Ag. Div. Bush House, Aldwych, London W.C.2.

ANNIS, C.W., Lincs. Aerial Spraying Co., Boston Aerodrome, Boston, Lincolnshire.

ANTONELLI, C., Sipcam, S.p.A., Viale Gian Galeazzo 3, Milan, Italy.

ARDANT, P., Eli Lilly Int. Corporation, Broadway House, The Broadway, Wimbledon, London S.W.19.

ARNOLD, G.I., Boots Pure Drug Co., Station Street, Nottingham.

ASHBY, D.G., Fisons Pest Control Ltd., Harston, Cambridge.

ASHER, B., Fisons Pest Control Ltd., Harston, Cambridge.

ASHTON, Miss P.J., Shell Internat. Chemical Co. Ltd., Shell Centre, York Road, London S.E.1.

ASHWORTH, R.E., Shellstar Ltd., 70 Brompton Road, London S.W.3.

ASPLIN, J.W., Asplin Chemicals Ltd., Boat Lane, Sprotborough, Doncaster, Yorkshire.

AUSTIN, M.D., Commercial Grower, 154 Fleet Street, London E.C.4.

BACHEM, K.E., Baywood Chemicals Ltd., Eastern Way, Bury St. Edmunds, Suffolk.

BAGNALL, B.H., Baywood Chemicals Ltd., Eastern Way, Bury St. Edmunds, Suffolk.

BAILEY, J.A. Rowntree & Co. Ltd., The Cocoa Works, Haxby Road, York.

BAILEY, P.F., Cyanamid of Great Britain Ltd., Ag. Div. Bush House, Aldwych, London W.C.2.

BAINBRIDGE, A., N.A.A.S., Government Buildings, Kenton Bar, Newcastle-upon-Tyne.

BAKKEREN, M., N.V. Aagrunol Chemische Fabrieken, Oosterkade 10, Groningen, Holland.

BALDWIN, B.J.T., Shell Int. Chemicals Co., Shell Centre, London S.E.1.

BALHUIZEN, F., Velsicol Internat. Corporation, Sophialaan 3-s, Zeist, Holland.

BALLE, J., Lindinger Agro. Co. Ltd., 239 Rodvrevej, Copenhagen-Vanlose, Denmark.

BANKS, D.R.B., Cyanamid of Great Britain Ltd., Ag. Div. Bush House, Aldwych, London W.C.2.

BARONTINI, A., Union Carbide Europa S.A., 40 Rue du Rhone, Geneva, Switzerland.

BARANYOVITS, Dr. F., Plant Protection Ltd., Jealott's Hill Research Station, Bracknell, Berks.

BARBER, Dr. M.S., Nat. Res. Development Corp., 66-74 Victoria Street, London S.W.1.

BARDNER, R. Rothamsted Experimental Station, Harpendon, Herts.

BARLOW, J.E., Agricola Chemicals Ltd., 30-32 Grays Inn Road, London W.C.1.

BARLOW, J.N., Berk Ltd., Berk House, P.O. Box No. 1 BL., 8 Baker Street, London W.1.

BARNES, T.R., Geigy (U.K.) Ltd., Simonsway, Manchester 22.

BARNSLEY, G.E., Geigy (U.K.) Ltd., Simonsway, Manchester 22.

BARWELL, D.M. Cyanamid of Great Britain Ltd., Ag. Div. Bush House, Aldwych, London W.C. 2.

BASTA, Mr. A.H., University College of North Wales, Agriculture Zoology Dept., Bangor, Caerns.

BATES, J.A.R., Ministry of Agriculture, Fisheries and Food, Hatching Green, Harpenden, Herts.

BEAN, K.W., World Crops, The Tower, Shepherds Bush Road, Hammersmith, London W.6.

BECK, Dr. W., Osterreichische Stickstoffwerke Akt., Postfach 296, A4021 Linz, Austria.

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ERRATA

Corrections to Volume 1

Page x - Contents (Session VA)

Paper on "Control of cereal rusts by fungicides containing nickel" by Dr. G. C. Hewitt withdrawn.

Page xii - Contents (Session VIB)

Alter authors of paper on "Determination of residues of bromophos and bromophos-ethyl" to read "G. LEBER and W. DECKERS".

Page xiii - Contents (Session VII)

Paper on "A new systemic fungicide" by Dupont Chemical Company withdrawn.

Pages 231, 232 and 233 (incl. Tables 3, 4 and 5)

"Ethyl ethoate" should read "ethoate-methyl".

Page 232 - Table 4

Alter heading of second column to read "Active ingredient in lb per 14,000 plants".