Wednesday afternoon

MODE OF ACTION OF HERBICIDES

CHAIRMAN: DR. E. E. CHEESMAN

SELECTIVE WEED CONTROL - SOME NEW DEVELOPMENTS AT WYE

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For some years now, one of our lines of research at Wye has been concerned with the breakdown of certain chemicals of the growth substance type within plant tissues. Most of the compounds we have studied are related to established growth promoters such as 2:4-D, MCPA and 2:4:5-T but they differ structurally in having more than one methylene (CH_2) group in the side chain. They form homologous series of acids starting with the acetic derivative with one methylene group and in most cases, all homologues up to the octanoic derivative with seven methylene groups have been prepared and examined. When the growth-regulating activity of these compounds is assessed, an alternation in activity is usually shown as indicated below for the ω-(2-methyl-4-chlorophenoxy) alkylcarboxylic acids.

Behaviour of homologues of 2-methyl-4-chlorophenoxyacetic acid ($C_6H_3(CH_3)ClO(CH_2)_n COOH$) in the wheat cylinder elongation, the pea curvature and the tomato leaf epinasty tests

Derivative	n	Activity	
Acetic	1	ACTIVE	
Propionic	2		INACTIVE
Butyric	3	ACTIVE	
Valeric	4		INACTIVE
Caproic	5	ACTIVE	
Heptanoic	6		INACTIVE
Octanoic	7	ACTIVE	

Such an alternation is fully consistent with the breakdown of the side chain by a β-oxidation mechanism as suggested by Synerholm and Zimmerman(1) in 1947. A similar oxidative breakdown of fatty acids is well known to occur in the animal body, the molecule being attacked at the β-position to the carboxyl group with the loss of two carbon atoms at each stage [2,3] e.g.,

$$RCH_2CH_2\overset{\beta}{CH_2}\overset{\alpha}{CH_2}COOH \rightarrow R\overset{\beta}{CH_2}\overset{\alpha}{CH_2}COOH \rightarrow RCOOH$$

Chemical evidence that β-oxidation of the side chain of ω-phenoxyalkylcarboxylic acids can occur in the flax plant has been obtained at Wye(4) and this has recently been supported by the results of biological and chromatographic investigations using other series of related compounds(5). Thus, the alternation in growth-regulating activity observed in homologous series is readily explicable; all acids with an odd number of methylene groups in the side chain are degraded by β-oxidation to the active acetic derivative whereas all other homologues are converted to the parent phenol, inactive as a growth substance(1). All our early experiments were in full agreement with such considerations. However, as the investigations proceeded, exceptional behaviour was found in certain series where although the expected alternation in activity was exhibited in the wheat cylinder test, in the pea curvature and tomato leaf epinasty tests only the acetic derivative was active. This could only mean that the β-oxidising enzyme systems present in pea and tomato tissue were incapable of degrading the side chain of these particular substituted phenoxy acids though with other types of ring substitution, they could do so. Further experiments involving chromatographic investigations, supported these indications that different plant tissues possess specific β-oxidase enzyme systems whose ability to operate with particular phenoxy acids depended on the nature and position of substituents in the ring (5,6). (Fig.1.)

Now all these, you may think, are academic considerations. If, however, the production of a positive growth response in intact plants is also related to the capacity of the tissue to degrade the side chain to yield an active acetic acid, then we have a logical approach to selective weed control based upon enzyme make up(6).

Our experiments carried out along these lines have given most encouraging results. Thus we have shown that various γ-phenoxybutyric acids, for example, will destroy certain plant species owing to their breakdown within the tissues to the active acetic derivative. On the other hand, plant species not possessing the specific enzyme to bring about this oxidative degradation of the side chain, are unharmed.

This new approach, which opens up the possibility of controlling weeds in a wider range of crops, has already been discussed in its fundamental aspects(5,6). In this paper, some of the more applied results will be considered. The first experiments on crops and weed were carried out with γ-(2:4:5-trichlorophenoxy) butyric acid (2:4:5-TB). As expected from its inactivity in the pea curvature test, this acid produced no growth responses when applied as a spray to peas at a rate equivalent to 2 lbs. of the acid per acre. Furthermore it killed Annual Nettle and affected certain other weeds. This acid, however, was slow in action and moreover it was without appreciable effect on many weed species. For this reason, attention was given to the butyric, caproic and octanoic acids derived from other chlorinated phenols. In particular, the 4-chloro-, 2:4-dichloro-, 2-methyl-4-chloro-, 3:4-dichloro-, 3-methyl-4-chloro-, 2:5-dichloro- and the 2:3:4-trichloro- derivatives of γ-phenoxybutyric acid were studied. The results obtained leave little doubt that some of these acids, especially γ-(2-methyl-4-chlorophenoxy)-butyric acid (MCPB) and γ-(2:4-dichlorophenoxy) butyric acid (2:4-DB) must be seriously considered for use as selective weed killers in commercial practice(7). It must be emphasised, however, that these compounds will not control as wide a range of weed species as MCPA and 2:4-D for unless the plant possesses the enzyme system necessary to degrade the side chain to the acetic derivative, no growth response would be expected (Fig.II and III).

Our experiments this season with the above butyric and a number of other acids have necessarily been of a preliminary nature. Nevertheless they have covered a fairly wide range of crop and weed plants growing in pots in the glasshouse and, in addition, a number of small scale field trials have been carried out. As might be expected certain compounds were found to be more effective for destroying specific weeds than others and also, the safety margin as far as a particular crop is concerned was shown to be dependent on the nature and position of the ring substituents.

Some results obtained by Mr. F. Wightman with potted plants this season are given in Tables 1 and 2. Treatment consisted in spraying the young plant usually 2-4" tall, to run off with a 1,000 p.p.m. solution of the γ-phenoxybutyric acid as its ethanolamine salt. In all cases 0.2 per cent. wetter was present in the spray. Observations were taken for four weeks after treatment.

Table I. Effect of spraying crop plants with 0.1% solutions of substituted γ-phenoxybutyric acids

Crop plant	Ring substituents							
	2:4-di-chloro	2-methyl-4-chloro	2:4:5-tri-chloro	3:4-di-chloro	4-chloro	2:3:4-tri-chloro	2:5-di-chloro	3-methyl-4-chloro
Lactuca sativa (Cabbage Lettuce)	xxx	xxx	xx	xxx	xxx	x	x	xxx
Phaseolus vulgaris (Runner Bean)	xxx	xxx	xx	xxx	-	xx	xx	xx
Vicia faba (Broad Bean)	xxx	xx	xx	xxx	-	xx	0-x	xx
Pisium sativum (Garden Pea)	xx	x-xx	0	xxx	xxx	0	0	xx
Fragaria x ananassa (Garden Strawberry)	xx	xxx	x	x	-	0	0	xx
Lycopersicon esculentum (Tomato)	xxx	xxx	0	xxx	xxx	x	0-x	xxx
Solanum tuberosum (Potato)	x	0	0	0	x	0	0	0
Brassica oleracea var. capitata (Cabbage)	xxx	xxx	xxx	xxx	xxx	0	0	0
B. oleracea var botrytis (Cauliflower)	xxx	x	xx	xx	xxx	0	0	x
Raphanus sativus (Raddish)	xxx	0-x	xxx	xxx	xxx	0	0	x
Zea mays (Maize)	0	0	0	0	0	0	0	0
Linum usitatissimum (Flax)	xx	x	0	xxx	xxx	0	0	0
Trifolium repens (White Clover)	0	0	x	x	xx	0	x	x
T. pratense (Red Clover)	0	0	0-x	xx	xxx	0	x	x
Medicago sativa (Lucerne)	x	xx	x	xx	xxx	x	x	x

Crop plant	Ring substituents							
	2:4-dichloro	2-methyl-4-chloro	2:4:5-trichloro	3:4-dichloro	4-chloro	2:3:4-trichloro	2:5-dichloro	3-methyl-4-chloro
Beta vulgaris (Beetroot)	xxx	x	xx	xx	x	0	0	x
Daucus carota (Carrot)	x	0	0	xx	xx	0	0	xx
Pastinaca sativa (Parsnip)	0-x	0	0	xxx	0	0	0	0
Allium cepa (Onion)	xx	xx	0	xxx	0-x	0	0	0
Apium graveolens (Celery)	0	0	0	0-x	0	0	0	0
Curcurbita pepo (Vegetable Marrow)	xxx	xxx	xxx	xxx	xxx	xxx	xxx	xxx
Gossypium sp. (Cotton)	xx	xx						

xxx Killed or severely damaged
x Slight effect

xx damaged
0 No effect

Table 2. Effect of spraying weeds with 0.1% solutions of substituted γ-phenoxybutyric acids

Weed Species	Ring substituents							
	2:4-dichloro	2-methyl-4-chloro	2:4:5-trichloro	3:4-dichloro	4-chloro	2:3:4-trichloro	2:5-dichloro	3-methyl-4-chloro
Urtica urens (Annual nettle)	xxx	xxx	xxx	xxx	xx	xxx	x-xx	xxx
Chenopodium album (Fat Hen)	xxx	xxx	x-xx	xxx	xxx	xxx	x-xx	xxx
Polygonum aviculare (Knotgrass)	xxx	xxx	x-xx	xxx		x-xx	0	x
Fumaria officinalis (Fumitory)	xxx	xxx	xx	xxx	xxx	x-xx	x	x

Weed Species	Ring substituents							
	2:4-dichloro	2-methyl-4-chloro	2:4:5-trichloro	3:4-dichloro	4-chloro	2:3:4-trichloro	2:5-dichloro	3-methyl-4-chloro
Stellaria media (Chickweed)	x	x	x	xx		0-x	0	x
Matricaria matricarioides (Rayless Mayweed)	0-x	0-x	0	0-x		0	0	x
Plantago major (Greater Plantain)	xx	xx	xx	xxx		xx	x	x
Mercurialis annua (Annual Mercury)	x	x	xx	0	x-xx	0	0	x-xx
Veronica spp. (Speedwell)	x	x	xx	x	xxx	x	x	x
Lamium purpureum (Red Dead-nettle)	xx	x	xxx	xx	xxx	0	0	x
Sonchus oleraceus (Sow Thistle)	xxx	xx	xx	xxx	xx	0	0	x
Spergula arvensis (Corn Spurrey)	0	0	0	x	x	x	0	0
Senecio vulgaris (Groundsel)	x	x	x	xx	x	0	0	x
Cirsium arvense (Creeping Thistle)	xxx	xxx	x	xxx	x	0-x	0-x	xx
Echium vulgare (Vipers Bugloss)	x-xx	0	0	0	0	0	0-x	0
Geranium spp. (Cranesbill)	xx	xx	xx	0-x	xx	0	0	x
Myosotis arvensis (Field Forget-me-not)	0	0	0	x	0	0	0	0
Euphorbia helioscopia (Sun Spurge)		xx						

xxx Killed or severely damaged
xx damaged
x Slight effect
0 No effect

It will be noted that some crops and many important pasture and arable weeds have not yet been studied. Also, the responses of the plants listed in Tables 1 and 2 still require investigation at different stages in growth and with higher levels of treatment.

In field experiments, control of Annual Nettle, Creeping Thistle, Fumitory and Fat Hen, has been achieved with MCPB and 2:4-DB applied at 2 lbs. per acre. As you will hear in a later paper, Mr. K. Carpenter in his more extensive field trials carried out this season, has successfully controlled a number of important arable weeds with MCPB without damage to the clover crop. These weeds include Fat Hen, Charlock (Sinapsis arvensis), Corn Poppy (Papaver rhoeas) and Knot grass (Polygonum aviculare) treated at the seedling stage and Creeping Thistle and Perrenial Sowthistle (Sonchus arvensis) as established plants.

At Wye, we have obtained a striking control of Annual Nettle infesting celery plants in the field with one application of either 2:4-DB or MCPB at 2 lb. per acre. No damage whatever to the crop occurred although 2:4-D and MCPA applied at a corresponding rate killed the plants outright within three weeks. (Figs. IV and V)

Carrot, lucerne, flax and clover have also been studied in the field this season. More detailed information, however, is required on the field performance of our more promising compounds with a wide range of crops and differing weed populations.

In summary, the indications from the present season's results may be stated as follows:-

1. Clover (red and white) and celery are but little affected by MCPB and 2:4-DB applied at rates up to 2 lbs. per acre.
2. Carrot, parsnip, flax and peas are much less damaged by MCPB than by MCPA or 2:4-D. The use of MCPB as a selective weed killer in these and other crops should be further investigated in the field.
3. 2:4:5-TB is safe to use on the pea crop at 2 lbs. per acre.
4. Lucerne is severely damaged by MCPB but to a much less extent by 2:4-DB. The latter compound might prove useful for killing weeds in this crop.
5. A range of important agricultural weeds including Annual Nettle, Creeping Thistle, Fumitory, Fat Hen and Charlock can be controlled by MCPB and 2:4-DB. 2:4:5-TB shows less activity as a weed killer than these two compounds.
6. Other phenoxybutyric acids, e.g. the 4-chloro- and 3:4-dichloro-derivative and certain phenoxy-caproic and octanoic acids may have specific uses in selective weed control.

I should like to express thanks to my colleagues at Wye, particularly Mr. F. Wightman and Dr. C. H. Fawcett who have been actively concerned with all aspects of this work and to Dr. K. Gaimster of May and Baker, Ltd., who synthesised three of the homologous series of phenoxy acids which formed the basis of these investigations.

Thanks are also due to the Agricultural Research Council in whose Unit at Wye, this work was carried out.

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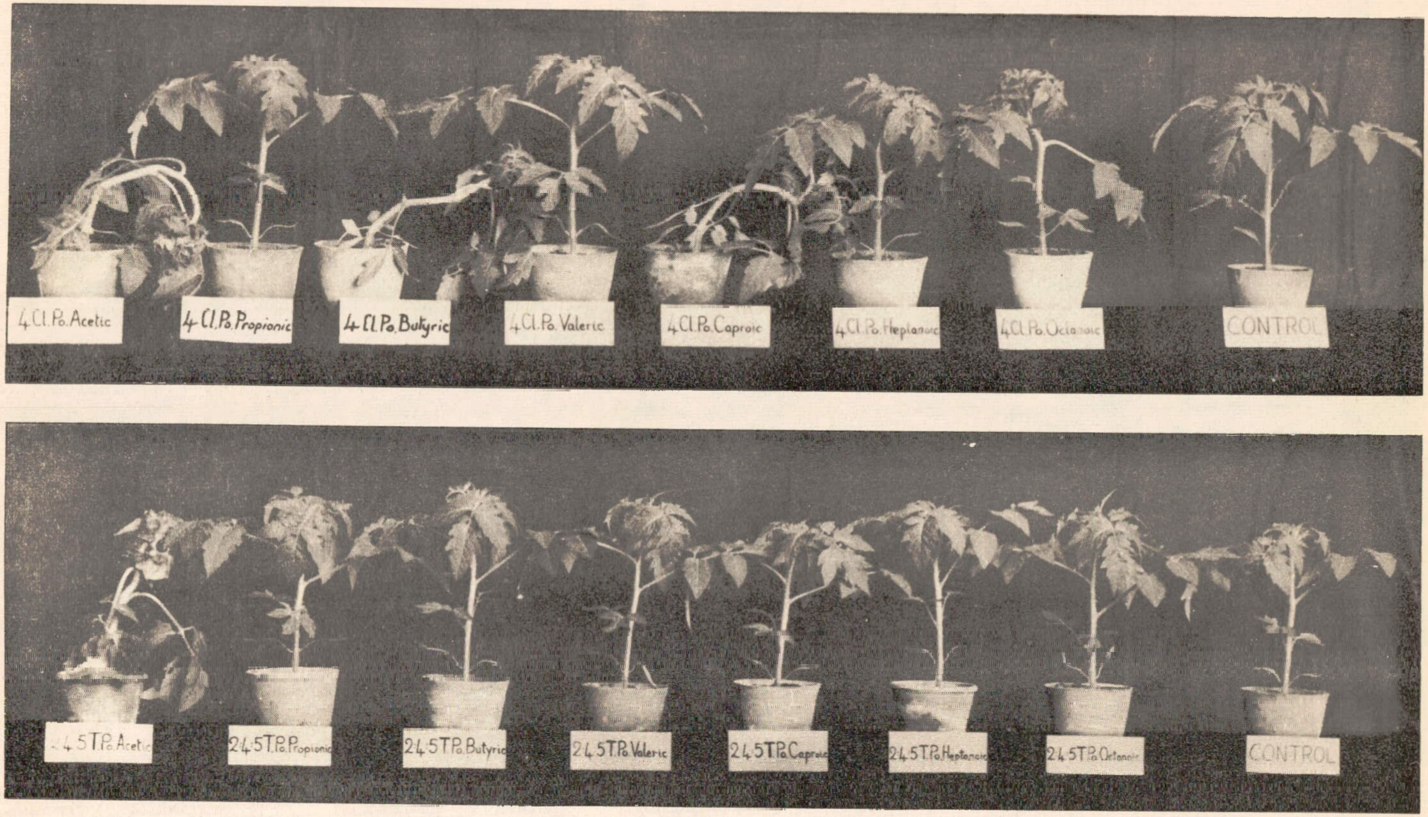

Fig. I. Responses of tomato plants 24 hrs. after treating in leaf axil with 2% solutions in lanolin of (top row) 4-chlorophenoxy- and (bottom row) 2,4,5-trichlorophenoxy acetic, prorionic, valeric, caproic, heptanoic and octanoic acids control plants on right.

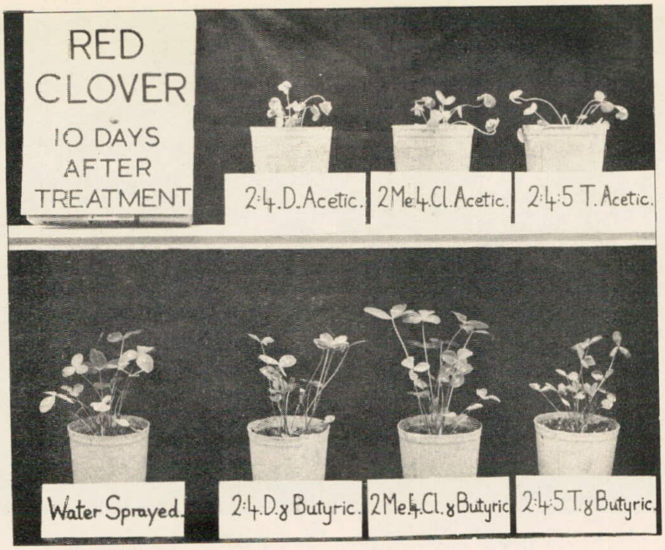

Fig.II. Top row Red clover plants sprayed with 2,4-D, MCPA and 2,4,5-T and Bottom row with 2,4-D B, MCPB and 2,4,5-TB witn control plant on right. Spray applications applied at 0.1% acid as sodium salt.

Fig.III. Top row White clover plants sprayed with 2,4-D, MCPA and 2,4,5-T and Bottom row with 2,4-DB, MCPB and 2,4,5-TB with control plant on right. Spray applications applied at 0.1% acid as sodium salt.

Fig. IV. Effect of spraying MCPB and MCPA at 2lb/acre on celery in the field with a control plant on right.

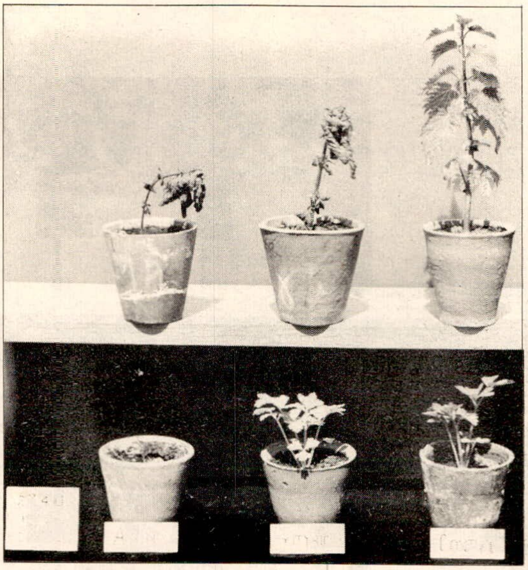

Fig. V. Effect of spraying MCPA and MCPB on Annual Nettle and celery plants with control plants on right. Spray applications applied at 0.1% acid as ethanolamine salt. Photographed 20 days after treatment.

ADSORPTION AND GROWTH REGULATION

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Summary

The forces involved in physical adsorption are outlined. The extent of adsorption between two molecular species can be measured with a Langmuir trough.

MCPA (2-methyl-4-chlorophenoxyacetic acid) was adsorbed to long-chain compounds containing a variety of polar groups and also to a protein (gliadin), lecithin and a lipoprotein. To determine the extent of its adsorption to various plant constituents, a simple technique is described whereby films were produced directly from a plant.

The extent of MCPA adsorption to constituents from a range of plants is given. The amount of these constituents in the plants is now being determined thus enabling an estimate of total adsorption within these plants to be made. Preliminary estimates indicate a correlation with their resistance to MCPA.

Introduction

Plants vary considerably in their susceptibility to 2-methyl-4-chlorophenoxyacetic acid (MCPA). Many of the monocotyledons are very resistant, other plants such as groundsel and mayweed are somewhat less resistant whilst many species are highly susceptible. In the work described, we have sought to determine how physidal adsorption of MCPA to various plant constituents contributes to their resistance.

After spraying MCPA on to a growing plant, adsorption might occur at several stages.

(1) Entry into the plant through the leaf or petiole may well depend on its adsorption (and desorption) to the various cuticular components.

(2) Adsorption to cell membranes may cause permeability changes.

(3) During translocation through the plant MCPA may be adsorbed to various surfaces as well as to soluble or colloidal components of the plant protoplasm.

(4) Adsorption to a site (possibly an enzyme) that brings about the observed biological response.

We shall only discuss in detail the adsorption outlined in item (3).

Adsorption Forces

Forces leading to adsorption may be classified in their order of strength as follows:-

The strongest association is that in which covalent bonds are formed, for example in the adsorption of oxygen or carbon monoxide on certain metals. This is usually an irreversible adsorption and biologically the following are more important:-

(a) Salt formation in which positive ions associate with negative ions. Long range forces are involved and the association is therefore relatively non-specific. The complex so formed is particularly stable if it is reinforced by other associations about to be described.

(b) Hydrogen bonds are formed between electronegative atoms such as oxygen and nitrogen through the medium of a hydrogen atom.

(c) Ion-dipole and dipole-dipole interactions are weaker still and are formed between molecules having pronounced dipolar properties.

(d) Finally, van der Waals forces exist even between non-polar molecules and groups such as $-CH_2$. They are very weak indeed but are additive. Thus the inter-attraction of two $-CH_2$ groups is very small but that of 16 $-CH_2$ groups as in stearic acid, is relatively large. They are short range forces and are largely responsible for the highly specific nature of some biological reactions. Thus small irregularities in the shape of a biological molecule may be suffieient to destroy van der Waals forces in that region.

We are mainly concerned in this work with ion-ion interactions reinforced by van der Waals attraction. Thus at pH 4-5, MCPA is almost entirely negatively charged and interacts readily with the positively charged amino groups of proteins. Van der Waals forces resulting from the benzene ring and its substituents further stabilise the complex.

The Langmuir Trough

Surface reactions may play an important part in the biological activity of plant cells because membranes, macromolecules, colloids, etc. all contribute to a large surface area within the cell. The Langmuir trough, which permits the study of surface reactions in vitro, was therefore selected.

This consists of a shallow pyrex trough, divided into three sections by a glass slide and also a mica barrier, which is part of a surface tension measuring device. The barriers and upper surfaces of the trough are waxed, and the trough is filled with buffer solution.

A monomolecular film can then be spread on the surface of the solution in the centre section. Almost all organic compounds containing a water-soluble group and a suitable non polar group will form a stable monolayer, (e.g.) stearic acid $C_{17}H_{35}COOH$, eicosylamine $C_{20}H_{41}NH_2$, cetyl alcohol $C_{15}H_{31}CH_2OH$, cholesterol, many proteins, lecithin, etc.

These films were studied by two methods.

(1) Surface Pressure

The film was compressed by means of the glass barrier and corresponding film pressures measured using the torsion device. This assessed the compactness and orientation of the surface molecules and enabled us to classify the films as solid, liquid or expanded.

(2) Surface Potential

A radioactive electrode enabled us to measure the surface potential of the films. The circuit comprises a platinum loop suspended about 1 mm above the water surface. The air gap thus formed is made conducting by attaching a capsule of radioactive mesothorium bromide to the loop. Current then flows through the water filled trough and a silver wire constitutes the second electrode. As the currents generated are extremely low, a direct current amplifier is also used.

The voltage produced which is essentially a contact potential between platinum and air, is modified by the presence of a surface film. The extent of modification gives information on the vertical component of the dipole moment of the film and hence on its structure.

Surface potential measurements are made in conjunction with those of surface pressure and deductions can often be made concerning the nature and disposition of the polar groups in the surface.

The Injection of MCPA

Having so characterised the monolayer spread on pure buffer solution, we then injected a solution of MCPA. After allowing about an hour for equilibrium to be established, surface pressure and potential measurements were again made. The following may then be observed:-

(1) No change in surface pressure or potential, indicating no interaction between MCPA and the film.

(2) No change in surface pressure but a significant change in surface potential. This indicated adsorption of MCPA to the monolayer without penetration, presumably by ion-ion forces.

(3) A significant change in both surface pressure and potential. This resulted from adsorption of MCPA by ion-ion forces coupled with film penetration due to large van der Waals attraction between the non-polar portions of film and MCPA.

Experimental Results

Initially, MCPA was injected beneath monolayers of simple long-chain molecules containig a variety of polar groups (e.g.) acids, amines, amides, ketones, quaternary ammonium salts, etc.

We found strong interaction between MCPA and amines and quaternary ammonium salts and weaker interaction with ketones.

This suggested a corresponding study with proteins which all contain ($-\overset{+}{N}H_3$) groups and lecithin containing the quaternary ammonium group. Strong interaction occurred with MCPA concentrations as low as 10^{-4} to 10^{-5}M. It did not however, interact strongly with a lipoprotein complex consisting of protein and lecithin. We inferred that the negative phosphate-ion of the lecithin molecule was preventing the MCPA from interacting with the positively charged protein groups. It was therefore suggested that the lipoidal status of a plant might influence the biological activity of the growth regulator. This may be involved in the varying susceptibility of plants to MCPA.

To determine the extent of adsorption to various plant components, a simple technique was developed for spreading films directly from a plant. A portion of the leaf, petiole, stem or root was well bruised and immediately applied to the surface of the trough. The procedure was repeated until a film of desired area was formed. The film was stable and reproducible.

Various parts of the resistant species, - oats, wheat, ryegrass, mayweed and groundsel were spread in this way and also the susceptible plants - rape, mustard, tomato, cress, onion, sugar beet and broad bean. Surface pressure and potential measurements were first made on the films alone and then after the injection of MCPA. The extent of adsorption to each film was estimated.

In general, the monocotyledons produced films of higher surface potential than those of the dicotyledons, and the films were usually more stable. On injecting MCPA at about 10^{-4}M, penetration of all the films occurred and there was a change of surface potential. The extent of the change however, varied from species to species and the following slide illustrates the relative extents of adsorption.

The resistant species, oats, wheat, ryegrass, mayweed and groundsel all gave rise to relatively high adsorption. Of the susceptible plants, several were low adsorbers (e.g.) tomato, cress, broad bean and sugar beet, but there were three notable exceptions. Thus rape, mustard and onions which are susceptible in the field, strongly adsorbed MCPA.

Discussion

Two other factors would influence the total amount of adsorption within the plant:-

(1) pH
(2) The amount of adsorbing material.

pH

Little precise work was done owing to the difficulty of measuring pH at the appropriate adsorbing site in the plant. Overall determinations however, indicated no significant difference of pH in the range of plants studied.

The amount of Adsorbing Material

Hitherto, the extent of MCPA adsorption to a given area of film on the trough was measured. The total amount of MCPA adsorbed however, is a function of this and of the amount of the material in the plant.

It is now being measured. A weighed amount of plant tissue is homogenised, filtered and the juice applied to the surface of the Langmuir trough with an Agla Microsyringe. The volume of solution required to give a certain area of film is noted.

The results so far which are of a preliminary nature indicate that plants resistant to MCPA contain up to 10 times the amount of material in the susceptible species. Rape, mustard and onion films which adsorbed MCPA strongly, contain only small amounts of adsorbing material. We may therefore have obtained a correlation between total adsorption within the plant and its resistance to MCPA.

Conclusions

The tentative conclusion is drawn that resistance is related to the presence of material which readily adsorbs the hormone weedkiller thus impeding its translocation to the vulnerable sites within the plant. Under field conditions therefore higher concentrations of MCPA must be applied to those species having higher potential adsorption in order to ensure a toxic concentration at the true site of action. It does not follow however, that compounds of lower adsorption would be more active since biological activity may ultimately depend on adsorption to a specific enzyme or membrane surface.

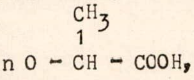
DISCUSSION ON TWO PREVIOUS PAPERS

Professor G. E. Blackman: It is quite clear that I have not to impress upon you the importance of Professor Wain's paper. It is particularly pleasing to see that a purely fundamental approach, an approach which set out to enquire how changes in the molecule produce changes in toxicity and which led on to an analysis of what were the reactions taking place at cell level, has brought to the world a new series of selective herbicides. I have said from time to time that we cannot expect the practice of selective weed control to become simpler but rather that it must become more and more complicated. It is quite clear from the slides that Professor Wain has shown us that these new compounds hold out great promise and that the next stage is to investigate them under field conditions. I am absolutely appalled at the size of the programme of the developmental work that this might entail when one considers the number of compounds, the number of crops and the number of weeds.

It does not look as if Dr. Brian's results are likely to produce a practical result in the near future. We have for many years at Oxford been interested in this balance between the physical and the chemical factors. For example, in trying to analyse the varying toxicity of oils to plants we have shown that if you take a whole series of hydrocarbons in the vapour phase it is not the change in structure that is important, it is the change in physical characteristics. It is possible to predict from such information which hydrocarbon will, in fact, kill the leaves of barley but will not kill the leaves of parsnips when they are exposed to the vapour. This study does not mean that there is going to be a new selective hydrocarbon because other factors are involved. Nevertheless, it is this type of fundamental approach which will eventually greatly expand the field of weed control.

Dr. Warren C. Shaw: I have one question I would like to ask Professor Wain. Did I interpret your statement correctly that the 2,4-dichlorophenoxy proprionic acids were not active in the test you used?

Professor R. L. Wain: The proprionic acids exist in two forms the α-substituted proprionic acids and the β-substituted. In my discussion I have been concerned solely with the β-derivatives with the side chain $- O - CH_2 - CH_2 - COOH$, which are inactive as growth substances. The α-substituted proprionic acids, however,



having the side chain $O - \overset{CH_3}{\overset{|}{C}H} - COOH$, are active and indeed they are optically active as well because the middle carbon atom is asymmetric. It may interest you to know that we have worked with such stereo-isomers at Wye: usually, one of them is highly active and the other inactive.

May I say another word about the paper I have just given. It is not my purpose to stand before you as an expert in weed control. I think we have done enough at Wye to indicate that there is something in this new approach to selective weed control and I do hope that Professor Blackman and his colleagues and others will now take these new chemicals and put them through their proper paces. Our results suggest that such further work would not be a waste of time.

Dr. J. T. Martin: We must congratulate Professor Wain on his work, which provides an example of results which may be of great practical importance arising directly from fundamental research. When investigating the biological effect of chemicals, there is the question of the extent to which they penetrate to the site of action. I gain the impression from Dr. Brian's paper that he assumed the MCPA went in to the same extent and then was locked up in some plants so that it could not be translocated.

Dr. R. C. Brian: I should have made it clear that we only consider these surface phenomena as one of many possible factors. There is penetration, translocation, decomposition and a host of other factors. At the moment we have only tackled absorption during translocation.

Unidentified speaker: I have the impression from Professor Wain's slides that the effect of the chemical on creeping thistle was not so strong or so clear as on other plants. Possibly there is an explanation for this that Professor Wain can give us.

Professor R. L. Wain: The photograph of the thistles was not taken at the best time though it shows the effect quite clearly. There is no doubt that creeping thistle succumbs to sprays containing alternate homologues of MCPA; the butyric acid, for instance, has destroyed thistle when applied at rates of 2 lb. per acre.

INVESTIGATIONS INTO THE PRACTICAL VALUE OF MCPB AS A SELECTIVE WEEDKILLER IN LEGUMINOUS CROPS

by

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Supplementary paper submitted after the Conference

SUMMARY

The herbicidal activity of a number of substituted ω(phenoxy) butyric acids was tested in the greenhouse early in 1954 and as a result, four:-

	ω(4-chlorophenoxy) butyric acid	(4-Cl B.)
	ω(2:4-dichlorophenoxy) butyric acid	(2:4DB)
	ω(3:4-dichlorophenoxy) butyric acid	(3:4DB)
and	ω(4-chloro-2-methylphenoxy) butyric acid	(MCPB)

were chosen for field evaluation in clover and pea crops. These experiments led to the choice of MCPB for commercial development and further experiments on its crop toxicity were set up.

Details of the results so far available for MCPB are given. Those for the other acids are summarised where appropriate.

The results show that MCPB offers a safe selective weedkiller for use in seedling and other clover crops. Much more work is necessary however, before its potentialities in the pea crop can be properly assessed.

Introduction

In his paper to this Conference(1) and elsewhere(2), Professor Wain has described the results of experiments on the growth regulating activity of homologous series of ω(4-chloro)-, (2:4-dichloro)-, and (2:4:5-trichloro)-phenoxy aliphatic acids.

Briefly these results indicated that whereas the wheat, pea and tomato tissues used in these tests were all able to break down, by β-oxidation, the alternate higher homologues of the 4-chloro- and 2:4-dichloro series to the highly active acetic acids, neither the tomato nor the pea tissue was able to produce a corresponding degradation in the 2:4:5-trichloro series. Professor Wain has described(1) how this suggested to him that, if similar or other differences were shown by intact plants, they might lead to new methods of obtaining greater or different selectivity in the growth regulator herbicides, and has outlined the course of his pot and field plot experiments to develop this idea at Wye College.

A. A. Greenhouse Experiments

As we have already indicated(4), we were aware of these developments through the contribution of Dr. K. Gaimster to the synthesis of the key series(1,3). We therefore planned at Ongar a series of greenhouse experiments on the herbicidal activity of some of these compounds, beginning with ω-2:4:5-trichlorophenoxy butyric acid (2:4:5-T.B.) as being the simplest member of what then appeared to be the most interesting series. The activity of this compound was compared with the corresponding acetic acid on a range of nineteen crop and weed species, using the laboratory spraying apparatus described at this Conference(4). The plants were treated at dose rates equivalent to 1, 2 and 4 lbs./acre in 50 galls. water, with four replicates of each treatment and kept in greenhouses controlled to a night temperature of 50°F. All were sprayed at the seedling stage to ensure maximum sensitivity.

The results of these first experiments showed that a number of crop plants (i.e. clover, peas, carrot and lettuce) were reasonably resistant to 2:4:5-T.B. but that some important weed or weed-like species were fairly susceptible (i.e. charlock, *Papaver sp.*, *Chenopodium sp.*, *Brassica alba*). All were rather less susceptible to the butyric than the acetic acid, the differences being most marked at 1lb./acre, much less so at 2lb., and hardly noticeable at 4lb.

The degree of reaction to the butyric acid derivative was highly specific and unsystematic. For example the four leguminous crops included in the tests, clover, peas, broad beans and french beans, covered the whole range of possible reactions. Whereas peas and clover were highly resistant to the butyric acid even at 4lbs./acre but very susceptible to the acetic acid, french beans were almost equally and rapidly susceptible to both acids even at 1lb./acre. Broad beans were intermediate in their reaction. A similar degree of variation occurred amongst cruciferous plants although all of these were fairy susceptible. The most susceptible cruciferous weed, charlock, was *relatively* much less susceptible to the butyric acid than poppy and fat hen. At this stage it was possible to draw the following inferences.

(i) Since some general loss in weedkilling power seemed probable it was advisable to move to ring systems with a greater weedkilling potential than 2:4:5-T. (i.e. for herbaceous or annual weeds).

(ii) That with the specificity experienced in these tests there was reasonable hope that the ω-2:4-D, and MCP butyric acids might show some useful selectivity even though the reactions of the former were quite normal in Professor Wain's original laboratory tests.

(iii) That with the trend of results so far the leguminous crops offered the most hopeful field.

As the search for selective weedkillers in leguminous crops was one of the main objects of our herbicide screening at that time, this lead was followed up immediately by a series of greenhouse tests on these lines. Other important arable crops such as beet, kale, linseed, carrot and strawberries, were included. By the end of April it was clear that the most promising compounds from our point of view were:-

ω(4-chloro-2-methylphenoxy) butyric acid	(MCPB)
ω(2:4-dichlorophenoxy) butyric acid	(2:4-DB.)
ω(3:4-dichlorophenoxy) butyric acid	(3:4-DB.)
ω(4-chlorophenoxy) butyric acid	(4-ClB.)

All had a reasonable degree of activity against the three test weeds. Seedling white clover was resistant to MCPB, 2:4-D.B. and 3:4-D.B., seedling peas to MCPB, 3:4-D.B. and the 4-Cl.B. compound. Their practical significance obviously depended on the range of weeds they could control under field conditions and on the rates of application at which the control could be achieved, bearing in mind the probable cost of the materials. Their effectiveness against perennial weeds, notably creeping thistle seemed to us to be one of the key questions to be answered.

Efforts were made, therefore, to prepare sufficient quantities of these acids for immediate field tests.

2:4:5-T.B. was included in case it should possess some special activity, e.g. against perennial weeds. The ethyl esters of MCPB, 2:4-D.B. and 2:4:5-T.B. were also prepared in case they provided greater activity without impairing selectivity.

B. Field Experiments

The first exploratory experiments were begun as soon as preparations were complete at the beginning of June, with the main aim of finding out which, if any, of these acids and esters had a practical level of weedkilling activity. The corresponding acetic acids were therefore not included as this would have made the experiments too unwieldy, and moreover, ample data on their performance was available. All treatments were applied to weeds in crops either specially grown or on neighbouring farms, but in the first place it was intended to make qualitative observations only on crop effects. As the experiments progressed and the practical possibilities of some of the compounds became more certain, the numbers of different compounds were decreased and MCPA and 2:4-D. included in the layouts as far as was practicable.

By the end of July it was fairly clear that the final choice would fall on a salt of ω(4-chloro-2-methylphenoxy)butyric acid (MCPB). Further experiments were then set up in the greenhouse and field to compare its activity and particularly its crop toxicity, more systematically with that of MCPA.

As the results of these experiments could not be prepared in time for presentation at the Conference itself, a preliminary note was included in the research report on the methods used(4). It has been possible, however, to include the present fuller report in the proceedings.

The full programme has involved observations on about 1,400 plots and about 4,000 pot plant assessments. Moreover, many of the experiments are still incomplete and many of the evaluations can only be regarded as preliminary. It has not been feasible, therefore, to include in this report all the results on all the compounds and crops tested. The data on MCPB are obviously the most complete and these are given in full as far as they are at present available. The relative activities of the other phenoxy butyric acids are given in detail for some of the more significant comparisons but are otherwise considered in the discussion where appropriate.

Results

Materials Used

(a) Formulation and Purity

In all the original greenhouse comparisons all the acids (butyric and acetic) were applied as aqueous solutions of the diethanolamine salts of the pure compounds. The same is true of the butyric acids applied to all the field experiments except 31/6 and 7 (Tables III & IV), where an approximately commercial formulation of the sodium salt was used but prepared from acid of high purity. The MCPA used in the field experiments was a commercial formulation of the potassium salt.

All the ethyl esters were applied as emulsions made up from self-emulsifiable concentrates in mineral oil containing 40% w/v acid equivalent and containing the same emulsifiers throughout.

(b) Distribution in Experiments

The first two field experiments (49/2, 49/12, Table I), included the full range of acids and some esters (not given in the table). Following the weed-killing and crop effects shown in Table I the experiments in undersown cereals and seedling clover were (except for the first one), confined to a study of the acids and esters of 2:4-D.B. and MCPB, and the experiments in peas to MCPB, 4-Cl.B., 3:4-D.B. and 2:4:5-T.B. and its ester.

Application Method

Applications were made through the experimental field crop sprayer described at the Conference(4). Rates of application varied from ¼ to 3lb./acre according to the compound and the crop, but all were in 15 galls./acre of water applied at 30 p.s.i. pressure.

Experimental Layouts

All were in the form of randomised block layouts with four blocks to each experiment with only two exceptions. Each block contained from 12 to 20 treatments but as the individual plots were 4'6" wide x 12-15' long, reasonably compact square layouts were possible.

Sites

Unsprayed weedy crops in the right stage of growth were naturally not readily obtained by the time these experiments began, (early June), and some had to be specially sown. Sites infested with creeping thistle were specially sought but the combination of weather conditions and lateness considerably limited the variety of other species encountered (Table II).

Weather Conditions

Weather conditions after the second week in June were uniformly poor and only the three earliest sites (49/2, 49/10 and 49/12, Tables I & II), were sprayed in anything approaching good spraying weather.

Methods of Assessment

(a) Weed Control

Weed populations (Tables I & II), were assessed by plant counts in two half-square yard quadrats in each plot. The quadrat positions were chosen by a systematic sampling method. Counts were made 6-8 weeks after spraying and the degree of control calculated by comparison between treated and control plot population at that time.

(b) Crop Tolerance

Clover densities (Tables III & IV) were obtained by counts of trifoliate leaves using a foot square quadrat. Clover population figures in Table V were obtained by the same method as the weed counts.

Clover hay yields (Table VI) were taken from the whole plot after removing a border of discard. The pea yields in Table VII were also whole plot yields in 47/12, but those in 49/8 & 9 were from two half-square yard quadrats in each plot.

Statistical Analysis

The considerable task of carrying out a full analysis of all the data obtained has only just begun. It seemed preferable, however, to publish the results as they stand rather than miss the opportunity of including them in these proceedings. All the quantitative results given here have been examined to make sure that variation between replicates is not sufficient to be misleading and confirmatory experiments are included wherever possible.

TABLE I.

INITIAL FIELD EXPERIMENTS COMPARING THE EFFECT OF RING SUBSTITUTION ON ACTIVITY

Species	Expt. No.	Stage of growth at spraying	% control given by each compound at rates in lb./acre															Control pop./sq. yd. & mean ht. at counting
			4-Cl.B.			2:4-D.B.			3:4-D.B.			2:4:5-T.B.			M.C.P.B.			
			½	1	2	½	1	2	½	1	2	½	1	2	½	1	2	
Creeping Thistle	49/2	15 - 18"	28	54	71	72	88	83	9	58	66	0	6	43	83	91	92	22 x 33"
	49/12	6"	76	78	76	-	-	-	76	73	91	45	0	20	80	84	100	14 x 20"
Knotgrass	49/2	3"	0	16	20	68	91	94	0	3	78	23	7	3	10	65	87	10 x 13"
	49/12	1½"	48	28	27	-	-	-	0	26	0	0	36	29	34	64	75	28 x 13"
Fat Hen	49/2	2"	76	100	100	86	100	100	71	100	100	62	15	43	96	96	86	7 x 11"

Experiment 49/2 was carried out in barley at the five leaf stage on 4th June 1954.
Experiment 49/12 was carried out in peas at 6" high on 14th June 1954.

Abbreviations used as follows:-

4-Cl.B.	ω(4-chlorophenoxy) butyric acid.
2:4-DB.	ω(2:4-dichlorophenoxy) butyric acid.
3:4-DB.	ω(3:4-dichlorophenoxy) butyric acid.
2:4-5-TB.	ω(2:4:5-trichlorophenoxy) butyric acid.
MCPB.	ω(4-chloro-2-methylphenoxy) butyric acid.

TABLE II

SUMMARY OF CONTROL BY MCPB OF WEEDS MOST FREQUENTLY OCCURING IN THESE EXPERIMENTS

Species	Expt. No.	Crop	Control pop./sq.yd. and mean ht. at counting	% control (dose rates in lb./acre)						
				MCPB				MCPA		DNBP
				¼	½	1	2	½	1	1
Creeping Thistle	49/2	Barley	22 x 33"	-	83	91	92	-	-	--
	49/4	Undersown S.Wheat	6 x 14"	-	57	83	91	61	65	--
	49/6	Barley	16 x 22"	-	73	68	71	79	83	-
	49/10	Direct sown Clover	14 x 33"	-	79	84	61*	-	-	-
	49/12	Peas	14 x 20"	-	80	84	100	-	-	-
Charlock	49/8	Peas	15 x 22"	69	62	94	-	96	-	100
	49/10	Direct sown Clover	10 x 34"	-	88	100	98	-	-	-
Knotgrass	49/2	Barley	10 x 13"	-	10	65	87	-	-	-
	49/4	Undersown S.Wheat	9 x 10"	-	39	28	61	42	56	-
	49/8	Peas	11 x 8"	35	47	77	-	53	-	71
	49/10	Direct sown Clover	4 x 14"	-	72	43	57	-	-	-
	49/12	Peas	28 x 13"	-	34	64	75	-	-	-
Fat Hen	49/2	Barley	7 x 11"	-	96	96	86	-	-	-
	49/10	Direct sown Clover	1 x 13"	-	0	88	88	-	-	-
	49/9	Peas	6 x 6"	0	12	24	-	47	-	0
Sowthistle (Perennial)	49/2	Barley	2 x 34"	-	100	100	100	-	-	-
	49/10	Direct sown Clover	4 x 27"	-	79	86	72	-	-	-

* Exceptionally large thistle population in one replicate - survivors all badly stunted and distorted.

The following species occurred too spasmodically to be included in the table, but appeared to be killed or severely damaged by doses of 1-2lbs./acre of MCPB where they did occur:-

Poppy	-	seedling plants only.
Perennial sowthistle	-	killed wherever it appeared.
Annual sowthistle	-	moderate control of small seedlings.
Black bindweed	-	typical stunting as with MCPA.
Seedling curled dock.		

Control of Ivy-leaved Speedwell was variable but in two later experiments where it was sprayed at the two-leaf stage in direct sown Clover a substantial reduction was obtained.

Groundsel appeared to be almost completely resistant to MCPB.

COMPARISON OF THE EFFECT ON SEEDLING CLOVER VIGOUR OF MCPB AND MCPA

Table III. Experiment 31/6

Variety	Compound	Clover-leaf density as percentage of control (dose rates in lb./acre)				
		½ lb.	¾ lb.	1½ lb.	2 lb.	3 lb.
Kentish Wild White	MCPB	140	190	187	194	141
	MCPA	77	79	90	73	30
Early Red	MCPB	73	98	91	105	68
	MCPA	48	44	72	71	-

Sprayed: 16.8.54. at 3-4 leaf stage.
Assessed: 26.11.54. (See also plate I).

Weeds present: Moderate population of creeping thistle killed by all rates above ½ lb. Dense population of ivy-leaved speedwell checked by rates above ¾ lb.

Table IV. Experiment 31/7

Variety	Compound	Clover-leaf density as percentage of control (dose rates in lb./acre)					
		½ lb.	1 lb.	1¼ lb.	1½ lb.	1¾ lb.	2 lb.
Kentish Wild White	MCPB	71	70	68	67	69	59
	MCPA	79	57	36	39	14	20
Late Red	MCPB	85	118	116	102	97	90
	MCPA	100	98	100	73	49	65
S.100	MCPB	104	113	114	52	56	94
	MCPA	104	45	34	36	14	47

Sprayed: 23.9.54. at 2-3 leaf stage.
Assessed: 27.11.54.

Weeds present: Species and degree of control as for Table III, but only slight infestation.

Very little clover growth after spraying at this late date.

Table V

EFFECT OF MCPB AND MCPA ON CLOVER STAND IN UNDERSOWN SPRING WHEAT

Experiment 49/4. Results expressed as percent. of control population.

Varieties	Compounds and dose in lb./acre				
	MCPB			MCPA	
	½	1	2	½	1
S.100 white	123	141	150	125	108
Late red	161	100	110	95	109

Treatments applied on 16th June, clover in 3-leaf stage.
Counts made on 10th August, 1954.

For weed infestation and control see Table II.

TABLE VI

EFFECT OF MCPB ON HAY AND SEED YIELDS FROM THREE-YEAR LEY.

Experiment 31/5. (All results expressed as percent. of control value)

	Compounds and doses in lb./acre								
	MCPB			2:4-D.B.			MCPA		
	½	1	2	½	1	2	½	1	2
Yield of hay	121	136	109	113	114	102	98	92	83
Wt. S.100 flower heads	-	-	71	-	-	-	-	-	3
Wt. S.100 seed	-	-	62	-	-	-	-	-	1
Germination S.100 seed	-	-	92	-	-	-	-	-	100

Treatments applied on 24th June 1954, clover two thirds in flower.
Yields taken 15th - 20th August, 1954.

TABLE VII

EFFECT OF VARIOUS COMPOUNDS ON YIELDS OF PEAS EXPRESSED AS PERCENT. OF CONTROL YIELDS

Experiment 49/12.

Variety	Compounds and doses in lb./acre								
	MCPB			3:4-D.B.			4-Cl.B.		
	½	1	2	½	1	2	½	1	2
Onward	77	86	75	77	72	60	109	71	47
Harrison's Glory	71	119	87	67	91	97	89	82	57

Sprayed on 14th June, peas 6" high.
Onward picked green and shelled on 11th August.
Harrison's Glory harvested dry, 2nd September and threshed 5th - 8th October.
For weed population and control see Table I. (see also plate III).

Experiments 49/8 & 49/9. (Kelvedon Wonder for deep freezing)

Experiment No.	Compounds and doses in lb./acre					
	MCPB			4-Cl.B.		MCPA
	¼	½	1	½	1	½
49/8	105	107	96	77	56	53
49/9	120	121	136	146	107	101

Experiment 49/8 - Sprayed on 15th June, peas 6" high, picked green, shelled on 5th August.

Experiment 49/9 -- Sprayed on 15th June, peas 7" high, picked green and shelled on 12th August.

TABLE VIII

A POT EXPERIMENT ON THE VARIETAL RESPONSE OF PEAS TO MCPB AND 2:4-D.B.

Compound and dose in lb./acre		Dry weights of each variety expressed as percent. of control, taken one month after treatment.				
		Kelvedon Wonder	Onward	Meteor	Harrison's Glory	Rondo
MCPB	½	120	100	118	102	70
	1	108	67	40	116	68
	1½	85	69	27	87	67
	2	89	60	28	75	51
2:4-D.B.	½	69	42	45	67	58
	1	58	36	48	53	60
	1½	46	30	27	57	45
	2	32	24	26	31	27
MCPA	1	7	4	21	16	28
	1½	4	8	15	6	22
	2	0	14	17	4	13
2:4-D.	1	0	12	6	7	11
	1½	0	5	6	2	9
	2	0	3	5	2	0

Peas sprayed at two expanded leaf stage.

2:4-D.B. and 2:4-D. applied as diethanolamine salt.

MCPB and MCPA applied as potassium salts.

All in 10 galls. water/acre.

DISCUSSION

A. Weed Control.

(i) Structure activity in the ω(phenoxy)butyric acids.

The initial comparative experiment (Table I) showed quite clearly that 2:4:5-TB. had negligible activity against creeping thistles (Fig. I). This was confirmed in three further experiments directed mainly against other weeds. Of the other compounds MCPB and 2:4-DB. were the most active against this weed giving good kills in all experiments. Apart from the poorest shoot kill given by 3:4-DB. and 4-Cl.B., the surviving plants from these treatments were only slightly affected except for blindness in the growing tip. This did not prevent them making fairly vigorous vegetative growth and presumably replenishing the root systems. Survivors from the 2:4-DB. and MCPB treatments were all seriously distorted and made little subsequent growth.

The very slight superiority of MCPB over 2:4-DB. shown against creeping thistle in experiment 49/12 has been confirmed at two out of three other sites. At the third there was no difference.

As far as annual weeds were concerned, 2:4:5-TB. was again markedly inferior even against charlock. Charlock and fat hen were roughly equally susceptible to all the remainder but knotgrass and black bindweed were much less susceptible to 4-Cl.B. and 3:4-DB.

2:4-DB. and MCPB were generally similar in activity, the differences detected in these experiments being parallel to the differences between 2:4-D, and MCPA (e.g. control of knotgrass). More exact methods of comparison will be necessary to evaluate the relative potency of these two compounds accurately.

(ii) The activity of MCPB as compared with MCPA

The number of direct comparisons (Table II) was very limited for reasons already given. If all the evidence from greenhouse experiments and the considerable information we already possessed on the activity of MCPA are taken into account, some general comparisons can be made.

MCPB appears to have been no less active than MCPA against the shoots of creeping thistle. The effect on the root system will obviously not be known until next year.

It was less active than MCPA against cruciferous weeds at rates of application of ½ lb. or less but at rates of 1 lb./acre or above the difference was negligible, control being virtually complete. MCPB was also very slightly less active against other annual weeds susceptible to MCPA such as fat hen, knotgrass and poppy, but these differences were again usually negligible, at doses of 1lb./acre and over. The nature and size of these differences has been most clearly demonstrated in the pot experiments.

A number of other species which are only moderately affected by MCPA, i.e. ivy-leaved speedwell, black bindweed, pale persicaria and annual sowthistle, all appeared to respond similarly to MCPB but occurred too infrequently to give quantitative estimates of kill. Notable exceptions were chickweed, scentless mayweed and groundsel which were almost completely resistant to MCPB.

More accurate comparisons between the two acids are desirable but the main purpose of the weed control investigations has been achieved - that is to show that MCPB gives good control of many growth-regulator susceptible weeds at an economic dose-rate (1 - 2 lbs./acre).

B. Crop Toxicity.

(i) Seedling clover

The first experiment on toxicity to seedling clover was carried out on an area known to be badly infested with creeping thistle and charlock (Table II) (49/10). Strips of Kentish wild white, S.100 white, broad red, late red, Alsike clover and lucerne were drilled with grass and sprayed at the 2-3 leaf stage with 2:4-DB., MCPB, 2:4:5-TB. and their ethyl esters at ½, 1 and 2 lbs. 15 galls./acre. The weeds offered only slight cover to the clover at that time. Weed control was excellent with 2:4-DB. and MCPB and their esters at the 1 lb. and 2 lb. rates and the young clovers grew very rapidly. At 2 lb./acre some curvature and darkening of red clover leaflets was observed but the new growth was free from distortion. None of the five clover varieties seemed to suffer more than a slight temporary check. Lucerne, however, seemed much less resistant and suffered some reduction in stand and vigour. The subsequent weed growth in the control plots was so vigorous that clover growth in them was very largely smothered (Table II, 49/10). The experiment was therefore valueless for quantitative measurement on direct toxicity to the clover and none was attempted. The vigour of all varieties eight weeks after MCPB treatment (Fig. II) left no doubt that this compound had practical possibilities not only for use in undersown cereals but for the control of creeping thistle and possibly other perennial weeds in direct seeded leys.

Four experiments were laid down in undersown cereals but at that late period good sites were difficult to obtain. Of these four, only two produced useful information on toxicity to clover. The results for 49/4, which contained a comparison with MCPA, are given in Table V. Experiment 49/5 gave very similar results for MCPB but did not include MCPA.

A field experiment to compare the toxicities of MCPA and MCPB on four clover varieties was therefore started in late July. Strips of Kentish wild white, S.100 white, late red and broad red clover were drilled with grasses and sprayed at the 3-4 leaf stage (Table III).

Wet weather made drilling conditions difficult on our heavy soil and emergence of both S.100 and late red was so patchy that quantitative assessments of these two varieties could not be made. An even plant of the other two varieties was obtained and counts of leaf density made later (Table III). These plots contained a moderate population of creeping thistle and a dense population of ivy-leaved speedwell. The former was killed and the latter, which was at the 2-3 leaf stage at the time of spraying, was severely checked by the three higher doses of both compounds. This check almost certainly accounts for the much larger densities of wild white clover in the MCPB plots three months after treatment as compared with controls. It was obvious from our periodic observations that the larger and faster growing red clover was much better able to cope with speedwell competition than the wild white. The balance between the two appeared to be fairly delicate, however, and the lower doses of MCPA had apparently upset it in favour of the weed. The reversal of the more usual relative susceptibilities of these two varieties to MCPA at the lower rates of application can be explained by this effect. Photographs taken six weeks after treatment (Fig. 1) give a more typical picture.

A further experiment designed to fill the gaps left by failures in the above was ready for treatment in late September, the clover being rather younger than before. As the weed population was small, assessments of this experiment were more in agreement with the usually accepted susceptibilities of red and white clover to MCPA (Table IV). The much lower densities of wild white clover given by all treatments are very probably due to the lateness of the experiment, which has not allowed this slower growing variety to recover from initial check.

Neither of these two experiments can be fully assessed until next year. The data obtained so far do demonstrate however, the much lower susceptibility of red and white clover seedlings, especially the latter, to MCPB as compared with MCPA. It must be emphasised that these results are based on leaf counts not plant counts, and are therefore a measure of check to growth and not kill. In a number of pot experiments on S.100 white clover no kill was obtained even at rates up to 4 lb./acre of MCPB. Susceptibility decreased rapidly with age. At the 6-7 leaf stage hardly any visible effect was obtained at 4 lb. beyond some darkening of the leaves and slight check to growth. Similar results have been obtained with red clovers.

The results with MCPA in the field experiments are in general agreement with those of Scragg(5), Holly(6) and Ochiltree(7).

There seems little doubt therefore that MCPB can be safely recommended for use in seedling clovers at the two trifoliate leaf stage and above, at rates not exceeding 1½ lb./acre.

(ii) Established clover

One experiment was carried out on a weed-free ley sown in May 1951 and consisting of perennial ryegrass, cocksfoot, timothy, S.100 white clover and S.123 red clover. MCPB, 2:4-DB. and MCPA were applied in June when the clover was about two-thirds in flower. The vigour of the S.100 clover was very considerably reduced by MCPA immediately after the treatment and flowering was almost completely stopped. Recovery was rapid, however, and by the time yields were taken, eight weeks later, the MCPA treated plots were not much inferior to those treated with MCPB and 2:4-DB., although the latter had never shown the slightest sign of check. The general increases in yield after the phenoxy butyric acid treatments, which were found on all replicates, probably resulted from changes in the interspecies competition balance. A general view of this experiment, showing some of the effect on clover vigour, is given in our report on the techniques used(4).

Seed yields of S.100 were also taken from the 2 lb. treatments of MCPB, MCPA and control and showed that although the MCPB had caused some loss this was very slight when compared with the effect of MCPA.

From this experiment it seems probable that MCPB could be used for the control of perennial weeds in high clover content leys for hay and silage without yield reduction and, once the effect of timing has been properly investigated, in seed production crops also.

C. Peas

The results of field and greenhouse experiments on the response of peas are given in Tables VII and VIII. The initial screening experiments (using Kelvedon Wonder) has suggested that MCPB, 3:4-DB., 4-Cl.B. and 2:4:5-TB. were all fairly non-toxic. 2:4:5-TB. and later 3:4-DB. were discarded because their weedkilling power was too low. (Fig. III).

The yield results with 4-Cl.B. show that this compound is somewhat toxic at weedkilling doses and it does cause some 'fern-leaf' symptoms as well as loss in yields.

MCPB is clearly the most promising member of the series. Even this compound produces some initial check and slight stem deformity but in the field recovery is rapid. Pot experiments tend to exaggerate this effect (c.f. Tables VII and VIII), assessments have to be made after about one month, i.e. before full recovery can be made. The importance of varietal response is obvious and the stage of growth probably has some influence.

These points will have to be more fully investigated before treatment of this crop can be recommended.

D. Other Crops

The only other crops examined in the field were carrots and lettuce which had both appeared to be fairly tolerant to 2:4-DB., MCPB and 2:4:5-TB. in the greenhouse tests. Field tests with three varieties of lettuce showed that these were only tolerant to a practical degree to 2:4:5-TB., which was insufficiently active as a weedkiller. The tops of the two varieties of carrots used did not react strongly to 2:4-DB. or MCPB although some typical growth regulator distortion and swelling was observed in the growing point. Between 70% and 85% of the carrots harvested, however, showed severe malformation of the roots at rates of 1 lb. and 2 lb./acre.

CONCLUSIONS

1. The evidence on the weedkilling powers of the substituted ω(phenoxy) butyric acids is sufficient to show that MCPB and 2:4-DB. will give good control of many of the important growth regulator susceptible weeds at dose rates of 1-2 lbs. per acre in the field. The other members of the series are less efficient in various ways.

2. Both MCPB and 2:4-DB. showed a very low degree of toxicity to clovers in preliminary experiments. Further experiments comparing MCPA and MCPB show that the latter could be used with a high degree of safety on red and white seedling clovers at the two-leaf stage and above, at dose rates of up to 1½ lbs. per acre.

3. MCPB also has a low degree of toxicity towards some varieties of peas but further work on varietal response and time of application are required before tentative recommendations can be made. 2:4-DB. is much more toxic than MCPB to this crop.

4. For these and certain chemical reasons, MCPB has been chosen by us as being the most promising member of this series for immediate commercial development.

Acknowledgements

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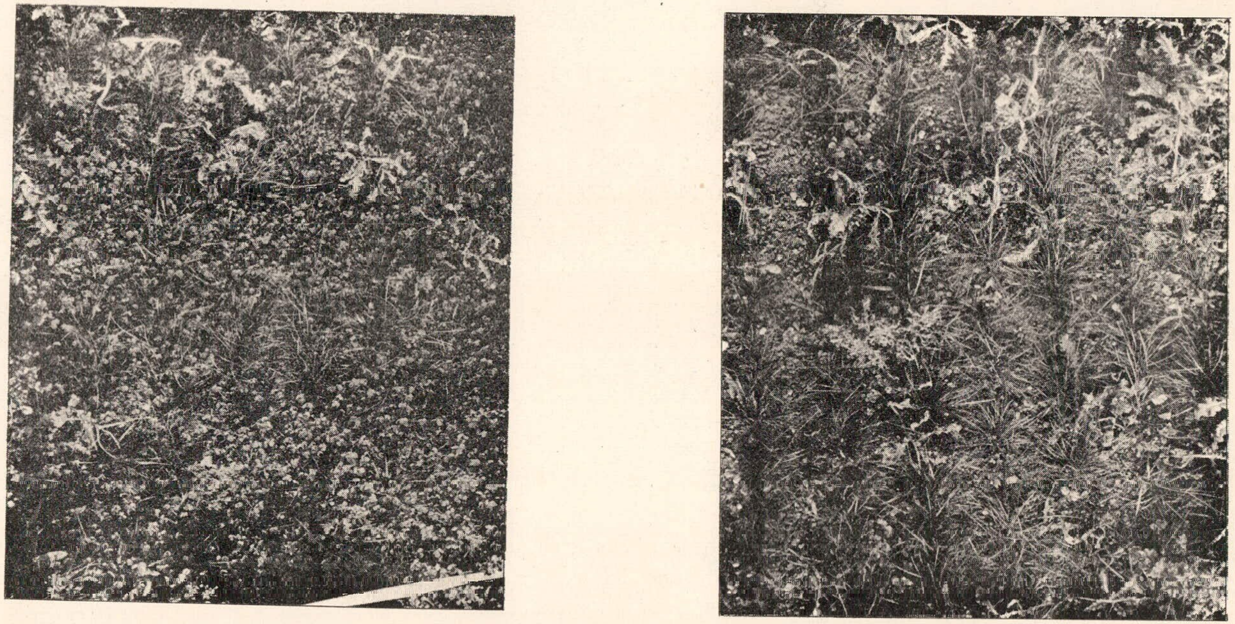
Fig. I. Tolerance of direct sown clover to MCPB and MCPA.
Experiment 31/6. (Table III).

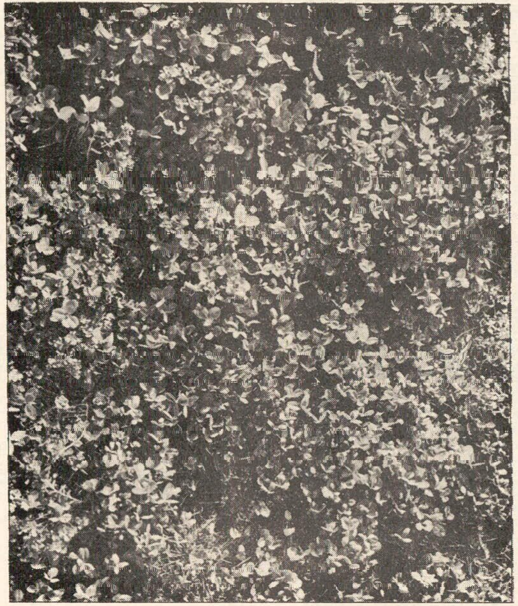
(a) Wild white clover ley.



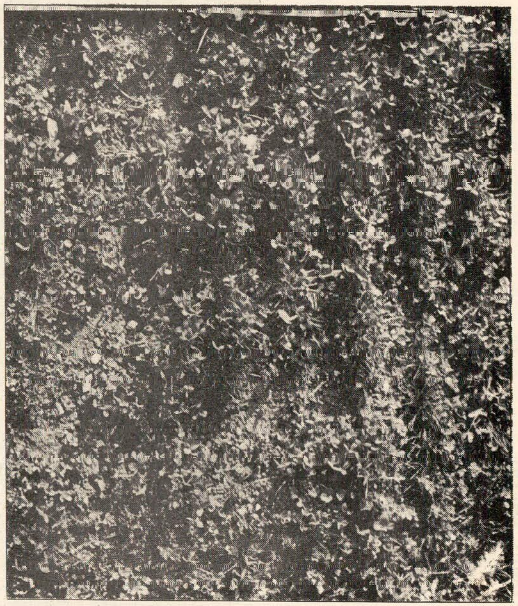
MCPB 3lb./acre

MCPA 2lb./acre

(b) Early red clover ley.



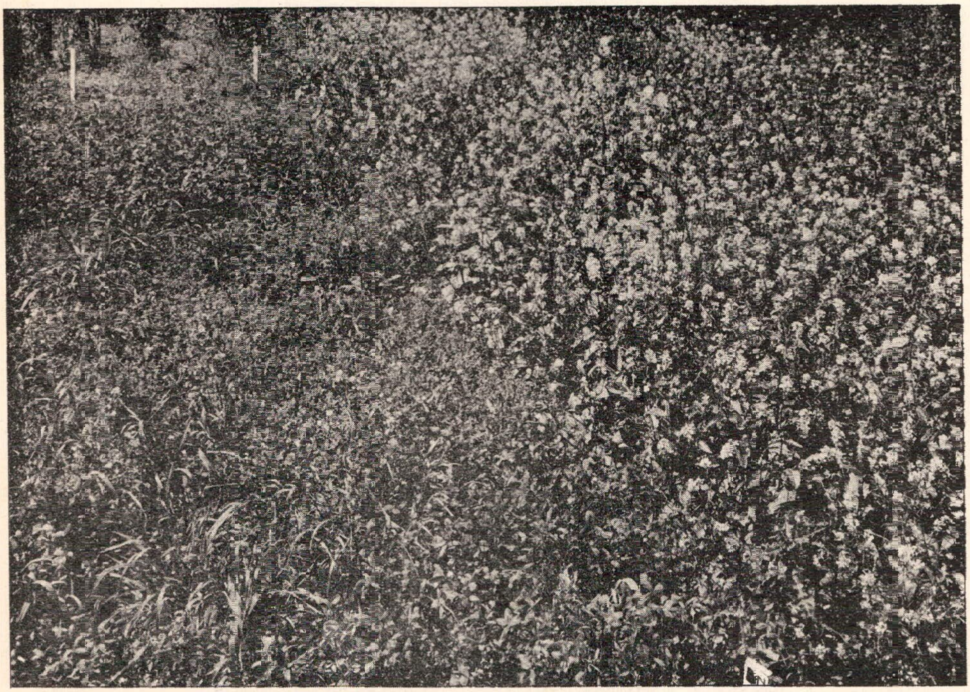
MCPB 3lb./acre



MCPA 2lb./acre

Clovers sprayed at 3-4 leaf stage on 16.8.54. Photographs taken six weeks later. Each photograph represents one variety plot, less discards, and covers an area 4° x 3°6".

Fig. 11. Control of Charlock by MCPB.
Experiment 49/10.



Top right - untreated (for weed density see Table 11).
Bottom left - MCPB at 1lb./acre.

Crops sprayed at two to three leaf stage. Photographs taken eight weeks later.

Clover in foreground is late red, that in the background S.100 white, containing uncontrolled groundsel.

This is part of the first field experiment on seedling clovers.

Fig.III. Control of creeping thistles in Harrison's Glory peas. Experiment 49/12.

2:4:5-T.B. 1lb./acre

MCPB ½lb./acre

Peas sprayed at 6" high. Photograph taken six weeks later. For weed control see Table I. (Knotgrass survivors hidden by peas). For pea yields see Table VII.