Research Report No. D.5.

# CHEMISTRY AND HERBICIDAL PROPERTIES OF TRIAZINE DERIVATIVES

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Geigy Co., Basle

## Summary

The synthesis and the plant growth influencing properties of a number of triazine derivatives have been described. If the three chlorine atoms of cyanuric chloride are replaced by one, two or three amino- especially low molecular aliphatic amino-, alkoxy- and alkylmercapto- groups, chemicals are obtained which have an influence on the growth of plants. The activity is best on the young plant and is mainly due to the chemical which is taken up from the soil through the root system. Some representatives particularly the more soluble ones are absorbed at least in part through the leaves also. Triazines having one halogen atom preferably chlorine or bromine and in addition ethylamino-, iso-propylamino- and diethylamino-groups show considerable promise as overall toxic as well as selective herbicides. Crops being tolerant to the more promising triazines in amounts which lead to a commercial weed control are maize, sorghum, milo, grapes, asparagus, sugar cane etc. Some other crops like peas, beans, potatoes and tobacco are relatively resistant to a number of triazines. G. 25804 is tolerated in addition by cotton, strawberries, carrots and onions.

Some relationship between structure and activity could be determined. The best herbicides of the triazine group have in addition to one halogen atom two amino-groups which are substituted with alkyl radicals having 4 - 8 carbon atoms for the 2 nitrogen groups together. The substitution of the halogen atom by alkoxy- or amino-groups decreases the activity of these compounds. The triazine ring is not the condition sine qua non to give products with plant growth influencing properties. In addition to the triazine-ring, especially some other 6-membered nitrogen containing heterocyclic ring compounds are of interest.

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When we started in 1952 to synthesize and to test triazine derivatives, weed-killers belonging to the following chemical groups were either on the market or under investigation as experimental compounds:

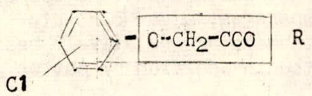
1. Arylhydroxy-fatty derivatives such as 2,4-D.
2. Urethanes of aromatic amines such as propham.
3. Aryldialkyl-ureas such as monuron.
4. Maleic acid hydrazide.

The inorganic chemicals are only mentioned here by the way; they are of no interest for us as we are dealing in this paper strictly with organic chemicals.

Among the above mentioned groups of chemicals only 2,4-D and propham were rather extensively tested and their spectrum of activity was already known at the beginning of our work. While 2,4-D had found a very wide use for the control of broadleaf weeds in all kinds of small grain, propham was tolerated fairly well by dicotyledons but it controlled grasses. In Great Britain and in the United States of America considerable work had been done in the herbicide field since the last world war, and a great number of 2,4-D analogues were synthesized and tested. In addition to 2,4-D especially 2-methyl-4-chlorophenoxyacetic acid (MCPA) was found to be a more specific herbicide in this country and a great number of papers deal already with the activity of this chemical. We were more interested in the urethane-type of chemicals. The first field results with DuPont's monuron indicated that not only aryl-urethanes of propham type but also aryl-ureas showed interesting herbicidal properties. It became evident that with the ureas a selectivity between monocotyledons and dicotyledons no longer existed to the same extent as with 2,4-D or propham.

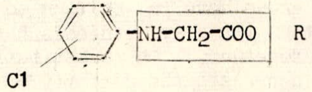
By comparing the structures of the following chemicals:

2,4-D-Type



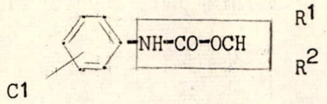
I acid, salts, esters

Glycine-Type



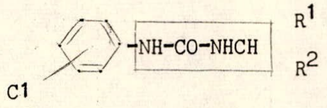
II acid, salts, esters

Propham-Type IPC



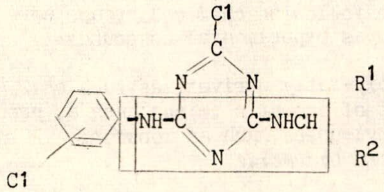
III $R^1$: H, alkyl; $R^2$: alkyl esp. $R^1 = R^2 = CH_3$

Monuron-Type



IV $R^{1,2}$: H, alkyl

Triazine-Type

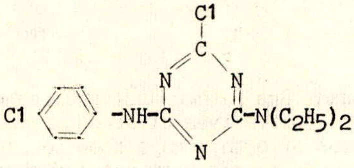


V $R^{1,2}$: H, alkyl

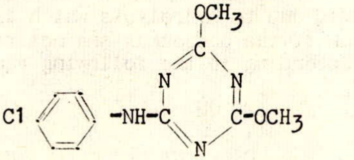
their similarities become obvious. From the 2,4-D-type (I) over the isosteric phenylglycine compounds (II) substances of the propham-series (III) are obtained by isosteric replacement. $N^1$-iso-propyl-$N^3$-phenyl ureas (IV) are also isosteric to compounds of the propham-type.

In the literature several examples are known in which it was found to be possible to substitute the carbonyl group of an urea by a triazine-ring without a fundamental change of the properties of these chemicals. We decided therefore to make an attempt in this direction and to synthesize compounds of the general structure (V). Cyanuric chloride with its three reactive chlorine atoms is an attractive intermediate for the synthetic organic chemist. The fact that it is possible to replace the chlorine atoms step by step with different substituents explains the enormous variety of chemicals which can be made by using cyanuric chloride as a starting material. Practically all hydroxy-, mercapto- and amino-compounds react with cyanuric chloride to give ethers, thioethers, amines or mixed products of the three classes of chemicals. Of all reaction products theoretically possible, only a limited number of chemicals was synthesized, i.e. a limited number in regard to those theoretically possible. These compounds were made in our laboratories by my co-worker E. Knüsli and tested by A. Gast for their plant growth influencing properties.

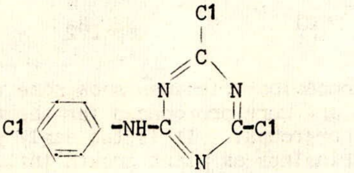
In a first series reaction products of cyanuric chloride with aromatic amines were made, in which the 2nd and 3rd chlorine atom of cyanuric chloride were either left unchanged or were substituted further with alcohols or aliphatic amines. One compound was made by replacing the first and the 2nd chlorine atom of cyanuric chloride with an aliphatic amine:



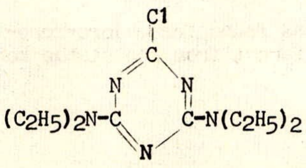
G. 27902



G. 25799



G. 25796

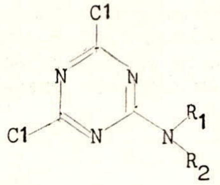


G.25804

Compounds G. 27902 and G. 25799 did not show any significant herbicidal activity. Compound G. 25796 had more interesting properties. In the routine screening test it showed only a very slight activity as a herbicide but its fungicidal properties were good enough that this chemical was tested further in the field. Here it became evident that its phytotoxic side reactions were such that this compound had to be dropped from field tests on grapes. Chemicals of this type have been published in the meantime by Wolf and co-workers of Ethyl Corp. The o-chloro-anilino-dichloro-triazine was tested as a fungicide quite extensively under the number B 622 in the U.S.A. but it shows some phytotoxicity too. A great increase in activity is reached with compound G.25804, derived from cyanuric chloride by replacing 2 chlorine atoms by 2 diethylamino-groups. Based on this result we made a rather extensive study of the reactions of cyanuric chloride with all kinds of aliphatic amines.

The chemicals as such are known in part, in part new ones. Their use as plant growth influencing compounds is covered by patent applications.

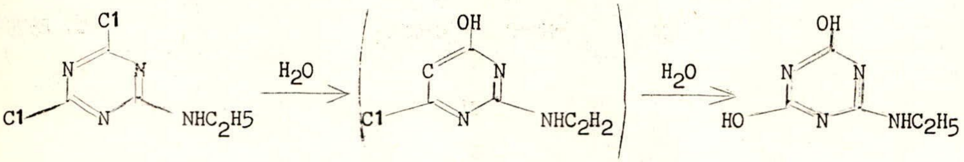
The substitution of one chlorine atom only with aliphatic amines has to be made very carefully in order to avoid the formation of diaminochloro-triazines. If the reaction-temperature is kept low enough, however, it is possible to get chemicals of the following general type:



$R_1$ = H or alkyl

$R_2$ = alkyl

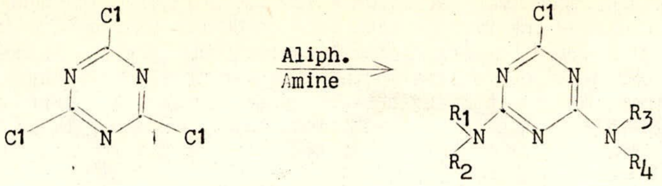
If $R_1$ is hydrogen the compounds are rather unstable, especially the members with low molecular-weights. Derivatives of secondary aliphatic amines are more stable. Representatives of both groups show considerable activity against a variety of weeds. We do not know yet for sure if it is only the formation of hydrochloric acid due to hydrolysis which is responsible for a rather severe leaf burning or if the compounds are active weedkillers as such. The hydrolysis takes place according to the following equation:



Several of these dichloro-monoamino-triazines show some very definite skin irritation properties which are more pronounced for the compounds having aliphatic than aromatic amino-groups. It is too early yet to judge the value of the dichloro-monoamino-triazines as plant growth influencing compounds.

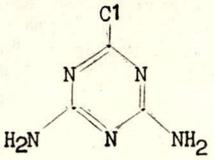
The same instability was found for chloro-mono- and dialkoxy-triazines, the latter being absolutely different from the stable monochloro-diamino-triazines.

If cyanuric chloride is substituted by two aliphatic amines chemicals of the the following type are easily formed:



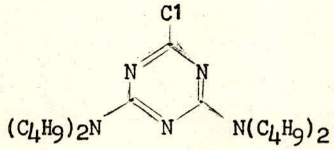
$R_{1-4}$ = H or alkyl

Their biological properties vary very much with the number of the carbon-atoms of the respective amines used for the substitution. A compound having two unsubstituted amino groups plus one chlorine atom



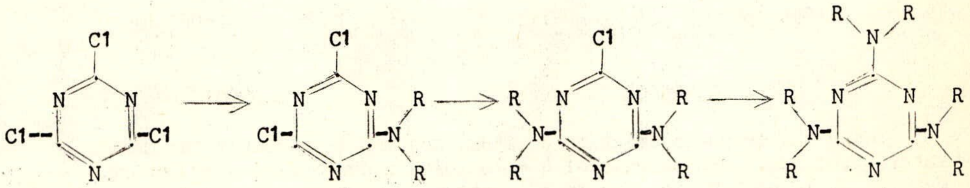
G. 28273

does not show any significant herbicidal activity. If the number of carbon atoms is as high as 16 in disubstituted chloro-amino-triazines, for example the chloro-bis-dibutyl-amino-triazine,



G. 27895

this chemical does not have any significant weed control property. Between these two extremes, however we found a number of mono-chloro-bis-alkylamino-triazines with good to very good herbicidal properties. It is this type of chemicals in which we are primarily interested as among these triazines we believe to have found the most promising products. In the preliminary screening tests practically all compounds have some activity so that a relatively high percentage of these products had to be tested further in secondary tests and in part in field-tests later. If in the formulae below the number of C-atoms for R is kept between 1 and 5 several hundred chemicals are theoretically possible among which the best candidates had to be selected:



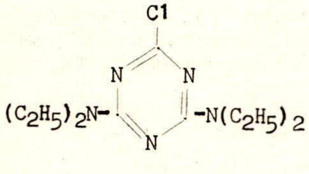
R : H, Alkyl $C_{1-5}$

From the very beginning we had two different goals in mind, namely to find if possible, a herbicide which could be used due to its overall toxicity against a large number of weeds and secondly a herbicide which was selective in regard to its activity towards crops. The first category of compounds should have in addition to a weedkilling effect a long residual activity in order to be competitive with existing cheap compounds like sodium chlorate or TCA which have a rather short activity and have to be used several times per season. For an overall toxic herbicide it is necessary in addition that the solubility of such a chemical be rather low, so that the risk of a transport from a treated to an untreated area is reduced as much as possible.

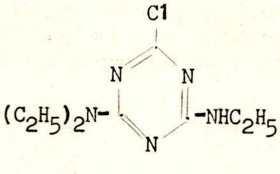
For the selective type it is necessary to have a compound or a series of compounds which are tolerant to one or several crops and have a sufficient herbicidal activity on the weeds present. In addition, it is desirable that such a chemical can be used both as a pre-emergence and as a post-emergence-herbicide. In cases where a crop-rotation is normal the carry-over effect from one year to another has to be as low as possible. To have all these requirements united in one chemical is a goal much more difficult to attain than to find an overall toxic compound. In addition to the difficulties which exist for the crops and the weeds the variability of the soils, the climatic conditions, the microfauna etc. have a great influence on the activity and the residual effect of a herbicide.

Among our triazine-compounds representatives of the overall toxic and the selective type were found. It became evident from our first field-test that maize (corn) is extremely tolerant to all triazine-derivatives tested by us so far. The tolerated dosages towards maize are so high that we consider this as a fundamental difference between these triazines and the aryl ureas of the monuron type. In addition brush and woody plants seem to be considerably more tolerant to the triazines which can be an advantage or a disadvantage, according to the purpose for which these herbicides are used.

From the weedkilling point of view among the chloro-bis-amino-triazines those having ethyl-, propyl-, i-propyl- or allyl- substituents show the best results. In regard to selectivity compounds having one or two diethyl-amino-groups are superior to all others.. Chloro-bis-diethyl-amino-triazine and chloro-ethylamino-diethylamino-triazine are the most interesting derivatives at the present time. These two compounds were tested rather extensively in Switzerland and in the United States.



G. 25804



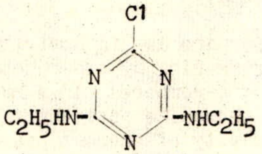
G. 27901

Among the crops tolerant to G. 25804, cotton is probably the most interesting one. In amounts of 4 - 10 lb/ac a commercial weed control is reached while no harm is done to the cotton. G.27901 is more active but definitely less selective on a number of crops. Grapes, beans, peas, potatoes, and cotton are tolerant to G. 27901 at dosages which give a commercial weed control. Due to their higher solubilities G. 25804 as well as

G. 27901 have the possibility of being absorbed at least in part from the leaves and the root-system faster than compounds having a lower solubility. This opens the field for triazine-derivatives to be used as post-emergence herbicides.

There is a considerable difference in the effect of triazines on annual and perennial weeds. The first category is controlled more easily than the latter. Deep rooted weeds like dandelions or bindweed are extremely difficult to control. Most of the active ingredient is kept near the soil surface so that it would be desirable for this purpose if the herbicide could be taken up by the shoot of the plant also.

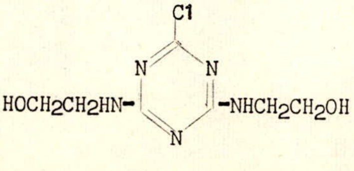
If cyanuric chloride is substituted with 2 moles of mono-alkyl-amines instead of diethylamine in G. 25804, the weedkilling potency of these chemicals is considerably increased. Chloro-triazines being substituted with 2-ethyl-amino- or 2-iso-propyl-amino-groups have the strongest activity. The chloro-bis-ethyl-amino-derivative has been tested in Switzerland as well as in U.S.A. in 1955 and especially this year under the common name simazin.



G. 27692

The dosages which give the same herbicidal effect are, compared with G. 25804, considerably lower. Amounts as low as 1 - 2 lb/ac are able to kill annual and perennial weeds when applied pre-emergence. Due to its insolubility in water very minute amounts only are absorbed through the leaves so that practically the whole activity comes from the uptake through the root-system. In order to bring the compound down to the rootlets it is necessary to use a sufficient quantity of water. In a soil having a large amount of humus the risk that the chemical is adsorbed at the very surface is rather high. A special particle size as well as a sufficient amount of emulsifier can help to bring the compound to the necessary depth. In regard to the mode of action we do not know at the present time how the compound interferes with the plant metabolism. The triazines do not have, however, a plant growth regulating activity in the classical sense of the auxins and antiauxins. Bean epicotyls treated with simazin and kept in a horizontal position developed normal negative geotropic reactions. All compounds of the triazine type have only a negligible influence on germination, so that the main effect is on the young plant. Germination of the weeds takes place in a normal way and the young plants are killed after a period of 4 - 6 weeks. The first sign of activity is a yellowing of the leaves which is significantly different from the albinism which is caused by amino-triazole.

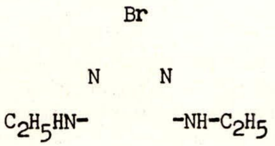
By replacing aliphatic amines by hydroxylated aliphatic amines, compounds of the following type are obtained:



G. 27693

Compared with the respective hydroxy-group-free chemicals as mentioned above they still have a significant but inferior effect, while the bis-morpholino- and bis-piperidino-derivatives have little or no influence on plant growth. The bis-cyclohexyl-amino- as well as the bis-arylalkylamino-monochloro-s-triazines are practically inactive, and the same is true for the corresponding compounds formed from aromatic amines, from glycines, or glycino-ethylester.

If one chlorine atom in the triazine-ring is replaced by bromine, compounds of the following structure are obtained:



G. 31132

for example is highly active. If the halogen atom is substituted by another amino-group, by an alkoxy- or by a substituted amino-alkyl-oxy-group the chemicals are still influencing the plant growth.

Derivatives of the isocyanuric acid-series are low in activity. In principle it is possible to replace the triazine ring by other heterocyclic ring-systems. Especially nitrogen containing 6-membered rings having halogen, amino-groups or alkyl-groups as substituents show some activity in preliminary tests. It is too early to report on the activity of these types of chemicals.

In regard to the effect of triazines towards warmblooded animals, insects or fungi we know that the toxicity towards animals depends on the solubility of the respective product but it is in general rather low. $LD_{50}$'s of 1 g to over 5 g/kg for mice or rats given per os are frequent. Some triazines have a significant activity on fungi while the insecticidal activity of the whole group is negligible. There is to our knowledge only one member of the triazine-group, the triallyloxy-triazine which was synthesized by the American Cyanamid Company and which is said to have an insecticidal activity. According to our screening-tests the insecticidal activity is practically zero, however.

## Acknowledgement

Grateful acknowledgement is given to A. Gast and H. Grob for the biological evaluation of the chemicals described. For very useful data also our best thanks to the staff of the biological laboratories of Geigy-New York.

Basle, September 1956.

## DISCUSSION ON THE PREVIOUS PAPER

Dr. B. J. Heywood (Introduction to discussion)

Dr. Gysin and his colleagues are to be congratulated on completing a very fine piece of research leading to the discovery of this new group of herbicides. The research staff of the Geigy Company has brought into play their experience gained in a number of other fields apparently unconnected with herbicides. Thus, research work with both dyestuffs and pharmaceuticals have played their part. In dyestuffs the amide linkage confers affinity for cotton when introduced into certain molecules and this 'substantivity' as it is called, is not lost when the amide linkage is replaced by the triazine ring linkage. The group does not profoundly alter the properties except in this one respect. It is apparently necessary with the triazine compounds to alter the type of the end groups attached to the triazine ring to obtain high herbicidal activity. The question one would therefore ask is: has the hypothesis been tested in reverse? That is, has the aminotriazine linkage in simazin been replaced by the amide linkage to give a symmetrical diethyl urea? What is the herbicidal activity of this compound? Also, since the triazine compounds are not plant growth regulators, does Dr. Gysin think that the original hypothesis is still tenable?

One final question concerns residues left on plants. In my opinion it is very proper that growing concern is shown regarding the dangers of pesticidal residues left on food products. Is there a suitable method of analysis available for estimating these harbicides in both plant and soil?

Dr. H. Gysin

One of the important reasons for making more toxic soil sterilants is that the inorganic products have to be applied at high rates. Analytical methods are available for amounts down to 0.1 p.p.m. in soil or plant tissues.

Dr. W. E. Ripper

Is there any toxicological information on the triazines.

Dr. H. Gysin

The LD 50 of chlorazin is 2 g/kg and of simazin 5 g/kg to mice.

Mr. G. G. Fisher

Has Dr. Gysin any information on the adsorption of triazines by different types of soils?

Dr. H. Gysin

On sandy soils adsorption is almost nil. On heavy and organic soils there is considerable adsorption near the surface.

# A NEW DEVELOPMENT IN SELECTIVE WEED CONTROL

## PART I: INTRODUCTION AND WEED CONTROL DATA

G. B. Lush

Boots Pure Drug Co. Ltd., Lenton Experimental Station

## Summary

An account is given of the activity of certain substituted α-phenoxy propionic acids against Galium aparine (cleavers).

Two of these compounds, namely, α(2,4-dichloro-3-methyl phenoxy) propionic acid and α(4-chloro-2-methyl phenoxy) propionic acid, formulated as amines and used at 2 lb/ac a.e. are shown to give in cereal crops a control of cleavers of the same order as DNC.

The compounds are non-toxic, pleasant to handle, easy to dilute and may be used through low volume spraying machines.

Of the two compounds, α(4-chloro-2-methyl phenoxy) propionic acid is the more useful since it gives as good a control as MCPA on a range of other weeds including perennials. It also gives an excellent control of Stellaria media (chickweed).

## Introduction

Galium aparine (cleavers) is a major cereal weed problem in the United Kingdom and to a varying extent in a number of overseas countries. In this country cleavers is traditionally a weed of winter wheat, but of recent years the increased use of selective plant growth regulatory herbicides to which cleavers is resistant, coupled with combine harvesting methods has intensified a problem in spring-sown as well as in autumn-sown cereals.

Apart from competition for soil nutrients, dense stands of cleavers have the only too familiar effect of pulling down the crop, often causing lodging with attendant harvesting difficulty and loss in yield. Cleaver seeds are difficult to remove from grain samples and thus propagation is assured.

The conventional method of control of cleavers includes cultivations and the use of DNC at 6 - 8 lb/ac in 50 - 100 gal of water. This treatment, whilst giving good control of cleavers and other annual weeds, is particularly dependent on weather conditions which are not always favourable at the early stage of weed growth necessary for good control. A more important disadvantage in the use of DNC is its poisonous nature, by reason of which the Agriculture (Poisonous Substances) Regulations 1954 and 1955 impose conditions which limit its use by farmers using their own machines.

It has therefore been clear for several years that a non-poisonous selective herbicide for the control of cleavers in cereal crops is a major requirement in agriculture and with this aim in view a screening programme was initiated at Lenton several years ago.

## Experimental methods and results

### Preliminary screening and extension tests

During late 1954 greenhouse screening tests showed certain substituted $\alpha$-phenoxy propionic acids to be capable of inducing in cleavers plant growth regulatory responses resulting in death. MCPA and 2,4-D under similar conditions induced only very slight responses in cleavers which rapidly recovered and became indistinguishable from the unsprayed plants.

The five most active compounds in these tests were taken forward to the extension stage in small plot field trials where they were sprayed at 1, 1.5 and 2 lb/ac a.e. at high volume and at several stages of growth. 2,4,5-TP was included in these trials.

Results showed two compounds, $\alpha$(2,4-dichloro-3-methyl phenoxy) propionic acid and $\alpha$(4-chloro-2-methyl phenoxy) propionic acid, coded respectively as R.D. 4501 and R.D. 4593 to be capable of effecting a good control of cleavers at 2 lb/ac a.e. R.D. 4501 was found to be practically specific to cleavers, whilst R.D. 4593 was found to have a much wider weed control spectrum. 2,4,5-TP though giving a good control of cleavers was ruled out on the grounds of gross cereal phytotoxicity.

In further extension tests the addition of 2,4-D and to a lesser extent MCPA to sprays of R.D. 4501 and R.D. 4593 at given doses, conferred upon these compounds, an activity greater than would have been expected of them used alone at those same doses. This synergistic effect was noted but has not been further investigated.

A note is relevant at this point concerning the definition of "acid equivalent" in relation to these compounds. On synthesis, $\alpha$-phenoxy propionic acids occur as mixtures of equal parts of the dextrorotatory and the laevorotatory optical isomers. Only the former is active but separation is not economically feasible. Acid equivalent data in this paper, therefore, refers to the mixed 'd' and 'l' isomers.

### Field trials

A description follows of the field trials designed to examine on large scale the weed control activity of the two compounds R.D. 4501 and R.D. 4593.

Extension work having indicated that R.D. 4593 had the greater margin of safety for cereals and the wider weed control spectrum, field work on the two compounds followed different patterns. The main objectives were -

1. R.D. 4593. To obtain as much information as possible on cleaver and other weed control at an economical dose at different volumes per acre.

2. R.D. 4501. To determine the optimum mixture of R.D. 4501 and 2,4-D or MCPA to give economical control of cleavers and other weeds in an attempt to confirm the synergistic effect noted in greenhouse tests.

Whenever possible DNC was included and it was customary to incorporate MCPA and/or 2,4-D as a check on the control of other weeds.

In the majority of trials an amine formulation was used. Other formulations were used in a limited number of trials.

The trials were sited in the following counties, where cleavers constitute a serious problem in cereals, Nottinghamshire, Derbyshire, Lincolnshire, Northants., Essex and Sussex.

Trials were predominantly in winter wheat but a number of trials was carried out in spring wheat and in spring oats.

Experimental layout consisted of three blocks of randomised tractor-sprayed plots, generally of the order of 100 yd long, each plot being spray-boom width. The majority of trials was carried out with an Allman 120 machine (rear tank only) mounted on a Ferguson tractor, fitted with a means of measuring land speed. The tractor with sprayer mounted was conveyed from site to site on a flat platform lorry, which was capable of carrying 240 gal of water - sufficient for an average trial.

Four other types of spraying machine were also used.

As a check on calibration, the amount of spray used and the area covered were always measured so that the actual quantity applied per acre was known in each case.

## Assessment methods

Assessment of cleaver control was made in three ways.

1. Using a visual scoring method.

2. Weighing the cleavers found in 10 x 1 sq. yd quadrats per 100 yd plot.

3. Classifying the cleavers into seven categories and counting the numbers in 1 sq. yd quadrats as in 2.

The visual scoring method was used for three post spraying assessments; the first within a week or so of spraying, the second three to four weeks later and the third just prior to harvesting. At this last assessment the square yard quadrat weighing method was used coupled with the categorising and counting method. The object of the latter method was to determine the make-up of the bulk collected for weighing, i.e. whether it comprised one or two large vigorous plants or a number of small moribund ones. Flower and fruit presence was noted. Available time permitted only three quadrats of the ten to be counted in this manner, but a useful indication was obtained from these counts.

The percentage reduction of cleaver figures appearing in this paper are based on the weighing method obtained by comparison with unsprayed control plots.

## Optimum dose and effect of volume

Both compounds gave a highly satisfactory control of cleavers at the 2 lb/ac a.e. rate as indicated in the table.

Volume of dilute spray did not seem to be of great importance and usually no difference was observed between the 20 gal and the 40 gal rate which were the rates most commonly employed. In one trial, however, a volume of 50 gal/ac gave a significant improvement in control as compared with 20 gal/ac. The crop in question was well-established winter wheat, but many of the other trials were carried out in equally advanced crops so the reason for this exception is not clear.

One notable feature of these trials was the good control of cleavers obtained at 20 gal/ac, in view of the fact that this weed is so frequently found in the rows climbing up the cereal crop.

### Timing

Timing of spray in relation to growth stage of cleavers did not seem to be critical in these trials. In the extension work it had been shown that spraying at the seedling stage gave less satisfactory results than when the weed was more established. In all field trials carried out in this series, spraying was subsequent to this stage and satisfactory results followed spraying from when the plant had three to four internodes up to the flowering stage. One satisfactory trial was carried out when the cleavers were in full flower. An 80% reduction of cleavers was achieved, but seeding, though checked, was not prevented. Such late spraying is not to be recommended.

### Control of other weeds

The trials emphasised the great difference in weed control spectrum of the two compounds. In addition to the control of cleavers R.D. 4593 at 2 lb/ac controlled as wide a range of weeds as did MCPA at 1.2 lb. Control of the following weeds was at least as satisfactory with R.D. 4593 as with MCPA.

Bindweed, black (*Polygonum convolvulus*)
Bindweed, field (*Convolvulus arvensis*)
Buttercup, creeping (*Ranunculus repens*)
Charlock (*Sinapis arvensis*)
Dock, Broad leaved (*Rumex obtusifolius*)
Dock, curled (*Rumex crispus*)
Fat hen (*Chenopodium album*)
Groundsel (*Senecio vulgaris*)
Knotgrass (*Polygonum aviculare*)
Nettle, annual (*Urtica urens*)
Orache (*Atriplex patula*)
Shepherd's purse (*Capsella bursa-pastoris*)
Thistle, creeping (*Cirsium arvense*)
Willow weed (*Polygonum persicaria*)

Chickweed stood out as being much more susceptible to R.D. 4593 than to MCPA. In two trials shown in the Table almost complete eradication of a dense stand of chickweed was achieved.

More work remains to be done on the reaction of other weeds to R.D. 4593, but these trials clearly showed that at the rate required to control cleavers an equally good control of weeds susceptible to plant growth regulators can be expected.

R.D. 4501 on the other hand was found to be virtually specific to cleavers. An unusual response to R.D. 4501 was observed with creeping thistle, where stem elongation virtually ceased after spraying followed by subsequent shortening of the internodes. The spiny lobes of the leaves elongated and a new growth of leaves sprouted from the axils, giving the whole an unnatural spiny bush appearance. Flowering was prevented.

### Combination sprays

In view of the synergistic effect on these compounds of 2,4-D and to a lesser extent MCPA observed in greenhouse experiments, a number of trials were carried out with a range of mixed sprays in the hope of producing a more economic control of cleavers and also, in the case of R.D. 4501, improving the weed control spectrum.

Whilst there were indications of enhanced activity with certain mixtures, no worth-while economic effect was found in any of the treatments included in these trials.

Comparison with DNC on weed control performance

The response of cleavers in the field to R.D. 4501 and R.D. 4593 was quite unlike that to DNC. The first noticeable symptoms were leaf epinasty, stem bending and curling which could occur an hour or so after spraying. The plant became limp and the aerial portion fell to the ground. Leaflets elongated and those formed subsequent to spraying were narrower and sometimes greyish in colour. Nodes became swollen and the stem took on a water-logged appearance in the basal region. Internodes elongated for a time and then became shorter. Plants often assumed a reddish colouration. A typical characteristic of moribund plants some weeks after spraying was a compressed apical tuft of leaves supported physiologically but not mechanically by a thin brown stem of dead appearance.

Cleavers response to the substituted $\alpha$-phenoxy propionic acids is understandably slower than that to DNC. The final result, however, compares very favourably as indicated in the Table.

As already indicated R.D. 4593 controls other weeds than cleavers. In this respect it has certain advantages over DNC in control of perennial weeds. There is also less likelihood with R.D. 4593 of a second germination of weeds some time after spraying as happens under some circumstances with DNC.

Undersown crops

R.D. 4501 and R.D. 4593 cannot be recommended for undersown crops in the light of present knowledge.

Effect of weather conditions

The effect of weather conditions is substantially the same for R.D. 4501 and R.D. 4593 as it is for MCPA. In several trials very satisfactory results were obtained, even though rain fell within a few minutes of spraying. Drought produced the usual delayed reaction and there is some indication that very low night temperatures were responsible for the only otherwise unaccountable unsatisfactory result.

## Discussion and conclusions

It is shown in this paper how the new and interesting activity of certain substituted $\alpha$-phenoxy propionic acids against Galium aparine (cleavers) was first observed in systematic greenhouse screening methods, substantiated by small plot extension trials and confirmed by large scale field trials, to be of practical value in the control of cleavers in cereal crops.

In these trials two compounds, viz. $\alpha$(2,4-dichloro-3-methyl phenoxy) propionic acid and $\alpha$(4-chloro-2-methyl phenoxy) propionic acid have been shown to give at a dose of 2 lb/ac a.e. a control of cleavers which compares very favourably with that given by DNC at normally recommended rates.

These compounds have very marked advantages over DNC. Possessing a very low mammalian/toxicity they present no hazards to the user and can be handled with the same ease and safety as the conventional 2,4-D and MCPA herbicides, now so universally used.

The amine formulation used in these trials is readily miscible with water and gave rise to no application problems when used in a number of commercial spraying machines under a wide range of conditions.

Low volume spraying at 20 gal/ac was found to be completely satisfactory, and although in one trial where the flag though considerable was by no means excessive, a statistically significant improvement in control was obtained by using 50 as against 20 gal/ac of water, it was generally found as indicated in the Table that no measurable advantage was gained by increasing the volume to 20 gal/ac even when spraying tall well-established winter wheat.

The two compounds differ in their effect on weeds other than cleavers. R.D.4501 is virtually specific for cleavers and although compatible with 2,4-D and MCPA no useful effect has been demonstrated in the field.

R.D.4593, however, at 2 lb/ac has controlled as wide a range of weeds in these trials as MCPA at conventional rates, and therefore control of cleavers, other annual weeds and perennial weeds can be conveniently combined.

The DNC season is a short one and the degree of cleaver control with DNC is very dependent on climatic conditions. With R.D.4593, however, there is more latitude and therefore greater opportunity to select optimum conditions for weed control.

Where thistles and docks and other perennial weeds occur with cleavers it is often necessary after spraying with DNC to spray with MCPA later in the season. This double spraying can be obviated by the use of R.D.4593 to which docks and thistles are particularly susceptible.

## Acknowledgements

Our sincere thanks are due to Dr. H. A. Stevenson and his colleagues, Mr. R. F. Brookes and Mr. M. D. Potter who synthesised these and the very many other compounds in connection with this work. To Mrs. T. A. Wharton (nee Myers) who initiated and to Mr. E. L. Leafe who carried on the initial screening; to the staff of the Plant Physiology Section and to Mr. John Frisby who carried out the major part of the tractor spraying involved in the field trials.

Thanks are also due to the farmers who so willingly offered facilities.

## Data from a selection of field trials

| Site | Compound | Dose lb/ac | Volume gal/ac | % Reduction Cleavers | Control of Other Weeds | Remarks |
|---|---|---|---|---|---|---|
| I | R.D.4593 | 2.0 | 20 | 98.0 | Very good control of charlock (*Sinapis arvensis*) Creeping thistle (*Cirsium arvense*) fat hen (*Chenopodium album*) | The control plots at harvest were heavily infested with cleavers and severely laid. |
|  | " " | 2.0 | 40 | 96.7 |  |  |
|  | R.D.4501 | 2.0 | 20 | 96.8 | No control of above weeds |  |
|  | " " | 2.0 | 40 | 98.3 |  |  |
|  | DNC | 6.0 | 80 | 100 | Very good control of above weeds |  |
| II | R.D.4593 | 1.7* | 86 | 97.4 | Almost complete eradication of chickweed (*Stellaria media*) | Control plots at harvest were heavily infested with cleavers and chickweed. |
|  | " " | 1.8* | 50 | 97.1 |  |  |
|  | " " | 2.0 | 20 | 90.6 |  |  |
|  | DNC | 6.0 | 86 | 99.4 | DNC not so effective on chickweed. | Significant difference between 20 gal rate and other rates. |
| III | R.D.4593 | 1.9 | 19 | 87.6 | No assessment of other weeds was possible. | Very heavy rain commenced 10 minutes after last plot sprayed and continued for 1 hour. Very heavy infestation of cleavers in control plots at harvest. |
|  | R.D.4501 | 1.9 | 19 | 86.0 |  |  |
| IV | R.D.4593 | 2.6* | 26 | 95.0 | Complete eradication of chickweed (*Stellaria media*). Very good control of groundsel (*Senecio vulgaris*), creeping thistle (*Cirsium arvense*), curled dock (*Rumex crispus*). | The control plots contained moderately heavy cleavers infestation. |
|  | " " | 2.2* | 44 | 95.0 |  |  |
|  | DNC | 6.0 | 80 | 99.0 (visually assessed) | DNC not so effective on chickweed |  |

* Variation in dose due to calibration speed not being maintained during spraying.

| Site | Compound | Dose lb/ac | Volume gal/ac | % Reduction Cleavers | Control of Other Weeds | Remarks |
|---|---|---|---|---|---|---|
| V | R.D.4593 | 2.0 | 20 | 95-98 (all visually assessed) | Knotgrass (*Polygonum aviculare*) significantly checked. | No sampling was carried out in this trial to avoid damage to yield plots. Very heavy cleaver infestation in control plots at harvest. |
|  | " " | 2.0 | 40 |  |  |  |
|  | R.D.4501 | 2.0 | 20 |  |  |  |
|  | " " | 2.0 | 40 |  |  |  |
|  | DNC | 6.0 | 80 | 98 " |  |  |
| VI | R.D.4593 | 1.8 | 18 | 84.6 | Good control of bindweed, field (*Convolvulus arvensis*), charlock (*Sinapis arvensis*), chickweed (*Stellaria media*), fat hen (*Chenopodium album*) | Control plots at harvest contained moderately heavy infestations of cleavers. |

| Site | Compound | Formulation | Dose lb/ac | Volume gal/ac | % Reduction Cleavers | Control of Other Weeds | Remarks |
|---|---|---|---|---|---|---|---|
| VII | R.D.4593 | Amine | 2 | 20 | 79.2 | Good control of bindweed, field (*Convolvulus arvensis*) | Spraying took place when cleavers were in full flower. Fruiting checked but not prevented. Moderately heavy infestation of cleavers. |
|  |  |  | 2.5 | 20 | 83.0 |  |  |
|  | R.D.4593 | Sodium | 2 | 20 | 80.7 | " |  |
|  |  |  | 2.5 | 20 | 81.3 |  |  |
|  | R.D.4593 | Sodium-ammonium | 2 | 20 | 80.4 | " |  |
|  |  |  | 2.5 | 20 | 83.0 | " |  |

# A NEW DEVELOPMENT IN SELECTIVE WEED CONTROL

## PART 2

## EFFECT ON CEREAL DEVELOPMENT

E. L. Leafe

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### Summary

Histograms are presented showing the percentage of abnormal plants occurring after treatment with the two substituted $\alpha$-phenoxypropionic acids referred to in the first part of this report. MCPA was included for comparison and two substituted $\gamma$-phenoxybutyric acids (MCPB and 2,4-DB) were also included in the trials. The three major cereals were sprayed at several stages prior to, and during the conventional non-susceptible period, with rates corresponding to 1, 2 and 4 lb/ac a.e. The types of abnormalities which occurred in each cereal are summarized and their significance discussed. The safety of these compounds is considered and suggestions are put forward with regard to the spray timing of these new herbicides.

### Introduction

This work was initiated with the discovery of the unique herbicidal value of certain substituted $\alpha$-phenoxypropionic acids in controlling weeds resistant to the substituted phenoxyacetic acids and $\gamma$-phenoxybutyric acids, more particularly cleavers (Galium aparine). Of some ten substituted $\alpha$-phenoxypropionic acids which showed activity in screening work, two were selected from extension work for further evaluation. They were $\alpha$-(2-methyl-4-chlorophenoxy) propionic acid and $\alpha$-(2,4-dichloro-3-methylphenoxy) propionic acid, coded as R.D. 4593 and R.D. 4501 respectively. The weed control aspect has been dealt with in the first part of this report and this part concerns the safety and spray timing of these compounds.

### Experimental

The extension work indicated that, for the two chemicals selected for further evaluation, the optimum rate of application lay between 2 and 3 lb/ac a.e. and that they were safe for use after the six leaf stage and up to the beginning of shooting. Accordingly, at the weed control sites, a number of varieties of the three major cereals were sprayed at high and low volume during this safe period. R.D 4593 caused no abnormalities at any of the sites but at some sites mild abnormalities followed the use of R.D. 4501. These trials were designed primarily for weed control assessment and no detailed investigation of the effect on cereal development was carried out. Part 2 of the report concerns the detailed investigation of these compounds on cereal development at a series of growth stages.

The trials were designed to compare the number and severity of abnormalities caused by these new herbicides and those caused by MCPA and further to compare and evaluate the substituted $\gamma$-phenoxybutyric acids. To this end six compounds were used, namely: MCPA, R.D. 4593, R.D. 4501, MCPB, 2,4-DB and a proprietary preparation of MCPB With the exception of the last, these compounds were used as diethanolamine salts at rates corresponding to 1, 2 and 4 lb/ac a.e. The volume of spray used was 20 gal/ac and the results given refer to a solution of the salt in water with no further additions. All compounds were applied at susceptible and non-susceptible stages of the three major cereals. It was intended, as far as possible, to spray at each of seven stages of the cereal, the leaf stage being determined by the number of fully expanded leaves and not by their first appearance. Thus the three leaf stage was that stage when the main stem bore three expanded leaves; the fourth was present but unexpanded. Weather and other factors made it impossible to spray every leaf stage and sometimes it was necessary to spray a leaf stage before the full expansion of the definitive leaf. This is noted in the results and discussion.

Wheat was sprayed at the 1, 3, 4, 5 and 7 leaf stages, barley at the 1, 2, 4, 6 and 7 leaf stages and oats at the 1, 3, 4 and 7 leaf stages.

The experimental design was a randomized block and the trials were sited on fields of spring cereals which showed even fertility and emergence.

Wheat var. - Peko

Barley var. - Carlsberg

Oats var. - Blenda

The plots were 2.5 x 5.25 yd and were sprayed with a sprayer equipped with Bray ceramic tipped nozzles. There were three replicates of each treatment at each stage.

In each cereal, and at each stage, the developing head was examined immediately prior to spraying and about 14 days later when abnormal differentiation could be determined. Final assessment was made after heading and this showed satisfactory correlation with the pre-heading examination. The percentages given are those from the post-heading examination and refer to the number of plants bearing abnormal leaves or heads, the average being calculated from 300 plants. In the case of oats, tubular leaves only were counted in the first stage and bunched heads in subsequent ones. Other abnormalities were insignificant in number.

The method of assessment was such that pre-heading assessment would be correlated to the post-heading assessment directly and independently of the amount of tillering. To do this only the main stem was used in both assessments; the inclusion of tillers in the final assessment would have destroyed the correlation between this and the pre-heading examination when, at the early stages, no tillers were present. This would account for the apparent discrepancy between the percentages given here and those given by other workers. The procedure of assessment varies from one worker to another and, whilst in no way affecting the validity of their results, this makes the inclusion of a standard treatment, such as MCPA, vital.

By dissection of the growing point of the cereal it was possible to recognize at an early date abnormal differentiation or absence of tissue and thus, broadly, the type of abnormality to be expected. Tubular leaves were detectable some 10 - 12 days after treatment by careful dissection of the lower leaves and aberrant differentiation of the spike and spikelet parts was easily seen by the technique described by Marjorie H. Myers in 1953. It was not possible, however, to recognise by this method the late sterilization of tissue which occurred with some treatments and which resulted in an excessive number of sterile spikelets. Nor was it easy to recognize the differentiation which led to bunching of the oat panicle.

## Results

The results are presented as histograms showing the percentage of plants bearing abnormal heads or leaves. These are further discussed with regard to the type of abnormality present.

### Wheat

One leaf stage. The second leaf was visible but not expanded. The apex was strictly vegetative and the abnormalities produced were almost all tubular leaves. Reference to the histograms shows clearly that, whereas MCPA, 2,4-DB and R.D. 4501 at the 4 lb rate caused over 50% of tubular leaves, neither R.D. 4593 nor MCPB caused a significant number. In the former case less than 2% resulted and in the latter less than 9%. At the lower rates the same relationship held, the difference between the two $\gamma$-phenoxybutyric acids being very marked.

Three leaf stage. At this stage transition from the vegetative to the reproductive phase had taken place. The apices bore up to three pairs of spikelet primordia and consequently the abnormalities occurred very largely in the lower part of the spike. Spikelets borne oppositely, in whorls and supernumerarily, in contrast to the normal alternate arrangement, were the predominant abnormalities. Some tubular leaves were present and a few heads were incomplete.

MCPA, 2,4-DB and R.D. 4501 caused a very high percentage of abnormal plants at the highest rate and an appreciable number at the lowest. Furthermore, both R.D. 4501 and 2,4-DB caused a serious general toxicity, the former at all rates and the latter at the high rate only. The general toxicity, to which reference is made here and subsequently, was an effect on the gross appearance of the plant in contradistinction to the more localized effect on the differentiation of ultimate or penultimate leaves or spike and spikelet parts, phenomena usually described as abnormalities. The symptoms of this general toxicity were retardation, absence of the normal laxity of the lamina, dark green, grey or even purple colouration, and excessive stiffness of the stem and faulty emergence of the head. R.D. 4593 and MCPB caused a small number of mild abnormalities at the 4 lb rate and a negligible number at others.

Four leaf stage. Up to six pairs of spikelet primordia were present and suppression of the lower part of the primordium was evident. This was the most sensitive stage, abnormalities being positioned intermediately on the rachis and comprising mainly opposite, whorled and supernumerary spikelets. MCPA and R.D. 4501 caused practically 100% of the plants to be abnormal at all rates, the latter causing severe general toxicity. 2,4-DB, whilst less severe, caused a considerable number of abnormal plants and some general toxicity. R.D. 4593 caused some abnormalities at the highest rate but a negligible number at the lower ones. MCPB behaved similarly.

Early five leaf stage. At this stage spikelet differentiation had just begun. Differentiation of the outer glume was evident in the most advanced spikelets and the type of abnormality found reflected this stage of differentiation in comprising mainly fusion and enlargement of glumes and pales. R.D. 4501 caused a large number of abnormalities and some general toxicity; MCPA caused an appreciable number even at the lowest rate. No other treatment caused a significant number of abnormal plants. It was only at this stage that 2,4-DB appeared markedly safer than MCPA.

Seven leaf stage. All spikelet parts had, by this time, differentiated to an extent to which they were no longer affected by any treatment.

Barley

One leaf stage. The second leaf, though visible, was not expanded. Although the growing point appeared to be elongating no spikelet primordia were discernible. The predominant abnormality was tubular leaf and a few opposite spikelets were present. In MCPA and R.D. 4501 plots, particularly the latter, there were a few whorled spikelets and few heads were incomplete. R.D. 4501 caused a very high number of abnormal plants even at the lowest rate and MCPA caused only a few less. 2,4-DB caused a few abnormalities even at the lowest rate. No abnormal plants were found at any rate of R.D. 4593 nor of MCPB.

Two leaf stage. Up to four pairs of spikelet primordia had been differentiated and all abnormalities were found in the lower part of the spike. While opposite, whorled and supernumerary spikelets were the most frequent abnormalities, the more severe treatments also caused a large number of heads with one or more spikelets missing. Other abnormalities occurred in small numbers. At the two higher rates both MCPA and R.D. 4501 caused practically 100% abnormality and this, in the latter, was accompanied by a severe general toxicity. R.D. 4593 and both $\gamma$-phenoxybutyric acids caused an appreciable number of mildly abnormal plants, 2,4-DB being the most severe.

Four leaf stage. Six row formation was well advanced and anther initials were just apparent. The notable feature of this stage of spraying was the excessive amount of late sterilization of tissue caused by R.D. 4501. This was accompanied by a severe general toxicity. No other treatment, with the exception of MCPA at the highest rate, caused a significant number of abnormalities.

Early six leaf stage. All spikelet parts were differentiated and the late sterilization of tissue present in R.D. 4501 plots at the four leaf stage was again evident but to a lesser extent. No other treatment caused any abnormal plants.

Seven leaf stage. No treatment caused a significant number of abnormal plants.

Oats

One leaf stage. The growing point was strictly vegetative and tubular leaves were the only abnormality present. MCPA and 2,4-DB caused an appreciable number of abnormal plants especially at the high rate. All other treatments caused only a negligible number of abnormal plants except at the highest rate.

Three leaf stage. Branch initials were present and elongating at this stage. The only abnormality present in significant amount was bunching of the panicle and, since this type of development also occurs in unsprayed crops, the control levels are given. 2,4-DB was outstanding at this stage in causing a high proportion of bunched heads even at the lowest rate. MCPA caused some increase of bunching but no other treatment increased the percentage significantly above the control level.

Four and seven leaf stage. No treatment increased the count of bunched heads significantly above the control level.

## Discussion and conclusion

### Substituted a-phenoxypropionic acids

#### R.D. 4593

In all three cereals the margin of safety with this compound is much greater than with MCPA and, rate for rate, as great if not greater than with MCPB. However, since for effective weed control a rate of 2 - 3 lb/ac a.e. is needed as against about half this rate for MCPB, similar recommendations cannot be made. R.D. 4593 has two optical isomers, the laevorotatory form being inactive but which occurs during manufacture in equal quantities to the active, dextrorotatory form. This gives rise to some ambiguity in the acid equivalent basis of dosage insofar as this compound is concerned. On the basis of this work the cereals may be sprayed with safety at earlier stages than is recommended mended for MCPA. It is necessary, however, to determine the behaviour of this compound, at these early stages, over a very wide range of conditions before early spraying can be recommended and, at present, its use should be confined to the period between the appearance of the sixth leaf on the main stem and the beginning of shooting. In oats, spraying may commence with safety when the main stem has four leaves.

In cases where primary tillers are counted instead of the leaf in whose axil they arise, the usual precaution must be taken to exclude secondary tillers and those arising below the mesocotyl.

#### R.D. 4501

In view of the severe toxicity and the hitherto unencountered late sterilization of tissue which occurred with this compound, no recommendations for its use can be made.

### Substituted $\gamma$-phenoxybutyric acids.

These compounds have been treated more adequately elsewhere but these results serve to confirm that MCPB has a wide enough margin of safety to be used at the early growth stages of the three major cereals. The position with 2,4-DB is quite different and clearly its use in cereals, prior to the conventional safe stage, cannot be recommended.

## Acknowledgements

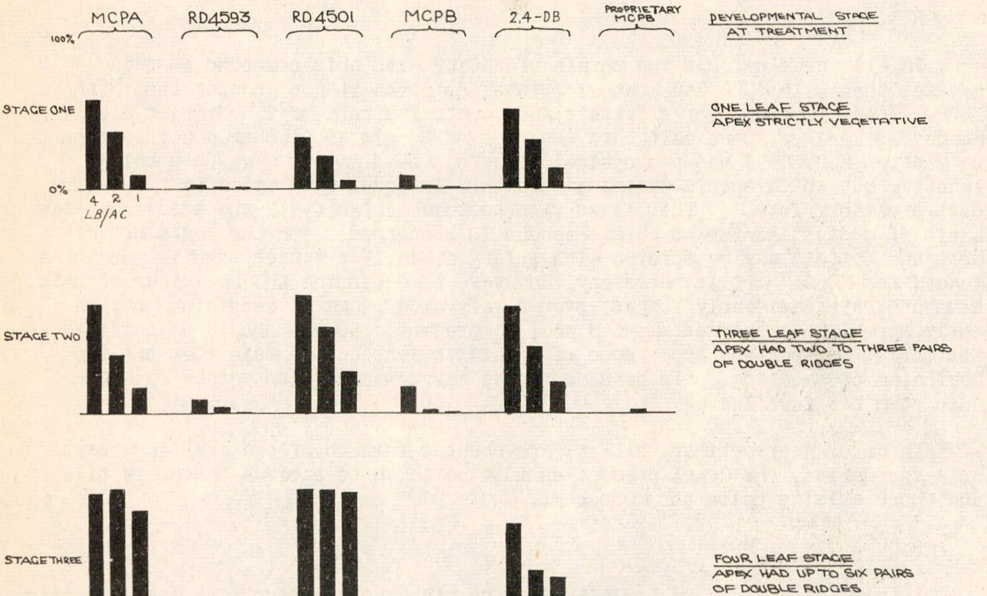
The author wishes to thank Dr. H. A. Stevenson and Mr. R. F. Brookes, Chemistry Research Division of Boots Pure Drug Co. Ltd., whose work made this new development possible, and Mr. A. J. Mayes, who was responsible for the greater part of the field work. Thanks are due also to Mr. G. B. Lush, Plant Physiologist, Agricultural & Horticultural Division, Boots Pure Drug Co. Ltd.

## Reference

(1) MYERS, M. H. (1954). Abnormalities produced by early applications of MCPA and 2,4-D to cereal crops and their pre and post heading examination. Proc. Brit. Weed Control Conf. 1953, 63 - 70.

## ABNORMALITY PERCENTAGES IN WHEAT

### PHENOXYACETIC, α PHENOXYPROPIONIC & γ PHENOXY BUTYRIC ACIDS.

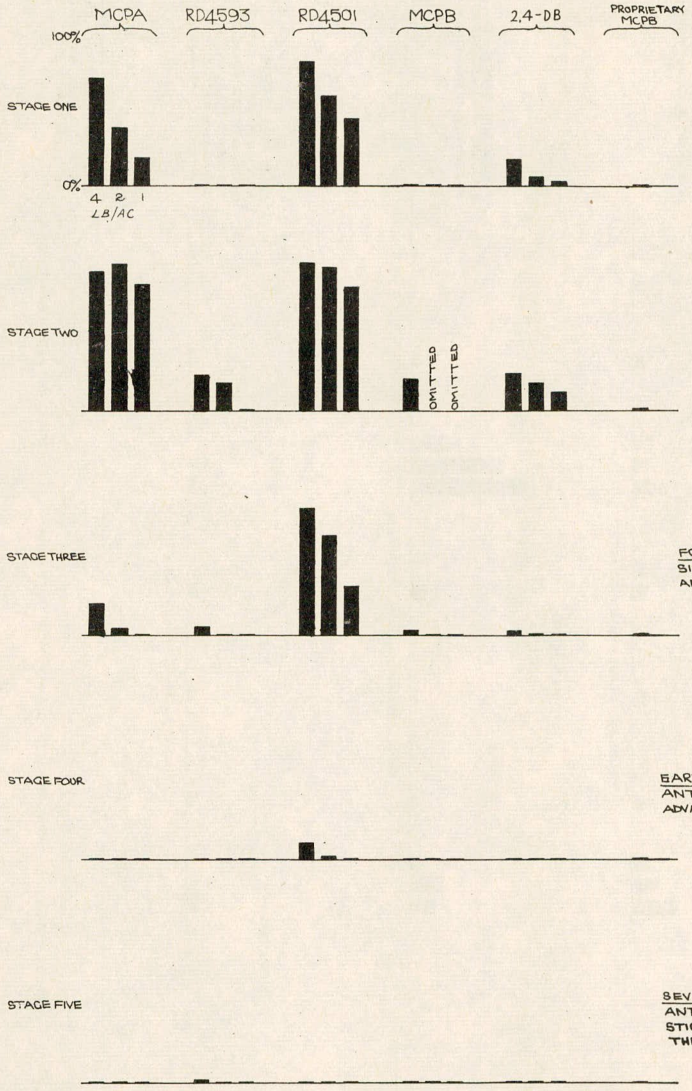


MCPA — 4-CHLORO-2-METHYLPHENOXYACETIC ACID.
RD4593 — α(4-CHLORO-2-METHYLPHENOXY)PROPIONIC ACID.
RD 4501 — α(2:4-DICHLORO-3-METHYLPHENOXY)PROPIONIC ACID.
MCPB — γ(4-CHLORO-2-METHYLPHENOXY) BUTYRIC ACID.
2,4-DB — γ(2:4-DICHLOROPHENOXY)BUTYRIC ACID.

} FORMULATED AS DIETHANOLAMINE SALT.

## ABNORMALITY PERCENTAGES IN BARLEY

### PHENOXYACETIC , α PHENOXYPROPIONIC & γ PHENOXYBUTYRIC ACIDS.



DEVELOPMENTAL STAGE AT TREATMENT

ONE LEAF STAGE
SECOND LEAF PRESENT BUT NOT EXPANDED. THE APEX SHOWED SLIGHT ELONGATION BUT DOUBLE RIDGES WERE NOT DETECTABLE.

TWO LEAF STAGE
APEX HAD FROM ONE TO FOUR PAIRS OF DOUBLE RIDGES.

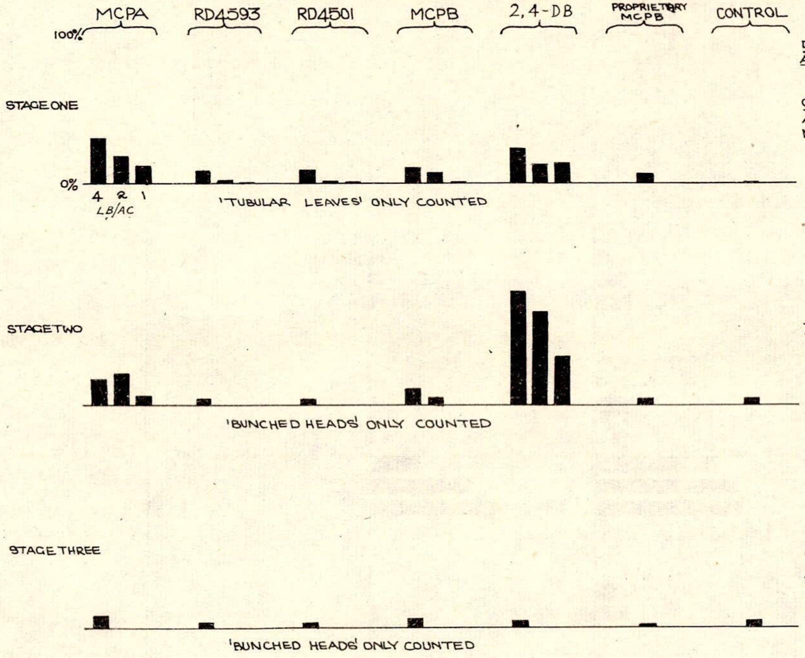
FOUR LEAF STAGE
SIX ROW FORMATION ADVANCED. ANTHER INITIALS JUST APPARENT.

EARLY SIX LEAF STAGE
ANTHER INITIALS LOBED IN THE MOST ADVANCED SPIKELETS.

SEVEN LEAF STAGE
ANTHERS LOBED AND STALKED. STIGMA RUDIMENTS ABOUT TWO THIRDS THE LENGTH OF THE CARPEL.

# ABNORMALITY PERCENTAGES IN OATS.

## PHENOXYACETIC, $\alpha$PHENOXYPROPIONIC & $\gamma$PHENOXYBUTYRIC ACIDS



STAGE FOUR. ABNORMALITY COUNT NOT IN EXCESS OF CONTROL IN ANY TREATMENT.

**DEVELOPMENTAL STAGE AT TREATMENT.**

**ONE LEAF STAGE**
APEX STRICTLY VEGETATIVE.
NO EVIDENCE OF BRANCHING.

**THREE LEAF STAGE**
BRANCH INITIALS WERE PRESENT AND ELONGATING

**FOUR LEAF STAGE**
BRANCHES OF THE FIRST & SECOND ORDER WERE PRESENT.
ANTHER INITIALS WERE JUST APPARENT IN THE MOST ADVANCED FLOWER.

**SEVEN LEAF STAGE**
STERILE GLUMES HAD ENCLOSED THE MOST ADVANCED SPIKELET.
ANTHERS LOBED AND STALKED IN THESE SPIKELETS,

## DISCUSSION ON THE TWO PREVIOUS PAPERS

### Prof. R. L. Wain

Mr. Lush and his colleagues are to be congratulated on finding this new use for 4-chloro-2-methylphenoxypropionic acid which, of course, is MCPA with a methyl group substituted in the side chain. A good deal is known about the effects on growth-regulating activity of substituting alkyl groups into the side chain of phenoxyacetic acids. In our investigations using three laboratory assay methods, we have found instances where the propionic acid is equal in activity to the corresponding acetic acid; in some cases it is more active and in others, less active. All these results and those for the corresponding butyric and isobutyric acids have been published.

What I should like to consider now is why 4-chloro-2-methylphenoxypropionic acid should be so much more active than MCPA against cleavers. All our work indicates that these two chemicals have a similar action within a plant; their growth response for example, are similar, and there is also evidence from studies on competitive antagonism. It may well be that the propionic derivative is superior on cleavers because it can move into the plant and to the site of action within the tissues better than the acetic acid. In this connection I should like to ask Mr. Lush how active MCPA is on cleavers - I should expect it to show some activity particularly at higher concentrations. However, if physical properties are one of the reasons why 4-chloro-2-methylphenoxypropionic acid is better than MCPA on this weed it might be worth while testing other members of the homologous series of alkyl substituted phenoxy acetic acids. In the case of the MCP series, the $\gamma$-substituted butyric acid is just as good in our three laboratory tests as 4-chloro-2-methylphenoxypropionic acid.

Incidentally, these active propionic and butyric acids might well be tried on bracken - for similar reasons.

From the economic point of view it is a pity that all these acids as prepared are mixtures of two forms, one of which usually has negligible activity. If the racemic mixture obtained by synthesis could be resolved economically it should be possible to reduce the dosage rate considerably.

On another point, mention was made by Dr. Åberg yesterday of the phenylthio acids and their possible use as herbicides. It is perhaps of interest that we have made some sixty of these compounds. In general, they show much lower growth-regulating activity than the corresponding phenoxy acids.

### Dr. R. de B. Ashworth

I should like to appeal to manufacturers to put forward suggestions for coined common names at an early stage. Such names should be based on the B.S.I. rules of nomenclature, so that when a new chemical becomes commercially important, the name has already been agreed. In this particular case, use of letter abbreviations is not only confusing, but also contravenes the recommendations of the B.S.I., thus when a common name is eventually adopted by the B.S.I. there will be yet more confusion.

### Mr. A. C. Tunstall

It would be helpful to know the effect of new spray materials on rubber and other materials used in the construction of spraying machines. The solvent is often more important than the new spray substance, but the tendency to use higher concentrations as for low volume applications does make this information desirable. We have been experimenting recently with coatings for metal parts - at present the use of these would not be economic but some progress has been made.

Mr. J. S. W. Simonds

Does 4-chloro-2-methylphenoxypropionic acid have any effect on mayweeds?

Mr. G. B. Lush

No

Dr. E. Åberg

I realise that the effect of 4-chloro-2-methylphenoxypropionic acid has only been studied on Galium aparine. It would be of interest to know the effect on Galium mollugo which species is also a serious weed in Sweden. 2,4,5-T is effective on Galium mollugo but not to the same extent on Galium aparine. It would, therefore, be of interest to know how the effect of this new compound compares on these two species of the same genus.

# FACTORS WHICH AFFECT THE PERFORMANCE OF CHEMICAL COMPOUNDS USED FOR INDUSTRIAL WEED CONTROL

Dr. L. E. Cowart

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Due to the advances made in chemical weed control in the past few years, the use of chemicals for selective weed control on agricultural soils is regarded as good farm practice. During this same period, there also has been a great deal of effort directed toward chemical control of vegetation on non-agricultural areas. Contributions of a research nature have been forthcoming from broad areas. Many research tools have been employed and a great deal of ingenuity has been apparent. As a result, a number of chemicals have been developed for use as non-agricultural herbicides and some of them also have been found useful.

The use of chemicals for industrial weed control is assuming an important place in an increasing number of the highly industrialized countries of the world. Government and industry have recognized that weeds can be a dangerous fire hazard as well as a hazard to public health. In addition, weeds have long been regarded by industry as an expensive obstacle to good maintenance practices. Railroads, petroleum installations, highway systems, power lines, inland waterways, and armed forces installations constitute a few of the many areas where economy and safety of chemical weed control have been amply illustrated.

Because of the growing importance of industrial weed control, it has become necessary to know as much as possible concerning the factors which will determine the success or failure of a commercial application of a chemical or chemicals made for that purpose.

Factors which affect the performance of these chemical compounds used for industrial weed control are basic to all weed control. The ones generally considered to be of the greatest practical importance in industrial weed control are species of weeds present, stage of growth, season during which the chemical is applied and the distribution and intensity of rainfall. The effect of the ever complex and dynamic soil system must be studied and evaluated. In addition, it is often helpful to consider the physiology, morphology and growth habits of a plant, together with the wetting characteristics, adsorption and translocation of the chemical applied.

With the possible exception of chemicals used for brush control on utility rights-of-way, the most important group of industrial weed control agents in use today are the so-called "soil sterilants". We are concerned with factors which affect the performance of industrial weed killers and as the name "soil sterilant" implies these are primarily connected with soil factors or soil properties.

When an herbicide is used for soil sterilization, its effectiveness is dependent on (1) movement, (2) activity, and (3) residual period in the soil. Soil sterilization is successful when the herbicide is distributed in the soil profile where the roots are active in absorption and when the herbicide remains in phytotoxic quantities for a sufficient period to allow absorption of a lethal dose. The residual period determines whether a compound is a temporary or relatively permanent soil sterilant.

The movement and action of herbicides in soils appear to be influenced by the rainfall pattern, formulation of the compound, and solubility of the compound, and a number of soil factors such as texture, structure, temperature, moisture and pH.

When an herbicide is applied to the soil surface, the amount that is absorbed by the roots of weeds depends to a large extent on the amount of herbicide in solution in the soil water at the root zone. A compound applied to the surface of soil is ineffective initially, except on seedlings rooted in the surface layer. In general, only that portion of material which is in solution is moved downward by the action of rainfall. At each level, the material in solution is in equilibrium with that adsorbed on the soil particles. Thus, the more strongly the material is adsorbed, the more slowly it is desorbed and moved downward. The amount of herbicide that is in solution in the root zone is influenced by the adsorptive capacity of the soil and the solubility of the compound. It follows that the rate of movement through the soil profile and the amount of compound available to the roots of plants is influenced by the degree to which a particular compound is adsorbed on a specific soil type. Strong adsorption results in slower downward movement with less material available in solution for absorption by the plants.

The effect of some of these factors on certain widely used soil sterilants is of importance in understanding how they may be expected to perform.

### A. Sodium chlorate

Although sodium chlorate can act as both a contact and a translocated herbicide (Robbins, Crafts, Raynor, 1952) its most important herbicidal action probably is that of a soil sterilant. Crafts (1938, 1939) in a series of experiments on chlorate toxicity showed that the effect of this herbicide is correlated inversely with soil fertility. Further work done in California has shown that sodium chlorate is readily mobile in soil and a given amount may be rather uniformly distributed if applied in solution sufficient to wet the soil. Root responses, however, vary according to nutrient content in the various soil horizons. The effect of soil texture on the duration of chlorate toxicity is not clearly understood. Schwendiman (1941) studying chlorate decomposition in soils observed that decomposition was greatest at high moisture levels and at the higher temperature levels. Further, that decomposition was apparently brought about by micro-organisms in the soil.

### B. Arsenic

Arsenic has been used for many years as a general herbicide. Although it has wide value for this purpose, its high mammalian toxicity makes its use hazardous. The principal soil factor affecting its performance as a herbicide in soils is texture (Ahlgren et al. 1951). Rosenfels and Crafts (1939), pointed out that, in general, light soils fix the smallest, and heavy soils, the greatest percentage of a given application of sodium arsenite. Fixation of arsenic in soils does not appear to be dependent upon moisture, but largely upon soil type. Besides the initial effect of arsenic, it is often fixed in soil against the leaching action of percolating water in a form available to plants. This is an important part of soil sterilization.

## C. Substituted ureas

Numerous workers have demonstrated that soil characteristics and rainfall distribution influence the herbicidal efficiency of 3-(p-chlorophenyl)-1,1-dimethylurea, and 3-(3,4-dichlorophenyl)-1,1-dimethylurea. Recent studies have shown that differences in solubility and the differential adsorption of these compounds on soil types help to explain the differences observed in herbicidal behaviour. (Note: These two compounds are commonly referred to by generic names. The compound 3-(p-chlorophenyl)-1,1-dimethylurea is identified as monuron, while the compound 3-(3,4-dichlorophenyl)-1,1-dimethylurea is identified as diuron.

Sherburne and Freed (1954), in a study on the adsorption of monuron on different soil types, showed that organic matter has a considerable affinity for this compound. They reported a correlation coefficient of 0.991 for the relationship between the amount of herbicide adsorbed by the soil and organic matter content, and a smaller but statistically significant correlation between adsorption and clay content. In biological studies, soils which were the highest adsorbers of monuron reduced the effectiveness of the chemical on rye grass. They predicted that on soils high in organic matter, a given treatment would be somewhat less effective, thus necessitating higher rates.

The influence of soil adsorption and water solubility on the herbicidal performance of monuron and diuron was studied by Bingeman and Hill (1955).

In leaching studies it was shown that the lower solubility of diuron (40 p.p.m. at 25° C compared to 240 p.p.m. for monuron results in slower movement in the soil.

In studies on the relationship of adsorption of monuron to soil properties it was found that adsorption increased as either clay content and/or organic matter content of soils increased.

Results from numerous tests and commercial applications show that when monuron is applied at "sterilant" rates of 40 to 80 lb/ac, a phytotoxic concentration may remain in the soil for 18 to 36 months, depending upon soil factors and the rainfall pattern.

Laboratory tests were conducted on mechanisms relating to disappearance of the substituted ureas (Hill, et al. 1955) from soils. These studies showed that leaching, chemical decomposition, and volatilization seem to play a minor role in disappearance. Photodecomposition (ultraviolet irradiation) of monuron was demonstrated in the laboratory and possibly is important when the compound remains on the soil surface for long periods of time. The action of micro-organisms was concluded to be the primary factor in the disappearance of monuron and diuron on the basis of Warburg studies, rate of decomposition in sterilized vs. non-sterilized soil samples, and the rate of decomposition of radio-labeled monuron. A soil bacterium of the Pseudomonas group was isolated which is capable of oxidizing monuron and using this compound as a sole source of carbon. In related studies, it was found that bacteria such as Xanthomonas, Sarcina, and Bacillus, and fungi such as Penicillium and Aspergillus can use monuron as a sole source of carbon in agar medium.

### D. Sodium trichloroacetate

Existing information does not show complete agreement on the effect of soil properties on the movement and activity of TCA. Most investigators are in agreement that TCA moves readily with soil water in most soils. However, Barrons and Hummer (1951) reported that the rate of leaching and extent of retention at different levels was observed to vary considerably with soil properties.

Blouch and Fults (1953) found that soil type influenced the selectivity of TCA and attributed this effect in part to adsorption by organic colloids.

Loustalot and Ferrer (1950) showed that 0.5 or 1 in. of rainfall following a 100 lb/ac application was sufficient to move TCA downward at least 8 in. in the soil. Ogle and Warren (1954) concluded that TCA leached very readily and that a fine sand, a silt loam, and a muck soil appeared to have little effect on its movement.

Existing information indicates that TCA disappears mainly by leaching and microbiological activity.

Ogle and Warren (1954) in laboratory studies showed that with a 16-lb rate of TCA, dissipation was a function of temperature and soil type. Little breakdown occurred in a sandy soil but marked dissipation occurred in a silt loam and a muck soil. Loustalot and Ferrer (1950) found that increased breakdown occurred with an increase in temperature or soil moisture.

### E. Compounds containing boron

Tests conducted with herbicides of this group indicate that it is the borate ion which produces a herbicidal effect. Therefore, the effectiveness of the various boron compounds usually can be estimated on the basis of the elemental boron contained.

The effects of boron when applied to soil appear to be reduced by leaching and by fixation in unavailable forms (Robbins, Crafts and Raynor 1952). Soil fertility does not seem to be a factor. However, the effectiveness of boron containing herbicides seems to be less apparent in soils high in clay content.

Borax and boric acid are non-poisonous to man and livestock and they are somewhat fire deterrent in action, and for these reasons are generally considered safe as soil sterilants. The phytotoxicity of boron varies widely, the grasses generally being more tolerant. High rates are usually required to produce sterility.

Much progress has been made in the last few years regarding factors which influence the performance of "soil sterilants". However, a great deal more must be learned before we are able to state exactly how much herbicide should be applied, and when and how it should be used for maximum efficiency.

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## DISCUSSION ON THE PREVIOUS PAPER

### Mr. R. C. Jennings (Introduction to discussion)

The question of non-agricultural sites is one common to many countries. It involves, however, consideration of climatic and soil conditions, difficulties of access and the most economical method of application of the appropriate chemical. The problem is far removed from normal agricultural spraying technique and each case has undoubtedly to be treated on its merits.

Dr. Cowart in his approach to this problem has plumped strongly for soil sterilants, and desirable as this may be I am not entirely convinced that the known commodities will produce the control and economic results on the very complex and varied sites involved. Doubtless there will be a need for both root contact and translocated herbicides to meet these conditions.

Arsenic, as we all know, is an extremely hazardous weedkiller to use and this naturally gives rise to caution and restricts its use.

Sodium chlorate formulations too have been widely used for many years, having as Dr. Cowart remarked both translocation and soil sterilization qualities. The search for more efficient non-selectives, however, continues and we have now had some experience of TCA, monuron and, to a very limited degree, boron.

TCA has not been utilized for industrial sites on a large scale and I have doubts as to whether it will ever do so. Reports upon monuron, however, confirm its effectiveness under certain circumstances. Relying upon root contact, this weedkiller is naturally dependent upon its persistence in the soil or substrate and is apparently very intolerant of certain soil conditions, especially upon what I term "man made" locations.

There is evidence also that reinfestation of shallow rooted weeds can occur where this soil sterilant has departed from the near surface level, the ultimate kill being obtained only if contact is made in the root zone area.

I believe we need to study still further the mobility of substituted ureas in varying soil conditions before we can make any definite recommendations. With the considerable and complex site conditions experienced on non-agricultural areas, especially where weeds emerge from closely sealed surfaces (i.e. concrete, tarmacadam) and conditions not conducive to soil sterilization exist, the answer may well be in utilizing monuron in formulation with other herbicides.

I cannot discuss the use of boron myself, having only a very limited knowledge of trials laid down, but perhaps others may like to refer to this commodity.

In conclusion, it would be interesting to learn from Dr. Cowart, whether in the U.S.A. the problem of weed infested non-agricultural sites is governed by any legislative requirements. The reaction one frequently encounters from people responsible for such sites and the apathetic response to the Weed Control Council's recent approach to a wide variety of organizations on this subject, may well be traced to a lack of appreciation of the situation. It is extremely doubtful if these people ever reflect upon the nuisance value of their weeds to the agricultural and horticultural community and experience shows that weed removal is often way down the maintenance list.

I cannot help wondering therefore, if success in this direction is not dependent upon careful official publicity and advice, to enlighten maintenance personnel as to the financial implications of their neglect. Whether this can be done without recourse to the revision and implementation of the 1921 Repeal Act is a sober thought.

Weeds to the farmer mean less profit, but to persons responsible for non-agricultural sites the same attitude does not and cannot apply. I do suggest, therefore, that some official approach to this problem may well be worthy of serious consideration, for without it there will surely be these sources of infestation to hamper the excellent work resulting from these Conferences.

Mr. P. Gregory

Would Dr. Cowart comment on surface wind erosion as a factor in removing monuron? I believe this is a factor of importance.

Dr. L. E. Cowart

Anything moving the soil is bound to remove the compound, whether it be wind or water. However, I think the danger is limited.

Dr. J. L. Harper

There are two important interactions which may occur between the weeds of agricultural and non-agricultural land. Firstly, the weeds on roadsides, railway banks, rubbish tips and in hedgerows may provide sources of seed which will spread into agricultural land. However, it must be remembered that 'a source of seed or weeds unselected by spraying which may spread into a sprayed field and compete successfully with the resistant remainder from spraying is valuable ....... such a reserve of unselected weeds provides a buffer, delaying the rapid evolution of resistance in outbreeding weeds'. (Harper, this Conference). This may be a significant argument against spraying much non-agricultural land.

Mr. R. Garrett-Jones

As none of the soil sterilants are really permanent in their effect I would suggest that they may have an outlet, if cheap enough, for bracken control; bracken, unlike other weeds, often forms a pure stand. In Wales a disease of bracken has been observed at several centres, which is giving good control of the weed and appears to be spreading; this may offer the possibility of biological control.

Dr. E. Holmes

I.C.I. recently made a survey of the potential demand for weed killers on its factory sites. Managers with new undeveloped sites were either not interested or preferred laying concrete; on developed sites they preferred lawns and flower beds on land not otherwise in use.

In the U.S.A. (Oregon, Washington and California) sodium chlorate is often used on agricultural land at up to 1200 lb/ac; this is regarded as economic where there are small compact infestations of noxious weeds, such as Convolvulus in very large fields. I know of one case where chlorate was applied at 1600 lb/ac to 4 acres of bindweed.

Mr. W. van der Zweep

Would Dr. Cowart care to say anything about the residual activity of the substituted urea herbicides?

Dr. L. E. Cowart

3-(3,4-dichlorophenyl)-1,1-dimethyl urea is used as an aqueous suspension in cotton. Present formulations aim at reducing the particle size which results in better suspension and hence easier application. Adsorption by clay depends on the type of clay e.g. those of the kaolin type are not important in this respect.

Bindweed is of importance in erosion and water conservation and farmers who have this weed are frequently given a subsidy to assist them in their efforts to control it.

Dr. W. Plant

No mention has been made of the use of herbicides for the control of water weeds. Would the speaker, or anybody else in the audience, care to make a statement of their experiments or experience in the above field?

Dr. L. E. Cowart

I have no experience in this field and therefore am unable to comment.