

EXPERIMENTS ON THE RATE OF DECOMPOSITION OF DNOC IN SOILS : THE
EFFECT OF PRE-TREATMENTS

K. Hurle and V. Pfefferkorn

Abteilung für Herbologie, Universität Hohenheim, 7 Stuttgart 70,
Federal Republic of Germany

Summary The rate of decomposition of DNOC in soil previously pre-treated with various concentrations of the same compound was greater than the rate of decomposition in similar soil treated for the first time. The rate of degradation depends on the concentration of DNOC used in the pre-treatment.

INTRODUCTION

For many herbicides degraded in the soil by microorganisms, the lag period and the effect of pre-treatment are well known phenomena. The lag period may be defined as the time in which the herbicide does not undergo any, or only relatively little decomposition. This period obviously is required for the development of a population of effective organisms. Subsequently, a quick degradation follows due to the proliferation or acclimatisation of the microorganisms concerned, the soil having become enriched with organisms capable of causing degradation. As a consequence, a subsequent treatment of the soil with the same compound results in a more rapid decomposition. Laboratory studies on the pre-treatment effect have been carried out with phenoxy derivatives by Audus (1951) and Brownbridge (1956, see Audus, 1964), with aminotriazol (Riepma, 1962), dalapon (Leasure, 1964), chlorpropham (Kaufman and Kearney, 1965), endothal (Horowitz, 1966) and pyrazone (Drescher and Otto, 1969). Under field conditions, more rapid degradation of subsequent applications was demonstrated for 2,4-D (Newman and Thomas, 1949; Newman et al, 1952; Hurle and Rademacher, 1970), for MCPA (Kirkland and Fryer, 1966; Kirkland, 1967) and for MCPB in soil previously treated with MCPA (Kirkland and Fryer, 1972).

Relatively little is known about the effect of different pre-treatment concentrations on the subsequent degradation. In the work described in this paper, DNOC was used, which is degraded by soil microorganisms (Gundersen and Jensen, 1956; Tewfik and Evans, 1966; Jensen and Lautrup Larsen, 1967; Hamdi and Tewfik, 1970), and shows pre-treatment effect in soils (Jensen, 1966; Hurle, 1969). The investigations were undertaken to show the influence of various pre-treatment concentrations on the rate of degradation of a subsequent application.

METHOD AND MATERIALS

"Soil" used in the experiment

A soil-sand mixture (1 : 1, dry wt) was used.

Soil characteristics: loam; silt 15.5%, clay 12.6%, organic matter (C) 0.93%, CEC 10.6 meq/100 g, pH 6.9 (CaCl₂).

Soil and sand were sieved to pass a 2 mm sieve. Addition of sand to the soil was necessary to avoid clodding.

Treatment of soil

A solution of DNOC in acetone was sprayed on sand and the sand mixed thoroughly after evaporation of the solvent. Water was then mixed with the treated sand. Soil and treated sand were combined and mixed again to make a total of 4 kg. Mixing was done in large size poly-ethylene bags, also used for subsequent storage in an incubator at 20±1°C. Water content was 8%.

In the text which follows "soil" stands for soil-sand mixture.

Treatment and sampling method

One sample of "soil" was treated with sufficient DNOC to give a concentration of 12.3 ppm; the sample was analysed daily throughout the rest of the experiment to show the rate of degradation in the absence of pre-treatment.

Four other "soil" samples were treated with sufficient DNOC to give concentrations of 0.005, 0.25, 1.25 and 2.5 ppm respectively. These samples were kept for 31 days at ambient temperature before being re-treated with sufficient DNOC to give 10 ppm. Thereafter, sub-samples were removed daily for subsequent analysis.

Analytical procedure

All sub-samples were kept at -20°C prior to analysis in two replications, using a method of detection of DNOC based on the intensive colour of its sodium salt, following a procedure as follows: Soil (25 g dry wt) was placed in 1 litre glass bottles which, after the addition of 2 ml n HCl and 50 ml water, were placed on a mechanical shaker for 30 min. Subsequently, 100 ml of benzene were added to the slurry and shaking continued for a further 30 min. The contents of the bottles were then centrifuged at 4,000 rpm for 20 min. Fifty ml of the supernatant liquid (repr. 12.5 g of soil) was evaporated to dryness in a vacuum evaporator. The residue was redissolved in 2 ml of acetone, 8 ml of 0.1% aqueous NaHCO₃ were added, and the solution was transferred to 2 cm cuvettes.

DNOC concentration was determined with a Zeiss PMQ II spectrophotometer at 440 nm. Beer's law was applicable. Recovery was 86±8% in the range of concentrations used in this study, with a limit of detection of about 0.5 ppm.

RESULTS

The various pre-treatment concentrations had a marked effect on the rate of degradation of the DNOC subsequently applied (Fig.1). The soil without pre-treatment showed a relatively rapid loss during the first two days, followed by a long lag period. The curve shows a degradation rate of 1.4% per day for the period from the second to the fifteenth day. After that, a much more rapid rate of breakdown of the

herbicide occurred, and assuming day 16 as the starting point for a more efficient degradation, the daily decomposition rate measured 15.6%. The soils which were pre-treated with DNOC showed lag periods of only one day, if any. All the degradation curves are more or less linear, and the rate of decomposition was clearly related to the amount of herbicide applied as pre-treatment. Pre-treatment to levels of 0.005, 0.25, 1.25 and 2.5 ppm resulted in degradation rates of 7.6, 13.1, 23.6 and 41.5% respectively, demonstrating a distinct effect of pre-treatment concentration.

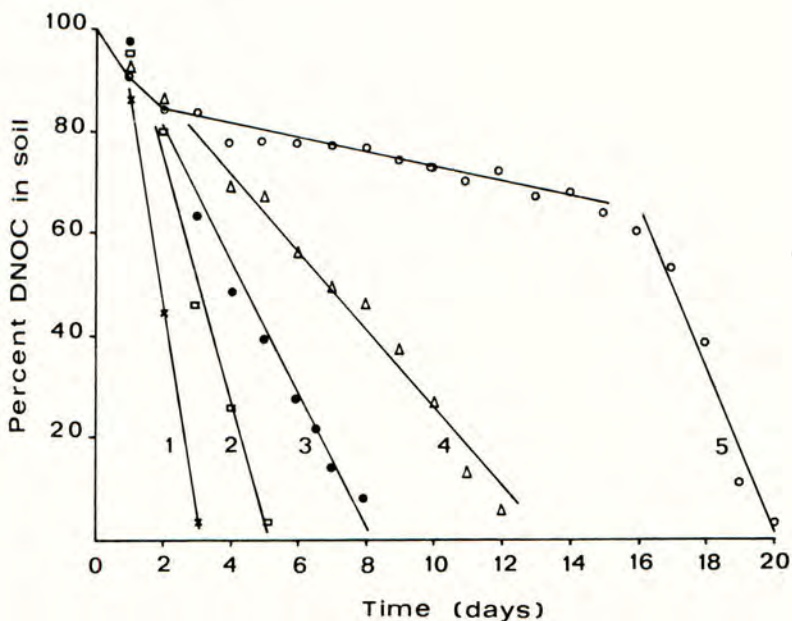


Fig.1. Comparison of DNOC degradation in soil previously treated, with degradation in soil without pre-treatment. Pre-treatment concentrations: 1=2.5 ppm; 2=1.25 ppm; 3=0.25 ppm; 4=0.005 ppm; 5=none.

DISCUSSION

The more rapid breakdown of DNOC observed in this experiment as the result of pre-treatment may be well explained by a proliferation and adaptation of microorganisms, suggesting that the rate of breakdown is a function of microorganism activity and enzyme concentration.

If pre-treatment concentrations are plotted against the observed rates of degradation per day, the curve obtained strongly suggests a linear relationship between pre-treatment concentrations and rate of breakdown (Fig.2). This in turn implies that in this experiment, the concentration of the microorganisms responsible for DNOC degradation depended directly and substantially on the pre-treatment concentration used.

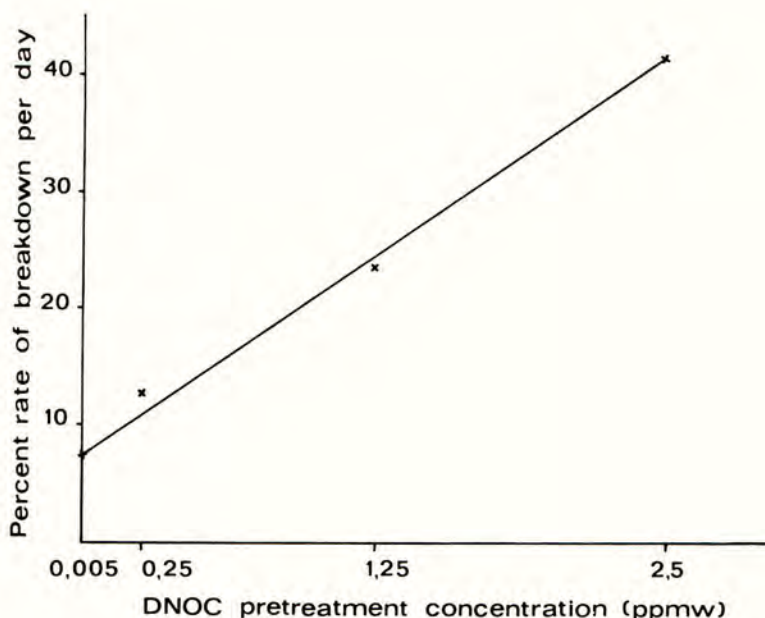


Fig.2. Relation between pre-treatment concentration and rate of breakdown per day.

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DEGRADATION OF 2-CHLORO-3-(4-CHLOROPHENYL) METHYLPROPIONATE (METHA-
CHLORPHENPROP) IN SOIL

H.Köcher, F.Lingens, and W.Koch

Abteilung für Mikrobiologie und Molekularbiologie und Abteilung für
Herbologie, Universität Hohenheim, 7 Stuttgart 70, Germany

Summary Methachlorphenprop was hydrolyzed in soil within a few hours. This rapid hydrolysis did not occur in autoclaved soil. The hydrolysis product 2-chloro-3-(4-chlorophenyl)propionic acid ("chlorphenprop") was 90% degraded within 20 days after addition to soil. The rate of its degradation was highest initially, and then gradually declined. 4-Chlorobenzoic acid was identified as an intermediate degradation product. The rate of chlorphenprop degradation was about the same in soil treated for the second time as in soil treated for the first time. Degradation of chlorphenprop was inhibited in soil which had been sterilized by autoclaving and addition of sodium azide.

INTRODUCTION

The herbicide methachlorphenprop (commercial product: "Bidisin") is used in agricultural practice to control wild oats (*Avena fatua*) in cereals and some other crops. The need of information on the fate of this herbicide in the soil was the reason for undertaking this study.

METHOD AND MATERIALS

The soil used in all experiments was a loam obtained near Stuttgart-Hohenheim with 27.3% clay, 1.0% C and pH (KCl) 5.9. The soil was sieved and then stored in a cold room until used. All experiments were performed with a mixture of one part loam and one part sieved sterile sand.

Analytical grade methachlorphenprop, 2-chloro-3-(4-chlorophenyl)propionic acid ("chlorphenprop"), 4-chlorocinnamic acid and 4-chlorobenzoic acid were obtained as a gift from Farbenfabriken Bayer AG, Leverkusen. In one experiment the commercial product "Bidisin" was used.

Thin layer chromatography was carried out on silica gel G and silica gel HF₂₅₄, primarily with n-hexane/acetic acid 96:8 as a solvent system. The detection methods used were: (1) Fluorescence quenching on silica gel HF₂₅₄; (2) Silver nitrate/ammonia spray; (3) Benzidine spray, prepared by dissolving 20 mg benzidine in 15 ml 96% ethanol.

+This method was developed by Dr. J.Kirchhoff, Abt. für Phytopathologie und Pflanzenschutz, Universität Hohenheim.

Upon UV-irradiation of benzidine-sprayed plates methachlorphenprop yields a brown spot and chlorphenprop a yellow one. Gas chromatography was performed on a Varian aerograph 1840-4 with FID on a glass column (1.6 m long, 2mm inner diameter) packed with 7.5%QF-1 on Gas Chrom Q 125-160 μ . Chlorphenprop and degradation product II had to be converted to their methyl esters prior to GLC by reacting them with diazomethane which was prepared following the procedure of de Boer and Backer (1963). IR-spectra were taken in KBr with Leitz spectrograph, using a beam condenser 6:1.

For experiments with enzymatically inactive soil, loam was autoclaved for 2 hours at 2 atm. Because of their instability in hot water methachlorphenprop and chlorphenprop had to be added after autoclaving. In the experiment on the stability of chlorphenprop in autoclaved soil the water content of the soil was adjusted by the addition of a 0.05% NaN_3 solution to avoid spreading of aerial infections.

The following extraction procedures were used for quantitative analysis. Method I: One hundred g loam/sand mixture were extracted with a mixture of 50 ml 0.075 N HCl and 100 ml acetone on the shaking machine, and after centrifugation reextracted with 150 ml chloroform. The combined extracts were partitioned in a separatory funnel, the organic phase drained and evaporated under vacuum. The residue was then taken up in an appropriate solvent for analysis. Method II: The main differences to method I were that 0.2 N HCl was used, and that after centrifugation the soil was rinsed only briefly with chloroform instead of an extended chloroform extraction.

For IR-spectroscopy degradation product I was extracted from soil with 0.075 N HCl. It was purified by chromatography on a silica gel column and recrystallized in petroleum ether. Degradation product II was extracted with a mixture of 0.3 N HCl and methanol and purified by TLC on silica gel.

For recovery determinations of methachlorphenprop and chlorphenprop, jars (200 ml volume) were filled with 50 g dry sterile sand. To each jar 2.3 mg methachlorphenprop (respectively 2.2 mg chlorphenprop) dissolved in acetone were added whilst stirring, the acetone evaporated and 50 g loam (8.5% water content) carefully mixed with the sand in the jars. The water content of the mixture was then adjusted to 10%. Nontreated controls were prepared in the same way. The jars were closed with screw caps and kept in a dark incubator at 21°C during the experimental period. The extraction followed method I.

In the studies on chlorphenprop degradation the compound was added to the soil as described in the previous paragraph, except that larger quantities of the loam/sand mixture were prepared. The chlorphenprop concentration in the soil was 22.0 ppm prior to the addition of water. Uniform distribution was obtained by shaking the soil on a tumbler. The water content was then adjusted to 10% using an atomizer. Portions of 100 g were placed in 200 ml jars which were kept under the conditions described in the previous paragraph. Also nontreated controls were prepared. Every second day the jars were aerated and two jars transferred to a deep freeze box until the soil was extracted following method II.

RESULTS

GLC analysis showed that already a few hours after addition to

soil the recovery of methachlorphenprop was practically zero. A degradation product I was detected by TLC which behaved in different solvent systems identical to the free acid chlorphenprop. Reacting product I with diazomethane yielded a product whose characteristics were in TLC and GLC identical with methachlorphenprop. The rapid hydrolysis of methachlorphenprop to chlorphenprop in soil was finally proven by IR-spectroscopy. Hydrolysis occurred also when methachlorphenprop was added to soil as an aqueous emulsion of the commercial formulation "Bidisin".

To obtain quantitative data, soil samples (4 replicates) were extracted 5 hours after addition of methachlorphenprop, and the extracts divided into two equal portions. One portion was analyzed directly by GLC, the other after methylation with diazomethane. Practically no methachlorphenprop was found in the non methylated portion, whereas from the methylated portion as much methachlorphenprop was obtained as from methylated extracts of soil samples which had been treated with an equimolar quantity of chlorphenprop (Table 1). Thus disappearance of methachlorphenprop after 5 hours in soil was entirely due to hydrolysis

Table 1

Recovery of methachlorphenprop and chlorphenprop from soil

Compound added to soil	Time (hours)	% Recovery
Methachlorphenprop	0.0	84 ± 4.7 without methylation
Methachlorphenprop	5.0	0 without methylation
Methachlorphenprop	5.0	79 ± 1.6 after methylation
Chlorphenprop	5.0	82 ± 3.2 after methylation

and not to irreversible adsorption to soil particles, 84% of methachlorphenprop were recovered when immediately added to the suspension of soil in the extraction solvents acetone/diluted HCl (Table 1, 0.0 hours). In a further experiment the time course of methachlorphenprop degradation was studied in autoclaved as compared to non autoclaved soil. In autoclaved soil there was no clear indication of methachlorphenprop degradation over the experimental period of 25 hours (Table 2).

The course of degradation of chlorphenprop in soil was followed by TLC and GLC. In soil treated for the first time with chlorphenprop considerable degradation had taken place already after 2 days. If there was any "lag-phase", it must have been very short (Figure 1). Almost 50% was degraded after 8 days, and 90% after 20 days. The losses of chlorphenprop during extraction were 26% on an average. In order to study the influence of a previous treatment of soil with chlorphenprop on the course of its degradation at the second treatment, soil was subjected to a second treatment 4 weeks after the first. For this purpose 10 parts loam/sand mixture which had already received one treatment were mixed with 3 parts non pretreated loam and 3 parts of sand to which the second dose of chlorphenprop had been applied, following the procedure already described above. The initial chlorphenprop concentration was the same in both treatments. The rate of degradation after the

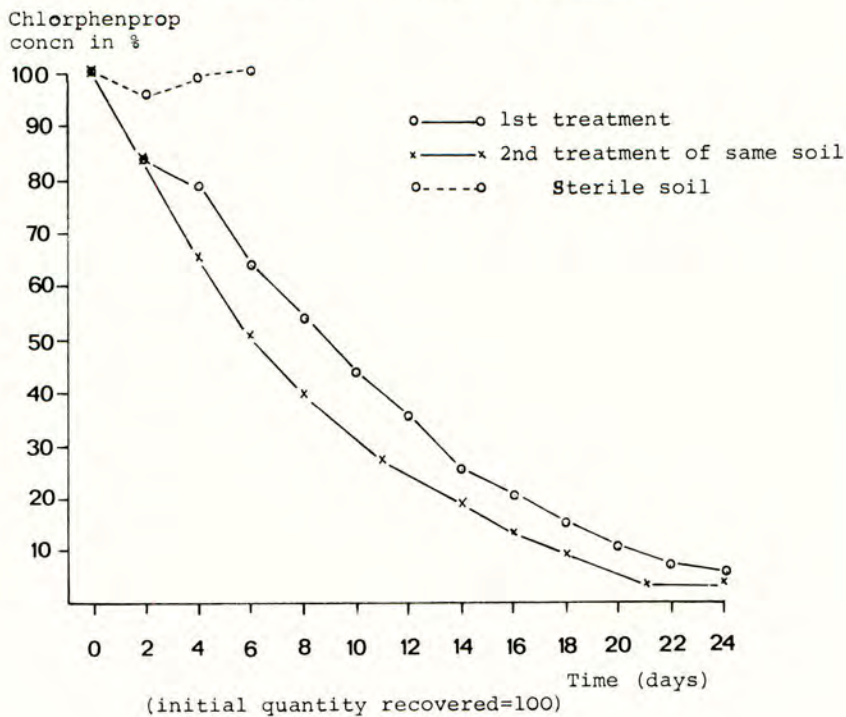
Table 2

Recovery of methachlorphenprop from autoclaved and non autoclaved soil in relation to time

Time (hours)	autoclaved	% Recovery	non autoclaved
0.0	86		84
5.0	80		0
15.0	85		0
25.0	81		0

Figure 1

Degradation of chlorphenprop in soil



second treatment was found to be very similar to the first treatment (Figure 1).

Between the second and eighth day - with a maximum at the fourth day - a degradation product II was found in soil treated for the first time. It did not appear, however, in soil treated for the second time (Table 3). This product could be separated from chlorphenprop by TLC and chromatographed identically with 4-chlorobenzoic acid. After treatment with diazomethane the resulting product was analyzed by TLC and GLC. The *rf*-values and retention times were the same as for 4-chlorobenzoic acid methylester. An IR-spectrum confirmed the identity of degrada-

Table 3

Quantity of degradation product II (4-chlorobenzoic acid) extracted from soil in relation to time

Time (days)	µg 4-Chlorobenzoic acid/100 g soil	
	1st Treatment	2nd Treatment
0	0	0
2	61	0
4	80	0
6	53	0
8	9	0
10	0	-

degradation product II with 4-chlorobenzoic acid. A second metabolite was found by TLC only. It occurred in very small amounts and chromatographed identically to 4-chlorocinnamic acid.

The degradation of chlorphenprop was completely inhibited in soil which had been sterilized by autoclaving and addition of NaN_3 (Figure 1).

DISCUSSION

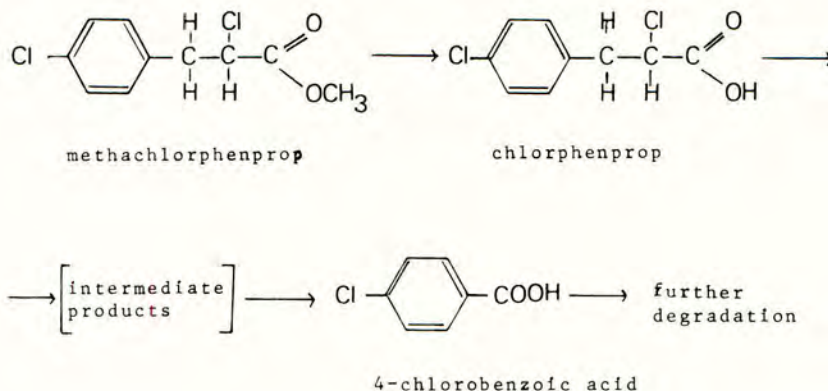
The fast hydrolysis of methachlorphenprop in loam is a striking result of our studies. We do not know yet whether this holds true for all types of soils, but mention that we obtained the same result in experiments (as yet unpublished) with a sandy soil high in organic matter and with low pH. Failure of autoclaved soil to hydrolyze an appreciable amount of methachlorphenprop within a 25 hr period points to the involvement of microbial hydrolytic enzymes in this degradation reaction. The production of these enzymes is obviously not dependent on the presence of methachlorphenprop in the soil.

The speed of degradation of the hydrolysis product chlorphenprop is highest initially and then gradually declines. This contrasts to the degradation curves which have been found for example for the herbicide 2,4-D (Hurle und Rademacher 1970): After an initial lag-phase the degradation of 2,4-D proceeded with rapidly increasing velocity. Assu-

ming that the degradation of chlorphenprop is due to the activity of soil microorganisms, we can conclude that unlike to 2,4-D the presence of chlorphenprop in the soil does not induce an increase of the degrading microbial potential of the soil. The similarity of the degradation curves for the first and the second treatment with chlorphenprop lends further support to this conclusion. The soil microorganisms which catalyze the first step of chlorphenprop degradation apparently do not respond by increased proliferation to the addition of this foreign substrate. In this context it is interesting that in liquid culture we have so far failed to select degrading microorganisms by addition of chlorphenprop as sole carbon source. It was not difficult, however, to select microorganisms able to grow on 4-chlorocinnamic acid or 4-chlorobenzoic acid as carbon source. On the basis of our experiments with loam we can characterize methachlorphenprop and chlorphenprop as foreign compounds with relatively little persistence in soil. We cannot yet answer the question as to what extent their degradation rate is influenced by the soil type. One should also bear in mind that oxygen and water supply are not always as favourable in the field as in our laboratory experiments, and these compounds may, therefore, have a longer persistence in the field environment.

4-Chlorocinnamic acid is possibly the first product of chlorphenprop degradation, but we have not yet been able to isolate and positively identify it. β -Oxidation of the side chain is likely to be the next step towards formation of 4-chlorobenzoic acid. During the first 4 days of chlorphenprop degradation the rate of 4-chlorobenzoic acid production appears to be faster than the rate of its degradation. The subsequent decline of its concentration in the soil can be explained by the proliferation of a 4-chlorobenzoic acid degrading microbial population after an initial lag-phase. The speed of its degradation was then accelerated to such an extent that it did not occur any more in detectable amounts. At the second addition of chlorphenprop to the soil the degrading population was still present from the previous treatment. This interpretation is valid only if 4-chlorobenzoic acid is formed as an intermediate product during the entire course of chlorphenprop degradation.

On the basis of our present results we want to suggest a possible pathway of methachlorphenprop degradation:



Acknowledgements

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THE BEHAVIOUR OF SIX SOIL-APPLIED HERBICIDES IN SOIL -
A COMPARISON

V. Steckó
Department of Plant Husbandry,
Agricultural College of Sweden, S-750 07 Uppsala 7, Sweden

Summary The persistence of linuron, monolinuron, buturon, prometryne, terbutryne and desmetryne was studied in field experiments on sandy and clay soils respectively by means of bio-assay on soil samples taken at intervals. The herbicides disappeared more rapidly from sandy soil infested by weeds than from clay soil which was nearly weed free. None of the compounds could be detected in the soil within a period of one year. Linuron, monolinuron and buturon moved to a depth of 10 cm down the soil profile. Terbutryne and prometryne were found only in the top 5 cm of the soil profile. Desmetryne was not detected in phytotoxic quantities at any point in the profile.

INTRODUCTION

The herbicides linuron, monolinuron, buturon, prometryne, terbutryne and desmetryne are used for selective weed control in Scandinavia. However, few experiments have been carried out to determine the persistence of these herbicides in soil under Scandinavian conditions.

The reports available suggest that persistence of these compounds varies according to the general geographic region where experiments are conducted. It appears that all compounds persist longer in the northern part of Europe where the soil is frozen for a prolonged period during winter. Linuron is considered to be more persistent than buturon or monolinuron and desmetryne and prometryne more persistent than terbutryne (Majumdar 1969, Hogue 1970, Steckó & Svensson 1970).

METHOD AND MATERIALS

The experiments were conducted at the Department of Plant Husbandry, Uppsala (60° N latitude) on both sandy and clay soils. The pH of the sandy soil was 6.7 and that of the clay soil 8.3. Organic matter in both soils was of the order of 3%. The experiments were started in June 1969. 1.5 and 3.0 kg/ha a.i. of linuron, monolinuron, buturon, terbutryne and prometryne, and 0.5 and 1.0 kg/ha a.i. of desmetryne were applied to land which had

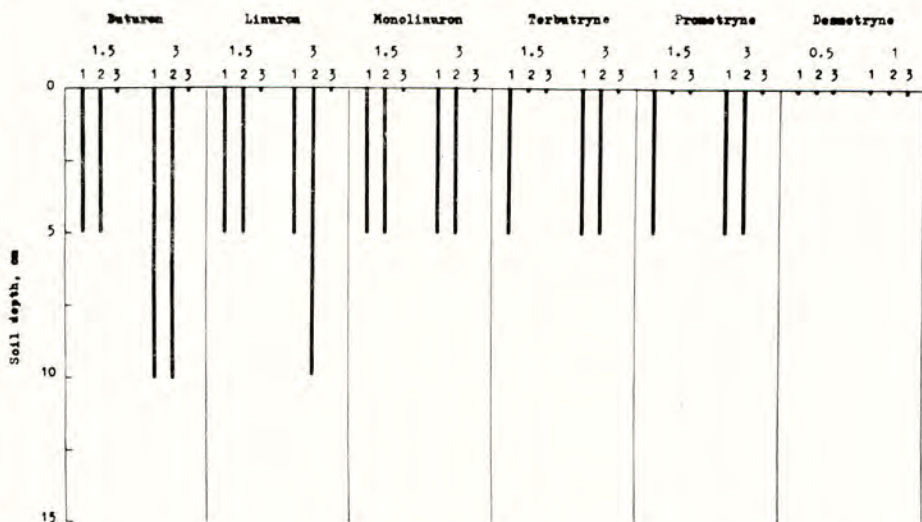
previously been cultivated and harrowed. The doses used are equivalent to "normal" and "double normal". The compounds were applied without incorporation. Soil samples were taken 43, 120 and 378 days after treatment. Between treatment and soil sampling the total precipitation was 43 mm, 192 mm and 442 mm respectively. The soil was frozen and covered by snow for about 5 months of the experimental period.

Soil samples were taken from 4 layers corresponding to depths of 0 - 5 cm, 5 - 10 cm, 10 - 15 cm and 15 - 20 cm respectively. Residual herbicide toxicity was determined by bio-assay using oats and white mustard. Seedlings of these species were grown on soil samples in plastic pots of 1 litre volume kept in the greenhouse at a temperature of 16 - 22°C. After 4 weeks, plant fresh weight and visual phytotoxic symptoms were used as a comparative measure of herbicidal persistence in the different soil layers.

Figure 1

The vertical movement and the persistence of six herbicides in clay soil

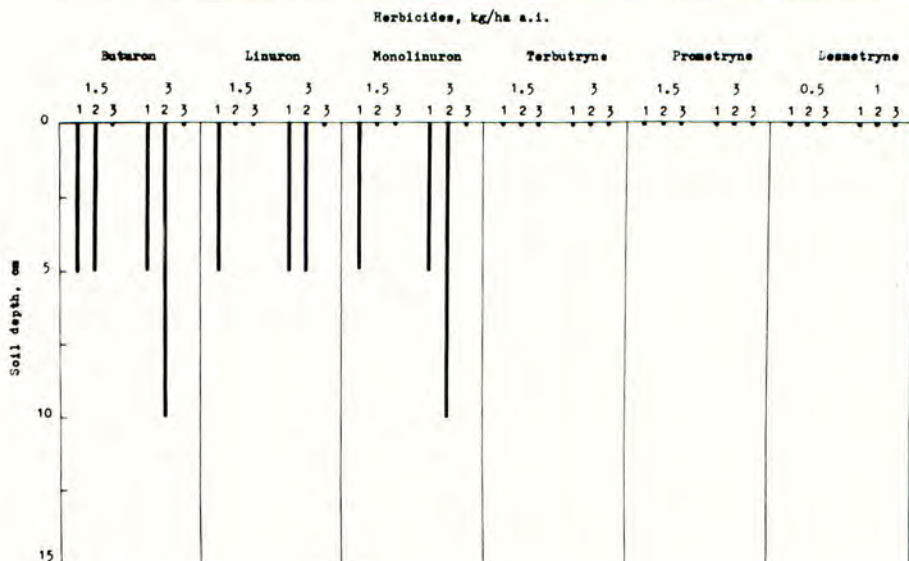
Herbicides, kg/ha a.i.



- The depth where the herbicides were detected in phytotoxic quantities.
- The herbicides were not detected in phytotoxic quantities.
- 1. Sampling 43 days after the treatment.
- 2. Sampling 120 days after the treatment.
- 3. Sampling 378 days after the treatment.

Figure 2

The vertical movement and the persistence of six herbicides in sandy soil



- The depth where the herbicides were detected in phytotoxic quantities.
 • The herbicides were not detected in phytotoxic quantities.
 1. Sampling 43 days after the treatment.
 2. Sampling 120 days after the treatment.
 3. Sampling 378 days after the treatment.

RESULTS

Data from the experiments are presented in Figures 1 and 2. They show that concentrations of all 6 herbicides fell below the level of detection in less than a year. Desmetryne was never detected in any phytotoxic quantity. Terbutryne and prometryne were only detected in the clay soil. The substituted urea herbicides were detected in phytotoxic quantities in both soil types.

The substituted urea herbicides showed the greatest vertical movement through soil. They were found in the 5 - 10 cm layer, but the greatest part remained in the top 5 cm. In no instance were compounds detected at a depth greater than 10 cm in the soil.

As a test plant, white mustard proved preferable as the visual phytotoxic symptoms occurred earlier and more clearly than in oats.

In the field, the herbicides applied to sandy soil had very little effect on Agropyron repens. Chenopodium album was only satisfactorily controlled by the highest rate of linuron and the highest rate of monolinuron.

DISCUSSION

Some of the herbicides used in these experiments are known to have shown a relatively long persistence in some parts of Sweden in certain years, and there are records of their causing serious damage on succeeding crops in a rotation. It appears that the persistence of the herbicides was particularly marked after a dry summer or in the absence of ploughing in preparation for the succeeding crop.

In the experiments described in this paper, however, compounds applied in "normal" and "double normal" doses did not persist longer than a single year. The trials results mainly demonstrate differences of persistence between sandy and clay soils. The substituted triazine herbicides were not present in detectable amounts in sandy soil, and even the substituted urea herbicides had generally a shorter residual effect and less toxicity in sand than in the clay soil. This might be partly explained by the presence of Agropyron repens and Chenopodium album in large numbers on the sandy soil having caused a favourable environment for the detoxification of the herbicides. Clay soil was nearly weed free during the experimental period.

The extent of vertical movement through the soil did not appear to show any direct correlation with the water solubility of the herbicides. Of the six, buturon has the lowest solubility, 30 ppm, followed by prometryne, 48 ppm, terbutryne, 58 ppm, linuron, 75 ppm and monolinuron and desmetryne, 580 ppm. As the figures show, only buturon, linuron and monolinuron were detected in the deepest layer of the soil profile sampled.

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A NEW SELECTIVE HERBICIDE FOR RICE, S-(2-METHYL-1-PIPERIDYL-CARBONYLMETHYL)-
O,O-DI-N-PROPYL DITHIOPHOSPHATE, FOR USE ALONE OR IN MIXTURES

D.H. Green & L. Ebner
Ciba-Geigy Ltd., Basle, Switzerland

Summary The above herbicide, coded C 19490, used at 1 - 1.25 kg a.i./ha alone, selectively controlled annual grasses and *Cyperus* spp. in the tropics. Used at 0.75 - 1.0 kg a.i./ha combined with the isopropylester of 2,4-D at 0.5 kg a.i./ha, it gave control also of annual broadleaved weeds.

A mixture, C 288, containing 4 parts C 19490 and 1 part C 18898, a triazine, demonstrated the same broad-spectrum activity without loss of selectivity both in the tropics and in temperate regions, and gave moderate - good control of semi-perennials in Japan. Rates ranged from 0.75 kg a.i./ha in the tropics to around 2 kg a.i./ha in Japan, depending on the weed species and the residual activity required. Activity was somewhat temperature dependent, but water management and soil type had little effect on performance. Transplanted, drilled and surface-sown flooded rice were tolerant, early post-weed emergence.

INTRODUCTION

At the end of 1969, Ciba-Geigy Ltd. began an intensive trial programme with several candidate herbicides in rice. The compound S-(2-methyl-1-piperidyl-carbonylmethyl)-O,O-di-n-propyl dithiophosphate (C 19490) emerged as a highly selective grass- and annual sedge killer. The most successful partners, which added greatly to the spectrum of weeds, were 2-(1',2'-dimethyl-propylamino)-4-ethylamino-6-methylthio-1,3,5-triazine (C 18898) and the isopropyl ester of 2,4-D. The two broad-spectrum mixtures, the phosphate + triazine in the ratio 4:1, coded C 288, and the phosphate + 2,4-D IPE mixture in the ratios 3:2 or 2:1, called C 19490 + 2,4-D in the text which follows, have now undergone 3 seasons of field testing. C 288 has been evaluated in more than 20 rice-growing countries, while C 19490 + 2,4-D trials have been confined to the tropical regions, because 2,4-D esters applied early are phytotoxic in temperate and sub-tropical climates, e.g. Japan and Taiwan.

Laboratory studies have shown that C 19490 and C 18898 are soluble to the extent of 12 - 15 and 50 ppm in water, respectively, both are oily liquids at room temperature.

Residue analysis methods for simultaneous determination of both components of either mixture have been worked out, sensitive to 0.05 ppm or less of any component in rice and soil. Rice grain and soil sampled 109 days after a post-emergence treatment with C 288 showed that no C 19490 residues were present in soil down to a depth of 20 cm. The C 18898 component was just detectable (0.04 ppm) in both soil and crop, as was C 19490 in the crop.

The acute oral LD₅₀ of technical C 19490 to mice was 410 mg/kg for males and 330 mg/kg for females; that of C 18898 was 3000 mg/kg for males and 3750 mg/kg for females. The toxicity of C 288 to all of four species of fish was similar to that of nitrofen or benthocarb, and around 25 times less than that of PCP. The two components formulated together on granules caused no skin irritation whatever to albino rabbits.

The mode of activity of C 288 and of C 19490 + 2,4-D are not yet clearly understood. The C 19490 appears to act at the soil surface, and is probably not readily translocated. The mobility in saturated soil of both components of C 288, determined by a standard technique (Gerber et al - 1970), is low. The triazine appears to function typically, as an inhibitor of the Hill reaction of photosynthesis. The 2,4-D component is known to affect a range of biochemical reactions, and can be presumed to be taken up, under flooded conditions, by both weed roots and emerged leaves.

METHOD AND MATERIALS

Greenhouse and field tests have been carried out by Ciba-Geigy personnel, cooperators such as the International Rice Research Institute (the IRRI) and by official research station staff, using many different methods, in approximately 20 important rice-growing countries.

All experiments reported below, however, have involved the use of complete randomised block designs involving at least 2, or, in field trials, 3 replicates.

Initial tests involved the use of simple plastic pots; later trials utilised large concrete or pot vessels in which it was possible to vary the depth of water as required. Field plots were usually separated by mud walls or plastic sheets and rows of plots were irrigated from a common canal with no communication between one plot and others adjacent. The size of field plots varied between 10 and 20 m².

The formulations discussed in this report were all granulars, applied evenly by hand to soil or water in pots or field plots. With little apparent effect on performance, different formulations were used in the three trial seasons; the latest formulations were made, for the 1972 season, with several different contents of a.i. calculated to give, with an application rate of 30 kg formulation/ha, the different doses of active ingredient found to be necessary to control different weed floras in different climatic regions. There were under test this season a 3.3 % granule of C 288 in the tropics and 5.5 and 6.5 % extruded granules in Japan. The 19490 + 2,4-D mixture has been formulated as a 4.2 % with ingredients in the ratio 3:2 and as a 5 % with an ingredient ratio of 2:1. Also available was a 2.5 % granule of C 19490 alone, to which could be added locally-formulated 2,4-D granules.

Scoring was carried out using, or converting scores to, the proposed EWRC scales of 1 - 9, where 1 represents perfect weed control and no damage to the crop, 4 represents the upper limit of acceptability (10 % of weeds remaining or a just acceptable degree of visible injury to the crop which was unlikely to affect yield, and 9 represents less than 33 % weed control or 67 % crop damage or more). In some trials carried out by cooperators weed weights, crop height measurements and tiller counts were made, in the majority of field trials, yield measurements were taken and usually analysed statistically, by the technique of analysis of variance, followed by the application of Duncan's multiple range test.

RESULTS

Work during 1969 and 1970 in the greenhouse clearly showed C 19490 to be among the most selective annual grasskillers for use in both seeded rice, post-emergence, and pre- or post-weed emergence in transplanted rice. A wide range of dosage rates, conditions of temperature, water management and timing were investigated. Selectivity between rice and Echinochloa crus galli was the main point of study.

Later trials, both in the greenhouse and in the field, tested mixtures of C 19490 and various possible partners, of which C 18898 proved to be the most advantageous against over 60 species of tropical and temperate aquatic weeds.

In 1970 came the discovery, for which we are indebted to Dr. S.K. De Datta and his team at the IRRI, Los Banos, Philippines, that early-applied mixtures of C 19490 with 2,4-D esters, especially the isopropyl ester, were completely selective, and achieved control of the whole tropical weed spectrum.

In the tables which follow, a sample of typical results has been made, to summarise the known properties of C 19490, C 288 and C 19490 + 2,4-D and the influence of important climatic and cultural factors on performance.

Table 1

Greenhouse results (Switzerland) with C 19490 and C 288. All formulations were granules. (Note: E.c-g is Echinochloa crus-galli)

Herbicide	Rate,kg a.i./ha	Timing(leaves of E.c-g)	Type of Rice	EWRC Scores for		
				Crop	E.c-g	Other Weed
						<u>Scirpus sp.</u>
C 19490	0.5	2 leaves	transplanted	1	1	6
	1.0			1	1	5
	2.0			3	1	5
	4.0			7	1	-
						<u>Fimbristylis</u>
C 19490	1.0	post-em.	--	-	-	9
	2.0			-	-	6
C 19490	0.5	pre-em.	seeded	5	1	-
	1.0			9	1	-
	0.5	2 leaves	seeded	1	1	-
	1.0			1	1	-
						<u>Eleocharis</u>
C 288	1.0	2 leaves	transplanted	1	3	5
	2.0			1	1	1
	4.0			4	1	1
						<u>Scirpus</u>
C 288	0.5	pre-em.	transplanted	2	1	5
	1.0			2	1	1
	2.0			3	1	1
C 288	2.0	2-3 leaves	--	-	1	-
	2.0	3-4 leaves	--	-	3	-

Table 2

Field results from yield trials in Japan with C 288 granular formulations. All scores are on EWRC scales. All trials on Transplanted Rice.

Rate of C 288 kg a.i./ha	Timing Leaf stage of E.c-g	EWRC Scores for			Yield Absolute tons/ha	%
		Crop	E.c-g	Other Weed		
				<u>Sagittaria</u>		
2.5	0 (pre-em.)	1	1	6	6.68	109
				<u>Perennials</u>		
2.5	0 (pre-em.)	2	3	8	7.83	105
				<u>Sagittaria</u>		
3.0	1.5 leaves	2	1	4	6.62	107
4.0	1.5 leaves	2	1	4	6.90	111
2.5	2 leaves	2	1	4	5.33	103
3.0	2 leaves	2	1	3	5.33	103
				<u>Sagittaria</u>		
2.0	0 (pre-em.)	2	1	7	6.02	102
3.0	0 (pre-em.)	2	1	5	6.19	104
2.0	3 leaves	1	2	4	5.92	100
3.0	3 leaves	2	2	4	5.97	100
				<u>Monochoria</u>		
2.0	0 (pre-em.)	1	1	1	4.80	102
3.0	0 (pre-em.)	2	1	1	4.97	105
2.0	2.5-3.5 leav.	2	3	1	4.77	101
3.0	2.5-3.5 leav.	2	2	1	5.41	115

* In the above table, yields are expressed as % of those from clean-handweeded controls; unweeded control yields varied from 77 - 93 % of these in different trials.

Only the semi-perennial weeds Sagittaria pygmaea, Cyperus serotinus and Eleocharis kurogawai in the above trials were not consistently at least 95 % controlled by the rates tested. Other weeds, well to completely controlled, were: Echinochloa crus-galli, Monochoria vaginalis, Eleocharis acicularis, Cyperus difformis, Rotala indica, Dopatrium junceum, Callitriche verna, Eriocaulon sieboldianum, Vandellia anagallis, Lindernia pyxidaria, Cyperus microiria, Polygonum hydropiper, Oenanthe stolonifera and Elatine triandra.

Table 3

Field results from trials in Tropical Asia with C 19490, C 288 and C 19490 + 2,4-D granular formulations on various types of Rice

Herbicide	Rate, kg a.i./ha	Timing DAS or DAT*	EWRC Scores for				Yield tons/ha
			Crop	Grasses	Sedges	Broad-leaves	
C 19490	0.75	1) 6 DAS	1	2	1	5	4.5 a
	1.5	1) 6 DAS	1	1	1	3	4.8 a
	1.5	1) 8 DAS	3	1	1	6	4.4 a
Control	--	--	unweeded				0.3 b
C 19490	0.75	3) 3 DAT	3	1	1	3	5.8 a
	0.75	4) 6 DAT	2	1	1	2	6.2 a
	Control	--	--	handweeded unweeded			
C 19490+2,4-D	0.75+0.5	1) 6 DAS	3	2	1	2	4.0 a
	0.75+0.5	1) 8 DAS	3	3	1	3	4.4 a
	Control	--	--	unweeded			
C 19490+2,4-D	1 + 0.5	3) 4 DAT	1	1	1	1	3.8 a
	1 + 0.5	4) 10DAT	1	7	4	8	1.2 b
	Control	--	--	unweeded			
C 288	0.75	3) 4 DAT	2	1	1	1	3.7 a
	1.5	4) 10DAT	1	3	1	3	3.4 a
	Control	--	--	unweeded			
C 288	1.5	1) 8 DAS	2	1	1	1	4.1 a
	1.5	1) 10DAS	3	2	1	2	4.1 a
	Control	--	--	unweeded			
C 288	0.75	4) 7 DAT	2	2	1	1	4.8
	1.5	4) 7 DAT	3	1	1	1	4.4
	Control	--	--	handweeded			
C 288	1.0	4) 7 DAT	1	2	1	2	5.2 a
	1.0	2) 7 DAS	1	2	1	3	4.7 a
	1.0	1) 7 DAS	1	2	1	2	4.9 a

Controls corresponding to the above plots yielded virtually no rice

* DAS = days after sowing DAT = days after transplanting

The main broadleaved weed was Monochoria vaginalis

Numerals before timing indicate : 1) broadcast-(surface-)seeded, flooded rice treated post-weed emergence 2) drilled, flooded rice, treated post-weed emergence 3) transplanted, flooded rice treated pre-weed emergence or at emergence 4) (transplanted, flooded rice, treated post-of weed) (weed emergence)

Yields followed by a common letter were not significantly different at P = 0.05

Table 4

Effects of various factors on performance of C 288 in the field

a) Temperature at low leaching intensity, transplanted rice; Japan

Mean of maximum temperature for 7 days after treatment C°	Percolation of water, cm/day	Scores for crop health (3 kg a.i./ha)	Scores for E.c-g (2 kg a.i./ha)	Control of Eleocharis
14	0	3	1	1
18-19	0.5	3	1	1
17	1.0	3	1	1
28	0.5-1.0	2	1	3
30	1.0	1	1	2

b) Leaching at constant low temperature, transplanted rice; Japan

Percolation of water, cm/day	Mean of maximum temperatures for 7 days after treatment C°	Scores for crop health (3 kg a.i./ha)	Scores for E.c-g (2 kg a.i./ha)	Control of Eleocharis
0	14	3	1	1
0.5	18	3	1	1
about 0.1	16	5	1	4
2.0	18	3	1	1
2.0-3.0	18	6	1	2

c) Water management, post-emergence, direct-seeded rice; Philippines

Seeding	Water depth at various stages (cm)					Yields of rice t/ha	
	6DAS	10DAS	20DAS	Panicle Initiation	Maturity	C 288 1 kg a.i./ha	Unweeded control
5	5	5	5	5	5	7.0	3.3
2.5	2.5	2.5	2.5	2.5	2.5	7.0	1.2
1	1	1	1	1	2.5	7.0	1.4
0	2.5	2.5	2.5	2.5	2.5	7.3	1.8
0	5	1	5	5	5	7.0	3.2
0	2.5	1	5	5	5	7.5	1.3
0	2.5	2.5	5	5	5	6.9	4.3
0	1	1	5	5	5	7.0	2.1
0	5*	5	5	5	5	6.4	1.6
0	2.5*	2.5	5	5	5	6.9	2.6

* These levels were maintained from 4 DAS (days after sowing)

Data in section c) published by kind permission of Dr. S.K. De Datta of the IRRI

DISCUSSION

From the results of the type summarised in table 1, it was soon learned that C 19490 was an excellent weedkiller for annual grasses and annual *Cyperus* spp., but that it did not control such weeds as *Fimbristylis miliacea* and many broad-leaved weeds. Results from the field, shown at the top of table 3 confirm this impression, at rates some 50 % higher than those used in the greenhouse. Also, C 19490 was not tolerated by seeded rice before it had emerged.

The mixture C 288 controlled *F. miliacea* and also *Scirpus* spp. at low rates, and both greenhouse and field trials with C 288, rapidly confirmed its broad spectrum of annual weed control, in transplanted rice at any stage from pre-weed emergence to the 4-leaf stage of grass weeds and in seeded rice at an early post-emergence stage of the weeds. In Japan, although higher rates were needed (table 2) than in tropical Asia, (table 3) the selectivity remained. The higher rates are necessitated by the generally lower temperatures, especially at night, which occur in Japan, and by the longer period over which weeds will germinate in a cooler climate (Noda - 1971).

The 19490 + 2,4-D combination (middle of table 3) proved to be nearly as active against the whole spectrum of weeds until these reached the 3-4 leaf stage, 10 days after transplanting or sowing, when both grasses and broadleaved weeds developed a strong resistance. For early post-emergence applications to both seeded and transplanted rice, the 19490 + 2,4-D treatments appear to be consistently as active and selective as those with C 288, the respective rates being 0.75 - 1.0 + 0.5 kg a.i./ha and 1.25 kg a.i./ha, or less when applied early.

Investigation of individual factors (table 4b) shows that low temperatures combined with high leaching can result in phytotoxicity with C 288 at rates only a little above those necessary for weed control. So far, only a few trials from northern Japan have demonstrated this. Under all other temperature and soil conditions, from 15°C to well over 40°C in Pakistan, adequate selectivity has consistently been observed on all soil types growing transplanted rice.

Greenhouse work and the trial summarised in table 4c have demonstrated the excellent consistency of C 288 under a wide range of water management practices. The much larger variation in control yields is shown there, and other products tested with C 288 were not as consistent.

Applied at - or post-weed emergence in transplanted rice, the rates of C 288 currently recommended for trials vary from 0.75 kg a.i./ha at or before the 3-leaf stage of *E. crus-galli* in many tropical countries to 1 or 1.25 kg for late applications or heavy stands of annual broad-leaved weeds and up to around 2 kg a.i./ha for annual weed control in Japan. From this rate upwards, a variable, often useful control of perennial weeds, e.g. *Sagittaria* spp. and *Cyperus serotinus* has been obtained in Japan. The 3-leaf stage is normally attained, in Japan, after 10-15 days.

In tropical countries, both C 288 at 0.75 - 1.25 kg a.i./ha or C 19490 + 2,4-D at 0.75 - 1.0 + 0.5 kg a.i./ha have given consistent control of all the major annual weed species, in transplanted rice between weed emergence and the 3-leaf stage of grasses, and in seeded rice at the 1-3 leaf stages. Emergence of weeds normally corresponds to 3 days after sowing (3 DAS) or transplanting, the 1-leaf stage is reached in 4 - 5 days, the 3-leaf stage in 7 days and 4-5 leaves in 10 days.

The phosphate C 19490 can only be used alone, also between weed emergence and the 3-leaf stage of grasses, where a pure stand of annual grasses and annual Cyperus spp. occurs; recommended rates, for seeded and transplanted rice, lie around 1 - 1.25 kg a.i./ha.

Acknowledgements

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Last but not least, the hard work and cooperation of our colleagues in the Ciba-Geigy Product Development groups in Pakistan, Indonesia, Egypt, Japan and Switzerland is gratefully acknowledged.

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HOE 2991, A NEW SELECTIVE UREA HERBICIDE

P. Langelüddeke & E.-F. Schulze
Farbwerke Hoechst AG, Frankfurt(Main), Germany

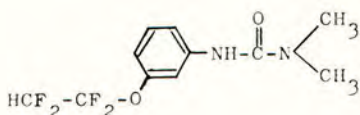
Summary. HOE 2991, a new urea herbicide, controlled in glasshouse and field trials a broad spectrum of broadleaved and grassy weeds and was found to be selective especially in cotton. Moreover, in glasshouse and laboratory experiments different aspects of soil behaviour and biological and physiological activity have been studied.

INTRODUCTION

Since the discovery of the herbicidal properties of monuron and diuron 20 years ago and their introduction into agricultural practice, numbers of other phenyl ureas have been developed by different companies. About 1960 in Germany Farbwerke Hoechst AG was the first to develop and commercialize the new ureas linuron and monolinuron. In further experiments in our laboratories a group of halogenated alkyloxyphenyl ureas has been studied in recent years (SCHERER et al, 1972) as regards their chemical and biological properties. HOE 2991 is the most interesting compound of this group.

CHEMICAL AND PHYSICAL PROPERTIES

Structure:



Chemical name: N-3-(1',1',2',2'-tetrafluoroethoxy)-phenyl-N',N'-dimethyl urea

Proposed common name: fluoretoxuron

Empirical formula: C₁₁H₁₂F₄N₂O₂; Molecular weight: 280

Physical form: white crystals; Odour: odourless

Meltingpoint: 115-117°C; Solubility in water: 225 ppm at 25°C

TOXICOLOGY

Acute oral toxicity:

rat LD₅₀ >6000 mg/kg bodyweight
 dog (beagle) >6000 mg/kg bodyweight

Dermal toxicity:

rabbit (5 consecutive applications) >5x800 mg/kg bodyweight

Subchronic toxicity (90 days feeding study):

rat no effect level 2000 ppm
 dog (beagle) no effect level 200 ppm

GLASSHOUSE TRIALS

1. Effects on weeds and crops

In preemergence applications HOE 2991 performed distinctly better than comparable compounds like linuron or fluometuron. The mean lethal dose for 15 mono- and dicotyledonous weeds studied in 44 single pot trials was:

HOE 2991 0.4 kg/ha
 fluometuron 0.7 kg/ha

GASSNER (not published) found a good selectivity on cotton and a limited selectivity on maize. The results of HOE 2991 on cotton and typical weeds found in cotton are given in table 1.

Table 1

Tolerated and lethal dosages of HOE 2991
 on cotton and weeds
 Pot trial, preemergence

Tolerated dosage cotton:	1.00 kg/ha a.i.
Lethal dosages <u>Amaranthus retroflexus</u>	< 0.15
<u>Bidens pilosa</u>	< 0.15
<u>Digitaria sanguinalis</u>	0.38
<u>Echinochloa crus-galli</u>	0.59
<u>Eleusine indica</u>	0.42
<u>Ipomoea purpurea</u>	0.15
<u>Leptochloa dubia</u>	0.50
<u>Polygonum persicaria</u>	< 0.15
<u>Sesbania sp.</u>	0.15 - 0.30
<u>Sida spinosa</u>	0.37
<u>Xanthium spinosum</u>	0.15 - 0.30

In postemergence screening trials HOE 2991 had a similar or slightly better herbicidal action than fluometuron.

2. Residual activity -^f bioassay

In a pot trial where the pots were sealed at the bottom to prevent leaching the residual activity of HOE 2991 was studied by measuring freshweight of oats. Oats were sown 1, 2, 3 and 5 months after treatment respectively. Between treatment and sowing soil moisture was kept at 80% field capacity of the soil. The trial was conducted in a glasshouse with a day temperature of 30°C and a night temperature of 15°C.

Table 2

Residual activity of HOE 2991
% damage on oats (freshweight)
means of 4 replicates

Date of sowing	kg/ha a.i.	
	1.25	0.62
1. immediately after treatment	100.0	99.9
2. 1 month " "	97.0	23.0
3. 2 months " "	72.0	11.0
4. 3 months " "	61.0	0
5. 5 months " "	39.0	0

Thus, 0.62 kg/ha HOE 2991 was completely decomposed within 3 months in a wet soil, whereas the activity of 1.25 kg/ha -which under these conditions is a high dosage- was appreciably reduced in the same time. As in a similar trial under dry soil conditions (30% field capacity) there was hardly any decrease of damage to the test plant, it seems that the active material is primarily decomposed biologically.

3. Other soil trials

The results of preliminary leaching studies conducted on a loamy and on a sandy soil with 1.8 and 3.3% organic matter content respectively indicate a stronger leaching of the active material in the sandy soil, although the organic matter content was higher than that of the loam.

On the other hand, a comparison of the herbicidal activity in different soil types showed, that the herbicidal activity seems to depend more on organic matter content than on the soil type.

Table 3

LD₅₀ of HOE 2991 on different soils
Test plant: Oats

soil type	organic matter	LD ₅₀
loamy soil	0.26%	0.27 kg/ha a.i.
loamy soil	2.7 %	0.47
sandy soil	2.7 %	0.50

In addition to this, we found that on a marshy soil there was hardly any herbicidal effect at rates lower than 5.0 kg/ha.

LABORATORY TRIALS

As manometric experiments showed, HOE 2991 is a potent inhibitor of the Hill reaction in green algae. The compound inhibits the photosynthesis of Chlorella vulgaris at the 50% inhibition level at a molar concentration of 1.4×10^{-5} .

Measurements of photosynthesis using infrared absorption methods and intact cotton plants indicated that after application to leaf and root (hydroculture) HOE 2991 has no adverse effect on photosynthesis of cotton at the earlier mentioned doses.

Experiments in growth chambers have demonstrated that the

biological activity of this new urea compound is increased by increasing temperature and light intensity.

FIELD TRIALS

In a preliminary logarithmic spray trial near Frankfurt (Germany) the herbicidal activity of HOE 2991 (50% wp) was compared with that of other urea derivatives, especially that of linuron. The preemergence results with HOE 2991 showed some advantages compared with linuron against Polygonum sp. (rates for kill of Polygonum sp.: 0.5 kg/ha a.i. HOE 2991, 0.8-1.0 kg/ha a.i. linuron). At a rate of 1 kg/ha a.i. nearly all annual weeds were controlled, whereas 2 kg/ha were tolerated by potatoes. In a number of other trials 3 to 5 kg/ha were sufficient to control some established perennial weeds for about one season, especially Agropyron repens and Agrostis alba.

In a series of preliminary preemergence trials which have been conducted abroad (Colombia and South Africa), a number of different crops especially cotton and maize were included. A summary of the effectiveness on weeds is given in table 4.

Table 4

Weed susceptibility at 1.5 to 2.0 kg/ha a.i. HOE 2991
Assessed on the proposed EWRC scale

a) Susceptible
1 - 3

Digitaria horizontalis
Eleusine indica
Leptochloa filiformis
Panicum laevifolium
Panicum maximum

Amaranthus deflexus
Portulaca oleracea
Scoparia dulcis
Spilanthes sp.

b) Moderately susceptible
4 - 6

Echinochloa colonum
Eleusine africana

Ipomoea congesta

c) Resistant
7 - 9

Cyperus esculentus

Cyperus rotundus

In these trials 2 to 3 kg/ha a.i. HOE 2991 were well tolerated by cotton and to some extent by maize.

In other experiments in Colombia it was found that HOE 2991 was tolerated by sugarcane up to 4 kg/ha pre- and up to 3 kg/ha post-emergent.

These results gave rise to a more intensive examination of the new compound especially on cotton in the U.S.A.

Acknowledgements

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Drs. Hörlein and Schönowsky on synthesis of the active material and supply of physico-chemical data and the work of Dr. Gutjahr on trials in Colombia is gratefully acknowledged, together with field data from co-workers in Germany and South Africa.

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HOE-2991 (3-tetrafluoroethoxyphenyl-N,N-dimethyl urea)
A NEW FLEXIBLE BROAD SPECTRUM HERBICIDE FOR COTTON

R. J. Marrese

American Hoechst Corporation, Somerville, New Jersey, U.S.A.

Summary HOE-2991 (3-tetrafluoroethoxyphenyl-N,N-dimethyl urea) is a new member of the fluorophenyl substituted ureas being developed by Farbwerke Hoechst.

HOE-2991 is a broad spectrum herbicide, effective against a wide range of annual grassy and broadleaf weeds. HOE-2991 can be applied postemergence and pre-emergence with or without soil incorporation. The same application rates are used for soil surface and soil incorporated treatments, since soil incorporation of HOE-2991 does not greatly alter its activity.

Pre-emergence rates of HOE-2991 range between 1.0-2.0 lb /ac a.i., depending upon soil type. The lower rate is employed on sandy loams and the higher rate on clays and clay loams. Effective postemergent control is obtained with 0.5-1.0 lb /ac a.i. employing 0.5% v/v of a suitable adjuvant.

HOE-2991 has been tested under a wide range of soil and climatic conditions of the U.S. Cotton Belt. The significant characteristic of HOE-2991 is its selectivity toward cotton and its consistency of weed control.

INTRODUCTION

In the Cotton Belt of the United States, the three commonly recommended substituted urea herbicides are diuron, fluometuron and norea. These materials are used primarily in a program approach. This involves concurrent use with a dinitroaniline herbicide such as trifluralin or nitralin, or pre-emergence and postemergence use of the particular urea herbicide. Postemergence use usually includes combinations with the arsenical MSMA.

The strengths of the dinitroaniline herbicides rest on their inherent activity against grassy weed species. Incorporation of these compounds also minimizes the danger of lessened weed control due to dry conditions following application. The urea herbicides, on the other hand, are effective against a wider range of broadleaf weed species. All these ureas may also be used as early and late postemergent treatments.

In general, the substituted ureas show specific and narrow crop selectivity. Crop tolerance is often not as wide as with some other classes of herbicides. Selectivity is rather a factor of overall biological activity, dosage rate, water solubility, soil type and moisture following application.

HOE-2991 would rank as one of the more biologically active of the ureas used in cotton. The water solubility of HOE-2991 is 225 ppm. This is approximately 1½-fold that of norea, 2½-fold that of fluometuron and 6-fold that of diuron.

The field evaluation program with HOE-2991 was initiated with the aim of proving whether or not it would become a useful tool in the battle to control weeds in cotton.

METHODS AND MATERIALS

Field studies were conducted on a program basis during the 1971 and 1972 growing seasons in eleven of the fourteen cotton growing states. These tests were primarily conducted with Experiment Station cooperators on a small plot basis.

Plot size consisted of two to four rows, twenty-five to fifty feet in length. Each experiment treatment was replicated three to four times. Plot design usually consisted of randomized complete blocks. Application equipment ranged from back-pack sprayers to small tractor-drawn spray units. Nozzles were usually of the Tee Jet 8002-8006 series. Applications were usually made with about 30 lb/in² pressure using 15-30 gal of spray per acre. Surfactants WK and X-77 were most often used with the postemergence sprays of HOE-2991 (on a 0.5% v/v basis).

Observations were made on crop stand, phytotoxicity, degree and nature of weed control, and in many cases, on cotton yields. Observations were usually made on weed control at two to three different periods following application. Cotton yields were sometimes divided into first and second pickings to study effects on date of maturity.

RESULTS

The 1971 growing season in much of the humid cotton south was characterized by excessive moisture following planting and herbicide applications. HOE-2991 exhibited only slight cotton phytotoxicity, mainly on very light sandy soils. This was only temporary in nature and no chlorosis could be found beyond the first 2-3 true leaf stages of cotton growth. The 1971 season also showed HOE-2991 to have longer weed control activity than would be expected due to its relatively high water solubility (Table 1). These weed control differences often carried through and were shown in yield differences (Table 2). No apparent differences in date of maturity were evident (Table 2).

Table 1. The preliminary evaluation of pre-emergence herbicides for use in cotton production, Rocky Mount, North Carolina, 1971.

Treatment and rate lb/ac a.i.	Percent cotton injury			Percent broadleaf control			Percent grass control		
	6/1 ¹	6/29 ¹	7/27 ¹	6/1	6/29	7/27	6/1	6/29	7/27
	HOE-2991 2.0	37	0	0	98	100	85	99	96
Fluometuron 2.0	23	0	0	98	100	28	98	80	27
L.S.D. .05	32	10	16	15	24	28	7	15	23
L.S.D. .01	43	14	22	19	31	38	10	21	31

1. Ratings 35, 64 and 92 days after planting.

Table 2. Cotton: Effect of pre-emergence treatments on cotton stand, seedling weight, hoe time and yield, Portageville, Missouri, 1971.

Treatment and rate lb /ac a.i.	Cotton stand per 4 meters	Cotton seedling weight g/20 plants	Hoe time sec/ plot	Cotton yield (lb /ac)		
				Total	1st pick	2nd pick
HOE-2991 1.5	193	396	82	10,545	6,914	3,631
Fluometuron 1.0	223	366	548	9,833	7,976	1,857
Trifluralin 0.5	217	415	736	8,987	7,064	1,923
Fluometuron + Trifluralin 1.0 0.5	207	260	775	9,088	6,700	2,388
L.S.D. (minimum)	12.94	146.8	454.4	616.1	494.0	294.1
L.S.D. (maximum)	15.82	179.4	555.3	753.0	603.8	359.4

HOE-2991 exhibits a broader range of activity than the commercially available herbicides for cotton. This is expressed more in degree and consistency of control, as well as spectrum of activity. The grasses, the broadleaf genera, *Abutilon*, *Cassia*, *Ipomea* and *Xanthium* all seem better controlled with HOE-2991. In situations where the easier to control weeds predominate, then efficacy of the urea herbicides is very similar (Table 3).

Table 3. Cotton: Secondary field evaluation of pre-emergence herbicides on Memphis silt loam, Marianna, Arkansas, 1971.

Materials and rate in lb /ac a.i.	Cotton stand ¹	Cotton injury after 5 weeks	Weed control after 5 weeks ²			Hoeing time h/ac	Seed cotton yield lb /ac
			Pigweed	other broad- leaf	Grass		
HOE-2991 1.5	52a	19b	99a	99a	97a	2a	2,698a
Fluometuron 1.5	52a	12b	99a	98a	96a	3a	2,698a
Norea 2.25	52a	6a	98a	78b	90a	11b	2,698a
Check -	29b	0a	0d	0d	0d	35c	710c

1. Average number of plants per 50 feet of row; for cotton stand, injury and yield:
a = no chemical injury, b = slight to moderate injury, c = moderate to severe chemical injury, d = severe injury to complete kill.
2. Rating percent. Average of three replications:
0 = no effect, 100 = complete plant kill

Preplant soil incorporated treatments of HOE-2991 have been used successfully in the furrow irrigated areas of west Texas, California and Oklahoma. HOE-2991 is sufficiently active that the dilution effect of incorporation is more than offset by the placement of the chemical near the susceptible germinating weed species so that root absorption may take place under these dryland conditions where irrigation water movement is upward.

Postemergence field use of HOE-2991 during 1971 showed this compound to be less dependent upon the combination with other herbicides such as MSMA, as seems to be necessary with most urea herbicides (Table 4). However, the presence of Johnsongrass from rhizomes and nutsedge would necessitate the use of MSMA in combination with HOE-2991.

Table 4. Cotton: Primary evaluation of postemergence herbicides, Fayetteville, Arkansas, 1971.

Treatments and rate lb a.i./ac ¹	Cotton stand ²	Cotton injury after 8 weeks	Weed control ³		Hoeing time h/ac	Cotton seed yield lb /ac
			Cocklebur (Xanthium)	Other broad- leaf		
HOE-2991 1.0	70b	3a	88a	95a	2a	1,517a
Fluometuron 1.0	96a	5a	70b	87b	7b	1,315b
Herbicidal Oil ⁴ 7 gal /ac	58b	7a	21d	85b	16c	268d
HOE-2991 0.5						
+ MSMA 1.5	98a	4a	85b	91a	3a	1,628a
Fluometuron 1.0						
+ MSMA 1.6	94a	1a	97a	95a	0a	1,955a

- Treatments applied at 3 inch stage of cotton growth; repeated at 6-8 inch stage. Treatments applied directed with a wetting agent.
- Number of cotton plants per 20 feet of row. For cotton injury ratings, stand and yield:
a = no chemical injury, b = slight to moderate injury, c = moderate to severe injury, d = severe injury to complete kill.
- Rating percent 0-100, where 0 = no effect, 100 = complete plant kill.
For weed control and hoe time:
a = good to complete control, b = moderate to good control, c = poor to moderate control, d = no to poor control.
- Herbicidal oil applied three times.

The 1972 season was generally drier following planting and herbicide application. In 1971, both grasses and broadleaf weeds were well controlled with pre-emergence soil surface applications of HOE-2991. However, in 1972 more escapes by *Digitaria* and *Echinochloa* were evident. In order to insure against this situation, many U. S. growers use a dinitroaniline preplant incorporated in conjunction with a banded pre-emergence application of ureas. During 1972, the consistency of good control was again exhibited by HOE-2991. The postemergence treatments of HOE-2991 were especially good in comparison to some of the weaker urea herbicides. Post-emergence field applications were generally made when the cotton was 3-6 in. tall and when the weeds were in the 2-4 leaf stage of growth. Postemergence sprays were directed rather than over-the-top. Table 5 lists the weed species, observed to date, which are controlled by HOE-2991.

Table 5. Weed species effectively controlled by pre- and postemergence applications of HOE-2991

Broadleaf Weeds

Abutilon theophrasti
Acalypha ostraefolia
Amaranthus dubius
Amaranthus palmerii
Amaranthus retroflexus
Amaranthus spinosus
Ambrosia artemisiifolia
Brassica kaber
Cassia tora
Chenopodium album
Chenopodium murale
Cuphea carthagenensis
Emilia sonchifolia
Euphorbia maculata
Euphorbia supina
Ipomea hederacea
Ipomea purpurea
Kochia scoparia
Mollugo verticillata
Physalis wrightii
Polygonum aviculare
Polygonum convolvulus
Polygonum persicaria
Portulaca oleracea
Richardia brasiliensis
Salsola kali
Salsola pestifer
Sesbania exaltata
Sida spinosa
Solanum nigrum
Stellaria media
Xanthium pennsylvanicum

Grass Weeds

Brachiaria platyphylla
Dactyloctenium aegyptium
Digitaria ischaemum
Digitaria sanguinalis
Echinochloa colonum
Echinochloa crusgalli
Eleusine indica
Eragrostis ciliaris
Leptochloa filiformis
Lolium multiflorum
Panicum capillare
Panicum texanum
Poa annua
Setaria glauca
Setaria viridis
Sorghum halepense (seed)

DISCUSSION

The structure of HOE-2991 differs from that of fluometuron in that it contains a tetrafluoroethoxy moiety in the meta position of the phenyl ring instead of the trifluoromethyl group. This increases its water solubility to 225 ppm, equivalent to that of monuron, which is too phytotoxic to be used on most cotton soils. Thus, it is apparent that the fluorine atoms may impart greater cotton selectivity than the chlorine atoms.

During years with excessive moisture, one might expect that HOE-2991 would be leached more rapidly from the soil. Results to date indicate that this does not happen. Other factors, such as chemical degradation and soil absorption may counteract the characteristic of greater water solubility compared to other ureas.

The pre-emergence soil surface use HOE-2991 has been more extensively evaluated than either the preplant soil incorporated or postemergence uses. However, both these latter uses look most encouraging. The greater activity of HOE-2991 when used postemergence in comparison to fluometuron cannot be explained at this time, but it does seem clear cut. Application method and timing of postemergence sprays need further investigation.

The flexibility and consistency of HOE-2991 make it a worthwhile addition to the cotton growers' efforts to control weeds and thus, more efficiently produce cotton.

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NEW SUBSTITUTED URACILS USED
AS SELECTIVE HERBICIDES

D. Bertin

Centre de Recherches Roussel-Uclaf, 93 Romainville, France

P. Carles, J. Lhoste, B. Raffray, G. Ratle, L. Roã

Département de Biologie Appliquée Procida, 5 rue Bellini, 92806 Puteaux, France

Summary The paper describes two compounds :

- 3-(2-tetrahydropyranyl) 5,6-trimethylene uracil (= RU.12068)
- 5-chloro 3-(2-tetrahydropyranyl) 6-methyl uracil (= RU.12709)

Both chemicals have a broad spectrum of herbicidal activity and are well tolerated by the following crops : wheat, cotton, sugar-cane, orchard-trees, pine-apple.

INTRODUCTION

Bucha *et al* (1962) found that molecules with a uracil nucleus had a useful herbicidal activity and herbicides in this group include :

- 3-cyclo hexyl 5,6-trimethylene uracil (= lenacil)
- 3-t butyl 5-chloro 6-methyl uracil (= terbacil)
- 5-bromo 3-isopropyl 6-methyl uracil (= isocil)
- 5-bromo 3-sec butyl 6-methyl uracil (= bromacil)

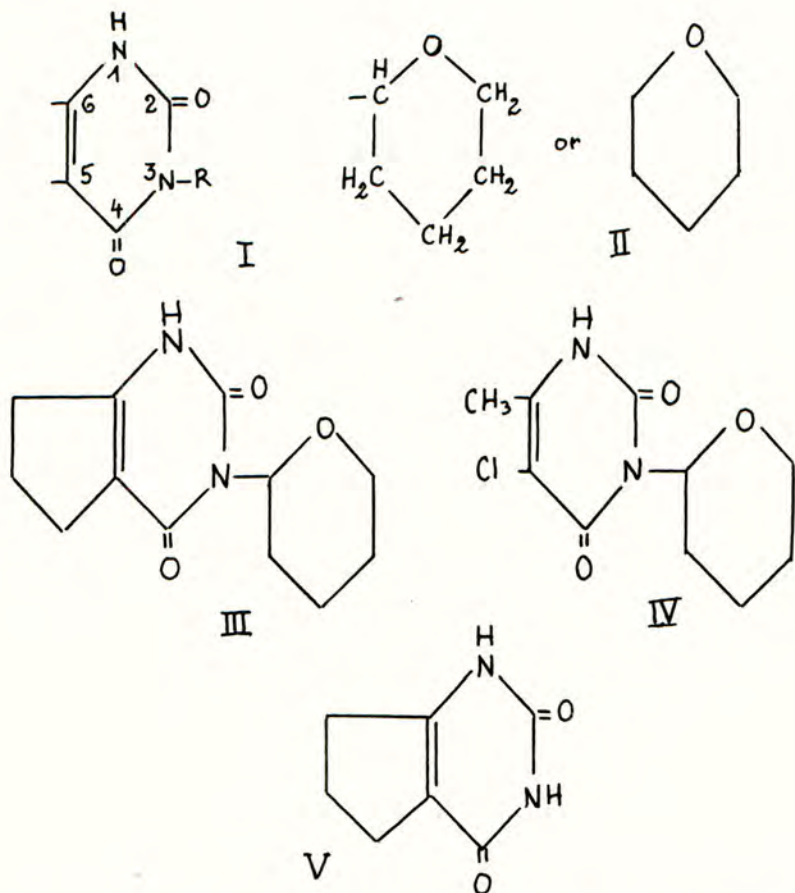
All these compounds show only a limited selectivity to specific crops : lenacil is used in strawberries and especially in sugar-beet (Durgeat and Lhoste, 1966; Durgeat *et al*, 1967); terbacil in potatoes, sugar-cane, orchard-trees; bromacil in orchard-trees (Van Staaldune, 1968), ...

Our objective was to increase the selectivity of such compounds in order to extend the technical performance of uracils. The description of the new synthesized compounds and the first results which were obtained are presented here.

CHARACTERISTICS OF THE NEW URACILS

The uracils inhibit photosynthesis (Hilton *et al*, 1964; Moreland, 1967) and this activity is associated with the presence of the heterocycle pyrimidine structure and seems to depend greatly on the type of substituents fixed on the nitrogen atom, position 3 (Fig.1 I).

Fig. 1



After numerous substitutions affecting position 3, the tetrahydropyran nucleus (Fig. 1 II) was chosen. The first of the compounds studied was 3-(2-tetrahydropyranyl) 5,6-trimethylene uracil (= RU.12068) and its structural formula is given in Fig. 1 III. This chemical can be considered as belonging to the lenacil family. The second compound, 5-chloro 3-(2-tetrahydropyranyl) 6-methyluracil (= RU.12709) (Fig. 1 IV), has structural similarities to *terbacil*.

The main characteristics of these two compounds are given in table 1.

Table 1

Physical and chemical properties of the uracils RU.12068 and RU.12709

Characteristics	RU.12068	RU.12709
Empirical formula	C ₁₂ H ₁₆ N ₂ O ₃	C ₁₀ H ₁₃ Cl N ₂ O ₃
Molecular weight	236.14	244.68
Physical nature	white solid	white solid
Melting point	269°C	225°C
Solubility at 25°C		
water	900 ppm	1100 ppm
cyclohexanone	0.75 ppm	2.4 ppm
ethanol	0.70 ppm	0.77 ppm
LD.50 on rat (oral)	7.3 g/kg	4 g/kg
Formulation	W.P. 25%	W.P. 25%

MODE OF ACTION

A number of trials were designed in order to determine the action of the tetrahydropyrene nucleus in the molecules RU.12068 and RU.12709. As an example, results obtained with RU.12068 are reported as follows.

Concentrations of 500 to 2000 ppm have been injected into the veins of tomato leaves or used for root dipping during 48 hours before replanting and the treated tomato plants were kept in a phytotron (1). Observations were made 7, 15 and 30 days after treatment and are summarized in table 2.

Table 2

Responses of tomatoes treated with concentrations at 1000 ppm

Chemical	After 7 days		After 15 days		After 30 days	
	on foliage	on root	on foliage	on root	on foliage	on root
RU.12068	++ (1)	+++	+++	++++	+++	++++
Lenacil	+	+	++	++++	+++	++++
Check	0	0	0	0	0	0

(1) + = very low phytotoxicity +++ = high phytotoxicity 0 = no effect
 ++ = low phytotoxicity ++++ = severe phytotoxicity

(1) Temperature : day = 24°C night = 17°C Humidity : 70 to 80% rh
 Photoperiod : 13 hours at 12 klx

Table 2 shows that :

- a) phytotoxicity occurred more rapidly with RU.12068 than with lenacil following both types of application;
- b) seven days after application of RU.12068 phytotoxic effects occurred more quickly following application to the roots than to the foliage;
- c) fifteen days after application of both products, phytotoxicity was greatest with root treatment.

The quicker action of RU.12068 compared to that of lenacil is probably due to the fact that the tetrahydropyran nucleus considerably increases the solubility of the molecule in water (6 ppm for lenacil compared with 200 ppm for RU.12068).

Furthermore, when the tetrahydro-pyranil group is included within the molecule, the partition coefficient between two solvents having different polarities (e.g. 1-octanol and water) is considerably lower than that for the unsubstituted molecule. Thus tetrahydro-pyranil-substituted compounds tend to favour solvents or phases of solvent mixtures with high polarities. This may help the compound to penetrate the plant more easily and so reach its site of action more rapidly.

The selectivity associated with RU.12068 may be due in part to the ability of tolerant plants to degrade it and when tomato plants are treated with this herbicide a metabolite of low phytotoxicity, 5, 6 trimethylene uracil (Fig. V) can be detected.

PROSPECTS OF APPLICATION

The possibility of using a selective herbicide depends on the resistance of the crops and on the susceptibility of weeds to the product. In table 3 are given the doses tolerated in field trials without phytotoxic effect in concordance with the mode of application concerning RU.12709; in table 4 are given the same data concerning RU.12068.

Table 5 and table 6 show, for both herbicides, the doses to be used in field plots for controlling a certain number of weeds at the young stage (2-4 leaves). The comparison between table 3 and table 5 and between table 4 and table 6 allows to foresee possible applications. In fact, some promising results have already been obtained on cereals, sugar-cane, pine-apple, asparagus, potatoes, fruit-trees, cotton...

CONCLUSION

The new uracils described, characterised by the presence of a tetrahydropyran nucleus, have special herbicidal properties which allow to consider the possibilities of selective weed control in many crops.

Table 3

Doses of RU.12709 in kg/ha tolerated by some crops

Doses kg/ha a.i.	Treatments	
	Pre-emergence	Post-emergence
0.3		Spring barley
0.5	Spring barley	Winter wheat Spring wheat
0.8	Spring oat Spring wheat Sorghum	Winter oat Lucern
1		Sugar-cane Cotton
2	Pineapple Asparagus Sugar-cane Orchards Vine	

Table 4

Doses of RU.12068 in kg/ha tolerated by some crops

Doses kg/ha a.i.	Treatments	
	Pre-emergence	Post-emergence
0.5	Oat Wheat Winter rape Maize Barley Sorghum	Oat Wheat Maize Sorghum
1	Ground nut Potatoes	Cotton
2	Pineapple Asparagus Sugar-cane Orchards Vine	

Table 5

Dosages of RU.12709 in kg/ha a.i. to be used
for the control of the most common weeds

Doses in kg/ha a.i.	RU.12709 : Spectrum of activity	
	Pre-emergence	Post-emergence
0.25	<i>Alopecurus agrestis</i> , <i>Digitaria sanguinalis</i> , <i>Galium aparine</i> , <i>Solanum nigrum</i> , <i>Stellaria media</i>	<i>Poa annua</i> , <i>Alopecurus agrestis</i> , <i>Agrostis spica-venti</i> , <i>Amaranthus retroflexus</i> , <i>Anagallis arvensis</i> , <i>Erodium sp.</i> , <i>Myosurus minimus</i> , <i>Polygonum convolvulus</i> , <i>Polygonum persicaria</i> , <i>Geranium sp.</i>
0.50	<i>Agrostis spica-venti</i> , <i>Chrysanthemum sp.</i> , <i>Sinapis arvensis</i> , <i>Raphanus raphanistrum</i> , <i>Rumex sp.</i> , <i>Atriplex sp.</i> , <i>Linaria sp.</i> , <i>Lolium perenne</i> , <i>Setaria glauca</i> , <i>Amaranthus retroflexus</i> , <i>Anagallis arvensis</i> , <i>Polygonum convolvulus</i> , <i>Veronica sp.</i> , <i>Matricaria sp.</i> , <i>Chenopodium sp.</i>	<i>Setaria glauca</i> , <i>Digitaria sanguinalis</i> , <i>Atriplex sp.</i> , <i>Chenopodium sp.</i> , <i>Galium aparine</i> , <i>Linaria sp.</i> , <i>Mercurialis annua</i> , <i>Polygonum aviculare</i> , <i>Sinapis arvensis</i> , <i>Solanum nigrum</i> , <i>Stellaria media</i> , <i>Viola tricolor</i> , <i>Diplotaxis erucoides</i> , <i>Capsella bursa-pastoris</i> , <i>Matricaria sp.</i> , <i>Alchemilla arvensis</i>
1	<i>Avena fatua</i> , <i>Diplotaxis erucoides</i> , <i>Portulaca sp.</i> , <i>Capsella bursa-pastoris</i> , <i>Erodium sp.</i> , <i>Mercurialis annua</i> , <i>Polygonum persicaria</i> , <i>Geranium sp.</i> , <i>Papaver sp.</i> , <i>Polygonum aviculare</i>	<i>Veronica sp.</i> , <i>Mariscus umbellatus</i> , <i>Eleusine indica</i> , <i>Paspalum scrobiculatus</i> , <i>Rottboellia exaltata</i> , <i>Hibiscus asper</i> , <i>Aspilia helianthoides</i> , <i>Ageratum conyzoides</i>
2	<i>Viola tricolor</i> , <i>Lepidium draba</i>	<i>Lolium perenne</i> , <i>Lepidium draba</i>
4	All weeds, excepted some perennial weeds such as <i>Cynodon dactylon</i> , <i>Convolvulus arvensis</i>	All weeds, excepted some perennial weeds such as <i>Cynodon dactylon</i> , <i>Convolvulus arvensis</i>

Table 6

Dosages of RU.12068 in kg/ha a.i. to be used
for the control of the most common weeds

Doses in kg/ha a.i.	RU.12068 : Spectrum of activity	
	Pre-emergence	Post-emergence
0.25-0.50	<i>Raphanus raphanistrum</i> , <i>Polygonum lapathifolium</i> , <i>Rumex</i> sp., <i>Spergula arvensis</i> , <i>Setaria glauca</i> , <i>Digitaria sanguinalis</i> , <i>Solanum nigrum</i>	<i>Agrostis tenuis</i> , <i>Sinapis alba</i> , <i>Trifolium</i> sp., <i>Poa trivialis</i> , <i>Solanum nigrum</i> , <i>Myosurus minimus</i>
1	<i>Alopecurus agrestis</i> , <i>Poa annua</i> , <i>Sinapis arvensis</i> , <i>Lolium perenne</i> , <i>Avena fatua</i> , <i>Echinochloa</i> sp., <i>Agrostis spica-venti</i> , <i>Amaranthus retroflexus</i> , <i>Anagallis arvensis</i> , <i>Atriplex</i> sp., <i>Chenopodium</i> sp., <i>Mercurialis annua</i> , <i>Papaver</i> sp., <i>Stellaria media</i>	<i>Alopecurus agrestis</i> , <i>Agrostis spica-venti</i> , <i>Digitaria sanguinalis</i> , <i>Poa annua</i> , <i>Alchemilla arvensis</i> , <i>Amaranthus retroflexus</i> , <i>Atriplex</i> sp., <i>Chenopodium</i> sp., <i>Capsella bursa-pastoris</i> , <i>Martica-ria</i> sp., <i>Mercurialis annua</i> , <i>Papaver</i> sp., <i>Polygonum aviculare</i> , <i>Polygonum convolvulus</i> , <i>Sinapis arvensis</i> , <i>Stellaria media</i>
2	<i>Lepidium draba</i> , <i>Eleusine indica</i> , <i>Alchemilla arvensis</i> , <i>Capsella bursa-pastoris</i> , <i>Polygonum convolvulus</i> , <i>P. persicaria</i> , <i>Viola tricolor</i> , <i>Diplo-taris portulaca</i> , <i>Erodium</i> sp., <i>Geranium</i> sp., <i>Fumaria officinalis</i> , <i>Galium</i> sp., <i>Lycopsis</i> sp., <i>Plantago</i> sp., <i>Polygonum aviculare</i> , <i>Veronica</i> sp.	<i>Lolium perenne</i> , <i>Avena fatua</i> , <i>Anagallis arvensis</i> , <i>Erodium</i> sp., <i>Geranium</i> sp., <i>Polygonum persicaria</i> , <i>Linaria</i> sp., <i>Viola tricolor</i> , <i>Lepidium draba</i>
3		<i>Cyperus sphacellatus</i> , <i>Mariscus umbellatus</i> , <i>Eleusine indica</i> , <i>Paspalum scrobiculatum</i> , <i>Rottboellia exaltata</i> , <i>Hibiscus asper</i> , <i>Aspilia helianthoides</i> , <i>Ageratum conyzoides</i>
4	<i>Sorghum halepense</i> , <i>Cirsium arvense</i> , <i>Oxalis</i> sp.	<i>Veronica</i> sp., <i>Oxalis</i> sp., <i>Cirsium arvense</i>

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2-(3,4,5-tribromopyrazol-1-yl)-NN-dimethylpropionamide

A NEW PRE-EMERGENT SELECTIVE HERBICIDE

G. E. Musgrove

Tuco Chemical Company, Division of Upjohn Limited
Fleming Way, Crawley, Sussex

H. J. Vostral

Herbicides and Growth Regulators, The Upjohn Company
Kalamazoo, Michigan 49001

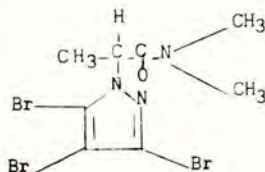
Summary U-27,267, 2-(3,4,5-tribromopyrazol-1-yl)-NN-dimethylpropionamide, is a promising herbicide. Its physical and chemical characteristics, toxicological and herbicidal properties are reported. U-27,267 shows low phytotoxicity to sugar beet, potato and other crops. The preliminary data available indicate it is a root absorbed herbicide and may be used in sugar beet, potato, transplanted rice and other crops. A summary of initial field trials carried out in 1971, is reported together with an indication of initial results from U.K. sugar beet studies.

INTRODUCTION

2-(3,4,5-tribromopyrazol-1-yl)-NN-dimethylpropionamide, coded U-27,267, was synthesised by Kornis in the laboratories of the Upjohn Company, Kalamazoo and previously reported by Chambers et al (1972). Initial screening indicated that product safety together with its broad spectrum weed control amply justified its further investigation. It is a pre-emergent herbicide for overall spraying or soil incorporation. Soil incorporation enhances effectiveness. U-27,267 is available as technical material (99.90% purity), and as a 75% wettable powder or as granules.

CHEMISTRY

The structural formula is:



2-(3,4,5-tribromopyrazol-1-yl)-NN-dimethylpropionamide.

Empirical Formula: $C_8H_{10}Br_3N_3O$

Molecular weight: 403.93

PHYSICAL PROPERTIES

U-27,267 is a white crystalline solid that is soluble in a variety of solvents (Table 1).

Table 1

<u>Solvent</u>	<u>mg/ml at 24°C</u>
Chloroform	880.0
Methylene Chloride	799.7
Acetone	203.0
Acetonitrile	187.6
Methyl Ethyl Ketone	185.0
Benzene	132.0
Methyl Alcohol, anhydrous	100.7
Ethyl Acetate	74.1
Toluene	60.0
Ethyl Alcohol, 95%	55.0
Hexane	0.8
Water, distilled	0.2

Under conditions of normal use U-27,267 is stable in solid state or solution. Hydrolysis occurs under alkaline conditions. This compound was stable for 2 years at temperatures of 4° and 37°C. Vapour pressure is 0.03 mm and volatility presents no problem in herbicidal use. Incorporation after application is not necessary to prevent photodecomposition. Compatibility with other herbicides and fungicides has not yet been fully established. In-tank mixes have, however, been explored and U-27,267 75% wettable powder appears compatible with the following formulated herbicides. Atrazine, benefin, bensulide, bromoxynil, chloroamben, chloroprotham, cycloate, 2,4-D, dicamba, dinoseb, diphenamid, diuron, linuron, MCPA, mecoprop, nitralin, nitrofen, pebulate, propachlor, propanil, trifluralin and vernolate.

TOXICOLOGY

A detailed programme investigating the toxicology of U-27,267 is in progress. Preliminary data indicate low toxicity:

The combined acute oral LD 50 of the technical material in rats is 3816 mg/kg (male 4472 mg/kg, females 3256 mg/kg) and for the 75% wettable powder is 4085 mg/kg (male 5125 mg/kg, females 3256 mg/kg).

14 day oral tolerance studies in the rat suggest 300 mg/kg to be the maximum no-effect level. The 90 day oral toxicity no-effect level in rats is 30 mg/kg day and in dogs 100 mg/kg day.

No teratological effects have been noted in rats fed at 6-16 days of gestation at levels of 1000 mg/kg/day.

Dermal toxicity in rabbits is negligible (> 20 g) and it is not considered to be a primary eye irritant. No evidence of systemic toxicity when applied to the skin of rabbits has been demonstrated and U-27,267 has not been shown to be a primary skin irritant.

BIOLOGICAL ACTIVITY

Early tests with U-27,267 indicated selectivity in the following crops (table 2)

Table 2

	Crop	Dose tolerated kg a.i./ha
Tolerant) Sugar Beet	3.36
) Potato	6.72
) Rice transplanted	2.24
) Sugar Cane	6.72
) Ground Nut	6.72
) Tomato	4.48
) Grape	5.60 - 11.20
) Strawberry	4.48
) Tobacco	3.36
) Pepper	4.48
Marginally Tolerant) Barley	< 1.12
) Cotton	1.68
) Pea	1.68
) Bean	1.68

Weed control was demonstrated over a wide range of grass and broadleaved species of weeds. (Tables 3 - 5)*

Table 3

Weeds susceptible to less than 1.12 kg a.i./ha:

Alopecurus myosuroides	Mollugo verticillata L.
Ambrosia artemisiifolia L.	Panicum capillare L.
Digitaria sanguinalis (L.)	Panicum dichotomiflorum Michx.
Eragrostis ciliaris (All.)	Paspalum boscianum Fluegge
Lolium temulentum L.	Poa annual L.
Sporobolus cryptandrus (Torr.)	

Table 4

Weeds susceptible to 1.12-2.52 kg a.i./ha:

Abutilon theophrastic Medic.	Lithospermum officinale L.
Achillea millefolium L.	Lolium multiflorum L.
Amaranthus retroflexus L.	Lychnis alba Mill.
Amaranthus spinosus L.	Oenothera biennis L.
Arthemis cotula L.	Panicum texanum Buck l.
Avena fatua L.	Paspalum dilatatum Poir

Table 4 - continued

Barbarea vulgaris R. Br.	Plantago lanceolata L.
Brassica campestris L.	Polygonum aviculare L.
Brassica niger (L.) Kach	Polygonum lapathifolium L.
Bromus tectorum L.	Portulaca oleracea L.
Capsella bursa-pastoris (L.)	Ranunculus sp. L.
Cenchrus echinatus L.	Richardia scabra L.
Cerastium vulgatum L.	Rumex acetosella L.
Chenopodium murale L.	Rumex crispus
Crotalaria mucronata Desv.	Salsola pestifer A. Nels
Croton capitatus Michx.	Scirpus californicus
Cyperus sp.	Sesbania exaltata (Raf.) Cory
Daubentonia texana Pierce	Setaria faberi Herrm.
Desmodium tortuosum (Sw.) D.C.	Setaria glauca (L.) Beauv
Echinochloa crusgalli (L.)	Setaria italica (L.)
Eleusine indica (L.) Gaertn.	Setaria viridis (L.)
Emilia sonchifolia (L.) D.C.	Sida carpinifolia
Heterotheca subaxillaris (Lam)	Sida spinosa L.
Kochia scoparia (L.) Schrad	Sorghum halepense (L.) Pers.
Lamium amplexicaule L.	Stellaria media (L.)
Lepidium campestre (L.) R. Br.	Striga lutea Lour.
Leptochloa filiformis (Lam.)	Urtica dioica L.
Xanthium pennsylvanicum Wallr.	

Table 5

Weeds susceptible to 2.25-6.72 kg a.i./ha:

Agropyron repens L. Beauv.	Oxalis stricta L.
Amaranthus blitoides	Polygonum coccineum Muhl.
Brachiaria ciliatissima	Polygonum convolvulus L.
Centaurea repens L.	Polygonum pennsylvanicum L.
Centaurea solstitialis L.	Polygonum persicaria L.
Chenopodium album L.	Potentilla canadensis L.
Chrysanthemum leucanthemum L.	Sagittaria calycina Engelm.
Cirsium arvense (L.) Scop.	Senecio vulgaris L.
Cynodon dactylon (L.) Pers.	Taraxacum officinale L.
Cyperus esculentus L.	Tragopogon porrifolius L.
Lactuca scariola L.	Vernonia altissima Nutt.

*Observations from field tests recorded 30-60 days after pre-plant incorporated treatments were made.

MECHANISM OF ACTION

U-27,267 kills the weed seedlings prior to or shortly after emergence from the soil without inhibiting germination. Susceptible plants may have restricted root development at sub-lethal concentrations. Absorption is through the root system and under ground stems of grass species. Foliar absorption is minimal resulting in little herbicide activity.

SOIL BEHAVIOUR

Field and greenhouse data obtained in the United States of America indicate U-27,267 is not readily leached through soils containing high clay or high organic matter levels. Low soil mobility of this compound was suggested by the improved consistency of results from mechanical incorporation. Incorporated treatments were also more effective against plants which emerged from underground vegetative organs. However, surface treatments receiving some rainfall were highly effective against shallow germinating seeds. Season long weed control was obtained on a sandy soil with 2% organic matter which received 50 cm of rainfall within one month following treatment, although leaching was noted in sandy soils with less than 1% organic matter. Placement selectivity results from low soil mobility and is used advantageously in moderately tolerant crops.

In temperate climates, rates greater than 3.4 kg a.i./ha may result in sufficient soil residual carry over to injure sensitive crops the following year. In sub-tropical climates the residual duration appears to be less than 6 months.

Application rates depend on soil type, organic matter, desired length of residual activity, and crop to be treated. In general as shown below, lower rates are advised on light textured soil low in organic matter, and on crops with moderate tolerance; higher rates are recommended on heavier soils and tolerant crops.

Table 6

<u>Soil Type</u>	<u>Organic Matter Percentage</u>	<u>Type of Crop</u>	<u>Incorporated Application Rate - kg ai/ha</u>
Sand Loamy sand	< 1		0.75-1.5*
Sandy loam Sandy clay loam	1-2	Moderately Tolerant	1.5-2.24
Silt and clay loams with low organic matter	2-3 3-4	Moderately Tolerant	1.5-2.25 2.25-3.0
—			
Silt and clay loams with medium to high organic matter and clays	4-10	Tolerant	3.0-4.5
Peat soils and high organic matter clay soils	> 10	Tolerant	4.5-6.0

*Surface applications on light textured soil followed by rainfall are as effective as incorporated treatments.

RESIDUES

Methods developed for determining soil and crop residues are currently undergoing further refinement and will be available for testing on 1972 crops. Analysis of sugar beet samples treated in the 1971 season showed no residue.

FIELD EVALUATION

Field trials carried out in 1971 demonstrated the product to be one of considerable promise. Preliminary 1972 information from 11 field trials carried out in the United Kingdom is presented below. The time of writing precludes inclusion of data on yields. Statistical analysis will be carried out when results are complete.

SUGAR BEET

1971 Trials - United States

Good weed control was demonstrated in 7 states. Incorporation was more effective than was surface application and with exception on sand, sugar beet emergence was not reduced. Beet toxicity one month after treatment was greater when U-27,267 was incorporated as a surface application for silt loam (3.2 om). However, yield was not reduced except at rates higher than 3.36 kg a.i./ha. Yield reduction did not occur when U-27,267 was incorporated 4-8 cm deep in a loam soil and incorporation depth was less important on this soil type than on sand.

Excellent weed control potential was shown with no yield loss when rates of 1.26-2.52 kg a.i./ha were incorporated to 5-8 cm deep.

Europe

1971 At rates of 1.5 to 2.0 kg a.i./ha, in 3 countries, U-27,267 selectively controlled many weeds. Retardation of individual plants was observed for 3-4 weeks but within 4-6 weeks recovery occurred. Incorporation improved activity of low rates but weed control at 4.5 kg a.i./ha was not improved over 3.0 kg a.i./ha.

1972 In the United Kingdom, U-27,267 was included in weed control trials being carried out at Experimental Husbandry Stations, by A.D.A.S. personnel and by the British Sugar Corporation. Climatic conditions and soil type play an important role in herbicide behaviour and we felt that trials to assess behaviour under practical use should be instigated as early as possible in the development programme. Eleven farm trials were, therefore, laid down using larger scale plots suitable for use with farm machinery.

Replicates were, however, kept to a minimum. Preliminary results are shown in table 7. For various reasons no untreated control was used in trials 5, 8 and 10 and these results have not been included in table 7. Standard rates of 1.5-2.25 kg a.i./ha were used in trials 1-10 and 2.25-3.36 kg a.i./ha on trial 11 (fen soil). Some crop damage occurred following severe retardation in trials 6 and 9 where U-27,267 was incorporated and this may be due to excessive rates used on very light soils. Retardation occurred in most trials to some extent but indications are that the crop recovered. Yield assessment will, however, be necessary to establish the transient nature of the retardation. On one site, *Avena fatua* control was achieved. Estimates of control are: (table 8).

Table 7

WEEDS TO THE SQUARE FOOT
 AVERAGE OF REPLICATES
 FIRST ASSESSMENT (28-47 days from spraying)

TREATMENT	Trial No.										3 ²
	1	2	3	4	6	7	9	11	Tot.	Ave.	
Overall Lower Rate	0.25	0.25	2.0	1.0	1.1	3.5	3.3	11.9	23.30	2.91	14.74
Overall Higher Rate	0.4	0.2	3.15	0.7	0.5	2.5	4.0	8.45	19.90	2.49	7.86
Incorporated Lower Rate	0.2	0.25	0.45	0.4	0.1	2.2	2.2	6.5	12.30	1.54	4.78
Incorporated Higher Rate	0.1	0.5	0.25	1.55	0	1.98	1.6	5.9	11.88	1.49	3.77
Untreated	2.9	4.2	5.2	2.0	5.0	7.17	3.3	19.3	49.07	6.13	26.99

Difference between treatments

Table of significance

Treatments Compared:	s	t	n	Significance	
Overall Lower Rate vs untreated	4.774	2.70	14	Highly significant	P > 0.98
Overall Higher Rate vs untreated	4.339	3.36	14	Highly significant	P > 0.99
Incorporated Lower Rate vs untreated	4.221	4.35	14	Highly significant	P > 0.99
Incorporated Higher Rate vs untreated	4.160	4.46	14	Highly significant	P > 0.99
Overall Lower Rate vs Incorporated Lower Rate	3.125	1.68	14	Possibly significant	P > 0.80
Overall Higher Rate vs Incorporated Higher Rate	2.411	1.66	14	Possibly significant	P > 0.80
Overall Lower Rate vs Overall Higher Rate	3.352	0.92	14	Not significant	P \approx 0.50
Incorporated Lower Rate vs Incorporated Higher Rate	2.068	0.97	14	Not significant	P \approx 0.50

Table 8

reduction of Avena fatua plants over untreated - 28 days from planting

Kg a.i./ha		Kg a.i./ha	
2.2 overall	50%	2.2 incorporated	61%
3.3 overall	27%	3.3 incorporated	93%

Extended evaluations on weed control in sugar beet and potatoes are in progress in France, Holland, Italy, Belgium and Germany.

RICE

1971 U-27,267 was under trial in the Philippines, Japan, Taiwan, Malaysia and Ceylon. 1.0 kg a.i./ha and above proved toxic to direct seeded rice, but not transplanted rice. 0.5 kg a.i./ha was insufficient for adequate weed control. Pre-emergent application of 1.0 to 2.0 kg a.i./ha applied 4-7 days after transplanting, however, showed good control of grass and broadleaved weeds without crop injury.

1972 More extensive trials are being conducted in the above countries. In addition to weed control and crop tolerance, information on yield and residue will be collected.

POTATOES

1971 Preliminary trials were conducted in Belgium, Italy, and Holland, in addition to the United States. Potato appears to be biologically the most tolerant crop to U-27,267. Excellent crop tolerance up to 6.72 kg a.i./ha was established. In Europe, selective control of grasses and broadleaf weed species was achieved. Incorporation to a depth of 5 cm may increase broadleaf weed control. Yields compared favourably with those from Linuron used at 1.5-2.0 kg a.i./ha and Monolinuron at 1.45 kg a.i./ha.

1972 Trial work was extended and includes several trial sites in the United Kingdom.

CONCLUSION

Preliminary testing has demonstrated U-27,267 weed control potential in sugar beet, potatoes, rice, and other crops. Trials work was extended during 1972. When results are finally analysed, more precise recommendations will be made.

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References

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