

## **SESSION 6C**

# **PLANT GROWTH REGULATORS AND HERBICIDES IN WARM-TEMPERATE AND MEDITERRANEAN CROPS**

SESSION  
ORGANISER      DR T. JONES

POSTERS

6C-1 to 6C-3

## DPX-M6316 + PYRIDATE, A NEW MAIZE HERBICIDE FOR POST EMERGENCE CONTROL OF BROADLEAF WEEDS RESISTANT TO ATRAZINE

P. IOOS, J.P. DOUCHET

Du Pont de Nemours (France) S.A., Paris, France

A. BASSI, A. BENCIVELLI

Du Pont Conid S.P.A., Bolzano, Italy

## ABSTRACT

DPX-M6316 (methyl 3-(3-(4 methoxy-6-methyl-1,3,5,-triazin-2-yl)ureidosulphonyl)thiopene-2-carboxylate) + pyridate is a new combination to be used in post emergence application on maize for control of broadleaf weeds. Trials carried out in France and Northern Italy showed that the product, at the normal use rate of 8 + 600 g ai/ha, was very effective on many species including biotypes resistant to atrazine : Amaranthus sp., Chenopodium sp., Solanum sp. and Polygonum sp. It was selective to the main maize varieties cultivated in these countries.

## INTRODUCTION

Atrazine has been widely used on maize in France and Italy for more than 25 years. The problem of broadleaf weeds resistant to atrazine appeared in France in the 1970's, and the acreage concerned was estimated to be equal to 1.2 million ha in 1988. In Italy, the problem occurred later and the acreage with resistant biotypes is now about 100,000 ha. A specific treatment is needed post emergence to control these weeds. A new combination has been developed for this market : DPX-M6316 (methyl 3-(3-(4 methoxy-6-methyl-1,3,5,-triazin-2-yl)ureidosulphonyl)thiopene-2-carboxylate) + pyridate. Pyridate is a foliar herbicide from Agrolinz Co, already developed on maize alone or in mixture with other partners. DPX-M6316 is a new sulfonylurea herbicide developed by Du Pont de Nemours presently sold for use on both cereals and maize. The chemistry of this herbicide and the work done on cereals have already been reviewed (Ambach *et al.*, 1984), (Hutchinson *et al.*, 1985) and (Sionis *et al.*, 1985). This paper reports the results of the trials carried out on maize with the combination in France and Italy.

## MATERIAL AND METHODS

A randomised block design was used. In trials for weed control evaluation, each treatment was replicated twice or three times and plot size was between 25 and 30 m<sup>2</sup>. In trials for yield evaluation, the number of replicate blocks was 4 and plot size was from 50 to 75 m<sup>2</sup>.

Applications were made with a hand-held plot sprayer using an inert gas propellant. Pressure was 300 KPa and spray volume between 150 and 300 litres per ha.

French trials for weed control evaluation were set up in fields of maize treated pre emergence with 2,500 g ai/ha of atrazine. Application was made on the emerged weeds which escaped from this treatment (resistant biotypes or moderately susceptible species). Sites for yield evaluation were chosen with very low weed population.

All products were sprayed at the 4 to 8 leaf stage of maize. Weed control assessment was made by visual scoring of biomass reduction versus untreated plot on a percentage scale (0 = no effect ; 100 = complete weed kill). In all trials, a visual evaluation of percentage crop injury was made regularly after treatment (0 = no effect ; 100 = complete crop kill). In crop safety trials, each plot was harvested with a farmer combine harvester and yield was calculated on a t/ha basis.

## RESULTS AND DISCUSSION

### Crop tolerance

Visual evaluations have been made in 52 trials at the normal use rate (8 + 600 g ai/ha) and 29 trials at the double rate (16 + 1,200 g ai/ha). The post emergence application of DPX-M6316 + pyridate on maize at the 4 to 8 leaf stage showed good selectivity to the varieties presently cultivated in France and Italy. Symptoms of slight leaf yellowing and growth delay were observed on maize in a few trials between 5 and 20 days after treatment, especially at the double rate but the crop appeared to recover quite rapidly. In trials where yield was recorded, there was no adverse effect on production.

Tables 1 and 2 summarize results of visual evaluation made respectively in France and Northern Italy in 1987 and 1988. Table 3 gives the yield results obtained in France.

TABLE 1. Crop selectivity to maize with post emergence application of DPX-M6316 + pyridate in France - 1987/1988.

Treatment	Rate g ai/ha	Mean crop damage %			Number of trials
		7 DAT	15 DAT	30 DAT	
DPX-M6316 + pyridate	8 + 600	4	3	0	41
DPX-M6316 + pyridate	16 + 1,200	6.5	4	0	18
pyridate	900	0	0.5	0	41
pyridate	1,800	0.5	0	0	18

TABLE 2. Crop selectivity to maize with post emergence application of DPX M-6316 + pyridate in Northern Italy - 1987/1988.

Treatment	Rate g ai/ha	Mean crop damage %			Number of trials
		15 DAT	30 DAT	45 DAT	
DPX-M6316 + pyridate	8 + 600	4	0.5	0	11
DPX-M6316 + pyridate	16 + 1,200	11	3	1	11
atrazine + bentazone	800 + 800	1	0	0	11

TABLE 3. Effect of DPX-M6316 + pyridate on maize yield in France - 1987/1988 (Fields with very low weed populations).

Treatment	Rate g ai/ha	Average yield t/ha	
		1987	1988
DPX-M6316 + pyridate	8 + 600	10.2	11.3
DPX-M6316 + pyridate	16 + 1,200	10.1	11.0
pyridate	900	10.3	11.1
pyridate	1,800	10.1	11.1
Untreated	-	10.1	11.3
Number of trials		7	11

## WEED CONTROL

Table 4 demonstrates that DPX-M6316 + pyridate at 8 + 600 g ai/ha was very effective on the main broadleaf weed species which have developed resistance to atrazine in France : Amaranthus sp., Chenopodium sp., Polygonum sp. and Solanum nigrum. The combination also provided good control of weeds which typically show only moderate susceptibility to atrazine, in particular Polygonum aviculare, Atriplex patula, Helianthus annua (sunflower regrowth).

Table 5 summarizes the results obtained in Northern Italy in 1987/1988. DPX-M6316 + pyridate provided a good control of the major broadleaf weeds present in the maize field, in particular on biotypes of Amaranthus retroflexus resistant to atrazine.

TABLE 4. Weed control given by a post emergence application of DPX-M6316 + pyridate on maize in France - 1987/1988.

Weeds	Number of trials	% weed control	
		DPX-M6316+pyridate 8 + 600 g ai/ha	pyridate 900 g ai/ha
<u>Amaranthus retroflexus*</u>	4	99	99
<u>Atriplex patula</u>	2	87	50
<u>Chenopodium album*</u>	11	94	97
<u>Chenopodium polyspermum*</u>	1	100	100
<u>Fumaria officinalis</u>	1	30	20
<u>Galium aparine</u>	1	80	100
<u>Helianthus annua</u>	1	95	75
<u>Papaver rhoeas</u>	1	57	55
<u>Polygonum aviculare</u>	1	90	60
<u>Polygonum lapathifolium*</u>	2	94	90
<u>Polygonum persicaria*</u>	6	93	57
<u>Rumex crispus</u>	1	75	30
<u>Senecio vulgaris</u>	2	100	94
<u>Solanum nigrum*</u>	9	100	100
<u>Spergula arvensis</u>	1	99	40

\* biotypes resistant to atrazine

TABLE 5. Weed control given by a post emergence application of DPX-M6316 + pyridate on maize in Northern Italy - 1987/1988.

Weeds	Number of trials	% weed control	
		DPX-M6316+pyridate 8+600 g ai/ha	atrazine+bentazone 800+800 g ai/ha
<u>Abutilon theophrasti</u>	3	86	99
<u>Amaranthus retroflexus*</u>	5	100	93
<u>Chenopodium album</u>	6	98	98
<u>Convolvulus arvensis</u>	3	67	67
<u>Galinsoga parviflora</u>	2	96	87
<u>Mentha arvensis</u>	2	75	65
<u>Phytolacca americana</u>	1	90	100
<u>Polygonum convolvulus</u>	3	69	71
<u>Polygonum persicaria</u>	1	80	100
<u>Portulaca oleracea</u>	1	98	100
<u>Solanum nigrum</u>	6	93	96

\* biotypes resistant to atrazine

#### CONCLUSION

Trials carried out in France and Northern Italy in 1987 and 1988 showed that the combination of 8 g ai/ha DPX-M6316 + 600 g ai/ha pyridate provided good control of broadleaf weeds usually present in maize crops and in particular of biotypes now resistant to triazine. The mixture was selective to the main varieties of maize cultivated in these two countries. The product has been already commercialised in France under the tradename "BINEX M".

#### REFERENCES

- Ambach, R.M. ; Toole, B.M. ; Zadorozny, S.A. ; Johnson, K.D. ; Ulrich T.S. ; Gorell, R.M. ; Schehl, S.E. (1984) DPX-M6316, a new herbicide for use in cereals, Proceedings North Central Weed control Conference Winnipeg, Canada, Volume 39, 120-126.
- Hutchinson, J.M. ; Levitt, G. ; Hageman, L.H. ; Schehl, S.E. (1985) DPX-M6316, a new selective post emergence herbicide for cereals - Meeting of Weed Science Society of America, Seattle USA, 1985. Volume 25, 10-15.
- Sionis S.D. ; Drobny H.G. ; Lefebvre P. ; Upstone M.E. (1985) DPX-M6316, a new sulfonylurea cereal herbicide, Proceedings British Crop Protection Conference Weeds, Volume 1, 49-54.

## GROWTH PATTERN OF ECHINOCHLOA SPECIES IN RELATION TO RICE AND BIO-EFFICACY OF 2,4-D AND DICAMBA COMBINATIONS

K. KRISHNAMURTHY, R. DEVENDRA, T.V. RAMACHANDRA PRASAD, S.L. MOHAN

Co-ordinated Research Programme on Weed Control, University of Agricultural Sciences, GKVK Campus, Bangalore 560 065, India

## ABSTRACT

Experiments were conducted to investigate the comparative growth pattern of four *Echinochloa* species in relation to rice and the bio-efficacy of 2,4-D and dicamba combinations in weed control of transplanted rice. Four species of *Echinochloa* namely *E. glabrescens* Munro ex Hook. F., *E. oryzoides* (Ard.) Fritsch, *E. picta* (Koen.) Michael and *E. colona* (L.) Link. showed higher growth rate and light interception from planting than two rice cultivars with different maturities (cv. Rasi, 120 days and cv. Jaya, 140 days). In addition, *Echinochloa* species possessed a low CO<sub>2</sub> compensation point and a high stomatal resistance, which helped them to compete more effectively with rice. The best fitted growth functions for leaf area and biomass showed a polynomial distribution in *Echinochloa* species.

In transplanted rice dominated by sedge (*Scirpus* sp.) and broad leaf (*Rotala verticillaris* Linn.) weeds, unweeded controls had rice yields 35% lower than hand weeded plots. The best herbicide combinations in lowering the density of sedges and broad leaf weeds were 2,4-D amine salt 0.5 kg a.i./ha with dicamba 0.125 kg a.i./ha post-emergence or 2,4-D amine salt 0.8 kg a.i./ha alone at pre-emergence. Combinations lowered the herbicidal dosages, besides enhancing the bio-efficacy.

## INTRODUCTION

*Echinochloa* species compete for light and nutrients in rice (*Oryza sativa* L.). In Karnataka (India) under lowland and upland conditions, levels of infestation are more frequent with *E. glabrescens* and *E. oryzoides* than *E. picta* and *E. colona* (Krishnamurthy *et al.*, 1983). Infestation of *Echinochloa* species have reduced grain yield by as much as 82% due to shading and reduction of stomatal conductance (Chang, 1970; Krishnamurthy *et al.*, 1988). As *Echinochloa* is the major competitor for rice, an attempt was made to understand the physiological growth parameters associated with four species of *Echinochloa* in competition with rice.

Under the red sandy soils of the southern dry region of Karnataka, the broad leaf weed *Rotala verticillaris* Linn. is a major competitor for transplanted rice. Herbicides, like pendimethalin 2.0 kg/ha, butachlor 1.25 kg/ha and oxadiazon 0.5 kg/ha have proved to be less effective on this weed (Krishnamurthy *et al.*, 1983). In order to investigate the comparative effectiveness of dicamba and 2,4-D combinations and to mitigate the broad leaf problem, a field study was conducted in transplanted rice.

## MATERIALS AND METHODS

In experiment I, 20-25 day old seedlings of four *Echinochloa* species namely *E.oryzoides*, *E.glabrescens*, *E.picta*, *E.colona* (70, 75, 90, 95 days from germination to maturity respectively) and two rice cultivars viz., cv. Jaya (140 days) and Rasi (120 days) were planted in separate plots of 3 m x 3 m using a spacing of 20 cm x 10 cm and supplied with a common fertilizer dose of 100N-22P-42K kg/ha. The treatments were replicated four times in a randomised block design (RBD). Periodical observations on leaf area/hill and total biomass/hill were made and growth parameters like net assimilation rate and crop growth rate were computed (Hunt 1982, Table 1). Stomatal conductance, light intensity and CO<sub>2</sub> compensation point were measured using Steady State Porometer (LICOR-LI-1600), Luxmeter model 300C and Table Model IRGA (ADC) respectively (Table 2).

In experiment II, 20 combinations of 2,4-D amine salt with dicamba were compared with 2,4-D amine salt alone at pre-emergence (2 days after planting:DAP), dicamba alone at 150, 200, 250 g a.i./ha, hand weeding twice (25 and 50 DAP) and an unweeded control. In addition, dicamba 120 g a.i./ha was applied as a sand mix 20 DAP (containing 240 g dicamba free + 240 g Oleyl propylene diamine salt of dicamba/litre). All 27 treatments were replicated three times in a RBD layout. Combinations of 2,4-D and dicamba were applied one after the other as a spray using a spray volume of 500-600 l/ha. Other cultural practices were followed as in experiment I. The data on grain yield and weed biomass at harvest have been presented (Table 3).

## RESULTS AND DISCUSSION

Experiment I

*Echinochloa* species showed higher growth rate than rice in terms of leaf area, crop growth rate (Table 1) and biomass production (Fig. 1) during the initial growth stages (up to 60 DAP). The *Echinochloa* species had a logarithmic growth phase much earlier than rice. This was perhaps due to the earlier maturity of *Echinochloa* (70-95 days) compared to rice (120-140 days). Further, the best growth function fitted based on biomass at different stages (T) showed a 2nd degree polynomial in all entries. The regression equations for rice and *Echinochloa* species are:

$0.031 + 0.030 (T) + 0.003 (T^2)$	for cv. Jaya	(R <sup>2</sup> = 100%)
$0.126 + 0.036 (T) + 0.002 (T^2)$	for cv. Rasi	(R <sup>2</sup> = 100%)
$-0.133 + 0.062 (T) + 0.003 (T^2)$	for <i>E.oryzoides</i>	(R <sup>2</sup> = 98%)
$0.023 + 0.069 (T) + 0.002 (T^2)$	for <i>E.glabrescens</i>	(R <sup>2</sup> = 99%)
$-0.322 + 0.122 (T) + 0.003 (T^2)$	for <i>E.picta</i>	(R <sup>2</sup> = 99%)
$-0.704 + 0.147 (T) + 0.016 (T^2)$	for <i>E.colona</i>	(R <sup>2</sup> = 92%)

Similarly, leaf area of rice cv. Jaya and all *Echinochloa* species showed 3rd degree polynomial growth function (R<sup>2</sup> of 95 to 98%), while cv. Rasi showed 2nd degree polynomial (R<sup>2</sup> = 100%). Thus *Echinochloa* species have a similar growth pattern to that of rice, with the exception of a higher growth rate in the initial stages indicating a smothering effect on the rice plants.

Further *Echinochloa* species showed higher photosynthetic efficiency (in terms of higher net assimilation rate of 3.3 to 5.5 g/m<sup>2</sup>/day at against 2.7 to 2.8 g/m<sup>2</sup>/day in rice cultivars), higher light interception due to greater plant height and larger leaf area, lower photorespiration (low CO<sub>2</sub> compensation point) and lower stomatal conductance (Table 2). Thus *Echinochloa* produced severe competition for light and moisture with rice during the early growth period. As observed in the present study, the higher adaptability of *Echinochloa* species with high water use efficiency has been well documented (Blake *et al.*, 1984), as well as the effect on lowering stomatal conductance and photosynthetic efficiency in rice (Krishnamurthy *et al.*, (1988). This indicates the physiological superiority of *Echinochloa* species over rice cultivars. Rice cultivars matured in 120-140 days as against 70 to 95 days in *Echinochloa* species. Due to the longer crop duration, rice produced a higher biomass and seed yield than *Echinochloa* at maturity. However, *Echinochloa* species had more seeds/panicle (378 in *E.picta* to 1651 in *E.glabrescens*) than rice cultivars (128-138). Hence, *Echinochloa* species have to be controlled at an early stage to avoid seed production.

### Experiment II

Major weeds observed in the experimental field were *Scirpus sp.* (sedge), *Panicum repens* L. (grass), *Rotala verticillaris* Linn. (broad leaf). Other weeds observed were 3 sedges, 3 grasses and 9 broadleaf species. Under unweeded conditions, the proportions of numbers of sedges-grasses-broadleaf weeds were 44-21-35% at 20 DAP, 73-3-24% at 50 DAP and 57-2-41% at harvest, respectively. Thus, *Scirpus sp.* and *R. verticillaris* accounted for more than 79-98% of sp. and *R. verticillaris* accounted for more than 79-98% of the total weed density. However, based on total weed biomass at harvest (18.8 g/0.25 m<sup>2</sup>), broad leaf species and sedges accounted for 71% and 28% of the biomass, respectively. The correlation worked out for weed biomass at harvest with grain yield of rice showed that broad leaf weeds had more detrimental effect on yield ( $r = -0.586^{**}$ ) than sedge ( $-0.446^{**}$ ). Further multiple regression of total weed biomass at 70 DAP with yield at harvest was 0.599<sup>\*\*</sup> and R<sup>2</sup> of 34%. This suggests that control of weed growth can save yield loss by 34%. Here, dry mass of *Rotala* was higher and eventually caused more competition to rice. Unweeded controls lowered yield by 35% compared to yield of 5074 kg/ha in two hand weedings. Pre-emergence application of 2,4-D amine salt at 0.8 kg/ha alone has given significantly better yield than the unweeded control, but similar to the two hand weedings, and to the post-emergence application of 2,4-D amine salt at 0.5 kg/ha with dicamba at 0.125 kg/ha (20 DAP, 5311 kg/ha, Table 3). As the major weed is *Rotala* by weight basis, 2,4-D and dicamba at lower doses controlled this weed better and produced higher yield.

Thus *Echinochloa* species showed better physiological superiority than rice. For weeds dominated with *Rotala verticillaris*, 2,4-D amine salt 0.8 kg a.i./ha as pre-emergence or 2,4-D amine salt 0.5 kg a.i./ha with dicamba 0.125 kg a.i./ha as post-emergence at 20 DAP have proved promising.

### ACKNOWLEDGEMENTS

Authors are thankful to PL-480/ICAR, New Delhi for funding the Weed Control Project. Also thanks are due to companies for sparing herbicides.



## REFERENCES

- Blake, T.J.; Schaplinski, T.J.; Eastham, A. (1984) Stomatal control of water use efficiency in popular clones and hybrids. Canadian Journal of Botany, 62, 1344-1351.
- Chang, W.L. (1970) The effect of weeds on rice in paddy field. I. Weed species and population densities. Journal of Taiwan Agricultural Research, 19, 18-28.
- Hunt, R. (1982) Plant Growth Curves - Functional approach to plant growth analysis, London, Edward Arnold, pp.55-60.
- Krishnamurthy, K.; Ramachandra Prasad, T.V.; Kenchaiah, K.; Narasimha, N.; Khan, T.A.; Dwarakanath, N. (1983) Integrated weed control in transplanted rice. Proceedings of Ninth Conference of Asian Pacific Weed Science Society, Philippines, pp.349-356.
- Krishnamurthy, K.; Devendra, R.; Ramachandra Prasad, T.V.; Narasimha, N.; Prasad, T.G. (1988) Competition of *Echinochloa* spp. on growth and productivity of transplanted rice. Proceedings of Second Tropical Weed Science Conference, Thailand, pp.132-142.

FIGURE 1. Growth curve of biomass of rice & *Echinochloa* species.

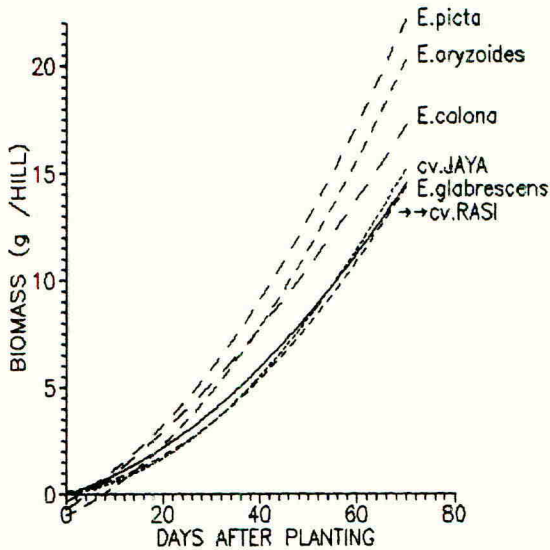


TABLE 1. Crop growth rate (CGR, g/m<sup>2</sup>/day) and leaf area in rice and *Echinochloa* species at intervals throughout the season.

Cultivars/ Species	CGR, g/m <sup>2</sup> /day			Leaf area, cm <sup>2</sup> /hill		
	20-30 DAP	40-50 DAP	60-70 DAP	10 DAP	40 DAP	70 DAP
cv. Jaya	5.5	8.2	10.9	61	503	811
cv. Rasi	5.4	7.8	10.2	66	363	739
<i>E.oryzoides</i>	8.0	11.3	14.6	84	622	530
<i>E.glabrescens</i>	6.4	8.4	10.4	71	611	623
<i>E.picta</i>	10.4	13.2	16.1	91	650	681
<i>E.colona</i>	9.8	11.3	12.8	75	812	717
LSD(P=0.05)	3.1	3.1	4.2	NS	234	NS

DAP - Days after planting

TABLE 2. Physiological parameters measured at the top of the canopy, biomass and grain yield in rice and *Echinochloa* species

Cultivars/ Species	55 days after planting				Biomass yield t/ha	Seed yield t/ha
	Stomatal conduct- tance, M/m <sup>2</sup> /sec	Light inter- ception %	CO <sub>2</sub> com- pensation point ppm	Plant height, cm		
cv. Jaya	0.63	30.9	74	88	10.5	3.88
cv. Rasi	0.71	25.9	70	92	11.2	2.92
<i>E.oryzoides</i>	0.33	59.4	25	140	10.7	0.64
<i>E.glabrescens</i>	0.42	61.3	22	143	7.6	0.38
<i>E.picta</i>	0.28	55.7	22	149	3.9	0.39
<i>E.colona</i>	0.43	70.8	20	154	5.0	0.40
LSD(P=0.05)	0.11	NA	NA	17	0.5	0.10

NA - Not analysed

TABLE 3. Effect of 2,4-D dicamba combinations on grain yield (kg/ha) and weed biomass at harvest (g/0.25 m<sup>2</sup>) in rice cv. IR-20, monsoon 1984, Nagenahalli.

2,4-D amine salt, g a.i./ha	Dicamba g a.i./ha										
	0		100		125		150		200		
	GY	WB	GY	WB	GY	WB	GY	WB	GY	WB	
300	3136	16.4	4216	9.2	4112	6.5	5074	8.0	4453	10.5	
400	4364	12.6	3994	15.3	4364	5.3	5053	8.3	4260	3.4	
500	4319	6.2	4142	13.3	5311	1.8	4305	3.2	4061	12.3	
600	3491	12.9	4290	6.5	4349	11.2	3869	5.5	4275	8.8	
Dicamba g a.i./ha											
150	4512	4.8	2,4-D amine 800 g a.i./ha				4719	7.7			
200	4394	15.0	Hand weeding								
250	3373	20.0	(25 and 50 DAP)				5074	11.0			
120	4009	22.8	Unweeded control				3315	18.8			
	LSD(P=0.05)				1271	6.2					

Herbicides applied post-emergence 20 DAP except 2,4-D alone which was used pre-emergence 2 DAP.

Dicamba 120 g a.i./ha applied as sand mix, 20 DAP.

DAP = Days after planting, GY = Rice grain yield, WB = weed biomass

## WEED CONTROL IN PADDY RICE WITH BENSULFURON METHYL + MOLINATE MIXTURES IN SPAIN AND PORTUGAL

L. MUNTAN

DU PONT IBERICA, S.A., Agricultural Chemicals Department, Tuset 23 - 3º;  
08006 Barcelona (Spain).

## ABSTRACT

Bensulfuron methyl, a new herbicide from Du Pont, has been tested during the last five years in paddy rice, in order to define its characteristics and possibilities of use.

It has shown a high level of activity at relatively low rates on the main weed species present in rice crops in Spain and Portugal.

Although its effect is clear on broadleaved weeds and sedges, bensulfuron methyl has also shown a significant effect on grasses.

Bensulfuron methyl can be applied during a long period (from presowing to early stem elongation of rice) alone or in mixtures with graminicides. These mixtures permit complete weed control with a single application, in most cases.

In addition, bensulfuron methyl has demonstrated a good level of crop selectivity on the main rice varieties cultivated in these countries.

The best level of weed control is obtained by applying a mixture of bensulfuron methyl plus molinate in a granule formulation type for direct application, containing 0.08 % and 8 % respectively, at the 1 to 3 leaf stage of rice.

## INTRODUCTION

Weed control in paddy rice has been achieved traditionally with two applications. The first one directed to control all species of Echinochloa: E. crus-galli, E. oryzoides, E. oryzicola and E. hispidula = E. phyllopoqon and carried out during the initial phase of crop growth (from presowing to 3 leaf stage). The second one, made generally during the normal drainage period, 30 to 60 days after sowing, is directed to control broadleaved weeds and sedges : Alisma plantago-aquatica, A. lanceolatum, Ammania coccinea, A. robusta, Berqia capensis, Scirpus maritimus, Scirpus mucronatus, S. supinus and Cyperus difformis.

Products used up to date are : molinate and thiobencarb for grass control and MCPA, bentazon and propanil alone or in mixtures for broadleaved weeds and sedges.

New compounds have been introduced recently such as : mefenacet, dimepiperate and quinchlorac for grass control.

Bensulfuron methyl is a sulfonylurea herbicide developed over the last few years with specific characteristics to be used in the rice crop. Its most important properties are : wide range of activity on the main weeds present in paddy rice, good selectivity on the most frequent rice varieties cultivated, flexibility of its application time, relatively low rates of application, adequate persistence, leaf and root absorption, translocation through the plant tissues and very favourable environmental safety profile.

Trials made in Spain and Portugal demonstrated good crop selectivity in most of the varieties cultivated such as : Bahía, Delta, Niva, Lido, Robino, Rubra and Ribe.

A wide development program has been carried out in Spain and Portugal during the last five years in order to define :

- 1) Crop selectivity in the rice varieties cultivated in these countries.
- 2) Time of application in relation to each weed species.
- 3) Water management needed in order to get the best product performance.
- 4) Mixtures with other compounds to obtain full weed control with a single application.

#### METHODS AND MATERIALS

Trials were conducted in the main rice areas of Spain and Portugal in order to obtain a broad range of data on the variables that can influence product results. In each area, the normal cultivation system was followed.

Plots were separated with ridges in order to avoid any kind of contamination from the neighbouring ones and irrigation was organized individually plot by plot.

A 10 % WP formulation of bensulfuron methyl was used for the spray applications and granules for direct application were prepared containing 0.08 % + 8 % (ref. 1), and 0.1 % + 6 % (ref. 2), of bensulfuron methyl + molinate respectively.

Spray applications were made with a knapsack motorsprayer equipped with an 8 fanjet nozzles boom and a working pressure of 200 kPa. Volume applied varied between 200 and 500 l/ha.

Evaluations were made of percentage of biomass reduction compared with untreated plots, and was given in a 0 % - 100 % scale, being 0 % = no effect and 100 % = complete weed control. A minimum of two assessments were made one at 20 to 30 days after sowing and a second at early ear emergence in order to differentiate Echinochloa species from rice and wild rice.

Application times varied from presowing to early stem elongation.

## RESULTS

Time of application

Six tests were carried out in order to obtain data from applications made at 75 g a.i./ha of bensulfuron methyl (10 % WP formulation) at the following times :

- 1) Preflood - 8 days before sowing
- 2) Sowing - just after sowing
- 3) One leaf stage of rice - 13 days after sowing
- 4) Two leaf stage of rice - 21 days after sowing
- 5) Beginning of stem elongation - 60 days after sowing.

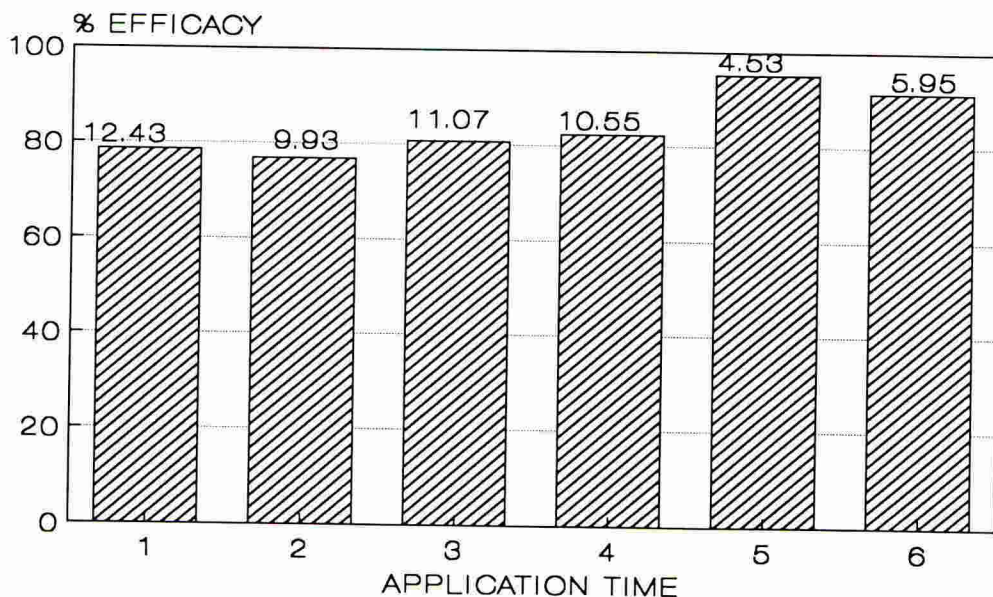
In order to avoid Echinochloa spp competition in plots treated at time 5, they were treated at the two leaf stage of rice with molinate in granules at 3750 g a.i./ha.

Species present were : Echinochloa spp., S. maritimus, S. mucronatus, A. plantago-aquatica, A. coccinea and B. capensis.

The standard treatment was one application of molinate in granules at 3750 g a.i./ha and a second treatment at the beginning of stem elongation with bentazon at 1920 g a.i./ha.

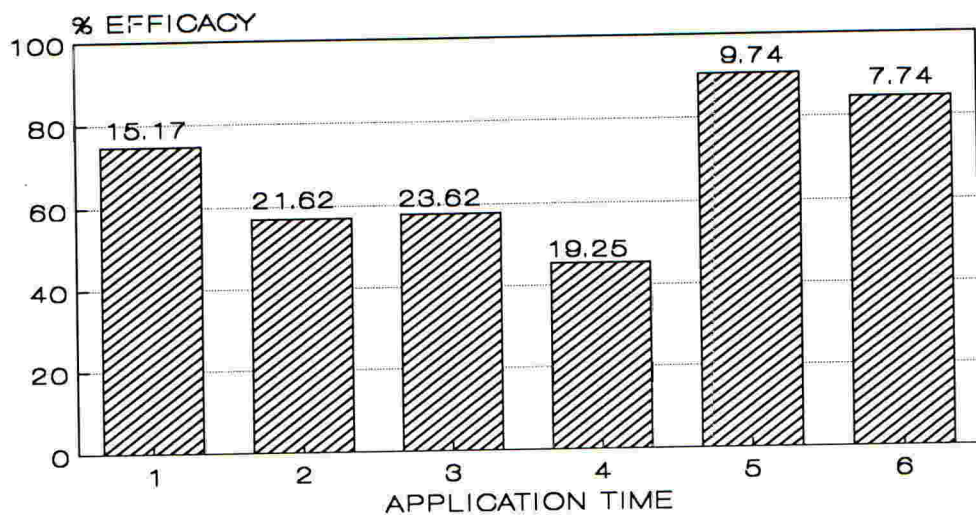
Figure 1 shows the average of efficacy results over all species mentioned. Figures on the top of bars indicate the standard error of means.

FIGURE 1. Results of bensulfuron methyl at 75 g a.i./ha at different application times : % efficacy over all weed species.



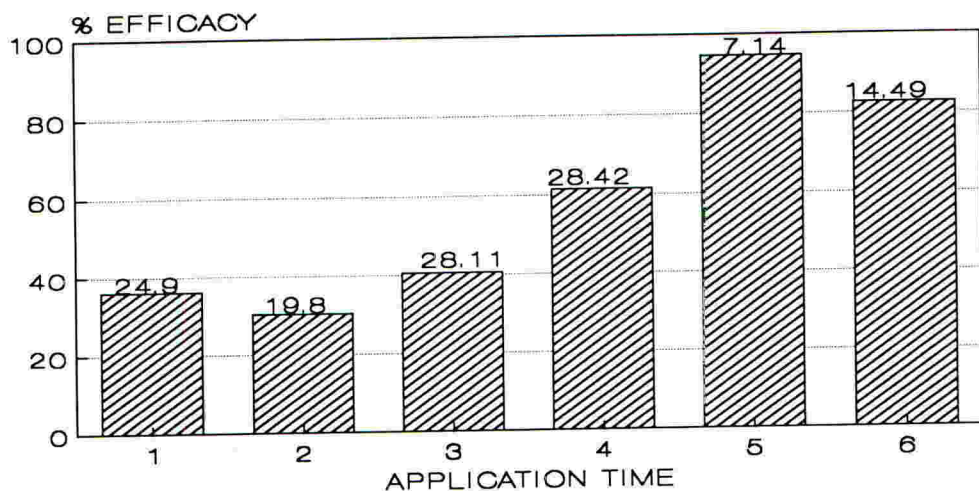
Since the biggest differences in performance were seen in the Echinochloa spp. and S. maritimus, the other species being consistently well controlled at all application times, the influence of the time of application on these two species was analyzed further and shown on figures 2 and 3.

FIGURE 2. Effect of timing of application of 75 g a.i./ha of bensulfuron methyl upon efficacy of control of Echinochloa spp.



In figure 2, considering times 1, 2, 3 and 4, where molinate was not used, bensulfuron methyl showed a significant effect on Echinochloa spp., especially when the application was made at the pre-flood time.

FIGURE 3. Effect of timing of application of 75 g a.i./ha of bensulfuron methyl upon efficacy of control of Scirpus maritimus.



In *S. maritimus* in figure 3, although at initial assessments a high level of activity (around 95 %) was recorded in all treatments, since it is a perennial, late germinating tubers were unaffected by the treatment and germinated after 20-40 DAT. The highest and most consistent level of effect was observed in plots treated at time 5.

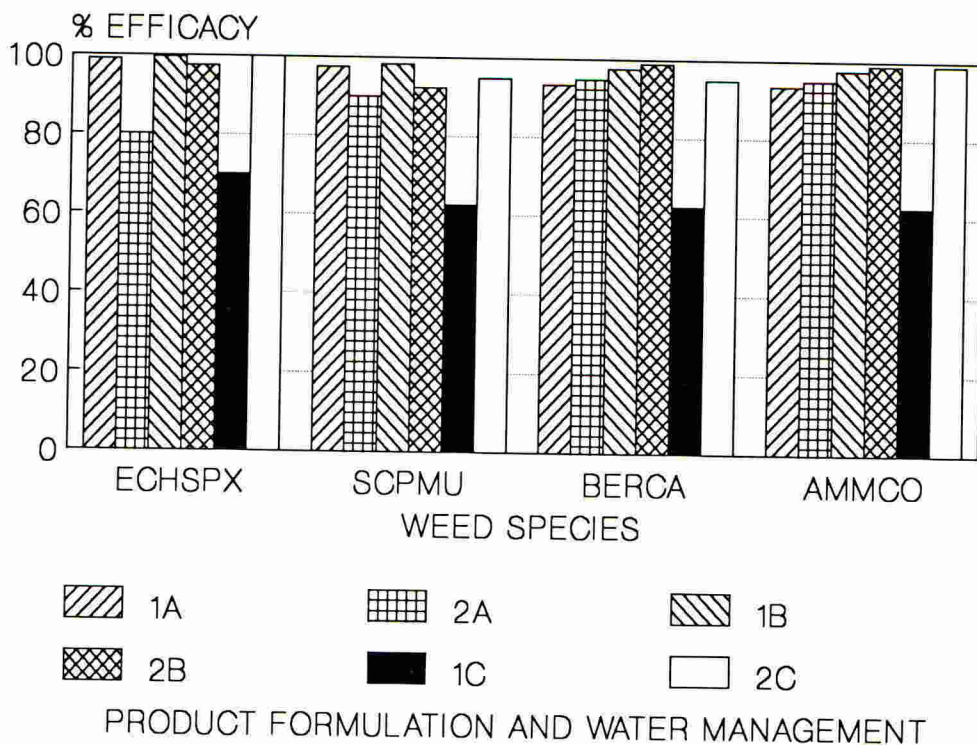
#### Molinate mixtures and water management

Since in previous tests (internal Du Pont report) it was proved that management of water was an important factor, a project using mixed formulations of molinate and bensulfuron methyl was carried out in order to establish product ratio in formulations and the required water management practices to obtain an acceptable level of weed control.

Granule formulations (Refs. 1 and 2 in figure 4), as described in methods and materials, were applied at the 2 leaf stage of rice at 50 kg/ha. Different types of water management practices were compared; since molinate applications require to keep the water held for a minimum of 2 days, we establish three different methods of water management practices:

- A) Inlet and outlet closed for 2 days
- B) Inlet and outlet closed for 5 days
- C) Inlet open and outlet closed for 5 days

FIGURE 4 : Effect of formulation ratio (bensulfuron methyl + molinate) and water management practices upon level of weed control.





The total weed coverage was 65%, the weed growth stages and percentage of ground coverage at treatment were:

Species	growth stage	% ground cover	code in Fig 4
<u>Echinochloa spp.</u>	1-2 leaves	12	ECHSPX
<u>Scirpus mucronatus</u>	2 leaves	20	SCPMU
<u>Ammania coccinea</u>	4 leaves	8	AMMCO
<u>Bergia capensis</u>	4 leaves	60	BERCA

In figure 4, comparisons of the different product mixtures performance (numbers 1 and 2) in the three different water management practices (A, B, C) illustrated that:

- There are no significant differences between formulations provided water is held for 5 days (1B and 2B).
- Holding water for 2 days (A) product efficacy on B. capensis and A. coccinea was similar with both formulations (93.5% in 1A and 95% in 2A). Nevertheless formulation 1 was clearly superior on Echinochloa spp. (99% in 1A and 80% in 2A) and slightly better on S. mucronatus (97.5% in 1A and 90% in 2A).
- A clear difference was noticed between formulations in the modality where water was maintained 5 days but with inlet opened (1C, 2C). In this case the best performance was obtained with the highest rate of bensulfuron methyl in the mixture (formulation 2).

#### CONCLUSIONS

Holding water for 5 days gives the best control of all species, but since farmers are not willing to hold water longer than 2 days, then formulation n° 1 (0.08 % of bensulfuron methyl + 8 % of molinate in granules) gave the most consistent effect with >93.5 % weed control in the species examined.

In particular cases where S. maritimus is present a second application of bensulfuron methyl may be needed in order to control late germinations, as explained in the S. maritimus analysis. This treatment should be done at the beginning of stem elongation of rice.

#### ACKNOWLEDGEMENTS

The author wants to thank the colleagues from Du Pont specially to V. Pereira who was encharged of the development work done in Portugal, all of them made this work possible, and also people from Agrop, Bayer and Sapec that collaborated in the development in Portugal.

# **SESSION 7A**

## **NOVEL ASPECTS OF WEED CONTROL**

**CHAIRMAN**      **MR D. TYSON**

**SESSION ORGANISER**      **MR M. E. UPSTONE**

<b>INVITED PAPERS</b>	<b>7A-1 &amp; 7A-2</b>
	<b>7A-6 &amp; 7A-7</b>
<b>RESEARCH REPORTS</b>	<b>7A-3 to 7A-5</b>

## CHIRALITY AND BIOLOGICAL ACTIVITY

P.A. CHALONER

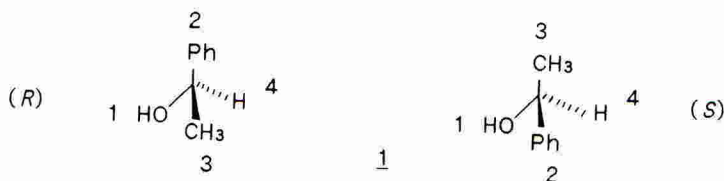
School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton

## ABSTRACT

Many of the chemical agents which are used to interact with biological systems show differing activity, depending on whether the "right" or "left" handed form of a chiral molecule is used. This results from the fact that biological receptors are themselves formed from chiral molecules, and have a distinctive shape. This effect has been known for many years in medical applications, has been shown for various insecticides, and has more recently come to be appreciated for herbicides and fungicides. This paper reviews examples from each of these classes, and considers methods for the synthesis of chiral biologically active agents.

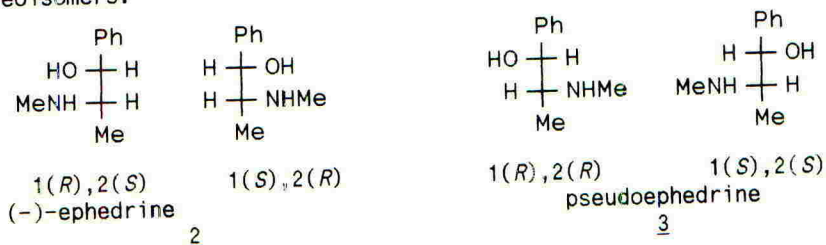
## INTRODUCTION

Chirality in organic compounds is generally associated with the presence in a molecule of an asymmetric or chiral centre in which a carbon atom is bonded to four different substituents as in 1. The two structures are mirror images, and the configuration at the chiral centre may be specified by reference to a set of rules as to the ordering of substituents (Cahn *et al.*, 1966). The substituents are ranked according to atomic number, with the attached atom with the highest atomic number ranked first. If a decision cannot be made on the basis of the first atom attached to the chiral centre, work outwards until a difference is found. There are special rules to deal with multiply bonded atoms, geometrical isomers, and further chiral centres. In 1 the assignment of priority 1 to the -OH group and priority 4 to the hydrogen is relatively easy. The phenyl group takes precedence over the methyl group on the basis of a "second atom out" consideration. If the molecule is viewed from the side remote from the lowest priority group, and in passing through groups 1, 2 and 3 in order, one describes a clockwise route, the configuration of the chiral centre is designated as (*R*). Conversely, if the circle traversed is anticlockwise, the configuration of the chiral centre is (*S*). The two compounds are described as enantiomers, and behave differently in the chiral environment found in biological systems.



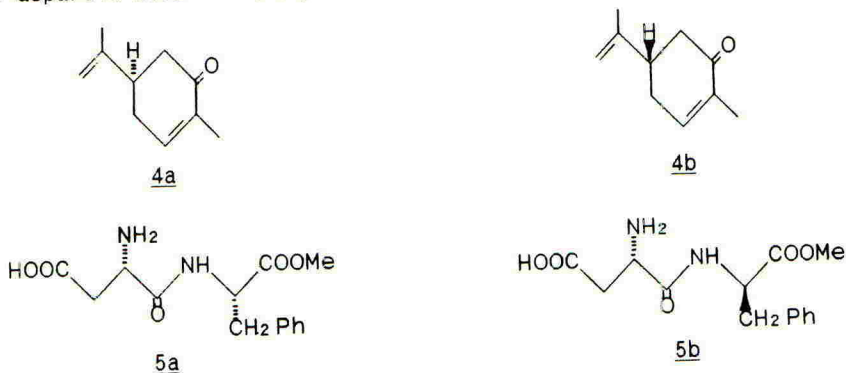
If a compound has more than one chiral centre, the number of possible isomers is increased; for  $n$  chiral centres the number is  $2^n$ . Within this manifold there are pairs of enantiomers, which are true mirror images; the

relationship of the other isomers is described as that of diastereoisomers. An example is provided by 2, ephedrine, and 3, *pseudo*-ephedrine, which are diastereoisomers.

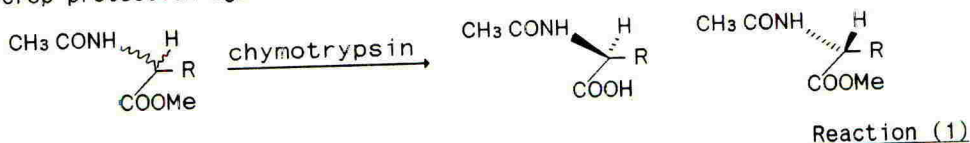


### INTERACTION OF CHIRAL MOLECULES WITH BIOLOGICAL RECEPTORS

All living systems, both plant and animal, have as their building blocks chiral molecules, in particular amino acids and sugars. Thus, receptors for bioactive agents are chiral, and enantiomeric molecules interact differently with them. For example, the (*R*)-enantiomer of carvone, 4a, tastes of spearmint, whilst the (*S*)-isomer, 4b, tastes of caraway (Russell and Hills, 1971). The dipeptide 5a was synthesised from (*S*)-aspartic acid, which has no taste, and (*S*)-phenylalanine, which is bitter. The product, aspartame, is extremely sweet, and its production as a non-nutritive sweetener is now a major industry. However, 5b, prepared from (*S*)-aspartic acid and (*R*)-phenylalanine (which is sweet) is bitter.



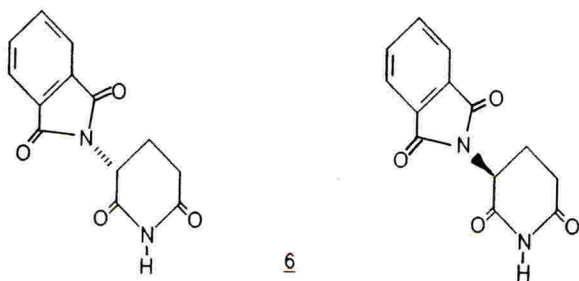
Studies of enzymes have greatly contributed to our knowledge of chiral biological interactions, and one of the best understood is the esterase enzyme, chymotrypsin, which catalyses ester hydrolysis, ((reaction (1)). Only the derivatives of (*S*)-amino acids are hydrolysed, and this observation was interpreted in terms of a model of the enzyme active site in which only these could be readily accommodated (Cohen 1969). Most organisms have a number of esterase and peptidase enzymes, and hydrolysis catalysed by esterases is one of the most important biotransformations for crop protection agents.



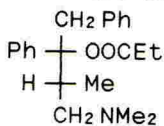
Why should the agrochemist be interested in the relative activities of the enantiomers of the crop protection agent which he is employing? The first consideration is an economic one. If one of the enantiomers is active (called the eutomer) and the other inactive (the distomer), double the materials are used in synthesis of the racemate, and application is less convenient, relative to the use of the pure eutomer. Additionally, the distomer may not have zero activity but may have an undesirable activity, or may be an antagonist for the eutomer. Also it may be biodegraded less rapidly, posing problems of persistence and residues in produce. At the very least, the inactive isomer can prove expensive and useless baggage; at worst it may have undesirable effects or be a serious pollutant.

#### THERAPEUTIC AGENTS

Perhaps the most famous, and certainly the most tragic, example of a drug in which the enantiomers proved to have different biological actions, is that of thalidomide, 6, marketed during the 1960's as an anti-emetic agent for use in pregnancy. The (*R*)-enantiomer does have a sedative and an anti-emetic effect, but the (*S*)-form is a severe teratogen, and caused miscarriage and serious birth defects (von Blaschke *et al.*, 1979).

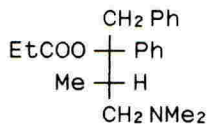


A happier example is that of propoxyphene, 7a, and 7b; dextropropoxyphene is an analgesic, whilst levopropoxyphene is an antitussive agent. These two actions are incompatible in a single drug, and the two isomers are marketed separately as pure enantiomers (Drayer, 1986).



2*S*,3*R*

7a



2*R*,3*S*

7b

With increasingly tight controls on the licensing of drugs it seems likely that most new therapeutic agents will need to be prepared and marketed in chiral form, unless the two enantiomers can be rigorously proven to have similar activities.

#### HERBICIDES

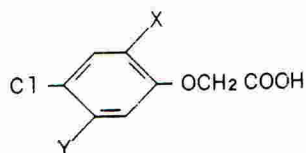
Many, if not most, synthetic herbicides are marketed in racemic form, and only in a few cases are there any data on the differential activities

of enantiomers. Further developments promise more selective herbicides, coupled with a better understanding of their mode of action at a molecular level.

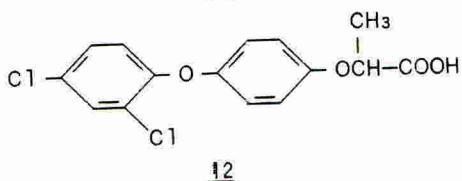
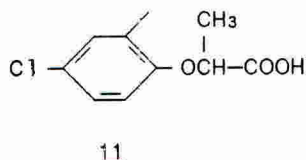
Herbicides which interfere with the action of the auxin plant growth hormones are among the most widely used. The auxin-type herbicides are more stable than the natural auxins, and induce the plant to "outgrow its strength". A complete description of the mode of action of auxins and the related herbicides is lacking, but the adsorption to the cell membrane, cell elongation and influences on enzyme systems have been investigated. Many auxin type herbicides have high levels of selectivity and can be used on broad-leaved weeds in cereal crops, whilst others are active against grasses and can be used on dicotyledonous crops.

#### Aryloxy carboxylic acid derivatives

Derivatives of acetic acid such as 2,4-D, 8, and 2,4,5-T, 9 were amongst the earliest auxin type herbicides. They suffer from having a relatively short half life, due to biodegradation at the CH<sub>2</sub> group; thus *Stellaria media* and *Galium aparine* are resistant to MCPA, 10 (Smith *et al.*, 1952). However, mecoprop, 11, is stabilised against degradation by the presence of a methyl group, and is effective against these weeds. In 11, moreover, we have introduced a new chiral centre, and it was shown that the activity lies mainly in the (*R*)(+)-form, with the distomer being virtually inactive, and inhibiting the activity of the eutomer by competing for a receptor site (Åberg, 1980). The effects of 2-(4-aryloxyphenoxy)propanoic acids on the incorporation of labelled acetate into fatty acids in chloroplasts has been studied (Hoppe and Zacher, 1985); (*R*)-diclofop, 12, is a more potent inhibitor than the (*S*)-enantiomer, in parallel with its herbicidal activity *in vivo*. This suggests that the mode of action of these herbicides is linked with the inhibition of fatty acid biosynthesis.

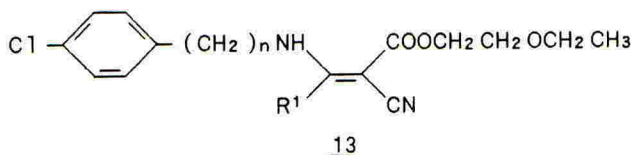


- 8 X = Cl, Y = H  
9 X = Y = Cl  
10 X = Me, Y = H

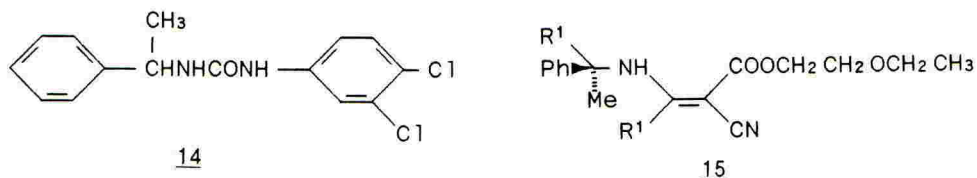


#### Photosynthetic Electron Transfer (PET) Inhibitors

The inhibition of photosynthesis is an attractive target for herbicides, in that this key energy process in higher plants is absent from mammals. The target in general is (PET) in photosystem II (PSII), and the mode of action is believed to involve binding to the thylakoid membrane in the chloroplast by displacement of the plastoquinone electron acceptor from its binding niche (Phillips, 1988). Many compounds are known which will effect such inhibition (for example, 13), but relatively few are chiral.



The effect of optically active PET inhibitors was first investigated using the diuron analogue, 14, and isolated chloroplasts (Moreland and Boots, 1971). The (*S*)-enantiomer is more active than the (*R*)-form, but the two do not compete. Inhibition was shown to take place at two sites, PS<sub>II</sub>, and a site concerned with the generation of ATP. However, for effective herbicidal use it is also necessary to worry about membrane permeability, and sensitivity to environmental and metabolic degradation. Unfortunately, 14 has little herbicide action at 8 kg ha<sup>-1</sup>.



A more interesting and more selective group of PET inhibitors is provided by 15. In this example the (*S*)-isomer is 200 times as active as the (*R*)-form, and twice as active as the racemate, for PET inhibition in isolated chloroplasts. These differences are reflected in effective herbicidal activity; the *S*-enantiomers give effective control of *Sinapis alba* at a post emergence application rate of 0.25 kg ha<sup>-1</sup>, whilst the (*R*)-enantiomer is essentially ineffective at 8 kg ha<sup>-1</sup>.

Currently these chiral PET inhibitors remain largely of academic interest, since the racemic compounds have good activity. They are, however, of considerable interest as a tool to probe the three dimensional structure of the PS<sub>II</sub> binding site and other receptors.

## FUNGICIDES

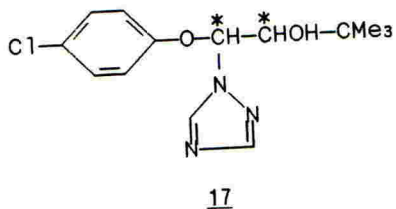
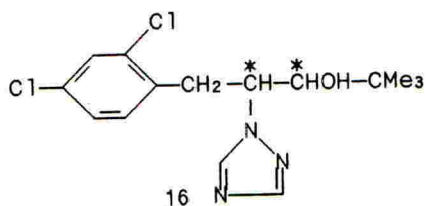
Recent years have seen the development of a range of systemic fungicides, which display both protective and curative activity. Biochemically and physiologically the system involved is complex, since we must consider receptors and metabolic pathways in both the pathogen and the host plant. Whilst many of the known fungicides contain chiral centres, studies on the differential activities of the enantiomers are relatively few.

### Ergosterol biosynthesis inhibitors (EBIs)

The EBIs are characterised by a common mode of action rather than a common structural type. As the name implies they inhibit the biosynthesis of ergosterol, a sterol with a significant role in fungal membrane ordering. It has also become clear that a number of fungicides of this type also inhibit the biosynthesis of gibberellin and sterols in plants, which has resulted in the development of some useful herbicides. The chirality of the material determines whether the herbicidal or fungicidal activity is

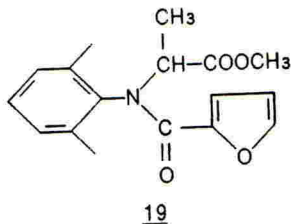
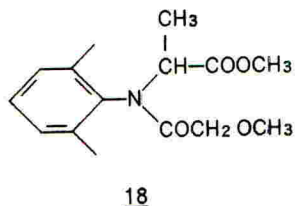
predominant (Fuchs, 1988).

The most important EBIs are the 1-substituted 1,2,4-triazoles, such as diclobutrazol, 16, and triadimenol, 17. Diclobutrazol has two chiral centres, and there are two diastereomeric pairs of enantiomers. Most of the activity resides in the (*R,R*):(*S,S*) diastereoisomer, and the recommended common name strictly applies only to this form. The (*R,R*)-enantiomer is the more active, with an activity ratio between 660 and 725. Apart from its fungicidal activity, paclobutrazol has proved to be an effective plant growth regulator, as shown with apple seedlings (Sugavanam, 1984). The PGR activity resides largely in the (*S,S*)-isomer. Computer modelling studies suggest that the (*R,R*)-isomer is superimposable on lanosterol, and the (*S,S*)-form on kaurene, a precursor of gibberellic acid in higher plants, which suggests that the enantiomers inhibit fungal ergosterol and plant gibberellin biosynthesis respectively (Marchington and Lambros, 1987).



#### Acylalanines and related compounds

This group of fungicides is characterised by a 2,6-dimethylaniline, substituted at nitrogen by an acyl group and a side chain with a chiral centre in the  $\alpha$ -position. Examples are provided by metalaxyl, 18 and furalaxyl, 19. *In vitro* it was shown that the (*R*)-enantiomer of metalaxyl was 1000 times as active as the (*S*)-isomer, but the difference *in vivo* was much less marked. Unlike a number of related compounds, the (*S*)-isomer does not have any significant herbicidal activity, and the use of the racemate is not in this case practically disadvantageous (Hubele *et al.*, (1983).



#### INSECTICIDES AND DISRUPTANTS

The nature of the chemicals used to control pests is very diverse, and there are numerous examples of stereoselection in their modes of action.

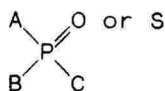
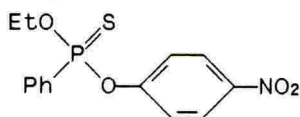
#### Organophosphates

Organophosphate compounds used as pesticides can inactivate acetylcholinesterase, by phosphorylation of a serine residue at the active site of the enzyme. The enzyme catalyses the hydrolysis of acetylcholine, which is responsible for the transmission of nerve impulses across synaptic



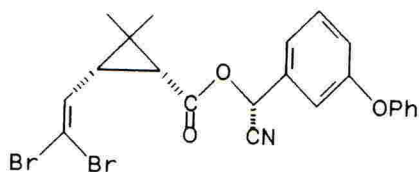
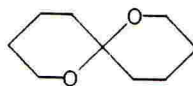
junctions. Inhibition of the enzyme causes an accumulation of acetylcholine, and poisoning due to disturbance of neurotransmission. Whilst many organophosphates are useful pesticides, others show such acute mammalian toxicity that they were developed as nerve gases for use in warfare.

The general structure of this class is 20, and the chiral centre which we must consider is at phosphorus rather than carbon. Most widely used pesticides have a non-chiral structure in which A and B are methoxy or ethoxy groups. Chirality is usual in the more toxic nerve agents. Many studies have been direct comparisons of *in vitro* anticholinesterase activity, and the data obtained can be rationalised on the basis of the "fit" of the organophosphate into the active site of the enzyme (Järv, 1984). In some examples, such *O*-ethyl *O*-4-nitrophenyl phenylphosphonothioate (EPN), 21, the desirable insecticidal activity dominates in the (*R*)-enantiomer, whilst the neurotoxic action in mammals dominates in the (*S*)-form (Ohkawa *et al.*, 1980).

2021

### Pyrethroids

The pyrethroid insecticides are related to natural compounds that occur in the flowers of *Chrysanthemum* species; most are chiral and contain a cyclopropane ring. The stereochemistry of the cyclopropane ring is critical in determining toxicity, both in insects and mammals. In general the most insecticidal isomers (also the most slowly metabolised) are the 1-(*R*)-*cis* compounds, especially when these bear an  $\alpha$ -cyano substituent at an (*S*)-chiral centre, as in deltamethrin, 22, one of the most powerful insecticides currently available (Elliott *et al.*, 1982). There is some evidence that the presence of other isomers reduced the efficacy of the most active compound.

2223

### Pheromones

Pheromones, or chemical messengers, have been most widely studied in insects. The use of such compounds to control insect pests is attractive because of the species specificity which may potentially be achieved. The problem is not simple, however, since most attractant agents are not a single substance but a rather complex cocktail; either one or both stereoisomers is active, and the other may act as a synergist or an inhibitor.

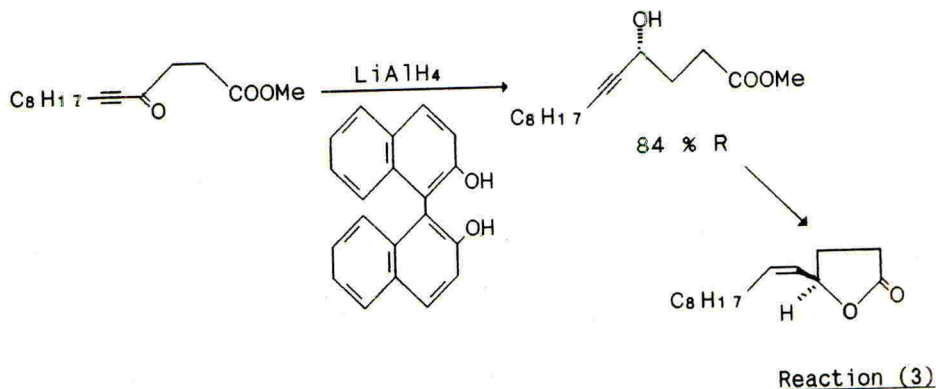
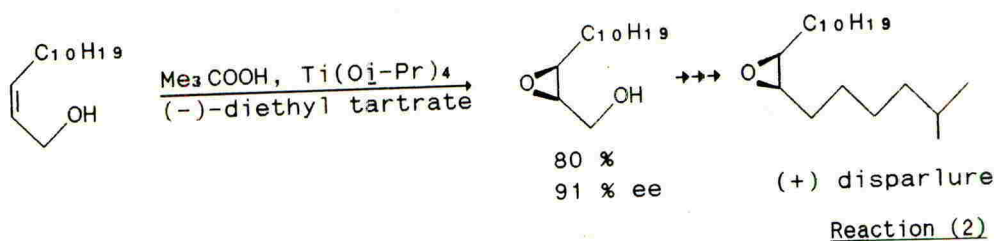
An interesting example of a sex-specific response is provided by the pheromone of *Dacus oleae*, olean, 23. The compound is emitted as a racemate by the female, but the male responds only to the (*R*)-enantiomer, which acts as a sex attractant. The females, by contrast, respond only to (*S*)-olean (Hanriotakis, 1986)

### ASYMMETRIC SYNTHESIS

Whilst asymmetric synthesis is currently used in the preparations of a wide range of chiral compounds, most of the practical applications have been in the biomedical area, or in the synthesis of pheromones. There is also a range of processes which leads to chiral material, which involve the separation of two enantiomers at some stage in the synthesis, by resolution. These are not generally economic for large scale production, since half of the material must be discarded or recycled.

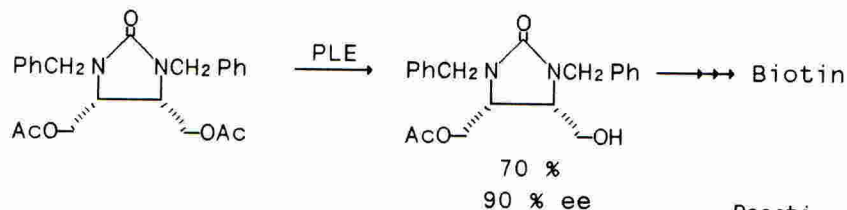
### Asymmetric Catalysis

The last ten years has seen an explosive growth in the range of reactions which use chiral catalysts, particularly transition metal complexes. Reactions which are high yielding and extremely enantioselective are now known (Brown, 1989). Reaction (2) (Rossiter *et al.*, (1981)) is an asymmetric epoxidation effected by *tert*-butyl hydroperoxide in the presence of a catalyst derived from  $[\text{Ti}(\text{OCHMe}_2)_4]$  and (-)-diethyl tartrate. The product was converted to disparlure, the pheromone of *Lymantria dispar*. Reaction (3) (Nishizawa *et al.*, (1981)) is not in practice strictly a catalytic process, but shows how a well-known reagent was modified to give a chiral reducing agent. The product was converted to the pheromone of *Popilla japonica*.

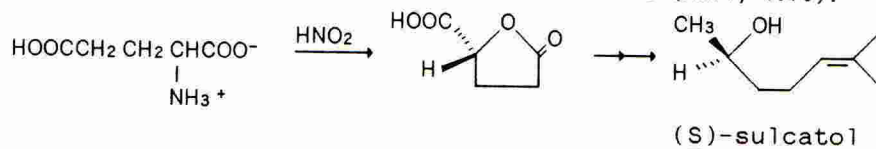


Use of enzymes

Enzymes are chiral catalysts *par excellence*, and operate under very mild conditions. Practical applications have largely been in the biomedical area, but there is clearly considerable further scope for this technique. Reaction (4) shows the selective hydrolysis of a diester by pig liver esterase to a chiral hydroxy ester, which was converted to biotin (Wang and Sih, 1984).

Compounds from the Chiral Pool

In designing asymmetric syntheses, it is useful to recall that there exists in nature a reservoir of chiral compounds, many of which are inexpensive, the so-called "chiral pool". These chiral centres might appear in the product, be transformed in a stereospecific manner, or be used to induce chirality at a neighbouring centre (Morrison and Scott, 1984). In reaction (5) the lactone is produced by diazotisation of (*R*)-glutamic acid. Successive manipulations gave (*S*)-sulcatol, the aggregation pheromone of *Gnathotrichus sulcatus*. The (*R*)-isomer was also prepared, since the natural pheromone is a 35:65 mixture of the two enantiomers (Mori, 1975).

Reaction (5)

## REFERENCES

- Åberg, B. (1980) Plant Growth Regulators XXXIX, Some nitro- and chloro-nitro-phenoxyacetic and optically active  $\alpha$ -phenoxypropionic acids. *Swedish Journal of Agricultural Research*, 10, 101-106.
- Brown, J.M. (1989) Asymmetric homogeneous catalysis. *Chemistry in Britain*, 25, 276-280.
- Cahn, R.S.; Ingold, C.K.; Prelog, V. (1966) Specification of molecular chirality. *Angewandte Chemie, International Edition in English*, 5, 385-415.
- Cohen, S.G. (1969) Active site and specificity of  $\alpha$ -chymotrypsin. *Transactions of the New York Academy of Sciences*, 31, 705-719.
- Drayer, D.E. (1986), Pharmacodynamic and pharmacokinetic differences between drug enantiomers in humans: An overview. *Clinical Pharmacology and Therapeutics*, 40, 125-33.
- Elliott, M.; Farnham, N.; Janes, F.; Khambay, P.S. (1982) Insecticidal activity of the pyrethrins and related compounds. part XII;  $\alpha$ -substituted-3-phenoxybenzyl esters. *Pesticide Science*, 11, 407-414.
- Fuchs, A. Implications of stereoisomerism in agricultural fungicides in *Stereoselectivity of Pesticides; Biological and Chemical Problems*, E.J. Ariens, J.J.S. van Rensen and W. Welling (Eds.) Amsterdam, Elsevier,

- 203-262.
- Haniotakis, G.; Francke, W.; Mori, K.; Redlich, H.; Schurig, V.S. (1986) Sex-specific activity of (R)(-) and (S)(+)-1,7-dioxaspiro[5.5]undecane, the major pheromone of *Dacus oleae*. *Journal of Chemical Ecology*, 12, 1559-1568.
- Hoppe, H.H.; Zacher, H. (1985) Inhibition of fatty acid biosynthesis in isolated bean and maize chloroplasts by herbicidal phenoxy-phenoxypropionic acid derivatives and structurally related compounds. *Pesticide Biochemistry and Physiology*, 24, 298-305.
- Hubele, A.; Kunz, W.; Eckhardt, W.; Sturm, E. (1983) The fungicidal activity of acyl anilines, in *Pesticide Chemistry: Human Welfare and the Environment, Proceedings of the 5th International Congress on Pesticide Chemistry, Kyoto, Japan, 1982*, J. Miyamaoti and P.C. Kearney (eds.), Volume 1, Pergamon Press, Oxford, 233-242.
- Järv, J. (1984) Stereochemical aspects of cholinesterase catalysis. *Bioorganic Chemistry*, 12 259-278.
- Marchington, A.F.; Lambros, S.A. (1987) Computer design of fungicides, in *Modern Selective Fungicides - Properties, Applications, Mechanisms of Action*, H. Lyr (ed.), VEB Gustav Fischer Verlag, Jena 325-336.
- Moreland, D.E.; Boots, M.R. (1971) Effects of optically active 1-( $\alpha$ -methylbenzyl)-3-(3,4-dichlorophenyl)urea on reactions of mitochondria and chloroplasts. *Plant Physiology*, 47, 53-58.
- Mori, K. (1975) The aggregation pheromone in the scolytid beetle, *Gnathotrichus Sulcatus*. *Tetrahedron*, 31, 3011-3012.
- Morrison, J.D.; Scott, J.W. (1984) *Asymmetric Synthesis, Volume 4*, Academic Press, Orlando.
- Nishizawa, M.; Yamada, M.; Noyori, R. (1981) Highly enantioselective reduction of alkynyl ketones by a binaphthol modifies aluminium hydride reagent. Asymmetric synthesis of some insect pheromones. *Tetrahedron Letters*, 22, 247-250
- Ohkawa, H.; Oshita, H.; Miyamoto, J. (1980) Comparison of Inhibitory Activity of various Organophosphorus Compounds against Acetylcholinesterase and neurotoxic esterase of Hens with respect to Delayed Neurotoxicity. *Biochemical Pharmacology*, 29, 2721-2725.
- Phillips, J.N. (1988) Stereo-selective photosynthetic inhibitor herbicides in *Stereoselectivity of Pesticides; Biological and Chemical Problems*, E.J. Ariens, J.J.S. van Rensen and W. Welling (Eds.) Amsterdam, Elsevier, 183-201.
- Rossiter, B.E.; Katsuki, T.; Sharpless, K.B. (1981) Asymmetric Epoxidation Provides Shortest Routes to Four Chiral Epoxy Alcohols which are Key Intermediates in Syntheses of Methymycin, Erythromycin, Leukotriene C-1 and Disparlure. *Journal of the American Chemical Society*, 103, 464-465.
- Russell, G.F.; Hills, J.I. (1971) Odor differences between enantiomeric isomers. *Science*, 172, 1043-1044.
- Smith, M.S.; Wain, R.L; Wightman, F. (1952) Studies on plant growth regulating substances. Part V: Steric factors in relation to mode of actions of certain aryloxycarboxylic acids. *Annals of Applied Biology*, 39 295-307.
- Sugavanam, B. (1984) Diastereomers and enantiomers of paclobutrazol; their preparation and biological activity. *Pesticide Science*, 15 296-302.
- von Blaschke, G; Kraft, H.P.; Finkentscher, K; Köhler, F. (1979) Chromatographic racemic separation of thalidomide and teratogenic activity of its enantiomers. *Arzneimittel Forschung*, 29, 1640-1642.
- Wang, Y.; Sih, C.J. (1984) Bifunctional synthons via biochemical methods 4. Chiral precursors to (+)-biotin and (-)-A-factor. *Tetrahedron Letters*, 25, 4999-5002

## THE SYNTHESIS, STABILITY AND BIOLOGICAL ACTIVITY OF THE ENANTIOMERS OF PYRIDYLOXYPHENOXYPROPRIONATES

D. CARTWRIGHT

ICI Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire RG12 6EY.

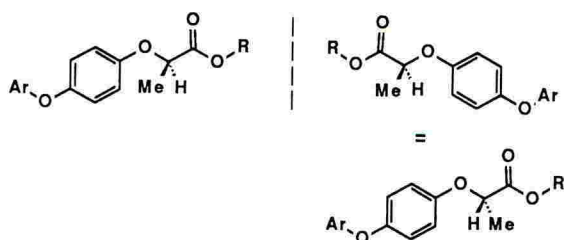
## ABSTRACT

Aryloxyphenoxypropionates possess a chiral centre and exist as a mixture of two optical isomers. Using the pyridyloxyphenoxypropionates as typical examples, the separation and synthesis of the two optical isomers is discussed and the stability of these under acidic and basic conditions is described. Although biological activity resides exclusively with the (R)-enantiomer in post-emergence situations, the (R) and (S)-enantiomers show equivalent activity when applied pre-emergence. This has been shown to be due to microbial conversion of the (S) to (R)-enantiomer in the soil. Recent biochemical studies are reviewed, which indicate that the grass/dicot selectivity lies at the enzyme level and that enzyme activity resides exclusively with the (R)-enantiomer.

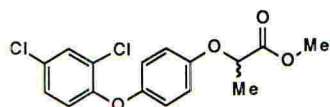
## INTRODUCTION

Aryloxyphenoxypropionates form an important weapon in the farmer's armoury to counteract unwanted grass species. The nature of the aryl group and its substituents influences both the overall activity and grass weed spectrum of the molecule, and products have been found which can be used to control grass weeds in cereals and to combat a wide spectrum of annual and perennial grasses in a large variety of broad leaf crops.

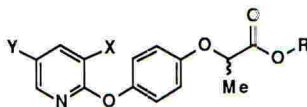
Chemical variation of the basic structure has shown that optimal grass weed activity and broad-leaf selectivity is obtained when the oxyacid side chain is substituted by one methyl group. The introduction of the methyl group creates a chiral centre and the resulting oxypropionates exist as one of a pair of mirror images (called enantiomers).



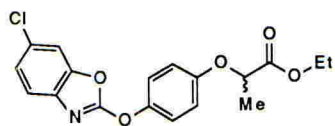
Synthetic procedures normally lead to a mixture of equal amounts of the two enantiomers called a racemate. The products diclofop-methyl, fluazifop-butyl, quizalofop-ethyl and fenoxaprop-ethyl were launched in their racemic forms.



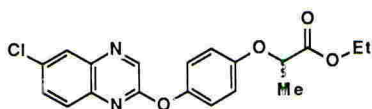
diclofop-methyl (RS)



Y=CF<sub>3</sub>, X=H, R=nBu; fluazifop-butyl  
 Y=CF<sub>3</sub>, X=Cl, R=EtOC<sub>2</sub>H<sub>4</sub>; haloxyfop-ethoxyethyl  
 X=Y= Cl, R=H; chlorazifop; (not commercialised)



fenoxaprop-ethyl



quizalofop-ethyl

From the outset it was of considerable interest to determine whether the herbicidal activity shown by the aryloxyphenoxypropionates was due to one or both of the enantiomers. Should the activity be due to only one enantiomer then it would be possible to use only that enantiomer as the herbicide. This would provide the opportunity to reduce application rates and to make more efficient use of the chemical building blocks.

The two individual enantiomers were separated (or separately synthesised) to allow comparison in biological tests and to allow their stability to interconversion to be studied. Independent studies were carried out by both Hoechst (Nestler *et al.*, 1979 and 1980) and ICI (Cartwright, 1979a and 1979b). Here I will concentrate on the work done within ICI. There are numerous examples of herbicidal compounds belonging to the aryloxy-phenoxypropionate group and subsequent work in other laboratories supports the results and conclusions that I will present in this paper. I will refer to the other work at the appropriate points during this review.

## PREPARATION OF THE ENANTIOMERS

### By Crystallisation

Separation of the enantiomers of an optically active acid can often be accomplished by formation of a derivative with one enantiomer of an optically active base. This creates two different species which can then be separated by standard techniques, for example crystallisation.



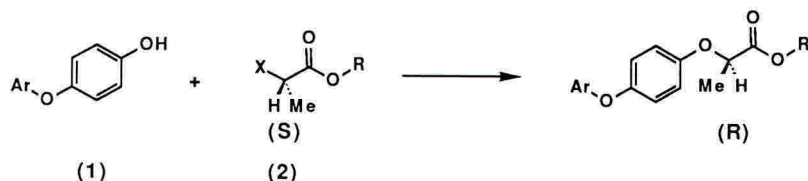
With an acid it is often most convenient to form a salt with an optically active base and to separate the two enantiomers by crystallisation. This is the approach we used with (RS)-chlorazifop. The acid was converted to its 1-(-) $\alpha$ -methylbenzylammonium salt which was crystallised repeatedly from toluene. After six crystallisations the salt was acidified to give an acid with a positive optical rotation. The acid was converted to its methyl ester using methanol with para-toluenesulphonic acid (PTSA) as a catalyst. The methyl ester obtained was examined by nmr using the optically active shift reagent praeeseodymium tris(3-D-heptafluorobutyryl)camphorate. This showed that the (+) methyl ester contained less than 1% of the (-) enantiomer. Using a similar approach, repeated crystallisation of the d-(+) $\alpha$ -methylbenzylammonium salt of (RS)-chlorazifop gave the (-) acid of similar purity which was converted to the (-) methyl ester as above without loss of optical purity.

The nmr analysis method was developed by M.R.Kipps at Jealott's Hill and has been described (Cartwright, 1979a; Sakata *et al*, 1985a). The method is very sensitive and allows the detection of less than 1% of each enantiomer. Subsequently, alternative analytical methods using HPLC have been developed (see for example Bewick, 1986 and Davy *et al*, 1987).

Similar approaches have been reported (Nestler *et al*, 1980; Sakata *et al*, 1985b) for separation of the enantiomers of diclofop and quizalofop.

#### By Synthesis

Aryloxyphenoxypropionates can be synthesised by reaction of an appropriate phenol (1) with a propionate derivative (2) where X is a leaving group such as halogen (Cl or Br), methanesulphonyloxy (MeSO<sub>2</sub>O) or para-tolylsulphonyloxy (pMeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>O). If an optically active propionate derivative is used the reaction gives the (+) or (-) propionate directly, and avoids the need to separate the two isomers by crystallisation. An inversion of stereochemistry takes place at the optical centre during the reaction so that an (S) propionate derivative gives the (R) aryloxyphenoxypropionate.



(R) and (S) propionate derivatives are readily available from natural sources. For instance (S)-(+)-lactic acid can be converted to its (S) mesyl or tosyl derivative (2, X=OSO<sub>2</sub>Me or OSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>pMe) and (R) and (S)-alanine can similarly be converted to the corresponding (R) and (S)-halopropionates (2, X=Br or Cl). Usually these reactions lead to a small amount of racemisation and this can give final products containing small amounts of the undesired isomer.

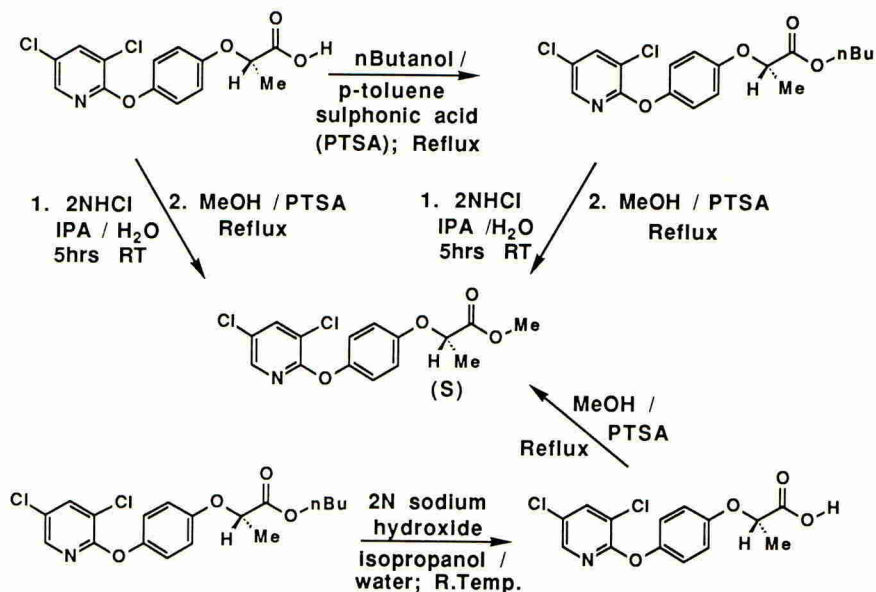
These methods were used for the synthesis of a range of (R) and (S) pyridyloxyphenoxypropionate esters, including esters of fluazifop, haloxyfop and chlorazifop (Cartwright, 1979a, 1979b). For example, reaction of methyl (S)-bromopropionate with 4-(3,5-dichloro-2-pyridyloxy)phenol gave (R)-(+)-chlorazifop-methyl. This compound was identical with the (+) enantiomer obtained by the fractional crystallisation method described above and established that the absolute stereochemistry of the herbicidal active form was (R) (in some literature the terms (D) and (L) are used rather than (R) and (S); in this particular case (R) is equivalent to (D) and (S) to (L)).

Similar synthetic approaches have been used in other laboratories for the synthesis of the (R) and (S) forms of diclofop-methyl, quizalofop-ethyl, haloxyfop and fenoxafop (Nestler, *et al*, 1979; 1980; Sakata *et al*, 1985a; Kleschwick, 1985; Foerster *et al*, 1986).

#### STABILITY STUDIES

The stability of the enantiomers of chlorazifop under acidic and basic conditions were investigated. The (R) and (S) acids were converted to their methyl and butyl ester derivatives using acid catalysis. Trans esterification of the butyl ester to the methyl ester and analysis by nmr using chiral shift reagent showed that no racemisation had occurred. Further experiments showed that treatment of both the (S) acid and (S) butyl ester with 2N hydrochloric acid in aqueous isopropanol for 5 hours at room temperature did not result in any racemisation. (S)-Chlorazifop-butyl was treated with two moles of 2N sodium hydroxide (1 molar excess) in aqueous isopropanol at room temperature for 5 hours. The ester hydrolysed to the acid which was then converted to the methyl ester for analysis. Nmr analysis showed that no racemisation had occurred. Similarly treatment of (S)-chlorazifop with two moles of 2N sodium hydroxide solution followed by conversion to the methyl ester and nmr analysis indicated that there was no loss of optical purity. Thus the enantiomers of chlorazifop and its esters are stable under acidic and basic conditions at room temperature.





## BIOLOGICAL ACTIVITY

### Post-emergence treatments

The post-emergence herbicidal activity of the arylphenoxypropionates resides largely with the (R)-enantiomer. This has now been demonstrated in many laboratories and fully reported (Cartwright, 1979a, 1979b; Nestler *et al.*, 1979, 1980; Dicks *et al.*, 1985; Barrett *et al.*, 1985; Uchiyama *et al.*, 1986; Bocion *et al.*, 1987; Gerwick *et al.*, 1988). The (R)-enantiomer is about twice as active as the (RS)-racemate and the (S)-enantiomer has little activity. Below is typical data from Dicks *et al.* (1985a) comparing the activity of (R), (S), and (RS)-fluzifop-butyl on maize. Although the (S)-enantiomer contained a small amount of the (R)-enantiomer as an impurity, the activity shown by the (S)-enantiomer could not be attributed entirely to the (R)-enantiomer present. It was not known whether the (S)-enantiomer is active *per se*, or whether it was converted to a limited extent to the (R)-enantiomer in maize. If this occurred it did so only to a small extent, which Dicks *et al.* estimated to be 6.4% based on the data in Table 1. There is no evidence for rapid or substantial enantiomer inversion in broad-leaf crops.

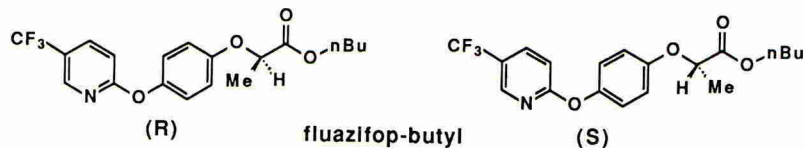


TABLE 1. Rates (g ha<sup>-1</sup>) for 50% and 90% reductions in fresh weight in maize post-emergence.

	50% ( $\pm$ S.E.)	90% ( $\pm$ S.E.)
(RS)-fluazifop-butyl	56 (3)	141 (5)
(R)-fluazifop-butyl	30 (2)	76 (3.5)
(S)-fluazifop-butyl	182 (6.5) (470)*	455 (10.5) (1200)*
(R):(RS) activity ratio	1.85	
95% confidence limits	1.53, 2.17	

\* Estimates for activity of the (S)-enantiomer alone (ie. contribution from the (R)-enantiomer contamination discounted)

No herbicidal activity was detected in post-emergence situations when the compounds were applied only to the soil. Thus 'foliar and soil' treatments were not different from 'foliar only' treatments.

#### Pre-emergence treatments

In complete contrast to the post-emergence situation the (R), (S) and (RS)-enantiomers of arylphenoxypropionates showed similar activity when applied to the soil. Results of tests have been reported (Cartwright, 1979a, 1979b; Nestler *et al.*, 1980; Dicks *et al.*, 1985; Gerwick *et al.*, 1988). Typical results for (R), (S) and (RS)-fluazifop-butyl taken from Dicks *et al.* (1985) are presented below.

TABLE 2. Pre-emergence activity of enantiomers and racemate of fluazifop-butyl (maize) - mean of replicates

Rate (g ha <sup>-1</sup> )	Visual assessments of % damage		
	(RS)	(R)	(S)
40	12	0	6
80	38	36	48
160	70	86	82
320	80	97	78
Relative activities	95% confidence limits		
(RS):(R) 0.99	0.51, 1.47		
(RS):(S) 1.02	0.58, 1.46		
(S):(R) 0.97	0.45, 1.49		

The equivalent activity shown by the enantiomers and racemate is not due to racemisation in the soil by microorganisms as first suspected (Cartwright, 1979a and 1979b; Nestler *et al.*, 1980). It is due to microbial conversion of the (S)-enantiomer to the (R)-enantiomer in the soil and will be discussed later.

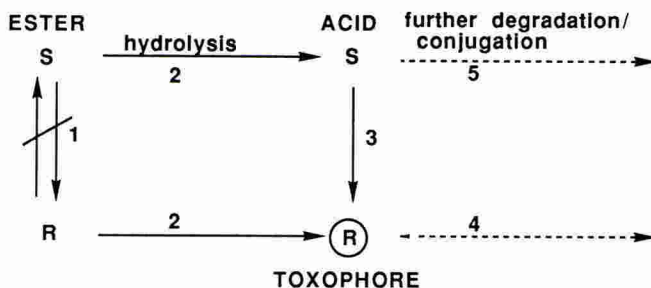
## TRANSLOCATION AND METABOLISM

Metabolic studies have shown that ester hydrolysis occurs rapidly once chemical is absorbed into plants and the acid has been implicated as the active principle (Boldt *et al.*, 1981; Shimabukuro *et al.*, 1979; Hendley *et al.*; 1985). It was shown for a range of pyridyloxyphenoxypropionates applied as the ester or acid (Hendley *et al.*, 1985) that within one day of application the majority of extracted material from plants was the acid. These results agreed with data obtained from *in vitro* experiments using *Agropyron repens* leaf homogenates in which esters of haloxyfop and fluazifop were shown to rapidly hydrolyse to the acid. In contrast the tertiary butyl ester of fluazifop was not significantly hydrolysed by the homogenates. In greenhouse tests this ester is significantly less active than the other esters.

## STEREOCHEMISTRY OF TRANSFORMATIONS IN THE SOIL

In moist anaerobic soils fluazifop-butyl is rapidly hydrolysed to fluazifop with a 'half-life' of less than 3 days. Fluazifop is further degraded with a half life of generally less than 12 weeks (Arnold *et al.*, 1982). It had been observed that although the (R)-enantiomer of fluazifop-butyl (fluazifop-P-butyl) was twice as active as the racemate in post-emergence applications the (R), (S) and (RS) forms had similar activity when applied pre-emergence. Studies have been undertaken to examine the fate of fluazifop-P-butyl and the (S)-enantiomer in the soil. It has been found (Bewick, 1986) that both (R) and (S) esters rapidly hydrolyse under aerobic conditions in moist sandy loam soil to their respective (R) and (S) acids with 'half-lives' of less than 2 hours. Interestingly, it was found that the (S) acid was then converted to the (R) acid with a 'half-life' of 1-2 days. The (R)-enantiomer retained high optical purity whether formed by inversion from the (S) acid or by hydrolysis of the (R) ester. It was found that the conversion of the (S)-enantiomer to the (R)-enantiomer did not occur in sterile soils, suggesting that the interconversion was microbially mediated. The interconversions are summarised in Scheme I (Dicks *et al.*, 1985).

SCHEME 1



1. Absent in soil and plants.
2. Rapid in soil and plant.
3. Fairly rapid in soil; absent or very slow in plant.
4. Predominant in soil; significant in plant.
5. Very limited in soil; significant in plant.

Recently it has been shown that similar effects occur with the enantiomers of diclofop-methyl, fenoxaprop-ethyl and the esters of haloxyfop (Wink *et al*, 1985; Gerwick *et al*, 1988). Further work has shown that the stereospecific inversion is due to micro-organisms present in the soil, and that the (R)-enantiomers of a range of aryloxyphenoxypropionates can be obtained by stereospecific conversion of the (S)-enantiomer using certain bacteria, cells or cell preparations (Bewick, 1985a and 1985b; Mori *et al*, 1985 and 1986).

#### BIOCHEMICAL STUDIES

Biochemical studies in various laboratories have indicated that the mode of action of aryloxyphenoxypropionates is due to the inhibition of fatty acid and hence lipid biosynthesis (Hoppe *et al*, 1985; Carr *et al*, 1985; Nakahira *et al*, 1988). Acetyl-CoA carboxylase has been shown to be the site of action of these herbicides (Burton *et al*, 1987; Walker *et al*, 1988a; Secor *et al*, 1988). Significantly it has been shown that haloxyfop inhibits acetyl-CoA carboxylase preparations from maize, but not from pea (Burton *et al*, 1987) and that diclofop and haloxyfop inhibit preparations from barley, maize and wheat, but not spinach or mung bean (Rendina *et al*, 1988). Similarly fluazifop inhibits acetyl-CoA carboxylase preparations from barley but not from pea (Walker *et al*, 1988a, 1988b). This suggests that the selectivity of the aryloxyphenoxy-propionates is at the enzyme level.

The activities of (R) and (S)-fluazifop on an acetyl-CoA carboxylase preparation from maize were also compared (Walker *et al*, 1988a). The (R)-enantiomer was very effective but no activity could be detected for the (S)-enantiomer (after allowing for the 7.5% of (R)-enantiomer present as impurity in the (S)). This may indicate that the low levels of plant activity noted for the (S) isomer of fluazifop in post-emergence tests may be due to a small amount of conversion to the (R)-enantiomer in the plant.

#### ACKNOWLEDGEMENTS

The author wishes to thank Roger Salmon and Vince Biggin for their help with compound synthesis; Martin Kipps for the NMR analyses and my colleagues whose publications I have relied upon in this paper.

## REFERENCES

- Arnold, D.J.; Poole, N.J.; Haga, T. (1982) *Abstracts of papers for the Fifth International Congress of Pesticide Chemistry, Kyoto, Japan. Vc-20.*
- Barrett, D.W.A.; Sutton, P.B.; (1985) Grass weed control in winter oilseed rape with isomers of fluzifop-butyl. *1985 British Crop Protection Conference - Weeds*, (1) 231-8.
- Bewick, D.W. (1985a) Optically active aryloxypropionic acids and their derivatives. *European Patent Publication No 133033.*
- Bewick, D.W. (1985b) Optically active aryloxypropionates and derivatives thereof useful as herbicides. *European Patent Publication No 133034.*
- Bewick, D.W.; (1986) Stereochemistry of fluzifop-butyl transformations in soil. *Pesticide Science*, 17, 349-356.
- Bocion, P.F.; Muehlethaler, P.; Winternitz, P.; (1987) Ro 17-3664, a new quinoxaline herbicide active against annual and perennial grasses in broad leaved crops. *1987 British Crop Protection Conference - Weeds*, (1), 55-62.
- Boldt, P.F.; Putman, A.R.; (1981) Selectivity mechanisms for foliar applications of diclofop-methyl. II Metabolism, *Weed Science*, 29, 237-41.
- Burton, J.D.; Gronwald, J.W.; Somers, D.A.; Connelly, J.A.; Gengenbach, B.G.; Wyse, D.L. (1987) *Biochemical & Biophysical Research Communications*, 148, 1039-1044.
- Carr, J.E.; Davies, L.G.; Cobb, A.H.; Pallett, K.E. (1985) The metabolic activity of fluzifop acid in exercised apical meristem sections. *1985 British Crop Protection Conference - Weeds* (1), 155.
- Cartwright, D; (1979a) Preparation of herbicidal 2-(4-(pyridyl-2-oxy)phenoxy)propionic acid derivatives and compounds thus obtained. *European Patent Publication No 0002925.*
- Cartwright, D; (1979b) Herbicidal pyridine compounds and compositions containing them. *European Patent Publication No 00003890.*
- Davy, G.S.; Francis, P.D.; (1987) Separation of the enantiomers of fluzifop and other 2-phenoxypropionic acids using chiral metal chelate additives in a reversed-phase high-performance liquid chromatography. *Journal of Chromatography*, 394, 323-31.
- Dicks, J.W.; Slater, J.W.; Bewick, D.W.; (1985) PP005 - The (R)-enantiomer of fluzifop-butyl. *1985 British Crop Protection Conference - Weeds*, (2) 271-280.
- Foerster, H.; Yanagi, A.; Santel, H.J.; Schmidt, R.R.; (1986) (R)-(Heterocyclyloxyphenoxy)propionic acid derivatives. *German Offenlegungsschrift 3502266.*
- Gerwick, B.C.; Jackson, L.A.; Handly, J.; Gray, N.R.; Russell, J.W.; (1988) Pre-emergence and post-emergence activities of the (R) and (S)-enantiomers of haloxyfop. *Weed Science*, 36, 453-456.
- Hendley, P.; Dicks, J.W.; Monaco, T.J.; Slyfield, S.M.; Tunnon, O.J.; Barrett, J.C. (1985) Translocation and metabolism of pyridinyl-oxyphenoxypropionate herbicides in rhizomatous quackgrass. *Weed Science*, 33, 11-24.
- Hoppe, H.H.; Zacher, H. (1985) Inhibition of fatty acid biosynthesis in isolated bean and maize chloroplasts by herbicidal phenoxyphenoxypropionic acid derivatives and structurally related compounds. *Pesticide Biochemistry and Physiology*, 24, 298-305.

- Kleschick, W.A.; (1985) Optically active esters of phenoxyphenoxypropionic acids or pyridyloxyphenoxypropionic acids. *United States Patent No 4532328*.
- Mori, H.; Yamada, S.; Kenji, K.; Tamai, K.; Yoshii, H.; (1985) (R)-4-substituted- $\alpha$ -phenoxypropionic acids. *Japanese Patent Kokai 60/120994*.
- Mori, H.; Yamada, S.; Kenji, K.; Tamai, K.; Yoshii, H.; (1986). Manufacture of optically active phenoxypropionates with bacteria. *Japanese Patent Kokai 61/1380*.
- Nakahira, K.; Uchiyama, M.; Ikai, T.; Igrashi, H.; Suzuki, K.; (1988). Mechanism of action of the herbicide quizalofop-ethyl. *Journal of Pesticide Science*, **13**, 269-76.
- Nestler, H.J.; Horlein, G.; Handte, R.; Bieringer, H.; Schwedtle, F.; Langeluddeke, P; Frisch, P; (1979) Optically active compounds, method for synthesis and use in plant protection. *European Patent Publication No 0002800*.
- Nestler, H.J.; Bieringer, H.; (1980) Synthesis and herbicidal activity of the (D)- and (L)-methyl-2-[4-(2,4-dichloro-phenoxy)phenoxy]propionate enantiomers. *Zeitschrift Fur Naturforschung*, **35b**, 366-71.
- Rendina, A.R.; Felts, J.M.; Beaudoin, J.D.; Craig-Kennard, A.C.; Look, L.L.; Paraskos, S.L.; Hagenhah, J.A. (1988). Kinetic characterisation, stereoselectivity and species selectivity of the inhibition of plant acetyl-CoA carboxylase by the aryloxyphenoxypropionic acid grass herbicides. *Archives Biochemistry and Biophysics*, **265**, 219-25.
- Sakata, G.; Makino, K.; Morimoto, K.; Ikai, T.; (1985a) Synthesis and herbicidal activity of optically active ethyl 2-[4-(6-chloro-2-quinoxalinyloxy)phenoxy]propanate. *Journal of Pesticide Science*, **10**, 69-73.
- Sakata, G.; Makino K.; Kusano, K.; Satow, J.; Ikai, T.; Suzuki, K.; (1985b) Preparation of optically pure ethyl (R)-(+ and (S)-(-) 2-[4-(6-chloro-2-quinoxalinyloxy)phenoxy]propionate by resolution method and their herbicidal activities. *Journal of Pesticide Science*, **10**, 75-79.
- Secor, J.; Cseke, C. (1988) Inhibition of acetyl-CoA carboxylase by haloxyfop and tralkoxydim. *Plant Physiology*, **86**, 10-12.
- Shimabukuro, R.H; Walsh, W.C.; Hoerauf, R.A.; (1979) Metabolism and selectivity of diclofop-methyl in wild oat and wheat. *Journal of Agricultural and Food Chemistry*, **27**, 615-622.
- Uchiyama, M.; Washio, N.; Ikai, T.; Igarashi, H.; Suzuki, K.; (1986) Stereospecific responses to (R)-(+ and (S)-(-)-quizalofop-ethyl in tissues of several plants. *Journal of Pesticide Science*, **11**, 459-467.
- Walker, K.A.; Ridley, S.M.; Lewis, T.; Harwood, J.L. (1988) Fluazifop, a grass-selective herbicide which inhibits acetyl-CoA carboxylase in sensitive plant species. *Biochemical Journal*, **254**, 307-310.
- Walker, K.A.; Ridley, S.M.; Harwood, J.L.; (1988b) The effects of the selective herbicide fluazifop on fatty acid synthesis in Pea (*Pisium sativium*) and barley (*Hordeum vulgare*). *Biochem Journal*, **254**, 811-17.
- Wink, O.; Luley, U. (1988) Enantioselective transformation of the herbicides diclofop-methyl and fenoxaprop-ethyl in soil. *Pesticide Science*, **22**, 31-40.

HOE 046360 - THE OPTICAL ACTIVE ISOMER OF FENOXAPROP-ETHYL  
FOR BROAD SPECTRUM GRASS-WEED CONTROL IN DICOTYLEDONOUS CROPS

H.P. HUFF, B. BOTTNER, E. EBERT, P. LANGELODDEKE

Hoechst Aktiengesellschaft, D-6230 Frankfurt (M), W-Germany

## ABSTRACT

Hoe 046360, the optical biologically active isomer of fenoxaprop-ethyl is described. The spectrum of biological activity and chemical and physical properties are the same as for the racemate. No significant differences were noted in the toxicological and ecological behaviour of the isomer versus the racemate. A degradation pathway is given. The amount of technical ingredient applied per hectare can be reduced to one half of the racemate.

## INTRODUCTION

In 1982 a publication of Hoe 33171 - the racemate of fenoxaprop-ethyl - was made by Bieringer et al. The molecule was presented in terms of its chemical and physical properties, toxicological and ecotoxicological data and mode of action. A survey of the biological activity demonstrated that fenoxaprop-ethyl is selective in all dicotyledonous crops:

TABLE 1: Crops shown to be tolerant to Hoe 033171  
at 1.5 kg/ha a.i. applied post-emergence

Clover	Potatoes
Beans	Soybeans
Groundnuts	Sugarbeet
Lucerne	Sunflower
Oil-seed rape	Tobacco
Peas	Cotton
Flax	etc.

The active ingredient controls the major grass weed species of economic importance.

TABLE 2: Grass weeds controlled with Hoe 033171  
0.05 - 0.25 kg/ha a.i. applied post-emergence

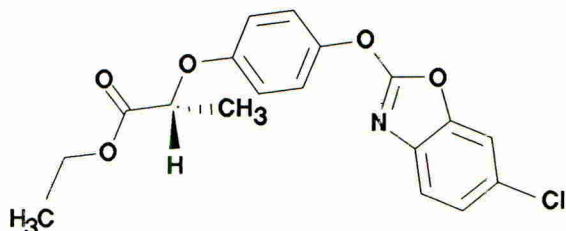
<i>Alopecurus myosuroides</i>	<i>Panicum capillare</i>
<i>Avena</i> spp.	<i>Panicum maximum</i>
<i>Brachiaria</i> spp.	<i>Phalaris</i> spp.
<i>Digitaria sanguinalis</i>	<i>Setaria</i> spp.
<i>Echinochloa</i> spp.	<i>Sorghum</i> spp.
<i>Eleusine</i> spp.	

In the laboratories of Hoechst AG Hoe 046360 was found to be the optical active (R)-isomer of the racemate fenoxaprop-ethyl.

By means of the following tests it was determined whether or not there were differences in physical and chemical properties, toxicological and ecotoxicological data. In field trials the optimal ratio of optical active ingredient in comparison to the racemate and the standard products was determined.

#### CHEMICAL AND PHYSICAL PROPERTIES

Structure and optical active point:



Common name: fenoxaprop-P-ethyl

Code number: Hoe 046360

Molecular weight: 361.8

#### TOXICOLOGICAL PROFILE OF FENOXAPROP-P-ETHYL

An important aspect of the toxicity testing with fenoxaprop-P-ethyl including acute and subchronic toxicity, embryotoxicity and mutagenicity, was to establish whether there were differences between the toxicological profile of the optical isomer and the racemate. For this reason the study protocols of the sub-chronic (4-week and 13-week) feeding studies in rats, mice and dogs and of the embryotoxicity studies in rats and rabbits with the isomer corresponded closely to the study with the racemate. This comparative toxicity testing revealed the following results:

##### Acute toxicity

Both isomer and racemate exhibited only slight toxic properties following acute treatment in rats and mice. As shown below, the LD<sub>50</sub> values of both compounds corresponded closely. In addition, the symptomatology of both compounds in the test animals was identical.

TABLE 3: Species Route LD<sub>50</sub> (mg/kg body weight)

mouse	oral	males >5000 ( 4670); females >5000 ( 5490)
rat	oral	males 3040 ( 2357); females 2090 ( 2500)
rat	dermal	males >2000 (>2000); females >2000 (>2000)
rat	inhal.	males & females >604 (>511) mg/m <sup>3</sup> air

( ) racemate values



Primary skin and eye irritation, dermal sensitisation

Both isomer and racemate proved to be slightly irritating to the skin and eye mucosa of rabbits and showed no sensitising properties.

Standard Mutagenicity

Neither isomer or racemate showed mutagenic potential in a variety of standard mutagenicity tests.

Repeated-dose and subchronic oral toxicity and embryotoxicity

Repeated-dose (4-week) and subchronic (3-month) feeding studies in rat, mouse and dog and testing for embryotoxicity including postnatal development in rats and rabbits also indicated that the isomer and the racemate had the same toxicological profile. The No Observed Effect Level (NOEL) and the Lowest Observed Effect Level (LOEL) in the studies with the optical isomer are given in the following table:

TABLE 4: No Effect Level and Lowest Effect Levels

Feeding studies:	NOEL	LOEL
(4-week) feeding study in mice:	3	12 mg/kg b.wt. per day
(4-week) feeding study in rats:	2	6 mg/kg b.wt. per day
(4-week) feeding study in dogs:	62	>62 mg/kg b.wt. per day
(3-month) feeding study in mice:	1.4	12 mg/kg b.wt. per day
(3-month) feeding study in rats:	0.8	6 mg/kg b.wt. per day
(3-month) feeding study in dogs:	15.9	81 mg/kg b.wt. per day

Embryotoxicity studies

Rat	: maternal / embryonic-foetal toxicity:	32/ 10 mg b.wt.
	: maternal / postnatal development	: 32/100 mg b.wt.
Rabbit	: maternal / embryonic-foetal toxicity:	32/100 mg b.wt.

Conclusion

When evaluating the toxicological data of the optical isomer and the racemate, it is concluded that there are no biologically significant differences between the toxicological profiles of the compounds.

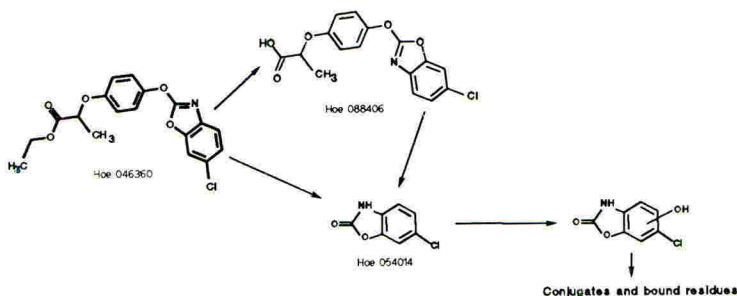
## ECOTOXICOLOGICAL BEHAVIOUR OF HOE 46360

Several plant and animal studies were performed with both fenoxaprop-ethyl and Hoe 046360 under identical conditions in order to compare their metabolic fate and degradation behaviour.

Degradation in plant and animal

Plant studies were carried out in soybeans, wheat and rice. They, in effect, show identical results for both test substances. Therefore, the metabolism of the racemate fenoxaprop-ethyl and the (R)-isomer Hoe 046360 follow the same basic steps in all investigated crops, i.e. hydrolysis of the ester to its free acid (HOE 088406) and cleavage of the benzoxazolyloxy linkage leading to the herbicidally inactive 6-chloro-2,3-dihydro-benzoxazol-2-one (HOE 054014). Moreover, hydroxylation of 6-chloro-2,3-dihydro-benzoxazol-2-one is a common reaction in all investigated crops.

Degradation-Scheme of Fenoxaprop-P-ethyl



Animal studies were carried out with rats, using dosages of 2 and 10 mg/kg. Fenoxaprop-ethyl and Hoe 046360 were both excreted rapidly. Rate and route of excretion were almost identical for both test substances, even after repeated dosing. A comparison of the metabolic pattern in the excretion of rats demonstrated clearly that the metabolic pathway for fenoxaprop-ethyl and Hoe 46360 is the same and tissue concentrations did not show any difference.

All the important plant metabolites were also identified in the rat. Therefore, the metabolic pathway in plants and animals is comparable. Furthermore, the degradation of fenoxaprop-ethyl and Hoe 046360 in soil leads to the corresponding free acid and to 6-chloro-2,3-dihydro-benzoxazol-2-one as main metabolites.

Plant and animal studies show no racemisation of the optical active Hoe 046360 or its free acid. Therefore, these compounds stay in their (R)-(+)-configuration as long as they are present.

Conclusion

There are no significant differences in the metabolic pathway of fenoxaprop-ethyl and Hoe 046360 either in plants or animals or in soil.

## BIOLOGICAL ACTIVITY

Methods and material

Field trials were carried out in Europe and North America in 1987 and 1988. The tested products were formulated as 90 g/l ec (Hoe 033171) and 75 g/l ew (Hoe 046360). The dose rates of the isomer were 60 and 50 % of that of the racemate.

The trials were randomised with a plot design using 3 - 4 replicates. The minimum plot size was 10 m<sup>2</sup>. All treatments were applied by means of air pressurized hand-carried plot sprayers using a water volume of 300 l/ha.

Visual assessment and weed counts were made to determine the herbicidal efficacy.

The crops were evaluated for vigour and injury.

TABLE 5: Comparison of a.i. ratio racemate to isomer in 1987/88  
Crops: soybeans, flax, canola in North America

g a.i./ha	% efficacy		
	racemate 80	Hoe 046360	
		40	50
Brachiaria ssp.	90 (2)	93	95
Panicum ssp.	80 (2)	86	95
Sorghum halepense	82 (5)	88	93
Setaria fabieri	99 (2)	99	99
Setaria viridis	99 (2)	99	99
Setaria lu.	86 (4)	85	94
Setaria fl.	40 (4)	50	50
Echinochloa crus-galli	77 (8)	83	95

( ) numbers of trials

No crop phytotoxicity was observed.

TABLE 6: Comparison of a.i. ratio racemate to isomer in 1987/88  
Crops: sugarbeets, oil-seed rape in Europe

g a.i./ha	% efficacy		
	Hoe 033171 (racemate) 180	Hoe 046360 (isomer)	
		90	108
Alopecurus myosuroides	94 (8)	95	95
Avena fatua	99 (5)	99	99
Echinochloa crus-galli	100 (2)	100	100
Setaria viridis	100 (2)	100	100
Volunteer barley	95 (5)	95	97

( ) numbers of trials

No crop phytotoxicity was observed with any treatment.

### RESULTS AND CONCLUSION

The results clearly demonstrate that it is possible to reduce the rate of technical ingredient for the isomer by 50 % of the racemate. This is possible on both annual and perennial grasses.

Fenoxaprop-P-ethyl (Hoe 046360) can be reduced by half of the technical ingredient compared with Hoe 033171.

### DISCUSSION

The results of the toxicological and ecotoxicological tests are essentially the same for the isomer and the racemate. The field results are demonstrate that the optical isomer is twice as active in biological tests as the racemate based on technical ingredient. This means that Hoe 046360 can completely replace Hoe 033171 without any loss of technical efficacy. A reduction of the applied amount of technical ingredient will consequently reduce any environmental burden.

### ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of other Hoechst technical and research personnel for generating and assimilating the information reported in this paper.

### REFERENCES

- Bieringer, H.; Hörlein, G.; Langelüddeke, P. and Handte, R. (1982):  
Hoe 33171 - a new selective herbicide for the control of annual and perennial warm climate grass weeds in broad-leaved crops.  
1982: British Crop Protection Conference - Weeds, 1, 11-17.
- Köcher, H.; Kellner, H.M.; Löttsch, K.; Dorn, E. and Wink, O. (1982):  
Mode of action and metabolic fate of the herbicide Hoe 33171  
1982: British Crop Protection Conference - Weeds, 1, 341-348.
- Schumacher, H.; Röttele, M. and Marrese, R.J. (1982):  
Grass weed control in soybeans by Hoe 33171  
1982: British Crop Protection Conference - Weeds, 2, 703-708.

## HOE 7113 - WORLDWIDE RESULTS ON SELECTIVITY AND GRASS WEED EFFICACY

P. HUFF, H. SCHUMACHER, H. VON OLFERS, M. BANKS

Hoechst Aktiengesellschaft, D-6230 Frankfurt (M), W-Germany

## ABSTRACT

Hoe 7113 represents a modified formulation of fenoxaprop-ethyl. As discussed in a previous paper (Bieringer et al. 1989), the addition of a new compound Hoe 070542 to fenoxaprop-ethyl allows selective control of the major species of grass weeds found in winter and spring varieties of wheat, durum wheat, rye and triticale to be achieved.

Excellent control of Avena spp., Alopecurus myosuroides, Apera spica-venti, Phalaris spp. and Setaria spp. has been demonstrated using rates of up to 180 g a.i. per ha.

Crop tolerance in all varieties tested to date of wheat, rye and triticale has proved to be very good.

## INTRODUCTION

It is widely accepted that grass weeds represent one of the most serious causes of yield reduction in cereals. Economic thresholds for Avena spp. and Alopecurus myosuroides have previously been set at just 12 plants/m<sup>2</sup> and 55 plants/m<sup>2</sup> respectively (North 1978).

Yield reductions as high as 40 % have been documented in the literature (Koch + Walter, 1983) and consequently the need for effective control is clear both from the point of view of optimising yields and in preventing seed return to the soil.

Throughout the major wheat growing areas of the world, Avena spp. is the most commonly occurring grass weed although it is common for one or more other grass weed species to be also present such as A.myosuroides (e.g. U.K., France, Germany), Apera spica-venti (Germany, Poland), Phalaris spp. (Australia, Italy, Spain, Portugal, Saudi Arabia), Setaria spp. (U.S.A., Canada, USSR), etc.

Consequently, there are strong technical advantages arising from the development of a broad spectrum grass weed product as opposed to a straight "Avenacide".

The discovery of fenchlorazole-ethyl (Hoe 070542) in the laboratories of Hoechst AG permitted the development of fenoxaprop-ethyl to take place as a selective postemergence grass weed herbicide for cereals. The mode of action of fenoxaprop-ethyl and Hoe 070542 is described by Köcher et al., 1989. Hoe 7113 is absorbed almost entirely through the leaves and leaf axils of grass weeds.

Hoe 7113 is formulated as a 60 g per litre emulsion in water formulation containing the racemic form of fenoxaprop-ethyl.

In 1985, the initial worldwide field work began evaluating crop selectivity with Hoe 7113 in order to determine the optimal dose rate by weed species, growth stage and environmental conditions.

## MATERIALS AND METHODS

Selectivity Trials

In all countries trials were conducted using rates of 180 g and 360 g a.i./ha Hoe 7113. Weed free sites were selected with 4 replications and a minimum 15 m<sup>2</sup> plot size.

Treatments were carried out at two different crop timings namely GS 13-26 and GS 27-32 (Tottman, 1987). Crops included winter and spring varieties of wheat, durum wheat, rye and triticale. Applications were made using either hand-carried or wheel-mounted boom sprayers fitted with flat fan nozzles delivering a water volume of between 100 - 300 litres/ha depending on the specific country.

Phytotoxicity to crops was evaluated at 8 and 14 days after application by means of visual ratings assessing levels of chlorosis and/or scorching and growth retardation on a percentage basis relative to the untreated controls.

Diclofop-methyl, isoproturon and flamprop-methyl were included in the trials programmes as standards.

All trials were taken to yield and harvested by means of small plot combines.

#### Efficacy Trials

The efficacy of Hoe 7113 was evaluated on commercially grown cereal crops for activity against naturally occurring weed populations. The trials were laid out using either 3 or 4 replicates and in all cases treatments were randomised. Plot sizes varied by country with the minimum size being 2 m x 5 m.

Treatments were generally carried out at three timings with the grass weeds being at GS 11-21, 22-27 and 28-32.

Application equipment, nozzles and water volumes were the same as reported under 'Selectivity Trials' above.

Efficacy assessments were generally made three times per season with all scores expressed in relation to the untreated controls. Final assessments involved recording the number of seed heads per treatment by means of 3 x 1 m<sup>2</sup> quadrats per plot. In the case of extremely high populations, visual assessments were used.

#### RESULTS

##### Selectivity

In general, little to no phytotoxicity was observed in either winter or spring wheat, durum wheat, rye or triticale. The worst individual selectivity ratings rarely exceeded 3-4 % phytotoxicity for both single and double rates and normally no phytotoxicity at all was observed.

TABLE 1

Yields of Wheat treated with HOE 7113  
in 1986 and 1987  
(Untreated = 100)

Product	g a.i./ha	Winter	Wheat Spring	Durum
HOE 7113	180	99 (48)	101 (8)	97 (22)
	360	102 (48)	100 (8)	100 (22)
Diclofop-m.	900			96 (18)
	1800		98 (8)	
IPU	1500	99 (36)	98 (8)	
Flamprop-M.	700	99 (36)		99 (10)

Treatments GS 13 - 27 a. GS 28 - 32 on weedfree plots  
( ) = number of varieties

The reported phytotoxicity can be described as minor leaf tip chlorosis which was seen some 3-4 days after application but in all cases symptoms were outgrown approximately 8 days following initial appearance.

#### Winter and Spring Wheat

Table 1 summarise relative yield scores for Hoe 7113 at 180 g a.i. and 360 g a.i./ha. There were no significant yield differences recorded for any of the varieties tested at either the early or late spray timing.

#### Durum wheat

No significant yield differences were recorded at either the single or double rates of Hoe 7113 even in the trials conducted in West Germany where relatively severe climatic conditions can often place durum wheat crops under stress (Table 1).

#### Rye and Triticale

The selectivity of Hoe 7113 has been confirmed by means of small plot and variety trials conducted in several European countries. Visual assessments revealed no significant varietal differences to Hoe 7113 at either single or double rates.

#### Efficacy

Figures 1,2,3,4 and 5 demonstrated the excellent efficacy of Hoe 7113 against the major grass weed species of importance in cereals.

Each figure represents a summary of the trials results for one or more countries where the particular weed is of importance. Treatment scores for Hoe 7113 and tralkoxydim represents an average control figure for all weed growth stages ranging between GS 11 and GS 32. For all other treatments, the control figures represent an average score only for weed growth stages falling within label recommendations for the particular product and country.

In terms of grass weed sensitivity to Hoe 7113 the order of susceptibility would rate as follows:

Increasing	↓	<u>Phalaris spp./A. spica-venti</u>
sensitivity		<u>A. myosuroides</u>
		<u>Avena spp.</u>
		<u>Setaria spp.</u>

Results documented in tables 4-8 indicate that Hoe 7113 provides either superior or equal results to the standard products tested. In all cases the rate of active ingredient required per hectare is considerably lower than the standards.

Whilst there is some fluctuation with regard to recommended rates of Hoe 7113 in the various countries (due mainly to climatical factors etc.) it can be clearly seen that there is rarely a need to exceed a rate of 180 g a.i. per ha. In fact, at this rate under good growing conditions in Europe, excellent control of both Avena spp. and A. myosuroides has been obtained with application made as late as full flag leaf emergence GS 39 (authors unpublished data).

#### DISCUSSION

Hoe 7113 has demonstrated a high degree of selectivity to all tested varieties of winter and spring wheat, durum wheat, rye and triticale. The levels of control and wide window of application against Avena spp., A. myosuroides, Phalaris spp., A. spica-venti, Setaria spp. in addition

Figure 1

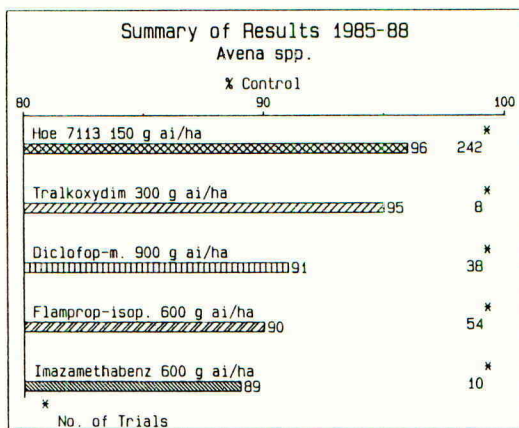


Figure 2

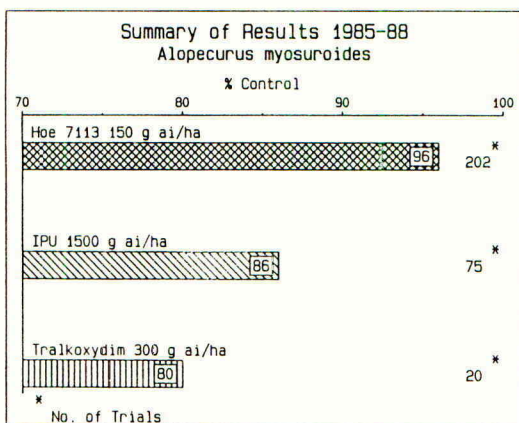


Figure 3

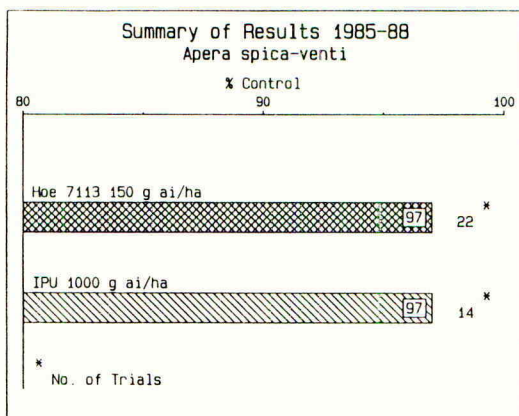




Figure 4

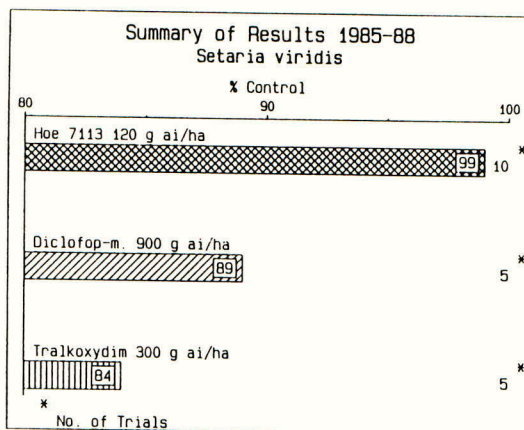
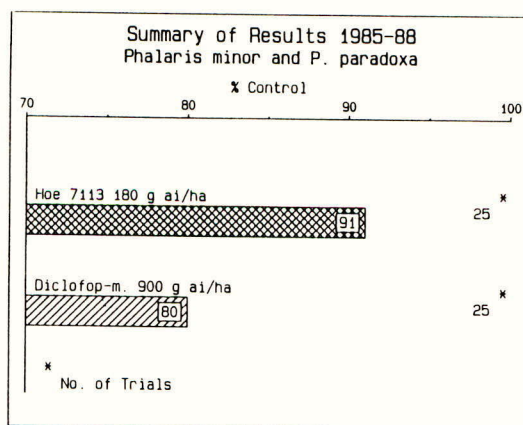


Figure 5



to other grass weed species known to be susceptible to fenoxaprop-ethyl such as Echinochloa spp., Eleusine spp. (Bieringer et al., 1982) and Poa trivialis, indicate considerable advantages in comparison to current standards.

The broad spectrum of susceptible grass weeds coupled with an extremely long period for application will mean that Hoe 7113 will allow the farmer to achieve improved standards in "one-pass" weed control through the addition of suitable broad-leaved weed products. This topic will form the basis of future publications.

#### ACKNOWLEDGEMENTS

The authors would like to thank all the farmers who co-operated in providing suitable sites as well as the numerous technical personnel of Hoechst AG and its subsidiaries involved in generating the reported data.

#### REFERENCES

- Bieringer, H., Hörlein, G., Langelüddeke, P., Handte, R. (1982):  
Hoe 33171 - a new selective herbicide for the control of annual and perennial warm climate grass weeds in broad-leaved crops.  
1982: British Crop Protection Conference - Weeds 1, 11-17
- Bieringer, H., Bauer, K., Hacker, E., Heubach, G. (1989):  
Hoe 070542 - a new molecule for use in combination with fenoxaprop-ethyl allowing selective post-emergence grass weed control in wheat.  
Brighton Crop Protection Conference - Weeds 1989
- Koch, W., Walter, H. (1983):  
The effects of weeds in certain cereal cropping systems.  
10th International Congress of Plant Protection 1983, 1, 90-97
- Köcher, H., Büttner, B., Schmidt, E., Löttsch, K., Schulz, A. (1989):  
Influence of Hoe 70542 on the behaviour of fenoxaprop-ethyl in wheat.  
Brighton Crop Protection Conference - Weeds 1989
- North, J.J. (1978):  
Pesticides in cereal production.  
Pesticide Science, 9, 234 - 239.
- Tottman, D.R. (1987); The decimal code for the growth stages of cereals with illustrations. Annals of Applied Biology 110, 441-454.

## THE EFFICACY AND CROP SAFETY OF A HERBICIDE + SAFENER COMBINATION IN CEREALS UNDER UK CONDITIONS.

D.W. CORNES, T. SCOTT, E.J. HENDERSON, P.J. RYAN

Ciba-Geigy Agrochemicals, Whittlesford, Cambridge, CB2 4QT

## ABSTRACT

CGA184927 is a new herbicide with activity against a range of grass weeds. Of particular interest in the UK is the excellent activity against Alopecurus myosuroides and Avena spp. up to at least GS 47 (flag leaf sheath opening). The mode of action is typical of the arylphenoxy-propionate graminicides widely used in broadleaved crops (e.g. fluazifop-butyl, quizalofop-ethyl). The initial activity is apparent in meristematic tissues with the subsequent death of the whole plant. The speed of action appears to be temperature related, with spring applications having the most rapid effects, although autumn applications are eventually equally effective.

Used alone CGA184927 is phytotoxic to cereal crops. However, a mixture with the herbicide safener CGA185072, allows use on all varieties of wheat, rye and triticale with the activity against A. myosuroides and Avena spp. being unaffected.

## INTRODUCTION

Alopecurus myosuroides (Blackgrass) and Avena spp. (Wild Oats) are generally regarded as being the most important grass weeds of cereal crops in the UK. A. myosuroides is predominately a weed of the heavier soils occurring throughout England although it is less common in the North. Avena spp. however are present throughout the UK.

The capacity of these species to reduce yields and to increase harvest difficulties has been described extensively, as has the need to prevent such yield losses and prevent weed seed return to the soil (Elliott, 1980; Wilson et al., 1985).

CGA184927 (2-propynyl (R)-2-[5-chloro-3-fluoro-2 pyridinyloxy-phenoxy]-propionate) + CGA185072 (5-chloro-8-quinolinoxy-acetic acid-1-methyl-hexyl-ester) is a novel herbicide and herbicide safener combination for the control of annual grass species in wheat, triticale and rye (Amrein et al., 1989). This combination is particularly effective in the control of A. myosuroides and Avena spp.

This paper presents results obtained in the UK during the 1988 and 1989 seasons.

## MATERIALS AND METHODS

Field trials were carried out on commercially grown cereal crops to determine the efficacy and safety of CGA184927 alone or in combination with CGA185072 under UK conditions.

Efficacy trials were located in fields infested with A. myosuroides and/or Avena spp. and were laid out as randomised complete blocks with three replicates and a plot size of 3 x 8m. Treatments were made using a precision plot sprayer incorporating 6 Lurmark F11002 nozzles delivering 200 l/ha at 233 kPa and a forward speed of  $1\text{ms}^{-1}$ . Growth stages at treatment, follow the decimal code (Tottman, 1987). Weed populations were evaluated using quadrat counts at application and each assessment timing.

Selectivity trials were located in crops with low or absent weed populations. Trials were of randomized complete block design with four replicates and a plot size of 3 x 12m. Visual crop damage was monitored throughout the growing season and yield data were obtained using a Claas Compact 25 combine harvester.

The chemicals evaluated in the trials were CGA184927 (100 g/l as an emulsifiable concentrate), CGA184927 + CGA185072 (100 + 25 g/l as an emulsifiable concentrate) and isoproturon (500 g/l as a suspension concentrate).

## RESULTS

Preliminary testing of CGA184927 alone resulted in severe damage to wheat and barley. This took the form of initial necrosis followed by retardation, death of individual plants and consequent crop thinning (Table 1). Addition of the herbicide safener CGA185072, to CGA184927 in these trials, using herbicide: safener ratios of 2:1 and 4:1, gave complete safening in wheat but not in barley, although in barley some safening effects were observed.

TABLE 1. Winter wheat and winter barley, visual assessment of percent crop phytotoxicity (necrosis and crop thinning) following applications of CGA 184927 + CGA 185072 (4 trials).

	Winter Wheat			Winter Barley		
	No safener	2:1 ratio	4:1 ratio	No safener	2:1 ratio	4:1 ratio
CGA 184927						
68 DAT						
75 g a.i./ha	10	0	0	70	50	40
150 "	50	0	10	80	60	50
300 "	70	5	15	90	75	70
97 DAT						
75 g a.i./ha	20	0	0	97	60	90
150 "	80	0	0	100	80	95
300 "	90	0	0	100	100	97
154 DAT						
75 g a.i./ha	0	0	0	-	-	-
150 "	60	0	0	-	-	-
300 "	80	0	20	-	-	-

Efficacy trials also carried out at this stage, showed no adverse effects on activity against A. myosuroides when CGA185072 was added to CGA184927 (Table 2).

TABLE 2. Percent control of A. myosuroides with CGA 184927 with and without CGA 185072 (mean of 2 sites based on head counts).

Treatment	g a.i./ha	% Control			
		Allopecurus myosuroides			
		DAT	30-34	91-95	195-200
CGA 184927	60		30	95	99
"	80		30	98	100
"	100		35	100	100
"	120		40	100	100
CGA 184927 + CGA 185072	60 + 30		35	90	99
"	" 80 + 40		38	97	99
"	" 100 + 50		45	100	100
"	" 120 + 60		43	100	99

Use of CGA184927 + CGA185072 was discontinued on barley and the rate of 60 + 15 g a.i./ha (4:1) was chosen for use in wheat and whilst 33 trials were carried out at a herbicide: safener ratio of 2:1, the results in this paper concentrate on the 4:1 ratio at 60 + 15 g a.i./ha respectively.

#### Autumn/winter applications

##### A. myosuroides control (Table 3)

Trials carried out in the autumn of 1988, with applications made mainly at GS 11-12, gave excellent control of A. myosuroides at 11 of the 12 sites. An assessment made in January at the one site where final control was poor showed CGA184927 + CGA185072 to be giving 97% control of the A. myosuroides plants present at application. The cloddy seedbed at this site encouraged spring germination of A. myosuroides which reduced the final level of control to 69%.

##### Avena spp. control (Table 3)

Application of CGA184927 + CGA185072 to Avena spp. gave generally good control. Germination of Avena spp. after application however reduced the final levels of control achieved at two sites, to a level below that which would be acceptable.

TABLE 3. Autumn/Winter Applications: Efficacy against A. myosuroides and Avena spp. Mean (and range) of percent control derived from head counts.

	g a.i./ha	<u>Alopecurus myosuroides</u>	<u>Avena</u> spp.
Application Period		Oct. - Dec.	Oct. - Nov.
GS at application		11 - 13	11 - 21
CGA184927+CGA185072	60 + 15	96 (69 - 100)	95 (81 - 100)
isoproturon	2500	90 (43 - 100)	85 (54 - 100)
Number of Trials		12	6
Heads per m <sup>2</sup> in the untreated		70 - 857	55 - 392

#### Spring applications

A. myosuroides control (Table 4)  
Applications of CGA184927 + CGA185072 during the 1988 and 1989 seasons gave excellent control of A. myosuroides at a wide range of growth stages, up to and including GS 37 (flag leaf emergence); however a trial carried out during 1987 gave 95% control of A. myosuroides at GS 47 (flag leaf sheath opening).

Two spring application timings were made at eight sites. At six of these sites application timing did not effect the final levels of control, which were excellent. At two sites however the early spring timing gave incomplete control (94%) due to weeds germinating after application. A later treatment applied at these sites gave complete control of A. myosuroides.

TABLE 4. Spring Application: Efficacy against Alopecurus myosuroides and Avena spp. Mean (and range) of percent control derived from weed counts.

	g a.i./ha	<u>Alopecurus myosuroides</u>	<u>Avena</u> spp.
Application Period		Feb. - May	Feb. - Apr.
GS at Application		14 - 47	21 - 37
CGA184927+CGA185072	60 + 15	98 (94 - 100)	99 (95 - 100)
isoproturon	2100	78 (33 - 98)	43 (26 - 97)
Number of Trials		22	15
Heads per m <sup>2</sup> in the untreated		215 - 916	97 - 558

#### Avena spp. control (Table 4)

Control of Avena spp. by CGA184927 + CGA185072 was excellent, with a

minimum of 95% at all sites. Growth stage at application did not affect the levels of control achieved, with excellent control being observed up to and including GS 37 (flag leaf emergence).

#### Crop safety (Table 5)

CGA184927 + CGA185072 applied in the winter or spring at the efficacy rate of 60 + 15 g a.i./ha and the double rate of 120 + 30 g a.i./ha, proved to be completely safe to winter wheat. No significant phytotoxicity or yield reductions were recorded at 14 winter wheat sites and 2 spring wheat sites harvested during the 1988 and 1989 seasons where CGA184927 + CGA185072 was applied at single (60 + 15 g a.i./ha) and double (120 + 30 g a.i./ha) rates. No crop damage was observed in the 29 efficacy trials also reported in this paper all of which were carried out in winter wheat.

TABLE 5. Winter wheat, crop yield following winter or spring application. Mean Percent yield (and range) relative to the untreated

Application Period GS at application	g a.i./ha	Nov. - Jan. 13 - 24	Mar. - Apr. 23 - 27
Untreated t/ha		6.6 (5.7 - 7.2)	7.4 (6.7 - 8.4)
CGA184927+CGA185072	60 + 15	102 (100 - 105)	103 (100 - 105)
CGA184927+CGA185072	120 + 30	104 ( 96 - 106)	103 ( 98 - 108)
isoproturon	5000	102 ( 95 - 106)	101 ( 97 - 103)
LSD (5%)		11.4 - 15.5*	9.3 - 15.6*
Number of Trials		7	3

\*No significant differences were recorded.

In three variety screens carried out in the field, during 1987, 1988 and 1989 no varietal effects were observed on thirty two varieties of winter wheat, eight varieties of spring wheat, four varieties of durum wheat, three varieties of rye and five varieties of triticale. Winter and spring barley and winter and spring oats were not tolerant of CGA184927 + CGA185072.

#### DISCUSSION

CGA184927 used alone causes severe necrosis, retardation, death of individual plants and ultimately, thinning of cereal crops. These effects are consistent with the contact and systemic action of CGA184927. The addition of CGA185072 however, produces a selective safening of CGA184927, allowing its use in wheat, rye and triticale crops, without compromising the excellent activity achieved against A. myosuroides and Avena spp.

The timing of application did not affect the final control of emerged weeds achieved by the CGA184927 + CGA185072 combination. Applications of CGA184927 + CGA185072 under both cold winter conditions

and warm late spring conditions have given excellent results against weeds at a large range of growth stages. The speed of action is however much slower in cold conditions with complete control taking up to 90 days compared with only 35-40 days in the spring.

Soil conditions at application and Kd values of the soil, whilst being of major importance for good performance of the residual herbicides currently used for control of A. myosuroides and Avena spp., are of less significance to the CGA184927 + CGA185072 combination which acts purely by foliar uptake. Soil conditions are only of importance where they promote subsequent weed germination, for example through the weathering of large clods as occurred at one site where an initial control of A. myosuroides of 97% declined to 69% due to such an effect. Due to the lack of residual activity from CGA184927 and its effectiveness under both cold and warm conditions, the optimal time of application for control of A. myosuroides and Avena spp. would appear to be from the late autumn with application possible until the late spring. CGA184927 + CGA185072 offers the potential for the early removal of A. myosuroides and A. fatua prior to the onset of yield reducing competition. However, where only spring treatment is possible or preferred, excellent control is obtained and the return of weed seed to the soil is virtually eliminated.

#### ACKNOWLEDGEMENTS

The authors would like to thank all the farmers who provided extensive assistance with field trials. The help of colleagues within Ciba-Geigy Agrochemicals was greatly appreciated.

#### REFERENCES

- Amrein, J; Nyffeler, A; Rufener, J. (1989) CGA184927 + S a new postemergence grasskiller for use in small grain cereals. Proceedings 1989 Brighton Crop Protection Conference - Weeds 1.
- Elliott, J.G. (1980) The economic significance of weeds in the harvesting of grain. Proceedings 1980 British Crop Protection Conference - Weeds 3.
- Tottman, D.R. (1987) The decimal code for the growth stages of cereals, with illustrations. Annals of Applied Biology, 110, 441-454.
- Wilson, B.J; Thornton, M.E; Lutman, P.J.N. (1985) Yields of winter cereals in relation to the timing of control of blackgrass and broadleaved weeds. Aspect of Applied Biology 9. 41-48.



## WEED CONTROL UNDER PLASTIC CROP COVERS

A J GREENFIELD

ADAS, Oxford Divisional Office, Marston Road, New Marston, Oxford, OX3 0TP

## ABSTRACT

The area of crops grown under low level film covers has increased dramatically over the past decade, now standing at an estimated 8000 ha of mainly vegetables in the United Kingdom. Few herbicide manufacturers make recommendations for the use of their products on such crops, and the growers involved generally use herbicides in the same way as for open grown crops. Trial work that has been carried out over the past few years on specific crops is summarised, and some of the effects of the crop covers on herbicide activity and persistence are discussed.

## INTRODUCTION

In the season 1988/1989 an estimated 8000 ha of vegetable crops were grown under a number of different types of film plastic crop covers in the United Kingdom. These covers are used mainly to advance crops early in the season, but will also aid crop continuity, protect crops from pest attack and from damaging weather conditions, extending the harvesting period into the autumn and aiding over-wintering, (Jones 1984, Antill 1987). Such conditions that are produced under the cover however, as well as being to the advantage of the crop will also be advantageous to weed growth. Indeed for non competitive crops, experience has shown that uncontrolled weeds can very easily swamp the crop, reducing its growth and eventual yield. The economically acceptable control of weeds is therefore widely acknowledged as an absolute requirement if optimum advantage is to be made of these crop covers.

Originally growers who made use of this technique of crop covering, extrapolated directly from their knowledge of the use of herbicides on the same crop grown in the open, using the same herbicides, mainly at the same application rates. No manufacturer until 1988 had any recommendation for the application use of any product on crops covered by plastic film, and to date only 2 manufacturers in Britain have such a recommendation for herbicides containing linuron, monolinuron and metribuzin. It is impossible to predict whether further manufacturer's recommendations are likely and what exactly might be the implications in the United Kingdom of the Control of Pesticide Regulations 1986. It does seem likely however, that some note will be taken by the Pesticide Registration Authorities of differences in crop, soil and herbicide interactions, when approval applications are dealt with.

Cover Types

Several manufacturers produce plastic sheets of various types which are used as crop covers. The majority of the covers are of clear polythene sheeting often, though not invariably perforated by holes of 1 cm diameter at a frequency of 200 or 500 holes per sq m. Historically

sheets were perforated by very closely spaced slits which would allow the sheet to expand greatly as a result of pressure from the crop below, thus forming a net-like cover. This type is now largely discontinued, not least because of the cost, and has been superseded by the non expanding types. As well as the solid plastic sheets whether perforated or not, a high and increasing percentage of the covers used are of non woven, fabric like materials. One advantage of these is that they are permeable to water, and may make irrigation of crops, should it be necessary, more easy to manage. It may also allow some herbicide application through the sheet.

### Crops

In the United Kingdom the major crops covered with film are carrots and potatoes, accounting for over 35% of the total covered crop area, with approximately 2,000 ha and 1,000 ha respectively. The various members of the brassica crops account for the next most important group, with an estimated 1,600 ha of cabbage, cauliflower, calabrese and Chinese cabbage being covered. Many other minor crops are also covered but the areas are less certain, as data from crop census in the UK does not differentiate between covered and uncovered crops.

TABLE 1. Estimated Area (hectares) of Crops Covered in the United Kingdom

Crop	1982	1985	1988	1989
Carrots & Parsnips	50	1200	2500	2000
Potatoes	200	1000	1400	1000
Sweetcorn	200	350	500	500
Lettuce/Celery	60	390	700	700
Brassicac	-	300	1200	1600
Cucurbit & Beans	50	175	450	500
Root Crops (others)	-	60	300	300
Miscellaneous Crops (onions, leeks, herbs tomatoes, spinach)	20	75	250	500
Areas covered specifically for weed control, storage or seed beds	20	90	600	800
Over-wintered Crops	-	75	100	100
TOTAL	600	3715	8000	8000

### Herbicide Usage

As is sometimes the case with new crop growing techniques, commercial practice can overtake technical information and recommendations that are available from scientifically executed experiments. In the few years since crop covers came into use in the United Kingdom some trial work has been carried out related to specific crops, and a small amount of basic work has been carried out investigating the behaviour of herbicides under

plastic covers. A survey summarised by the author carried out on covered crops in 1988 showed that potatoes were most often treated with linuron, monolinuron or terbutryne plus terbuthylazine; carrots with linuron; brassicas with propachlor plus chlorthal-dimethyl; and onions with chloridazon plus chlorbufam or propachlor plus chlorthal-dimethyl, chlorpropham or pendimethalin.

#### HERBICIDE TRIALS AND RESULTS

In trial work carried out in the UK up to 1987 growing season it has been shown that whilst for some crops the recommended herbicide treatments for uncovered crops are both effective and safe eg trifluralin plus linuron for carrots, in other crops this was not so, and whilst no crop damage may have occurred, weed control was not always commercially acceptable. In some cases the use of treatments not approved under the Control of Pesticide Regulations 1986 gave the best results eg propyzamide plus propachlor, tank mixed and applied post planting but pre covering to iceberg lettuce (Antill 1987).

Further trial work has been carried out since that time, investigating some of those crops reported on, and also introducing other crop/herbicide combinations.

##### 1. Runner Beans - Weed Control on Mulched Crop - Efford EHS 1987

Trials have compared various pre-emergence herbicide treatments and soil sterilisation under clear mulches with light inhibiting mulches. Beans were sown through the mulches in mid April, following application of treatments and laying of plastic sheets. Promising results were gained from some of the treatments not approved in the UK at the present time.

Diphenamid + chlorthal-dimethyl treatments were successful on their own and in conjunction with a low rate of pendimethalin, giving acceptable weed control, crop growth and yield. Terbutryn + terbuthylazine gave excellent weed control but unacceptable damage and reduced yield. Black plastic mulch, with and without a clear plastic crop cover gave acceptable weed control but yields were reduced, particularly early in the season.

TABLE 2. Runner Bean Trial - Efford EHS 1987

Treatments as rates a.i/ha	Weed Control 1-no control 9-total control	Growth Crop 1 poor 9 good	Total Yield t/ha
Under clear polythene mulch			
dazomet-220kg	4.0	3.7	4.1
diphenamid + chlorthal dimethyl 6 kg + 8 kg	5.3	6.7	5.4
diphenamid + chlorthal dimethyl 7.5 kg + 11.25 kg	5.0	5.3	5.0
pendimethalin - 0.66 kg	3.0	5.7	4.7
pendimethalin - 0.99 kg	4.3	6.7	5.2
pendimethalin - 1.32 kg	5.7	6.3	5.1
control - no herbicide	1.7	4.0	3.1
diphenamid + propyzamide 4.5 kg + 1.125 kg	4.0	7.0	4.5
diphenamid + chlorthal dimethyl + pendimethalin 4.5 kg + 4 kg + 0.66 kg	6.3	6.0	5.2
terbutryne + terbutylazine 0.7 kg + 0.3 kg	5.3	3.0	2.7
Under black polythene mulch			
no cover	6.0	5.3	3.9
clear polythene cover	6.0	6.7	4.5

## 2. Iceberg Lettuce - Herbicides under Film Cover - Efford EHS 1987

Pre planting soil sterilisation applied at two timings, was compared with post planting herbicide treatments both in uncovered crops and crops covered with non woven, porous sheets. The variety Saladin was sown on 26 February into 3.1 Hassy trays. Propagation followed standard commercial practice. Polythene sheeting was removed on 14 April from sterilised plots and cultivation carried out following fertiliser application. Planting took place on 15 April, post planting treatments were applied and irrigation given for establishment. The crop covers were laid on 16 April, and further irrigation given on 21 April.

Dazomet gave best weed control and heaviest head weights on the covered plants, but was less consistent on the uncovered crop. The post planting tank mix of propyzamide + propachlor gave better weed control than propyzamide alone, but reduced mean head weights.

TABLE 3. Iceberg Lettuce Trial - Efford EHS 1987

Treatments as rates a.i/ha	Weed Control 1-9		Head Wt (g)	
	Crop cover	Bare soil	Crop cover	Bare soil
dazomet (Dec) 220 kg	8.7	9.0	614	565
dazomet (Feb) 220 kg	8.7	8.8	653	664
propyzamide 1.4 kg	5.7	6.2	592	595
propyzamide + propachlor 0.7 kg + 2 kg	7.3	5.7	537	563
control - no herbicide	2.3	2.0	512	533
SED (5%)	0.51		34.7	

### 3. Courgettes - Weed Control for Early Production with Plastics - Efford EHS 1987

Soil sterilisation was applied in the autumn and compared with pre planting or post planting herbicides, and with light inhibiting mulches, for both direct seeded and transplanted crops.

TABLE 4. Early Courgettes - Efford EHS 1987

Treatment rates of a.i/ha	Weed control 1-9	Early Yield	Total Yield
Clear mulch:			
dazomet 220 kg			
field drilled	4.5	4	17
transplanted	7.5	8	25
Perforated polythene cover:			
diphenamid + chlorthal dimethyl 4.5 kg + 6.75 kg pre planting	2.8	1	10
diphenamid + chlorthal dimethyl 3 kg + 4.5 kg post planting	3.0	4	18
control - no herbicide:	2.5	6	21
Black polythene cover:			
low polytunnel	8.0	6	22
non woven porous cover	7.8	6	22

Dazomet and black plastic mulches were the only treatments giving acceptable weed control. The diphenamid + chlorthal dimethyl pre planting caused more damage than post planting, but neither treatments gave acceptable results.

4. Early Summer Cauliflower - Use of Herbicides under Polythene covers - Kirton EHS 1988

Seven herbicide treatments and a control, hand weeded to avoid weed competition effects, were compared on a crop of early summer cauliflower raised in a standard manner in Hassy 308 cellular trays or 6 cm peat blocks, shown in October 1987 and transplanted early April. Pre planting herbicides were applied immediately before planting; pendimethalin was applied to the soil surface; trifluralin was applied to the soil surface and incorporated according to the product recommendations using a rotary harrow. Post planting herbicides were applied immediately after planting and crop covers of perforated polythene laid. Polythene was removed after 6 weeks.

TABLE 5. Early Summer Cauliflower - Kirton EHS 1988

Treatment rates of a.i/ha	% Weed cover		Marketable yield (crates/ha)
	20 May	7 June	
propachlor + chlorthal dimethyl 4.5 kg + 2.25 kg	7	38	2304
pendimethalin + propachlor 0.99 kg + 4.5 kg	6	25	2244
trifluralin + propachlor 1.1 kg + 4.5 kg	2	6*	2376
metazachlor + chlorthal dimethyl 0.75 kg + 4.5 kg	10	45	2475
pendimethalin + metazachlor 0.99 kg + 0.75 kg	10	55	2007*
propachlor + tebutam 4.5 kg + 2.88 kg	5	11*	2172
trifluralin + tebutam 1.1 kg + 2.88 kg	4	8*	2321
control (hand weeded after 20 May count)	95	40	2376

\*Denotes significant difference at 5% level from control

Treatments which included trifluralin or tebutam all gave good weed control; other treatments were all poor by 7 June. Only the pendimethalin + metazachlor treatment gave any significant difference in yield from the control, though there were some differences in quality, with trifluralin + tebutam causing more bracting, but fewer loose heads.

5. Leeks - Evaluation of Herbicides on Transplanted Crop under Crop covers - Luddington EHS 1987/1988

Seven herbicide treatments and a control were compared on leeks sown between mid December and mid February and planted late April or early May. Herbicide treatments were applied post planting and perforated polythene crop covers laid immediately after. Polythene covers were removed after 3 weeks in 1987 and 4 weeks in 1988.

TABLE 6. Transplanted leeks - Luddington EHS 1987 and 1988

Treatment rates as a.i/ha	Total yield (tonnes/ha)	
	1987	1988
chlorbufam + chloridazon		
0.9 kg + 1.125	19.5	22.6
monolinuron 0.84 kg	20.7	23.4
prometryne 1.15 kg	18.2	22.1
propachlor + chlorthal dimethyl		
4.5 kg + 4.5 kg	21.9	24.3
propachlor + pendimethalin		
4.5 kg + 0.66 kg	21.7	22.1
propachlor + chloridazon		
4 kg + 0.86 kg	18.9	22.5
propachlor + chlorpropham		
4.5 kg + 3.36 kg	19.6	22.6
control	17.6	23.7
LSD 5%	1.97	NS

Propachlor + chlorthal dimethyl or pendimethalin gave the highest yields in 1987, but there were no significant differences in 1988. Control plots were significantly weedier than the herbicide treatments, between which there were no significant differences.

6. Comparison of Herbicides for Film Covered Crops of Celery. Arthur Rickwood EHF 1988

This Horticulture Development Council sponsored trial investigated 2 application methods of 2 herbicides on transplanted celery grown under a non woven porous crop cover, in particular investigating the feasibility of spraying foliar active herbicides through the cover. This method of application could be useful on organic soils where soil acting residual herbicides are less effective, thereby avoiding the need to remove sheets when applying herbicide. The crop was sown on 29 January and raised in a standard manner in Hassy 104 cellular trays. Planting took place on 11 April and herbicides were applied where appropriate. The crop cover was either laid immediately, or on plots where herbicides had been applied after a delay of one day. The treatments through the film cover were applied on 5 May at first emergence of weed seedlings. Covers were removed at the end of May and a further herbicide applied to the appropriate treatments.

TABLE 7. Celery - timing and application methods - Arthur Rickwood EHF 1988

Herbicide Treatment Rates in kg a.i./ha	% Weed cover	
	2 June	28 June
<u>At planting</u>	<u>Through cover</u>	<u>Post uncovering</u>
Control - hand weeded		0      1
prometryne 1.15		linuron 1.1      100      6
linuron 1.1		prometryne 1.15      100      25
	prometryne 1.15	57      19
	linuron 1.1	53      21
prometryne 1.15		prometryne 1.15      100      15
linuron 1.1		linuron 1.1      100      3
	prometryne 1.15	prometryne 1.15      37      18
	linuron 1.1	linuron 1.1      18      9
Control - non weeded		100      -

The best weed control early was where herbicides were sprayed through the crop cover, all other treatments were similar. At the later assessment the differences were not significant and Galium aparine which was not controlled by either herbicide had become dominant. No significant yield differences were seen between any treatment.

#### PERSISTENCE AND ACTIVITY OF HERBICIDES UNDER COVERS

The use of plastic film cover over the soil and crop will alter the environment in which the herbicide is to work. Temperatures and water movement in the soil will be affected, and these in turn will affect crop and weed growth. The changed environment can also have a direct effect on the herbicide movement and breakdown with possible increased volatility and the dry soil surface under the polythene reducing its activity. Soft crop growth under the sheeting may also increase the susceptibility of crop, as well as weeds, to contact herbicides applied immediately after removal of the sheet (Antill 1987), necessitating great care when using these products.

It has also been shown that residues of herbicides can remain longer in the soil when covered, and as increased temperatures will accelerate breakdown, it is assumed that the longer persistence is largely a result of reduced moisture levels and water movement under the covers (Bond and Walker 1989). Such increased persistence, could lead to higher chemical residues in crops, and therefore must be evaluated for this use by the Registration Authorities.

#### CONCLUSIONS

Whilst our knowledge of the use of herbicides under plastic crop covers is increasing, many crops have yet to be investigated in comparative experimental work. So far little work has been completed



investigating basic effects that the covers have on the environment beneath or on the manner in which this may effect the activity, movement and persistence of herbicides. Few herbicide manufacturers are likely to look seriously at the problem, and the pesticide approval and Registration Authorities may require further information relating to efficacy persistence, and chemical residues in crops, before approving such uses.

## REFERENCES

- Antill D.N. (1987) Problems of herbicide use on field grown vegetables under low level plastics. Proceedings 1987 British Crop Protection Conference - Weeds 2 617-624
- Bond W. & Walker A. (1989) Aspects of herbicide activity and persistence under low level polythene covers. Annals of Applied Biology 114, 133-140.
- Jones S (1984) Plastic film covers for vegetable production ADAS Booklet No. 2434 MAFF Publications.

## HERBICIDE GRANULES - REVUE OF PROCESSES AND PRODUCTS

G A BELL

ICI Agrochemicals, Formulation Process Department, Yalding,  
Kent, ME18 6HN

## ABSTRACT

The five major methods of forming granules are described. The methods are compared with regard to process ease and product quality.

Some examples of currently available products are given.

INTRODUCTION

Safety was the driving force which led to the introduction of "Weedol" (paraquat) and "Pathclear" (see below) granules in the early sixties. Although there are now many commercially available granules, and indeed most Agrochemical manufacturers now market them, the formulation type has failed to displace earlier types such as wettable powders, suspension concentrates and emulsion concentrates. The reason for this is probably economic as granules are more expensive to manufacture. However, safety issues are becoming more important and it seems likely that granules, which are dry, non dusty and do not contain solvents, will become a more dominant formulation type in the future.

The main advantages of dispersible granules over wettable powders, suspension and emulsion concentrates are:

Spillages easy to deal with without loss

No splashes

Low dermal toxicity

Non dusty

Easy to pour and measure

No long term stability problems

Protection against frost not necessary

Low residue left in packaging, which can be simple and cheap

Attractive uniform presentation

There are currently five basic types of granulation process:

Extrusion granulation

A powder mix and water are combined to form a paste which is extruded through a mesh screen with holes of about 1 mm diameter. The water content of the paste is 10 to 30% and the various ingredients can be dry milled or presented as liquids,

suspensions or solutions. A variety of extruder types are available, with selection depending on the required compaction, the rheology of the paste used, etc. After extrusion the granules can be dried either by using heat, or by designing a curing system into the formulation.

Examples of this type of formulation are:

"Pathclear" - (25 g/kg paraquat, 25 g/kg diquat, 50 g/kg simazine, 30 g/kg aminotriazole) ICI Agrochemicals.

"Atradex 900 WDG" (900 g/kg atrazine) Agtech Developments (NZ) Ltd

#### Pan granulation

A powder blend is fed onto an inclined rotating dish. Water or a solution is sprayed onto the powder which rolls and agglomerates into spherical granules. A take off removes the granules when they get to the desired size which is usually 2-4mm diameter. This method is popular in the USA and Canada where there are many contract manufacturers which have adapted the technology used for coal and steel granulation.

Examples of this type of granule are:

"Aatrex Nine- 0" (900 g/kg atrazine) Ciba-Geigy Corporation, USA

"Princep Caliber" (900 g/kg simazine) Ciba-Geigy Corporation, USA

"Sencor Sprayule" (750 g/kg metribuzin) Mobay Corporation, USA

#### Spray drying

A fine aqueous dispersion of the active ingredient is pumped to a nozzle at the top of a large spray drying tower. The resultant droplets are dried as they fall through a current of hot air. The size of the granules is usually 200 - 500 um.

This process is suitable for high tonnage, continuous production of one active ingredient. It is particularly suitable when the initial dispersion can be produced in situ during synthesis.

Examples of this type of granule are:

"Dicurane 75 Solurapide" (750 g/kg chlorotoluron) Ciba-Geigy AG, Switzerland

"Gesaprime 90 Solurapide" (900 g/kg atrazine) Ciba-Geigy AG, Switzerland

A/S Niro Atomiser, Denmark, market a multi-stage drier which combines spray drying at the top of the tower with fluid bed agglomeration at the bottom.

#### Fluid bed granulation

This granulation can be carried out in two different ways:

##### Agglomeration

A powder blend is fluidised by hot air and agglomerated by spraying a binder solution into the bed. Granules of 1-2mm diameter are produced.

DuPont, USA, are though to be using this process for "Lexone DF" (750 g/kg metribuzin).

##### Spray coating

A fine aqueous dispersion of the active ingredient plus dispersing agent is sprayed into a bed of inert water soluble particles which are fluidised by hot air. Coated particles of 0.5-2.0 mm diameter are produced.

At the present time there do not appear to be any commercial products of this type. However ICI used to product "Super Verdone" (2,4-D, dicamba and ioxynil) by this method.

#### Mixing or High shear Agglomeration

Water or a solution are sprayed onto a powder blend which is being kept in motion by mechanical means.

Various devices are available such as pin mixers and matrix mixers. In recent years the Shugi Flexomixer originally marketed by Schuurmans and Van Ginneken of the Netherlands has been used commercially. Powder is fed to the top of the Shugi mixer where it is carried down in a turbulent airstream as liquid is sprayed through radial nozzles. The atomised liquid is distributed through the solid particles and it is claimed they are en-robed in particles of powder (the so called "crumbing effect"). The irregular shaped granules are dried and the required offtake sieved out.

Various devices are available such as pin mixers and matrix mixers. In recent years the Shugi Flexomixer originally marketed by Schuurmans and Van Ginneken of the Netherlands has been used commercially. Powder is fed to the top of the Shugi mixer where it is carried down in a turbulent airstream as liquid is sprayed through radial nozzles. The atomised liquid is distributed through the solid particles and it is claimed they are en-robed in particles of powder (the so called "crumbling effect"). The irregular shaped granules are dried and the required offtake sieved out.

Shell UK used to make "Envoy" (110 g/kg cyanazine and 540 g/kg MCPA) by this method.

#### CHOICE OF A GRANULATION PROCESS

Granulation has been used in other industries before it was applied to agrochemicals. Most manufacturers seem to have used the processes they had experience of, and this probably explains the diversity of production types in use.

Several factors are normally taken into account when deciding which type of plant to use:

- a) The physico chemical properties of the powders and liquids used in the formulation. Spray drying for example would not be recommended for a heat sensitive active ingredient. Fluid bed granulation would not be ideal if the powders were difficult to fluidise.
- b) Availability of plant and expertise. Known technology is usually seen as being less of a risk than new. Change is often brought in only where problems have forced it. Production plant is expensive and it is often difficult to justify new purchases.
- c) Environmental aspects. Highly toxic or irritant dusts may need to be contained and considerations such as the size of recycle loops and the volumes of air used can be important. Spray driers and fluid bed granulators both form and dry the granules in one step. They can also be specially designed for dust containment.

A general comparison of the five basic processes is given in Table 1.

TABLE 1. Comparison of granulation processes

Method	Product	Plant	Restrictions	Comments
Extrusion	Hard compact granules	Optional size easy scale up small recycle	Suitable for heat sensitive materials	Versatile
Pan	Spherical usually soft	Optional size scale up small recycle.	Suitable for heat sensitive materials	High operator skill required
Spray Drying	Small spheres like coarse powder	Large scale only small recycle	Not for heat sensitive materials	Large air throughout
Fluid bed	Uniform spheres optional size	Optional size easy scale up small recycle	Suitable for materials of M.P. > 80C	Large air throughout
Schugi	Irregular shaped granules	Large scale only large recycle	Suitable for heat sensitive materials	

#### PROPERTIES OF DISPERSIBLE GRANULES

Granule quality depends as much on formulation expertise as it does on the equipment used. CIPAC are working on a model specification for water dispersible granules but at the present time there are no agreed physical test methods for these formulations. The following properties are examined by ICI Agrochemicals.

## Suspensibility

Standard CIPAC method as for wettable powders (Raw, G.R.)

## Disintegration time

5 g of granules in 500 ml of CIPAC D hard water at 20 C and stirred at a fixed agitation rate. Method under review.

## Friability

50 g of granules are rotated end over end for 45 minutes in a 9 inch stainless steel tube. The amount of dust produced is determined by sieving through a 60 mesh sieve.

## Sieve residue

Method under review. 30 g of granules are dispersed in water and passed through a 100 mesh sieve. The retained fraction is washed until the water passing through is clear, then the residue is dried and weighed.

## Dustiness

A commercially available dust tester supplied by Heubach GmbH of West Germany is used. Method under review.

## Storage stability

Samples are stored at 10, 25, 37 (or 40) and 50 C (or 54) and tested for chemical and physical changes, notably for caking and for changes in disintegration or sieve residues.

A list of herbicidal granules is given in Table 2. In general spray drying and fluid bed granulation tend to give fast disintegrating granules whereas extrusion produces harder, slower dispersing ones. Nevertheless this is by no means a set rule and product quality tends to depend on the nature of the active ingredient and the abilities of the design chemist.

## GRANULATION PROCESS CONSIDERATIONS

The decision to manufacture a granule formulation should be taken with the following points borne in mind.

- Product cost will be higher than for SCs or WPs
- May require capital expenditure
- Formulation may be sensitive to process and raw material variables.
- Requires skilled operators
- Need to recycle off-size or out of specification material
- Tighter control of toxic dusts
- Need to educate the consumer in proper use

In addition to these factors the selection of a suitable process should take account of existing expertise within the company, and likely future requirements. If product improvement or new products are envisaged then process flexibility and the availability of semi-technical or pilot plant scale equipment will be necessary. Product quality can be measured by simple physical tests but this has to be balanced with the requirements of the end user. It is easy to base calculations on cost grounds, and these, along with physical test measurements are the normal basis for process selection. It is more difficult to assess ease of manufacture, and the costs which arise from time and effort expended developing existing or new products.

An examination of Table 2 shows that atrazine WG's are produced by several different methods. Extrusion and spray drying provide very fast dispersing granules, whereas pan or Shugi granulation are slower. As far as the farmer is concerned these differences may be less important than the cost of the product. Granulation of atrazine is straightforward because the active ingredient has suitable physical properties. Process selection is more difficult when the active ingredient is highly toxic, irritant, unstable is a liquid or has heat stability problems. Comparison of physical test results for different granules must therefore be made very carefully.

## REFERENCES

Raw, G.R. (1970) CIPAC Handbook. Published by W Heffer and Sons Ltd.



TABLE 1. Several commercial water dispersible granule products.

Productname	ActiveIng	Man.	Process	Dispersion (sec)
Aatrex nine o	atrazine	1	pan	120
Gesaprime 90 solurapide	atrazine	2	spray	40
Princep caliber	simazine	1	pan	90
Lexone 75 DF	metribuzin	3	fluid bed	40
Lorox DF	linuron	3	fluid bed	45
Glean 75 DF	chlorsulfuron	3	pan	70
Finesse	chlorsulfuron + metsulfuron methyl	3	fluid bed	100
Bladex 90 DF	cyanazine	4	pan	110
Griffex 9 DF	atrazine	5	pan	60
Sencor DF	metribuzin	6	pan	85
Sencorex	metribuzin	7	fluid bed	50
Goltix	metamitron	7	spray	15
Atradex 900 WDG	atrazine	8	extrusion	30
Simadex 900 WDG	simazine	8	extrusion	30

- 1 Ciba-Geigy Corporation, USA
- 2 Ciba-Geigy AG, Switzerland
- 3 E I DuPont de Nemours and Company, USA
- 4 Shell Oil Company, USA
- 5 Griffin Corporation, USA
- 6 Mobay Corporation, USA
- 7 Bayer AG, FRG
- 8 Agtech Developments (NZ) Ltd