THE IMIDAZOLINONE HERBICIDES

R. PAXMAN¹, A.M. ANNAND², S.C. LEE³,
P.L. ORWICK⁴ and T.R. PEOPLES⁴

¹Cyanamid (N.Z.) Ltd, Private Bag, Onehunga, Auckland

²Cyanamid Australia Pty. Ltd, Baulkham Hills, N.S.W. Australia

³Cyanamid International, Singapore

⁴American Cyanamid Co., Princeton, N.J., U.S.A.

SUMMARY

Four imidazolinone herbicides are currently under development by American Cyanamid Company. Imazapyr (AC 252,925, ARSENALTM) is a broad-spectrum post-emergence herbicide with residual activity for use in non-cropland areas. AC 222,293 (ASSERTTM) is a selective post-emergence herbicide with residual activity for control of wild oats (*Avena fatua* or *Avena sterilis* spp *ludoviciana*), blackgrass (*Alopecurus myosuroides*), and several important broadleaved species. Imazaquin (AC 252,214, SCEPTERTM) and AC 263,499 are selective broad-spectrum herbicides with residual activity that can be either soil- or foliar-applied. Soybeans are the major market targeted for imazaquin while AC 263,499 has shown selectivity in leguminous crops such as lucerne, clovers, beans (*Phaseolus* spp. and *Vicia* spp.), peas, soybeans, and peanuts.

INTRODUCTION

The imidazolinones are a new class of herbicides discovered by scientists at American Cyanamid Company, Princeton, N.J., U.S.A. (Los *et al* 1982, 1983, 1984; Cross *et al* 1983). These herbicides have a broad spectrum of weed control, with activity against both monocotyledonous and dicotyledonous weeds. They can be absorbed either by foliage or roots and are translocated systemically within weeds. Several members of the new class have demonstrated selectivity within major crops. From this class of herbicides, imazapyr, AC 222,293, imazaquin, and AC 263,499 are currently being developed globally by American Cyanamid and its subsidiaries (Kirkland and Shafer 1982; Orwick *et al* 1983a, 1983b; Malefyt *et al* 1984). This paper presents an overview of these products and their uses.

CHEMICAL AND PHYSICAL PROPERTIES

Chemical Names

Imazapyr	2- 4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 <i>H</i> -imidazol-2-yl-3-pyridinecarboxylic acid
AC 222,293	<i>m</i> -toluic acid, 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester and <i>p</i> -Toluic acid, 2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-, methyl ester
Imazaquin	2- 4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 <i>H</i> -imidazol-2-yl-3-quinolinecarboxylic acid
AC 263,499	2- 4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 <i>H</i> -imidazol-2-yl-5-ethyl-3-pyridinecarboxylic acid

CHEMICAL STRUCTURES

Proc. 38th N.Z. Weed and Pest Control Conf.

Herbicide

Where R equals

Imazapyr

AC 222,293

Imazaquin

AC 263,499

Toxicology

All four herbicides have a low level of acute mammalian toxicity. All have an oral LD₅₀ to rats of >5000 mg/kg b.w. and a dermal LD₅₀ to rabbits of >2000 mg/kg. Imazapyr, AC 222,293, and AC 262,499 are reversible eye irritants in rabbits. Imazaquin is non-irritating to the rabbit eye. Imazapyr, imazaquin, and AC 263,499 are mildly irritating to rabbit skin while AC 222,293 is a non-irritant. All are non-mutagenic in the Ames test. Tests on fish and wildlife have shown that imazapyr, imazaquin, and AC 22,293 present no hazard to non-target species. Fish and wildlife tests on AC 263,499 are in progress. Rat metabolism studies with each herbicide using ¹⁴C-labelled material have indicated low potential for residual accumulation in tissues or blood because of rapid excretion in urine and faeces.

Mode of Action

The imidazolinones are absorbed by the roots and foliage of plants and translocated in the xylem and phloem, with accumulation in the meristematic regions. With foliar application, susceptible weeds stop growing soon after treatment and die within 2 to 4 weeks depending upon species and size. With soil application, some susceptible weeds may emerge from the treated soil and persist as stunted plants before they die.

The imidazolinone herbicides act by inhibiting acetohydroxyacid synthase, the first enzyme in the pathway leading to the biosynthesis of the branched-chain aliphatic amino acids, valine, leucine, and isoleucine (Shaner *et al* 1984).

Differential metabolism of imidazolinones in plants is important in determining species susceptibility. Tolerant species metabolize the herbicide more rapidly than susceptible ones.

METHODS

Imazapyr has been extensively evaluated worldwide as a non-cropland or industrial herbicide utilizing commercial application equipment. In general, applications of imazapyr were made in 250 to 1000 litres of water/ha as broadcast, post-emergence treatments to various annual and perennial weed species. A non-ionic surfactant was added to the spray solution at 0.25% (w/v).

AC 222,293 has been tested worldwide in cereal-growing regions as an early post-emergence treatment. Treatments were applied in 50 to 300 litres of water/ha and a non-ionic surfactant was added to the spray solution at 0.25% (w/v) to aid penetration.

Imazaquin and AC 263,499 have been tested as pre-plant soil-incorporated, pre-emergence and post-emergence applications in soybeans and other leguminous crops. Treatments were applied in 100 to 400 litres of water/ha and a non-ionic surfactant was added to the spray solution at 0.25 (w/v) for post-emergence applications.

RESULTS

Post-emergence applications of imazapyr at dosages from 0.5 to 2.0 kg ae/ha, provided effective control of a broad spectrum of annual and perennial herbaceous and woody weed species (Table 1). Highly susceptible species included *Sorghum halepense*, *Panicum maximum* and *Elytrigia repens*. Weed species demonstrating moderate susceptibility included *Digitaria* spp, *Ipomoea* spp and *Rosa multiflora*. *Acacia* spp and *Eucalyptus* spp were less susceptible to post-emergence applications of imazapyr however control of these woody species can be obtained with the appropriate dosage.

TABLE 1: Weed susceptibility* to imazapyr following post-emergence application.

Highly susceptible (0.5 to 0.75 kg ae/ha)	
<i>Bromus tectorum</i>	<i>Taraxacum officinale</i>
<i>Sorghum halepense</i>	<i>Daucus carota</i>
<i>Paspalum arvillei</i>	<i>Rumex crispus</i>
<i>Elytrigia repens</i>	<i>Conyza canadensis</i>
<i>Panicum maximum</i>	<i>Convolvulus arvensis</i>
Moderately susceptible (0.75 to 1.0 kg ae/ha)	
<i>Digitaria</i> spp	<i>Xanthium strumarium</i>
<i>Eleusine indica</i>	<i>Ipomoea</i> spp
	<i>Rhus radicans</i>
<i>Rosa multiflora</i>	<i>Smilax</i> spp
Less susceptible (1.0 to 2.0 kg ae/ha)	
<i>Cynodon dactylon</i>	<i>Cirsium arvense</i>
	<i>Acacia</i> spp
<i>Rubus</i> spp	<i>Eucalyptus</i> spp
<i>Equisetum</i> spp	

* >85% control

AC 222,293 at 0.3 to 0.75 kg ai/ha controlled several important cereal weeds including the highly susceptible *Avena fatua*, *A. sterilis* spp *ludoviciana*, *Alopecurus myosuroides*, and *Brassica* spp (Table 2). *Phalaris paradoxa*, *Polygonum convolvulus* and *P. persicaria* were moderately susceptible while *Lolium* spp were tolerant.

TABLE 2: Weed susceptibility* to AC 222,293 following post-emergence applications at dosages between 0.3 and 0.75 kg ai/ha.

Highly susceptible	Moderately susceptible
<i>Avena fatua</i>	<i>Phalaris paradoxa</i>
<i>Avena sterilis</i> spp <i>ludoviciana</i>	<i>Polygonum convolvulus</i>
<i>Alopecurus myosuroides</i>	<i>Polygonum persicaria</i>
<i>Raphanus raphanistrum</i>	Tolerant
<i>Brassica</i> spp	<i>Lolium</i> spp

* >85% control

Imazaquin and AC 263,499 can be applied pre-plant soil-incorporated, pre-emergence or early post-emergence for the control of a variety of grasses and broadleaved weed species (Tables 3 and 4). The major agronomic crop which has shown tolerance to imazaquin is soybeans. The control dosage range was from 0.14 to 0.28 kg ae/ha. AC 263,499 has shown selectivity in numerous leguminous crops including lucerne, clover, beans (*Phaseolus* spp and *Vicia* spp), peas, soybeans and peanuts at dosages from 0.036 to 0.14 kg ae/ha.

These four compounds are the first herbicides to be developed from the new imidazolinone family. They represent important new chemicals in the fight against weeds that infest cereals, leguminous crops, and non-cropland areas.

TABLE 3: Weed susceptibility* to imazaquin following application pre-plant incorporated pre-emergence and early post-emergence at dosages between 0.14 and 0.28 kg ae/ha.

Highly susceptible	
<i>Digitaria</i> spp	<i>Chenopodium album</i>
<i>Setaria</i> spp	<i>Hibiscus trionum</i>
<i>Eleusine indica</i>	<i>Polygonum persicaria</i>
<i>Cyperus esculentus</i>	<i>Xanthium strumarium</i>
<i>Amaranthus</i> spp	
Less susceptible	
<i>Eriochloa villosa</i> (pre-emergence only)	

* >85% control

TABLE 4: Weed susceptibility¹ to AC 263,499 at various application timings.

Application Timing ²	PPI	PRE	E.POST
Highly susceptible (0.036 to 0.071 kg ae/ha)			
<i>Chenopodium album</i>	Yes	Yes	No
<i>Solanum ptycanthum</i>	Yes	Yes	Yes
<i>Datura stramonium</i>	Yes	No	Un ³
<i>Amaranthus retroflexus</i>	Yes	Yes	Yes
<i>Amaranthus hybridus</i>	Yes	Yes	Yes
Moderately susceptible (0.071 to 0.11 kg ae/ha)			
<i>Echinochloa crus-galli</i>	Yes	No	No
<i>Setaria faberi</i>	Yes	Yes	Yes
<i>Setaria viridis</i>	Yes	Yes	Yes
<i>Ipomoea hederacea</i>	Yes	Yes	Un
<i>Datura stramonium</i>	Yes	Yes	Un
Less susceptible (0.11 to 0.14 kg ae/ha)			
<i>Echinochloa crus-galli</i>	Yes	Yes	Yes
<i>Panicum dichotomiflorum</i>	Yes	Yes	Yes
<i>Digitaria sanguinalis</i>	Yes	Yes	Yes
<i>Xanthium strumarium</i>	Yes	Un	Yes
<i>Chenopodium album</i>	Yes	Yes	Yes

¹ >85% control²PPI = preplant incorporated

PRE = pre-emergence

E.POST = early post-emergence; weeds 3 to 5 cm tall

³UN = undetermined; not enough data available to determine susceptibility**REFERENCES**

- Cross, B., Johnson, J.L., Los, M. and Orwick, P.L., 1983. *o*-(5-oxo--2-imidazolin-2-yl) arylcarboxylates: A new class of herbicides 3. Quinolines. *Abstracts, 185th National Meeting American Chemical Soc.*, Seattle, Washington, USA, March 20-25.
- Kirkland, K. and Shafer, N.E., 1982. AC 222,293, A new post-emergence herbicide for cereals: Field studies. *Proc. 1982 Brit. Crop Protection Conf.* — Weeds, 33-38.
- Los, M., Ciarlante, D.R., Ettinghouse, E.M. and Wepplo, P.J., 1982. *o*-(5-oxo-2-imidazolin-2-yl)arylcarboxylates: A new class of herbicides. *Abstracts, 184th National Meeting American Chemical Soc.*, Kansas City, Mo, USA, September 12-17.
- Los, M., Orwick, P.L., Russell, R.K., and Wepplo, P.J., 1983. *o*-(5-oxo-2-imidazolin-2-yl)arylcarboxylates: A new class of herbicides. 2. Pyridines. *Abstracts, 185th*

- National Meeting American Chemical Soc.*, Seattle, Washington, USA, March 20-25.
- Los, M., Wepplo, P.J., Russell, R.K., Lences, B.L. and Orwick, P.L., 1984. *o*-(5-oxo-2-imidazolin-2-yl)arylcarboxylates: A new class of herbicides. 4. AC 263,499, A herbicide for use in legumes. *Abstracts, 186th National Meeting American Chemical Soc.*, Philadelphia, Pennsylvania, USA, August 26-31.
- Malefyt, T., Marc, P.A., Umeda, K., Los, M. and Orwick, P.L., 1984. AC 263,499 - A new broad spectrum herbicide for soybeans and other leguminous crops. *Proc. 1984 Weed Sci. Soc. America*, Abstract 49, 18.
- Orwick, P.L., Marc, P.A., Umeda, K., Tafuro, A.J., Lamb, G., Ballard, T.O., Walls, F.R., Colbert, D.R., Rabby, J.C., Watkins, R.M. and Ciarlante, D.R., 1983a. AC 252,925 — A new broad spectrum herbicide: Field studies. *Proc. 36th Southern Weed Sci. Soc.*, USA, 291.
- Orwick, P.L., Martin, P., Fine, R.R., Baroni, O. and Rowcotsky, R.G., 1983b. Field studies on AC 252,214 — A new broad spectrum herbicide for soybeans. *Proc. 9th Asian-Pacific Weed Sci. Soc.*, 461-466.
- Shaner, D.L., Anderson, P.C. and Stidham, M.A., 1984. Imidazolinones, potent inhibitors of acetohydroxyacid synthase. *Plant Physiol.* 76: 545-546.