Relative Phytotoxicity of Some Picloram Derivatives

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Picloram (4-amino-3,5,6-trichloropicolinic acid), a relatively persistent and highly phytotoxic herbicide, is effectively used in the control of many broad-leaved weeds and woody plants. Although very little is known regarding its metabolism in the environment, a number of intermediary metabolites have been suggested (MEIKLE et al. 1966; HALL et al. 1968; REDEMANN et al. 1968; RIECK 1969; MEIKLE et al. 1974). Recently, using a root bioassay technique, the 6-hydroxy derivative of picloram was reported to be of equal phytotoxicity to picloram (NAIK et al. 1972). In the present study, the phytotoxicity of three picloram derivatives which are potential metabolites is examined, using sunflowers (Helianthus annuus L.) a picloram sensitive species.

MATERIALS AND METHODS

Synthesis of 4-amino-3,5-dichloro-6-hydroxypicolinic acid (II). Five grams of picloram in 300 ml of 20% NaOH was heated under reflux for 20 hr. The cool solution was acidified to pH 1 and filtered. The solid was extracted with 0.1 N NaOH (3 x 150 ml) and the combined filtrates were acidified to yield crude 4-amino-3,5-dichloro-6-hydroxypicolinic acid (4.16 g:90%:m.p.250 -252°C). Passage through an alumina column, using 0.1 N NaOH as an eluent, yielded pure II (m.p.251-252°C).

Synthesis of 4-amino-2,3,5-trichloropyridine (III). Picloram (4.5 g) in 125 ml of dimethylformamide was heated under reflux for 1 hr and filtered. Addition of water to the filtrate yielded crude 4-amino-2,3,5-trichloropyridine (1.9 g:51%:m.p.152-154°C). Recrystallization from ethanol raised the m.p. to 154-155°C.

Synthesis of 4-amino-3,5-dichloro-6-hydroxypyridine (IV). One gram of 4-amino-3,5-dichloro-6-hydroxypicolinic acid (II) in 20 ml of dimethylformamide was heated under reflux for 30 min. The condenser was removed, the solution allowed to boil until the volume had decreased to 5 ml, and cooled. Ether (40 ml) was added, and the solid collected by filtration to yield crude 4-amino-3, 5-dichloro-6-hydroxypyridine (580 mg:72%:m.p.243-245°C). Recrystallization from ethanol raised the m.p. to 246-247°C. This derivative (IV) was also prepared from the trichloropyridine (III) by heating 1.9 g of III in 100 ml of 20% NaOH under reflux for 17 hr, and treating the cooled solution as described above for

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synthesis of II. However, the yield was low (100 mg:6%:m.p. 246-247°C).

The reaction pathways for the three derivatives are outlined in Fig. 1. In addition to the m.p. determinations, the structure of the three derivatives was confirmed by IR-Spectrophotometry and NMR spectroscopy.

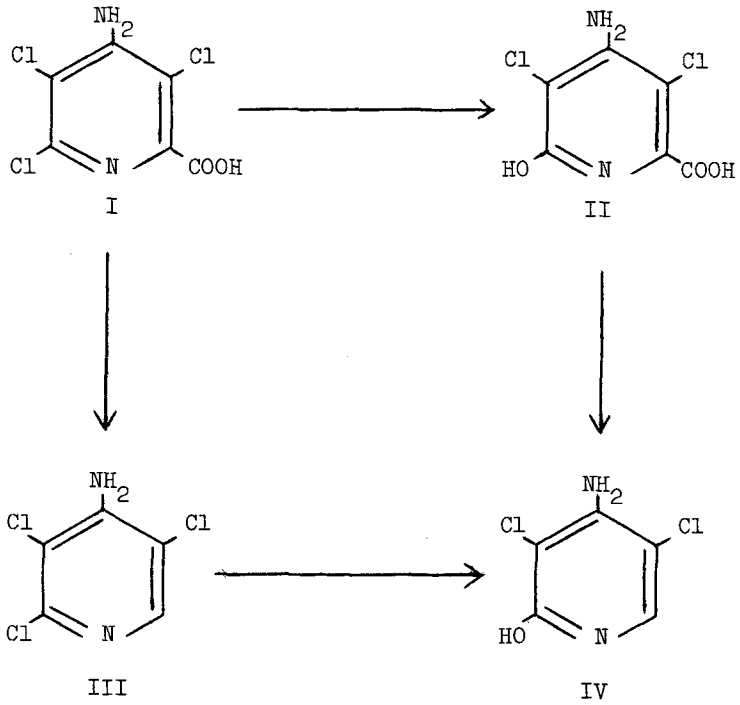

FIGURE 1. Structural configuration of picloram and its three derivatives showing the reaction pathways.

Phytotoxicity Evaluation. Uniform sunflower seedlings, approximately 5 cm in shoot height and germinated in sand, were transferred to glass jars of about 2 liter capacity containing one-quarter strength, Hoagland and Arnon (1950) nutrient solution. The nutrient solutions were prepared containing various concentrations of picloram, I, (0, 0.025, 0.05, 0.1, 0.2 ppm); 6-hydroxy-picloram, II, (0, 0.5, 1, 2, 4, 5, 10, 15, 20 ppm); decarboxy-picloram, III, (0, 1, 5, 10, 15 ppm); or 6-hydroxy-decarboxy-picloram, IV, (0, 10, 20, 40, 60, 80, 100 ppm). The glass jars were painted on the outside with black asphaltum followed by aluminum enamel. Two seedlings were grown in each jar, with four

replicates for each treatment. The seedlings were supported by two-hole paraffin-coated corks, and held in place with non-absorbent cotton. Since aeration of the culture solutions, over the short 6-day test period, was found to have no beneficial affect, all tests were carried out without aeration of the nutrient solutions. The glass jars were kept in a growth chamber maintained at a 16 hr day-length. The light intensity was 1800 ft-candles at 30 cm from the top of the jars. The day and night temperatures were 23 $\pm$ 1°C and 10 $\pm$ 1°C, respectively. On the 6th day, the shoots were cut and fresh weights of the shoots recorded.

RESULTS AND DISCUSSION

Fresh weights of sunflower shoots, expressed as percent of check, for picloram and the three derivatives, were plotted on a probability x 3 log cycles paper (Fig. 2) and their GR_{50} values (concentration in ppm for a growth reduction of sunflower shoots of 50% as determined by fresh weight) were calculated.

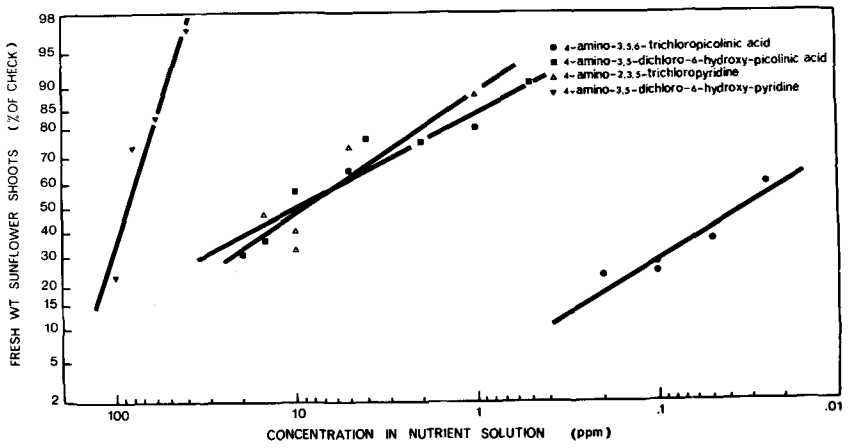

FIGURE 2. Logarithmic/probability growth curves of sunflower seedlings grown in various concentrations of picloram or one of its three derivatives.

The GR_{50} values for the four chemicals, their phytotoxicity rating relative to picloram, and comparable data from NAIK et al. (1972) are given in Table 1.

TABLE 1

Observed GR_{50} values for picloram and three of its derivatives and their relative phytotoxicity rating, using sunflower seedlings.

Chemical	No.	Sunflower bioassay		Lucerne root bioassay*	
		GR_{50}	rating	non-lethal	lethal
		(ppm)		(ppm)	
picloram	(I)	0.03	1	> 0.001	1
6-hydroxy-	(II)	10	333	> 0.001	1
decarboxy-	(III)	9	300	1	> 40
6-hydroxy-decarboxy-	(IV)	86	2,867	-	-

* Calculated from NAIK et al. (1972).

The bioassay curves (Fig. 2) show that for each chemical there is a linear relationship between the growth of the sunflower seedlings and the concentration of the chemicals in the nutrient solution. However, the GR_{50} values for the 6-hydroxy (II) and the decarboxy (III) derivatives increased by about 300-fold as compared to picloram, with a further 10-fold increase when the sunflower seedlings were grown in solutions containing the 6-hydroxy-decarboxy derivative (IV) (Table 1). NAIK et al. (1972), on the other hand, using a root bioassay technique and giving only the lethal and non-lethal concentrations, have reported that the 6-hydroxy derivative (II) and picloram were equally phytotoxic, with the decarboxy derivative (III) being 40 to 1,000 times less phytotoxic (Table 1). These workers did not include 6-hydroxydecarboxy derivative (IV) in their study.

The picloram concentrations required to inhibit root elongation of lucerne (Medicago sativa L.) and the shoot growth of sunflower seedlings, were in the same range, i.e. 0.001 to 1 ppm. However, the response of the two species to the 6-hydroxy derivative was markedly different. These results point out the importance of selecting the bioassay test species and/or the growth parameters when determining the phytotoxic effects of herbicides or their metabolites.

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