Influence of BAS-145138 on the Activity of Sulfonylurea and Imidazolinone Herbicides*

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This study demonstrates that corn can be partially safened by BAS-145138 against sulfonylurea and imidazolinone herbicides. The corn seeds were impregnated with BAS-145138 by soaking the seeds for 6 h in solutions of the safener. BAS-145138 had no effect on corn growth. However, corn shoot and root growth in length, fresh weight, and dry weight was partially protected by BAS-145138 from the phytotoxic effects of the sulfonylurea herbicides thiameturon and CGA-136872. Similar protection was given to corn against the phytotoxic activity of the imidazolinone herbicides imazapyr, imazaquin, and imazethapyr. This study suggests that corn could be safened with BAS-145138 against the phytotoxic effects of residual amounts of sulfonylurea and imidazolinone herbicides found in fields where wheat/corn or soybean/corn rotations take place.

Introduction

The sulfonylurea and imidazolinone herbicides are highly active and have a broad spectrum of weed control. Sulfonylureas, for example, have use rates as low as 2 g/ha [1], an astonishingly low rate when compared with conventional herbicides. Although chemically dissimilar, both herbicide groups have the same mode of action. Sulfonylureas and imidazolinones block the activity of acetolactate synthase (ALS), an enzyme which is necessary for the synthesis of three essential amino acids, valine, leucine, and isoleucine. Consequently, protein synthesis, so necessary for plant growth, is eventually terminated and the treated plant dies. Thus a compound that would provide a safening influence on these herbicides would be most valuable.

A moderate amount of study has been done concerning the influence of safeners on the herbicidal activity of sulfonylurea herbicides. Parker *et al.* [2] were the first to observe a safening effect on a sulfonylurea herbicide when they were able to show that naphthalic anhydride (naphthalene-1,8-dicarboxylic acid anhydride) could partially protect corn (*Zea mays* L.) from chlorsulfuron {2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide} activity. Following the work of Parker's group, a number of other studies demonstrated the safening effect of naphthalic anhydride on chlorsulfuron in corn [3–7]. In addition, Hatzios [4] found that the oxime safeners, cyometrinil {(*Z*)-α[(cyanomethoxy)imino]benzeneacetonitrile} and CGA-92194 {α-[(1,3-dioxolan-2-yl-methoxy)-imino]benzeneacetonitrile}, could protect grain sorghum (*Sorghum bicolor* (L.) Moench) from chlorsulfuron damage, but not as effectively as naphthalic anhydride. Devlin and Zbiec [8] showed that the safener BAS-145138 [1-dichloroacetyl-hexahydro-3,3,8-trimethylpyrrolo-(1,2-α)-pyrimidin-6-(2H)-one] could moderately protect corn against chlorsulfuron, chlorimuron {2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-benzoic acid}, and sulfometuron {2-[[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoic acid}.

There has been very little study of the effect of safeners on the herbicidal activity of imidazolinones. Barrett and Olson [9] have shown that grain sorghum can be protected from imazaquin {2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid} toxicity by treating seed with CGA-92194. Protection against imazaquim toxicity with corn and sorghum has been demonstrated in greenhouse experiments [9, 10]. In those experiments naphthalic anhydride showed the most promise.

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In the present study we have shown that BAS-145138 can provide some protection to corn from the herbicidal activity of the sulfonylureas thiameturon {3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid} and CGA-136872 {2-[[[[[4,6-bis(difluoromethoxy)-2-pyrimidinyl]-amino]carbonyl]amino]sulfonyl]benzoic acid} and the imidazolinones imazaquin, imazapyr {(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 H-imidazol-2-yl]-3-pyridinecarboxylic acid}, and imazethapyr {(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1 H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid}.

Materials and Methods

Corn seeds were soaked for 6 h in different concentrations of BAS-145138. The treated seeds were sown in 8 cm styrofoam pots (15 seeds per pot) containing moist vermiculite that had been previously treated on the surface with 7.4 ml of herbicide solution. For herbicide application a small atomizer was used at a pressure of 70 kPa. The bottoms of the pots were punctured several times to allow good drainage and the seeds were covered with untreated moist vermiculite to a depth of about one cm. Petri dish halves were used as holders for the pots to catch drainage and as an indirect method of providing water and nutrients. The plants were grown in a growth chamber under constant conditions of light (152 μE m^{-2} s^{-1}, 16 h light and 8 h dark) and temperature (22 ± 1). After shoot emergence 30 ml of 1/2 strength Hoagland solution was applied daily to each pot. After 12 days the seedlings were removed from the pots and the roots thoroughly washed. The ten largest seedlings (determined by shoot length) from each pot were selected and their shoot length, root length, fresh weight, and dry weight determined. All experiments were replicated four times and the data were subjected to analysis of variance.

Results

Over a wide concentration range (0.5 to 1.5 mM), BAS-145138 had little effect on the growth of corn. A slight decrease in shoot length and fresh weight was observed (Table I). Thus we can assume that any effect of BAS-145138 on the growth of corn when used in combination with the herbicides tested in this study is due almost solely to its properties as a safener.

A. Sulfonylureas

Measurements of shoot length, fresh weight, and dry weight of corn treated with thiameturon and BAS-145138 all indicated the safening influence of BAS-145138. Shoot length of corn treated with 50, 100, and 200 μM thiameturon was inhibited 26, 42, and 54%, respectively. When treated additionally with 1.5 mM BAS-145138 these inhibitions were reduced to 21, 20, and 24% (Table II). The safening effect was also observed when shoot fresh weight and dry weight were measured. For example, shoot dry weight of corn treated with 50, 100, and 200 μM thiameturon was reduced 7, 20, and 36%, respectively. However, no reduction in shoot dry weight occurred when the corn was also treated with 1.5 mM BAS-145138 (Table II).

Root growth of corn treated with thiameturon was partially protected by BAS-145138 (Table II). Corn treated with 50, 100, and 200 μM thiameturon had root lengths inhibited 44, 55, and 83%, respectively (Table II). When also treated with

Table I. Effect of BAS-145138 (BAS) on the growth of corn.

BAS [mM]	Shoots Length [mm]	Shoots Fr Wgt [mg/pl]	Shoots Dry Wgt [mg/pl]	Roots Length [mm]	Roots Fr Wgt [mg/pl]	Roots Dry Wgt [mg/pl]
0	199	675	52	207	713	46
0.5	186	600	48	199	687	45
1.0	185	617	47	213	729	47
1.5	186	627	48	217	670	45
LSD 5%	10	55	4.4	24	89	4.6
1%	14	77	6.2	34	125	6.5

Table II. Safening influence of BAS-145138 (BAS) on the herbicidal effect of thiameturon (Herb) on the growth of corn.

Herb [μM]	BAS [mM]	Shoots Length [mm]	Shoots Fr Wgt [mg/pl]	Shoots Dry Wgt [mg/pl]	Roots Length [mm]	Roots Fr Wgt [mg/pl]	Roots Dry Wgt [mg/pl]
0	0	140	393	31.8	197	628	36.3
50	0	104	318	29.5	110	213	20.0
50	0.5	115	374	31.8	156	325	27.3
50	1.5	110	360	31.0	182	359	27.8
100	0	81	259	25.5	89	172	20.5
100	0.5	108	372	33.0	139	235	22.0
100	1.5	112	379	33.0	163	289	24.3
200	0	65	201	20.5	34	139	22.0
200	0.5	92	294	28.5	113	208	20.0
200	1.5	107	356	34.3	124	226	21.7
LSD 5%		13.8	53.3	5.4	22.0	54.1	3.4
1%		18.5	71.4	7.3	29.5	72.4	4.6

1.5 mM BAS-145138 root length inhibitions at the above rates of thiameturon were only 8, 17, and 37%, respectively. Root fresh weight and dry weight recovery was not as pronounced. In fact, at 200 μM thiameturon corn roots were not protected against loss of dry weight by BAS-145138 (Table II).

Shoot length of corn treated with 100, 200, and 400 μM CGA-136872 was inhibited 27, 43, and 59%, respectively. With the addition of 1.5 mM BAS-145138 these inhibitions were reduced to 17, 17, and 28% (Table III). Shoot fresh and dry weight reductions due to CGA-136872 were partially offset by the safener. For example, the shoot dry weight of corn treated with 400 μM CGA-136872 was reduced 34%, but when treated additionally with 1.5 mM BAS-145138 the dry weight actually exceeded that of the untreated control. Partial protection of root growth from CGA-136872 by BAS-145138 was also observed (Table III).

Table III. Safening influence of BAS-145138 (BAS) on the herbicidal effect of CGA-136872 (Herb) on the growth of corn.

Herb [μM]	BAS [mM]	Shoots Length [mm]	Shoots Fr Wgt [mg/pl]	Shoots Dry Wgt [mg/pl]	Roots Length [mm]	Roots Fr Wgt [mg/pl]	Roots Dry Wgt [mg/pl]
0	0	173	491	34.5	215	661	41.0
100	0	126	450	39.0	112	211	21.3
100	0.5	139	446	36.5	133	262	24.3
100	1.5	144	463	37.8	146	311	25.8
200	0	99	338	31.5	64	123	15.0
200	0.5	123	405	34.7	112	216	21.5
200	1.5	144	483	40.5	124	256	23.0
400	0	71	235	22.8	43	107	13.3
400	0.5	113	386	34.0	93	170	17.0
400	1.5	125	426	38.0	102	186	19.0
LSD 5%		8.5	47.2	3.8	2.4	52.5	2.9
1%		11.4	63.5	5.1	3.3	69.3	3.9

B. Imidazolinones

The safening effect of BAS-145138 on imidazolinones was similar to that on sulfonylureas. Imazapyr at 5, 10, and 20 μM caused reductions in corn shoot length of 20, 36, and 63%, respectively (Table IV). However, when 1 mM BAS-145138 was also applied percent inhibitions of shoot length were reduced to 5, 11, and 33%. A similar safening effect was observed when shoot fresh and dry weights were measured and when root growth was studied (Table IV).

Corn seed treated with BAS-145138 was protected to a large extent from the herbicidal effects of imazaquin. Application of 2, 5, and 10 μM imazaquin reduced shoot length 19, 56, and 81%, respectively. But when 1 mM BAS-145138 was added these inhibitions were reduced to 0, 6, and 26% (Table V). Shoot fresh and dry weight measurements also gave evidence of the strong safening effect of BAS-145138 on imazaquin. For example, shoot fresh weight of corn treated with 2, 5, and 10 μM imazaquin was reduced 20, 51, and 77%, respectively. With the addition of 1 mM BAS-145138 the inhibitions were reduced to 0, 3, and 14%. Shoot dry weight measurements as well as root growth studies produced similar results (Table V).

Protection of corn from imazethapyr toxicity was demonstrated. However, the degree of protection was less than that found in studies with imazapyr and imazaquin. Shoot length of plants treated with 10, 20, and 30 μM imazethapyr was inhibited

Table IV. Safening influence of BAS-145138 (BAS) on the herbicidal effect of imazapyr (Herb) on the growth of corn.

		Shoots			Roots		
Herb [μM]	BAS [mM]	Length [mm]	Fr Wgt [mg/pl]	Dry Wgt [mg/pl]	Length [mm]	Fr Wgt [mg/pl]	Dry Wgt [mg/pl]
0	0	196	709	50	162	673	46
5	0	157	506	35	131	531	34
5	1	186	650	45	183	569	36
10	0	126	425	29	125	424	30
10	1	175	624	44	170	546	38
20	0	72	297	22	88	288	26
20	1	131	516	36	156	451	35
LSD 5%		9	73	5.2	32	60	4.2
1%		13	96	6.8	42	80	5.6

Table V. Safening influence of BAS-145138 (BAS) on the herbicidal effect of imazaquin (Herb) on the growth of corn.

		Shoots			Roots		
Herb [μM]	BAS [mM]	Length [mm]	Fr Wgt [mg/pl]	Dry Wgt [mg/pl]	Length [mm]	Fr Wgt [mg/pl]	Dry Wgt [mg/pl]
0	0	224	889	60	167	618	42
2	0	182	715	49	126	432	31
2	1	228	981	63	207	556	38
5	0	99	434	32	91	274	26
5	1	211	864	57	181	551	36
10	0	42	205	16	52	150	20
10	1	166	764	54	143	405	31
LSD 5%		14	71	4.6	16	51	4.1
1%		19	97	6.2	22	69	5.5

9, 31, and 63%, respectively. The addition of 1 mM BAS-145138 reduced the inhibitions to 2, 4, and 14% (Table VI). Shoot fresh and dry weight measurements and root growth studies all indicated that BAS-145138 could parially protect corn from the herbicidal effects of imazethapyr.

Discussion

Although a great deal is known about the physiological activity of most safeners, their mode of action has not been completely elucidated. This is especially true for the effect of safeners on the activity of sulfonylurea and imidazolinone herbicides in protected plants.

Studies by a number of investigators have shown that the herbicidal activity of sulfonylureas and imidazolinones can be reduced by safeners [3, 5, 7–9, 11, 12]. Both of these herbicide classes inhibit the activity of ALS, the first common enzyme in the biosynthetic pathway of the essential amino acids valine, leucine, and isoleucine [13–15]. Komives and Dutka [16] showed that there was a significant increase in ALS activity in the roots and shoots of corn treated with dichlormid (2,2-dichloro-N,N-di-2-propenyl-acetamide). Rubin and Casida [12] suggested that the increase in ALS activity was sufficient to partially counter the herbicidal effect of chlorsulfuron. However, other studies by Sweetser [7] on the metabolism of sulfonylureas and by Barrett and Olson [9] on imidazolinones indicate that safeners protect corn from these herbicides by enhancing their metabolism.

Ezra *et al.* [17, 18] found that BAS-145138 raised the level of glutathione-S-transferase activity in corn and in so doing increased the metabolism of chloroacetamide and thiocarbamate herbicides when they are applied to corn. Fuerst *et al.* [19] have shown that BAS-145138 increases corn shoot and root tolerance to metazachlor [N-(2,6-dimethylphenyl)-N-(1-pyrazolyl-methyl)-chloroacetamide], a chloroacetanilide herbicide. In addition, they also showed that BAS-145138 enhanced the activity of glutathione-S-transferase in corn shoot extracts assayed using metolachlor and glutathione as substrates. The work of Ezra *et al.* [17, 18] and Fuerst *et al.* [19] suggests that the safener activity of BAS-145138 is similar to that of other safeners such as dichlormid.

Although the work of the above mentioned investigators indicates that BAS-145138 protects corn from the phytotoxic influence of chloroacetamide and thiocarbamate herbicides through enhanced metabolism of the herbicides, it does not indicate how the safener protects corn against sulfonylureas and imidazolinones. At the present time the strongest evidence supports the general observation that BAS-145138, when applied to corn, enhances the metabolism of sulfonylurea and imidazolinone herbicides [7, 9].

Information from this study and the studies of other [7–9, 17, 18] suggests that BAS-145138 could serve to protect corn from the phytotoxic effects of residual amounts of sulfonylurea and imidazolinone herbicides found in fields where wheat/corn or soybean/corn rotations take place.

Table VI. Safening influence of BAS-145138 (BAS) on the herbicidal effect of imazethapyr (Herb) on the growth of corn.

Herb [μM]	BAS [mM]	Shoots Length [mm]	Shoots Fr Wgt [mg/pl]	Shoots Dry Wgt [mg/pl]	Roots Length [mm]	Roots Fr Wgt [mg/pl]	Roots Dry Wgt [mg/pl]
0	0	193	692	50	165	608	40
10	0	175	651	48	150	510	36
10	1	189	714	50	156	566	36
20	0	133	479	36	130	374	28
20	1	185	661	47	165	512	35
30	0	71	254	20	81	176	18
30	1	166	621	43	166	443	30
LSD 5%		12	53	4.6	24	50	3.2
1%		17	72	6.2	32	68	4.3

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