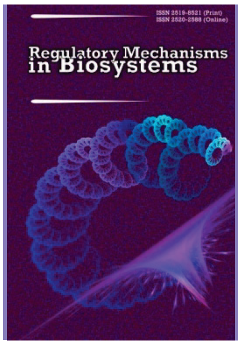

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Identification of acetolactate synthase resistant *Amaranthus retroflexus* in Ukraine

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The problem of weed resistance to herbicides has become very important in the last decade and threatens to dramatically reduce the productivity and profitability of modern crop production. Herbicides – ALS inhibitors dominate among current herbicides and are used annually on large areas of sunflower, wheat, corn, soybean, and rapeseed. Also, in recent years, Clearfield seeds of sunflower, corn, canola, soybean and wheat have been sown in large areas. In recent years, there has been a sharp decrease in *Amaranthus retroflexus* L. control levels by imidazolinone class herbicides. Thus, the effects of herbicides with different modes of action on the development of *A. retroflexus* on sunflower after imidazolinone application were investigated in field research. In the conditions of the Cherkasy region of Ukraine, the biotype *A. retroflexus* was identified, which is resistant to the post-emergence application of herbicides - acetolactate synthase (ALS) inhibitors of the imidazolinone class – imazapyr and imazamox. Weed plants treated with imidazolinone derivatives in the maximum doses registered in Ukraine did not differ from untreated control plants. Also, in the conditions of field experiments, cross resistance of the weed biotype to herbicides – ALS inhibitors of the sulfonylurea class – foramsulfuron and iodosulfuron-methyl-sodium, thifensulfuron-methyl, tribenuron-methyl, nicosulfuron was established; and also, to the triazolinone derivative – thiencarbazone-methyl; to triazolpyrimidine derivatives – florasulam and flumetsulam. Multiple resistance of the *A. retroflexus* biotype to herbicides of the classes of glycine derivatives – glyphosate, phenoxycarboxylates – 2,4-D, benzoic acid – dicamba has not been established; compositions of dicamba with triketone – topramesone; diphenyl ethers – aclonifen; pyridine carboxylates – clopyralid, picloram and aminopyralid. It was shown for the first time that herbicide compositions with selected nutrients (ammonium pool) can increase the level of effectiveness of controlling resistant weed biotypes. Thus, the addition of ammonium sulfate increases the effectiveness of controlling ALS-resistant *A. retroflexus* with herbicides – a derivative of benzoic acid (dianate) and a derivative of benzoic acid with a 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibitor (stellar – dicamba + topramesone). Thus, the *A. retroflexus* biotype resistant to ALS-herbicides of the imidazolinone class was identified for the first time in Ukraine, which is cross-resistant to other ALS-inhibitors of the sulfonylureas, triazolinones, and triazolpyrimidine classes. Multiple resistance of *A. retroflexus* to herbicides of the classes of glycine derivatives – glyphosate; phenoxycarboxylates – 2,4-D; benzoic acid – dicamba, triketones – topramesone; diphenyl ethers – aclonifen; pyridine carboxylates – clopyralid, picloram and aminopyralid has not been established. The identification of a highly harmful weed species resistant to widely used herbicides – ALS inhibitors in the central part of the "grain belt" of Ukraine requires a significant revision of the principles of crop rotation formation and ways of controlling weeds in the country in order to maintain high levels of profitability and productivity of agrophytocenoses.

Keywords: weed control; herbicides; cross and multiple resistance; common amaranth; redroot pigweed; weed resistance management.

Introduction

Agriculture has been the main branch of Ukraine's economy in recent years and provides more than 40% of revenues to the budget from exports. Ukraine is one of the guarantors of food security in the world and has the potential to further increase the production of agricultural products.

However, reduced crop rotations in all soil and climatic zones and the dominance of herbicides with one site of action - acetolactate synthase inhibitors – in weed control systems, creates a threat of emergence of herbicide-resistant weed biotypes. Due to the emergence and widespread spread of herbicide-resistant biotypes of weeds (www.weedscience.com), the costs of growing cultivated plants can increase significantly, up to the rapid loss of profitability of agriculture (Green, 2014; Heap, 2022).

Enzyme acetolactate synthase (ALS, EC 2.2.1.6, also referred to as acetohydroxy acid synthase; AHAS) (Duggleby, 2008; Powles & Yu, 2010) is found in plants and microorganisms. ALS catalyzes the first step synthesis of amino acids with a branched carbon chain (valine, leucine, and isoleucine). In the world, numerous cases of ALS resistance among weed species have been identified, which significantly limits the productivity of crop production (herbicides – ALS inhibitors – HRAC Group 2 (Legacy HRAC Group B); The Global Herbicide Resistance Action Committee (HRAC), www.hracglobal.com). By 2022, for example, 160 cases of resistance to ALS herbicides have been identified worldwide, with 65 species among monocotyledonous weeds and 104 species among dicotyledonous weeds.

Herbicides – ALS inhibitors are mainly used for all major crops weed control in Ukraine – sunflower, wheat, corn, soybeans, rapeseed, etc. Thus, 6,428,770 hectares were allocated for sunflower in 2021, and 6,142,220 hectares were sown in 2020. In Dnipropetrovsk region alone, 601,000 hectares of sunflower were sown, significant areas of the crop were sown in Cherkasy, Vinnytsia and other regions of the country. At the same time, the use of soil and post-emergence herbicides – photosynthesis inhibitors or protein synthesis inhibitors is limited by the reduction of tillage before sowing and the annual moisture deficit at the beginning of the growing season of the crop. Therefore, significant areas of sunflower fields are treated foliarly with ALS inhibitors: imidazolinone and sulfonylurea derivatives dominate the application. In recent years, under difficult economic conditions, sunflower acreage has been steadily increasing, while the foliar use of herbicides – ALS inhibitors is an important, and in some regions, the main component of weed control systems in crops.

In 2019 and 2020 on a number of farms of Cherkassy region it was found that the composite ALS-herbicide MaysTer Power, Bayer Crop Science Ukraine (foramsulfuron, 31.5 g/L + iodosulfuron-methyl-Na, 1.0 g/L + thiencarbazon-methyl, 10 g/L + antidote cyprosulfamide, 15 g/L) was not effective on maize crops. Prior to 2019, herbicides – ALS inhibitors – were used on wheat, soybean, sunflower and corn every year for more than 7 years in these fields. In 2021, composite herbicides of ALS-inhibitor imidazolines – Euro-Lightning, BASF (imazamox, 33 g/L + imazapyr, 15 g/L) were applied to sunflower crops in the same fields, which turned out to be ineffective in controlling a population of highly harmful *Amaranthus retroflexus* L. (Fig. 1, 2).

Redroot pigweed (*A. retroflexus* L.) is a widely distributed species worldwide (Mitich, 1997) and in Ukraine (Mosyakin, 1995; Ivaschenko, 2013; Ivaschenko & Ivaschenko, 2019). *Amaranthus retroflexus* is a powerful competitor to cultivated plants in crops for nutrients and water (Lindsey et al., 2013). With insufficient control, the weed often intercepts photosynthetically active radiation also from many cultivated plants (Knezevic et al., 1999).

Fig. 1. Damage to sunflower field of the NK Neoma CRU Clearfield hybrid, resistant to imidazolinone herbicides, by the imidazolinone-resistant biotype *Amaranthus retroflexus* L. (Cherkasy region, 2021)

Fig. 2. Plants of the ALS-imidazolinone-resistant *Amaranthus retroflexus* L. biotype dominate in the sunflower NK Neoma CRU Clearfield hybrid (Syngenta) after application of imidazolinone-class herbicide Euro-Lightning (imazamox, 33 g/L + imazapyr, 15 g/L), 1.2 L/ha (BASF), June 29, 2021 (Cherkasy region, Ukraine)

Usually, *A. retroflexus* in crops is controlled by the vast majority of dicotyledon weed killer herbicides: photosynthesis inhibitors, derivatives of phenoxyacetic and benzoic acids, as well as derivatives of ALS (Schwartau & Mykhalska, 2013; The Pesticide Manual, 2021).

Amaranthus retroflexus plants are very sensitive to synthetic auxins such as 2,4-D or dicamba, and sulfonylurea, and imidazolinone herbicides such as imazethapyr, thifensulfuron-methyl, rimsulfuron, and nicosulfuron. Most other broadleaf herbicides that are mitotic cycle inhibitors or bleaching herbicides also provide reasonably good *A. retroflexus* control in crops.

According to our observations, damage to agrophytocenoses of *A. retroflexus* decreased somewhat in the 1960s and 1980s due to the large-scale application of 2,4-D and benzoic acid derivatives (Table 1).

Thus, in 1983–1988, on the experimental farm of the Institute of Plant Physiology and Genetics, there were only 8–47 plants per m^2 of *A. retroflexus* plants in the experimental fields. Note that even when significantly high doses of mineral fertilizers were applied in the 1980s, the number of *A. retroflexus* plants on the experimental fields was, for the most part, small. In 2019 and 2021 on the farms of Kyiv and Vinnytsia regions the number of weed plants increased significantly. At the same time, the highest levels of infestation of crops were observed on the fields of holdings with large land banks. It is likely that agricultural holdings fields are dominated by sunflower, and weed control on sunflower exclusively with post-emergent herbicides – ALS inhibitors: imidazolinones and sulfonylureas may be a factor in the sharp increase of *A. retroflexus* infestation in recent years. It should also be considered that the systematic application of mineral nitrogen fertilizers contributes to the competitiveness of *A. retroflexus* as a pronounced N-phile. It is known that *A. retroflexus* in the presence of high levels of nitrogen nutrition significantly increases the level of competition with cultivated plants (Lindsey et al., 2013). It is also worth noting the increase in the number of plants of the weed in the central part of Ukraine, in the "grain belt", where its harmfulness may be significant.

Table 1
Amaranthus retroflexus L. density in the Central Ukraine (plants/m^2)

Year of research	Agrophytocenoses of farms	Agrophytocenoses of agricultural holdings	Non-agricultural land
		Kyiv region	
1988*	8–47	–	–
2019	12–70	35–90	5–25
2021	15–85	25–150	15–40
		Cherkasy region	
2021	25–60	55–180	10–20
		Vinnytsia region	
2021	7–55	35–120	5–12

Note: data from Victor Schwartau's PhD thesis (1988).

Amaranthus retroflexus is classified as a neophyte plant that easily occupies new territories. According to the data of Ivaschenko & Ivaschenko (2019), *A. retroflexus* was first discovered on the territory of Ukraine only in the 18th century in the south, where it grew on arable land.

It should also be noted that, in recent years, the avoidance of treatment with soil herbicides and the dominance of foliar treatments has led to an sharp increase in damage by the *Amaranthus* species due to high levels of weed germination in 2–3 waves from the beginning of the growing season. Both in Ukraine and in the world, the high levels of weed growth are being controlled by the annual use of ALS inhibitors, which can lead to the emergence of herbicide-resistant biotypes of *A. retroflexus*.

In the last decade, *A. retroflexus* has been one of the most noxious weeds in the Americas, in Europe, in China (Mitich, 1997; Huang et al., 2020). Climate change in the last decade may significantly increase the harmfulness of many drought-resistant weed species in cultivated crops. The competitiveness of *Amaranthus* spp. in crops is predicted to increase with increasing temperatures and moisture deficits. Bioclimatic models predict a significant advance of Palmer amaranth (*Amaranthus palmeri* S. Wats.) to the north of America and Europe (Kistner & Hatfield, 2018).

During the period of active use of triazines, corn was taken out of crop rotation on many fields. For the first time, the *A. retroflexus* biotype resistant to herbicides – inhibitors of photosynthesis (atrazine) was identified in Canada in 1980 on corn. Atrazine-resistant populations of *A. retroflexus* were also reported in the USA, France, Germany, Hungary, Switzerland, Spain, Poland, Chile, and the Czech Republic (Table 2). High doses of herbicides were used annually on the crop, which led in 1980 to nearly simultaneous identification of resistance in two provinces of Canada, France, Germany, and the USA. The incidence of *A. retroflexus* biotypes that have been resistant to photosynthetic inhibitors since the early 1980s may indicate a significant increase in the annual use of single mechanism of action herbicides on both monocrop (corn) and non-crop fields. Despite a significant reduction in the specific percentage of PSII inhibitors, Serine 264 Binders HRAC Group 5 (Legacy C1 C2), in the 2000s numerous cases of resistance to them were identified in the United States, Canada and Greece. Many of the identified resistant biotypes have cross resistance to metribuzin and linuron.

For the first time *A. retroflexus* biotype resistant to ALS herbicides (chlorsulfuron) was identified in Israel in 1991, in the USA in 1998 (imazaquin, imazethapyr), etc. Between 1991 and 2021, extensive and annual use of ALS inhibitors, primarily the imidazolinone and sulfonylurea classes on soybean, corn, cotton, wheat, and sunflower, resulted in numerous cases of ALS resistance in *A. retroflexus*. Populations *A. retroflexus* resistant to ALS inhibitors, sulfonylureas, and imadizolinones have been reported in the United States and Israel.

Protoporphyrinogen oxidase (PPO) resistance to herbicides in the *A. retroflexus* biotype has also been determined. It has been shown in cross and multiple resistance analyses, which indicated that the R population was cross resistant to lactofen and carfentrazone-ethyl but was sensitive to imazethapyr, thifensulfuron-methyl, atrazine, and glyphosate. It has been demonstrated that that the Arg-128-Gly substitution is the main reason for *A. retroflexus* resistance to fomesafen (Huang et al., 2020).

Only four cases of multiple resistance in *A. retroflexus* biotypes from 1998 to the present are known worldwide, but in all cases, chemical control of the weed in corn, soybean, tomato, and cotton crops is becoming exceedingly difficult (Beckie & Tardif, 2012; Hao et al., 2019). When identifying multiple resistance to herbicides of PPO and ALS classes, we also found cross resistance to classes of imidazolinones, sulfonylureas, and triazolopyrimidines. It is known that the ALS-resistance trait in *A. retroflexus* and *A. blitoides* is not associated with yield penalty and did not incur ecological cost in the field. At the same time, limiting the ability to control the harmfulness of the weed significantly reduces the productivity of crops (Sibony & Rubin, 2003).

Over the past 20 years, *A. retroflexus* biotypes resistant to 15 herbicides have been registered in 17 countries (Heap, 2022; The International Herbicide-Resistant Weed Database). ALS-herbicides currently make up the largest group by site of action (with 54 active substances of five chemical groups) and are widely used in Ukraine, and in the world. The evolution of weed resistance to AHAS inhibitors has been rapid and identified in populations of many weed species. The emergence of ALS-resistant biotypes is associated with numerous point mutations in the target ALS gene. The emergence of resistance has also been identified due to enhanced metabolism of herbicide active ingredients to non-phytotoxic metabolites. This multiplicity of resistance mechanisms creates prerequisites for the emergence of numerous biotypes both with cross resistance to ALS-herbicides of other chemical classes and for the emergence of multiple resistance to herbicides with a different mechanism of action (Yu & Powles, 2014).

Table 2
Identification of resistance of *Amaranthus retroflexus* to herbicides in countries of the world (Heap, 2022, www.weedscience.org with amendments)

Country	Resistance identification year	Crop/Situation	Active Ingredients	Site of Action
		Identification of resistance to herbicides - inhibitors of photosynthesis on corn		
Canada (Ontario)	1980	corn (maize), and cropland	atrazine	Site of Action
Canada (Quebec)	1980	corn (maize)	atrazine, and metribuzin	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
France	1980	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Germany	1980	corn (maize), railways, and roadsides	atrazine, and fenuron	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Indiana)	1980	cropland	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Switzerland	1982	grapes, orchards, and vegetables	simazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Colorado)	1982	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Bulgaria	1984	corn (maize), cropland, grapes, and orchards	atrazine, metribuzin, and simazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)

Country	Resistance identification year	Crop/Situation	Active Ingredients	Site of Action
Bulgaria	1984	cropland	linuron	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Connecticut)	1984	corn (maize)	atrazine, and cyanazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (New Hampshire)	1984	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Czech Republic	1985	corn (maize), railways, roadsides, and sugar beets	atrazine, cyanazine, metamitron, prometryne, terbuthylazine, and terbutryne	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Maine)	1985	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Spain	1986	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
China	1990	cropland	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Poland	1991	orchards, and sugar beets	atrazine, and metamitron	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Minnesota)	1991	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Vermont)	1991	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Virginia)	1993	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Oregon)	1994	mint	terbacil	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Kansas)	1995	corn (maize), and sorghum	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Italy	1999	corn (maize), soybean, and sugar beets	chloridazon/pyrazon, metamitron, and terbuthylazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Greece	2000	potatoes	metribuzin	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (West Virginia)	2000	corn (maize)	atrazine	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Canada (Ontario)	2001	carrots, and vegetables	linuron	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Canada (Quebec)	2001	carrots	linuron	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Michigan)	2001	asparagus	atrazine, and diuron	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Canada (Ontario)	2005	corn (maize)	bentazon, and bromoxynil	PSII inhibitors – Histidine 215 Binders HRAC Group 6 (Legacy C3)
United States (Idaho)	2005	potatoes	metribuzin	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
United States (Washington)	2010	mint, and potatoes	metribuzin, and terbacil	PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Identification of resistance to herbicides - acetolactate synthase inhibitors				
Israel	1991	forests	chlorsulfuron	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
United States (Arkansas)	1995	cropland, and soybean	imazaquin	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Canada (Ontario)	1998	corn (maize), cropland, and soybean	imazethapyr, and thifensulfuron-methyl	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
United States (Maryland)	1998	unspecified	imazaquin, and imazethapyr	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
United States (North Dakota)	1999	soybean	imazethapyr	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Canada (Manitoba)	2002	wheat	florasulam	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Serbia	2002	soybean	imazethapyr	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Italy	2003	soybean	imazamox, imazethapyr, nicosulfuron, oxasulfuron, and thifensulfuron-methyl	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Canada (Quebec)	2009	soybean	imazethapyr	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Canada (Saskatchewan)	2010	wheat	thifensulfuron-methyl, and tribenuron-methyl	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
United States (Mississippi)	2010	railways	imazethapyr, pyrithiobac-sodium, and trifloxysulfuron-Na	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Brazil	2012	cotton	pyrithiobac-sodium, and trifloxysulfuron-Na	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Germany	2012	corn (maize)	nicosulfuron	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)

Country	Resistance identification year	Crop/Situation	Active Ingredients	Site of Action
Ukraine	2020	corn (maize), and sunflower	florasulam, flumetsulam, foramsulfuron, imazamox, imazethapyr, iodosulfuron-methyl-Na, thiencarbazone-methyl, thifensulfuron-methyl, and tribenuron-methyl	Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B)
Identification of Protoporphyrinogen Oxidase resistance to herbicides				
Brazil	2014	cotton, and soybean	fomesafen	Inhibition of Protoporphyrinogen Oxidase HRAC Group 14 (Legacy E)
Identification of multiple resistance to herbicides				
United States (Pennsylvania)	1998	corn (maize), soybean, and tomatoes	atrazine, chlorimuron-ethyl, cloransulam-methyl, imazamox, imazaquin, imazethapyr, primisulfuron-methyl, and thifensulfuron-methyl	Multiple Resistance: 2 Sites of Action, Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B), PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
Brazil	2011	cotton	atrazine, prometryne, and trifloxysulfuron-Na	Multiple Resistance: 2 Sites of Action, Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B), PSII inhibitors – Serine 264 Binders HRAC Group 5 (Legacy C1 C2)
China	2017	soybean	acifluorfen, fluoroglycofen-ethyl, fomesafen, imazethapyr, and lactofen	Multiple Resistance: 2 Sites of Action Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B), Inhibition of Protoporphyrinogen Oxidase HRAC Group 14 (Legacy E)
United States (North Carolina)	2020	soybean	fomesafen, imazamethabenz-methyl, lactofen, and thifensulfuron-methyl	Multiple Resistance: 2 Sites of Action Inhibition of Acetolactate Synthase HRAC Group 2 (Legacy B), Inhibition of Protoporphyrinogen Oxidase HRAC Group 14 (Legacy E)

In Ukraine, we began to observe resistant biotypes of common *Echinochloa crus-galli* (L.) P. Beauv. in fields in the south of the country in 2014. In 2017, information on the identification of the ALS-resistant biotype of the monocot *E. crus-galli* was included in the International Herbicide-Resistant Weed Database/Ukraine/2017 (www.weedscience.org). No herbicide-resistant dicot biotypes of weeds were identified until 2019. However, it is necessary to take note of the limited effectiveness of *A. retroflexus* control after ALS inhibitor herbicides were applied in the Central part of Ukraine in corn and sunflower in 2019 and 2020.

Therefore, the purpose of this research is to study, in the conditions of field experiments, the reaction of *A. retroflexus* to the action of herbicides with different mode of action in order to identify the resistance of the *A. retroflexus* biotype.

Materials and methods

In the central part of the "grain belt" of Ukraine, in Cherkasy region, the effectiveness of herbicides with different mechanisms of action was studied on the fields of sunflower hybrid NK Neoma CRU Clearfield (Syngenta), resistant to imidazolinone class herbicides, with a high density of *A. retroflexus* emergence (Fig. 1). Development phase of sunflower BBCH15-20, development phase of *A. retroflexus* plants before processing 1–2 pairs of real leaves.

The location of the experiment is GPS 48.988098º N, 30.424638º E.

Herbicides were applied with a professional manual sprayer, manufactured by Gloria, Germany. The spraying fluid consumption rate was 200 L/ha (80 mL/plot). The area of the site is 4 m^2, the repetition was 4 times. The location of the experimental plots was randomized. Processing was carried out in the first half of the day, the air temperature was 23–24 ºC, there was no wind, it was sunny. Phytotoxicity of herbicides (www.weedscience.org) was evaluated by changes in dry matter accumulation and the results were presented in % of the control variant (Burgos, 2015; Heap, 2022).

Data from field assays were subjected to analysis of variance (ANOVA) using StatPlus, AnalystSoft Inc. Version v.7 in Excel 2019 and means compared by Tukey's test ($P < 0.05$).

Results

The level of control of *A. retroflexus* with the application of herbicides in the maximum doses registered in Ukraine – imidazolinone derivatives, imazamox, or the composition of imazapyr + imazamox, in terms of the amount of inhibition of the development of weed plants, did not differ from the state of plants on the control variant (Table 3). Nor was phytotoxicity to *A. retroflexus* observed with sulfonylurea derivatives (nicosulfuron, tribenuron-methyl). When applying triazolpyrimidine sulfoanilides (florasulam, flumetsulam), an initial weak inhibition of plant development was observed, but over time, effective control of the weed species was not observed. Thus, there was no phytotoxicity of florasulam + flumetsulam herbicides to control *A. retroflexus* at day 30 after application. A similar dependence was determined regarding the effectiveness of the composition of ALS herbicides foramsulfuron + iodosulfuron + thiencarbazone-methyl: leaf weak burns after spraying with no control of *A. retroflexus* a month after treatment.

The dominance of tribenuron-methyl, which is widely used in Ukraine, in compositions with thifensulfron-methyl caused a weak level of control of the *A. retroflexus* biotype immediately after spraying, and the absence of phytotoxicity a month after treatment. Reduced doses of tribenuron-methyl in the composition with thifensulfuron-methyl were non-phytotoxic to *A. retroflexus* even in the first days after spraying.

Application of glyphosate, an inhibitor of the enzyme 5-enolpyruvyl-shikimate-3-phosphate-synthase (EPSPS), led to a high level of control of *A. retroflexus*.

A high level of weed control was also achieved with the introduction of a derivative of diphenyl ethers – aclonifen, which, according to the mechanism of action, disrupts the synthesis of chlorophyll in plants by bleaching (discoloration).

The introduction of herbicide formulations with the addition of synthetic auxin derivatives (2,4-D 2-ethylhexyl ether, clopyralid, picloram, dicamba) to the ALS inhibitor made it possible to control *A. retroflexus* biotype at a sufficiently high level.

Identified levels of phytotoxicity of herbicides are well demonstrated visually (Table 4). On the control variant dense cover of weed sprouts dominated in the crop throughout the study period. The application of the composition imazamox + imazapyr or imazamox alone did not change the level of contamination of the experimental plots. A slight yellowing of the weed after application of flumetsulam + florasulam was not observed after 30 DAT. Application glyphosate, or aclonifen, or dicamba dimethylamine salt, or dicamba + topramezone produced high levels of *A. retroflexus* biotype control.

It has been established (Table 5) that for herbicides with an acidic fragment in the structure (dicamba dimethylamine salt), adding ammonium pools to the spraying solution led to an increase in phytotoxicity of the composition. Thus, the addition of ammonium sulfate (5.0 kg/ha) increased the effectiveness of controlling *A. retroflexus* biotype with herbicides – a benzoic acid derivative (dianate, 0.5 L/ha) and a benzoic acid derivative with a 4-hydroxyphenylpyruvate dioxygenase inhibitor (HPPD) (stellar, 1.25 L/ha – dicamba, 160 g/L + topramezone, 50 g/L).

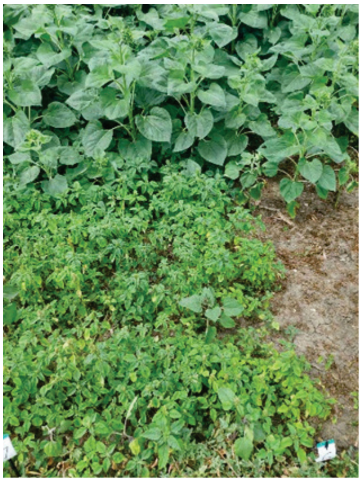
Table 3
Evaluation of the effectiveness of different herbicides on *Amaranthus retroflexus* L. control; Cherkasy region, Central part of Ukraine, 2021

Herbicide	Active ingredients	Herbicide doses, L(g)/ha	The effectiveness of herbicides on *Amaranthus retroflexus* L. control; dry matter accumulation (%), 0% – no efficiency, 100% – weed plants died	
			7 DAT	30 DAT
Without herbicide application	–	–	0^a	0^a
Acetolactate synthase inhibitors				
Euro-Lightning, BASF	Imazamox, 33 g/L + imazapyr, 15 g/L	1.2	0^a	0^a
Pulsar 40, BASF	Imazamox, 40 g/L	1.0	0^a	0^a
Derby 175 SC, Syngenta	Flumetsulam, 100 g/L + florasulam, 75 g/L	0.07	25 ± 10^b	5 ± 5^a
Granstar Gold, Corteva Agriscience	Tribenuron-methyl, 562.5 g/kg + thifensulfuron-methyl, 187.5 g/kg	(35)	20 ± 5^b	0^a
Calibre, FMC	Tribenuron-methyl, 250 g/kg + thifensulfuron-methyl, 500 g/kg	(60)	0^a	0^a
Milagro 40 OD, Syngenta	Nicosulfuron, 40 g/L	1.25	0^a	0^a
MaisTer Power, Bayer Crop Science Ukraine	Foramsulfuron, 31.5 g/L + iodosulfuron-methyl-Na, 1.0 g/L + thiencarbazone-methyl, 10 g/l + antidote cyprosulfamide, 15 g/L	1.5	25 ± 5^b	10 ± 10^a
Composition of inhibitor of acetolactate synthase + synthetic auxin or synthetic auxin				
Prima, Adama	Florasulam 6.25 g/L + 2,4-D 2-ethylhexyl ester, 452.5 g/L	0.6	50 ± 10^c	90 ± 5^b
Galera Super, Corteva Agriscience	Clopyralid, 267 g/L + picloram, 80 g/L + aminopyralid, 17 g/L	0.3	80 ± 10^c	90 ± 5^b
Dianat, BASF	Dicamba dimethylamine salt, 480 g/L	0.5	80 ± 5^c	100^c
Stellar, BASF	Dicamba, 160 g/L + topramezone, 50 g/L	1.25	70 ± 10^c	100^c
Inhibitor of 5-enolpyruvylshikimate-3-phosphate synthase				
Roundup Max, Bayer Crop Science Ukraine	Glyphosate in acid equivalent 450 g/L (551 g/L in glyphosate potassium salt form)	3.0	100^d	100^c
Inhibitor of chlorophyll synthesis (bleaching/discoloration)				
Challenge (Emerger) + Mero, Bayer Crop Science Ukraine	Aclonifen, 600 g/L + agricultural wetting agent (oil (rapeseed fatty acids esters) / Fatty acids, $C_{16\text{-}18}$ and C_{18}-unsatd., Me esters, 81.44%)	2.0 ± 0.5	70 ± 10^c	95 ± 5^c

Notes: herbicides that are registered for use in Ukraine were studied; DAT – days after treatment, hereinafter; letters serve for comparisons of samples (Tukey test, $P < 0.05$); the same letters indicate variants without statistically significant differences, hereinafter.

Table 4
Visual assessment the effectiveness of selected herbicides on *Amaranthus retroflexus* L. control

Variant/herbicide	Active ingredients	Plants' condition after application of herbicides: 07 DAT, 30 DAT	
Control, without using herbicides	–		
Euro-Lightning, BASF	Imazamox, 33 g/L + imazapyr, 15 g/L		

Variant/herbicide	Active ingredients	Plants' condition after application of herbicides: 07 DAT, 30 DAT	
Pulsar 40, BASF	Imazamox, 40 g/L		
Derby 175 SC, Syngenta	Flumetsulam, 100 g/L + florasulam, 75 g/L		
Granstar Gold, Corteva Agriscience	Tribenuron-methyl 562.5 g/kg + thifensulfuron-methyl 187.5 g/kg		
Roundup Max, Bayer Crop Science Ukraine	Glyphosate in acid equivalent 450 g/L (in glyphosate potassium salt form, 551 g/L)		

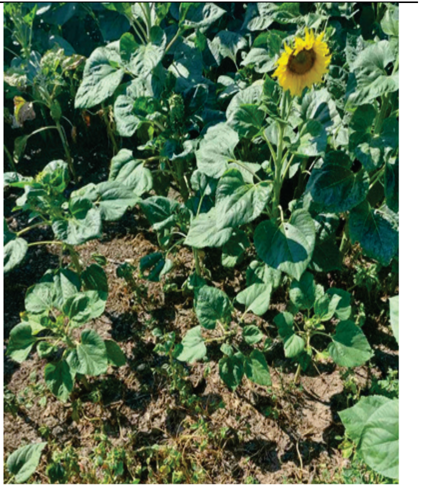
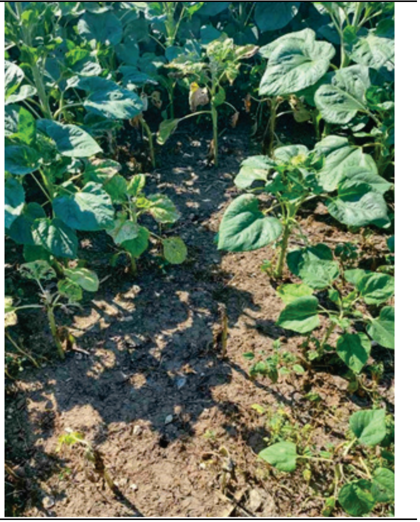
Variant/herbicide	Active ingredients	Plants' condition after application of herbicides: 07 DAT, 30 DAT	
Challenge (Emerger) + Mero, Bayer Crop Science Ukraine	Aclonifen, 600 g/L		
Dianat BASF	Dicamba dimethylamine salt, 480 g/L		
Stellar, BASF	Dicamba, 160 g/L + topramezone, 50 g/L		

Table 5
Ammonium sulfate increases effectiveness of ALS resistant *Amaranthus retroflexus* L. biotype control by herbicides – synthetic auxins

Herbicide/fertilizer	Active ingredients	Herbicide/ fertilizer doses, L/ha + kg/ha	The effectiveness of herbicides and ammonium on *Amaranthus retroflexus* L. control on 7 DAT; dry matter accumulation (%); 0% – no efficiency, 100% – weed plants died
Without herbicide application	–	–	0^a
Dianat, BASF	Dicamba dimethylamine salt, 480 g/L	0.5	80 ± 10^a
Dianat + ammonium sulfate	Dicamba dimethylamine salt, 480 g/L + $(NH_4)_2SO_4$	0.5 + 5.0	100^b
Stellar, BASF	Dicamba, 160 g/L + topramezone, 50 g/L	1.25	70 ± 10^a
Stellar + ammonium sulfate	Dicamba, 160 g/L + topramezone, 50 g/L + $(NH_4)_2SO_4$	1.25 + 5.00	95 ± 5^b

Discussion

Amaranthus retroflexus is a highly noxious weed in all countries with advanced crop production. The efficacy of controlling this species with herbicides is quite high. At the same time, the widespread introduction of the Clearfield system has dramatically increased the area of application of herbicides – ALS-inhibitors. The widespread dominance of ALS-inhibitors among herbicides with other mechanism of action is a problem in Ukraine, and is also observed in other countries (Dekker & Duke, 1995; Duke, 2018).

ALS-herbicides in modern crop production of the world and Ukraine constitute the largest group by site of action: 54 active substances from five chemical groups. The evolution of weed resistance to ALS-inhibitors has been rapid and identified in populations of many weed species. Often, the evolution of resistance is associated with point mutations in the target ALS gene, but there is also an increase in off-site herbicide metabolism. In several well-studied cases, off-target resistance is due to an increased rate of herbicide metabolism, and often involving cytochrome P450 monooxygenases (Yu & Powles, 2014).

ALS-herbicides of the imidazolinone group, which include imazapyr, imazapic, imazethapyr, imazamox, imazamethabenz and imazaquin, effectively control weeds mainly in foliar sprays. Imidazolinone-resistant corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), rice (*Oryza sativa* L.), canola (*Brassica napus* L.), and sunflower (*Helianthus annuus* L.) plants are now established by mutagenesis and breeding. These crops have been developed using traditional breeding methods and commercialized as Clearfield crops since 1992 (Tan et al., 2005). The Clearfield system is also very popular in crop production in Ukraine. For Ukraine, the Clearfield system is especially important and is widely used on sunflowers, which is the dominant crop in cost-effectiveness and planted areas.

Widespread use of herbicides with the same mode of action on different crops every year has caused the emergence of ALS-herbicide-resistant weed populations since 1990 (Table 2). At the same time, we note multiple occurrences of ALS-resistant *A. retroflexus* in countries with high levels of fertilizer and pesticide use. Importing seeds between countries considerably increases the risk of infecting local agrophytocenoses with seeds of weeds with already formed resistance. This circumstance should be taken into account when importing seeds to Ukraine, which in recent years is critically dependent on seeds produced in the EU countries. Seed imports from European countries to Ukraine will increase significantly in recent years. At the same time, the probability of infection of agrophytocenoses in Ukraine by herbicide-resistant weed species from Europe is increasing sharply. There are already examples of transfer of weed seeds between regions in the world. Thus, a significant amount of seeds in Ukraine comes from Italy: rice, wheat, soybeans and other crops. In Italy, several herbicide-resistant *Amaranthus* spp. were found: *A. retroflexus* with an Asp(376)Glu substitution in the ALS gene with resistance to thifensulfuron methyl. *Amaranthus tuberculatus* (Moq.) J. D. Sauer, and *A. hybridus* L. were cross resistant to thifensulfuron-methyl and imazamox; most ALS-resistant plants had a point mutation at position 574. In *A. hybridus*, a Trp(574)Met substitution, new to the genus *Amaranthus*, was observed. All ALS-resistant plants were controlled with glyphosate and metribuzin. *Amaranthus retroflexus* was controlled with bentazone, while *A. hybridus* and some specimens of *A. tuberculatus* were not. Thus, the main mechanism of resistance in the three *Amaranthus* species is the target site. It should be noted that ALS resistance was found in *A. tuberculatus* outside the species' native North American habitat (Scarabel et al., 2007; Milani et al., 2022).

In Canada and the United States, three species of *Amaranthus* are noxious: *A. retroflexus* L., *A. powellii* S. Watson and *A. hybridus* L. These are weeds introduced into Canada from Southern North America. The plants show high phenotypic plasticity and genetic variability. These plant species can germinate throughout the growing season, in 2–3 waves of weed emergence, and produce large numbers of viable seeds. All three species are multiply resistant to photosynthetic and ALS inhibitors (Costea et al., 2005). According to our long-term data, the seeds of *A. retroflexus* do not germinate for the first 3–5 months after maturation, the germination rate in the first month after maturation does not exceed 1–2%. The identification of ALS-resistant *A. retroflexus* biotypes in China is known also. ALS-resistant populations of *A. retroflexus* were found in Heilongjiang Province, China. High resistance (RI > 10) to imazetapyr was shown in all three populations. Three nucleotide mutations resulted in three known amino acid substitutions affecting the manifestation of resistance, Ala-205-Val, Trp-574-Leu, and Ser-653-Thr in the three resistant populations, respectively. Thus, ALS action site mutations in resistant *A. retroflexus* biotypes may be responsible for the formation of resistance to imazetapyr from the imidazolinone group (Chen et al., 2015).

High levels of *A. retroflexus* crop damage and differences in the values of yield reductions of major crops have also been found in other Asian countries (Hamideh et al., 2015). Competition from weeds can significantly reduce yields of major crops. Studies by the authors showed differences in the harmfulness of the species for major crops and concluded that the lowest levels of harmfulness were observed in wheat (*Triticum aestivum* L.) and bean (*Phaseulus vulgaris* L.), while higher levels of yield reduction were observed in alfalfa (*Medicago sativa* L.).

The problem of the increasing harmfulness of the species under climate changes observed in the last decade was discussed above.

Thus, the harmfulness of *A. retroflexus* is of global importance, and the formation of ALS-resistant biotypes significantly limits the possibilities of increasing the productivity and profitability of cultivated plants.

In Ukraine, the biotype *A. retroflexus* was identified in Cherkasy region which is resistant to the post-emergence application of ALS herbicides of the imidazolinone class – imazapyr and imazamox. Weed plants treated with imidazolinone derivatives in the maximum doses registered in Ukraine did not differ from control plants. That is, the absence of symptoms of phytotoxicity of imidazolinones at the given doses of application indicates the formation of ALS resistance in the weed population on experimental fields. Note that differences between ALS-resistant and imazetapyr-sensitive populations (*A. retroflexus*) were relatively low. The resistant (R) population was shown to show 19.16-fold resistance to imazetapyr compared to the susceptible (S) population. qRT-PCR analysis showed that there was no difference in ALS gene expression between the R and S populations. Sequence analysis revealed an Asp-376-Glu substitution in ALS in the R population (Huang et al., 2016). Previously, it was shown that resistant and sensitive biotypes of *A. retroflexus* have only limited differences in response to doses of herbicides – imidazolinone derivatives (Chen et al., 2015; Huang et al., 2016).

Also, in the conditions of field experiments, the cross resistance of the weed biotype to herbicides – ALS inhibitors of the sulfonylurea class – foramsulfuron and iodosulfuron-methyl-sodium, thifensulfuron-methyl, tribenuron-methyl, nicosulfuron was established; and also to the triazolinone derivative – thiencarbazone-methyl; to triazolpyrimidine derivatives – florasulam and flumetsulam. The composition of florasulam + flumetsulam can be used to control dicotyledonous weed species in 2–3 waves in the growing season, as well as species that are insensitive to herbicides – sulfonylurea derivatives (*Fumaria officinalis* L., *Centaurea cyanus* L., *Consolida regalis* Gray, *Papaver rhoeas* L., *Papaver somniferum* L., *Veronica* spp., *Matricaria* spp.).

The established cross resistance to other classes of ALS-inhibitors is dangerous in terms of the impossibility of achieving proper levels of the weed control in winter and spring wheat, corn, soybeans, barley.

Multiple resistance of the *A. retroflexus* biotype to herbicides of the classes of glycine derivatives – glyphosate, phenoxycarboxylates – 2,4-D, benzoic acid - dicamba has not been established.

EPSPS (EC No. 2.5.1.19) is a key enzyme in the synthesis of aromatic amino acids tyrosine, tryptophan and phenylalanine, which are components in the synthesis of proteins and numerous compounds of secondary metabolism (phenols, lignates, etc.). Thus, the application of glyphosate was effective in controlling the *A. retroflexus* biotype.

Compositions of dicamba with triketone – topramesone have been shown ; diphenyl ethers – aclonifen; pyridine carboxylates – clopyralid, picloram and aminopyralid.

Thus, in the Central part of Ukraine, in the "grain" belt of the state, a highly harmful biotype of *A. retroflexus* was identified, which is resistant to the post-emergence application of ALS herbicides of the imidazolinone class – imazapyr and imazamox (Fig. 2). Given that the use of imidazolinones is dominant in weed control in sunflower crops, the identification of a resistant biotype of *A. retroflexus* may reduce the effectiveness of weed control in subsequent crops in the rotation and the productivity and profitability of sunflower production. The multiple resistance of *A. retroflexus* to herbicides of the classes of derivatives of glycine – glyphosate, phenoxycarboxylates – 2,4-D, benzoic acid – dicamba; triketones – topramesone; diphenyl ethers – aclonifen; pyridine carboxylates – clopyralid, picloram and aminopyralid has not been established. The identification of a highly harmful weed species resistant to widely used herbicides – ALS inhibitors in the Central part of Ukraine indicates the limited effectiveness of weed control exclusively with herbicides with one mechanism of action and requires a significant revision of the principles of crop rotation formation and ways of weed control in the country to maintain high levels of profitability and productivity of agrophytocenoses. The level of effectiveness of controlling ALS-resistant weed biotypes is important in view of the limited time intervals of additional application of herbicides after the identification of resistance and, accordingly, the ineffectiveness of pretreatment. It is known that the phytotoxicity of herbicides with an acid fragment in the molecule can be enhanced by adding ammonium to the working solutions for spraying. In order to increase the effectiveness of controlling ALS-resistant *A. retroflexus*, the effect of ammonium sulfate on the activity of dicamba and its composition with topramesone was studied.

It was shown for the first time that herbicide compositions with selected nutrients (ammonium pool) can increase the level of effectiveness of controlling resistant weed biotypes. Thus, the addition of ammonium sulfate increases the effectiveness of controlling ALS-resistant weed with conventional herbicides - a derivative of benzoic acid (dianate) and a derivative of benzoic acid with a 4-hydroxyphenylpyruvate dioxygenase (HPPD) inhibitor (stellar – dicamba + topramesone). Previously, the possibility of increasing the phytotoxicity of herbicides when ammonium cations are added to spraying solutions has been shown.

It is shown that phytotoxicity of foliar spraying with glyphosate to *Phaseolus vulgaris* L. and some other species can be enhanced by treatment with compositions with butyric acid phosphate and ammonium sulfate. Ammonium salts, especially ammonium sulfate, have obvious advantages because of their availability, low cost and nontoxicity to mammals (Turner & Loader, 1975; O'Sullivan et al., 1981).

Ammonium sulfate in compositions with herbicides for use on ALS-resistant crops can also be considered as a fertilizer with nitrogen and sulfur (Pline et al., 2000; Schwartau & Mykhalska, 2013).

So, ammonium pool in foliar application is an important component of increasing the efficiency of benzoic acid derivatives and its compositions with HPPD inhibitor. Also, the pools of ammonium and sulfate due to the introduction of ammonium sulfate are important for the nutrition of crop plants, for example, sunflower, winter wheat or corn. The mechanism of this increasing in the phytotoxicity of the herbicide can be the activation of the protonation of H$^+$-ATP-ase of the plasmalemma under the influence of the ammonium cation. By adding ammonium salts to the working solutions of herbicides (dicamba, probably – 2,4-D derivatives), it is possible to achieve higher levels of control of ALS-resistant weeds and shorten the period of evidence of phytotoxicity of the compositions.

Thus, the *A. retroflexus* biotype resistant to ALS herbicides of the imidazolinone class was identified for the first time in the Central part of the "grain belt" of Ukraine, which is cross-resistant to other ALS inhibitors of the sulfonylureas, triazolinones, and triazolpyrimidine classes. The multiple resistance of *A. retroflexus* to herbicides of the classes of derivatives of glycine – glyphosate, phenoxycarboxylates – 2,4-D, benzoic acid – dicamba; triketones – topramesone; diphenyl ethers – aclonifen; pyridine carboxylates – clopyralid, picloram and aminopyralid has not been established. The identification of a highly harmful weed resistant to widely used herbicides – ALS inhibitors in the Central part of Ukraine indicates the limited effectiveness of weed control exclusively with herbicides with one mechanism of action (ALS) (Fig. 2) and requires a significant revision of the principles of crop rotation formation and methods of weed control in the country to maintain high levels of profitability and productivity of agrophytocenoses.

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