# Sunflower protection from negative effects of 2,4-D

Vladimir Strelkov<sup>1</sup>, Ludmila Fyadyuchenko<sup>1</sup>, Lidia Isakova<sup>1</sup>

<sup>1</sup>All-Russian Research Institute of Biological Plant Protection, 350039, Krasnodar, Russia, e-mail: vniibzr@internet.kuban.ru

#### ABSTRACT

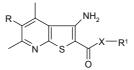
Twelve novel chemical derivatives of thieno[2,3-*b*]pyridines were synthesized and tested, aiming to find new compounds to protect/increase crop selectivity from herbicide impacts. Among these compounds, those with positive effect in reducing the toxicity of 2,4-D on sunflower are herein described.

Key words: 2,4-D – antidote – sunflower – thieno[2,3-b]pyridines.

### INTRODUCTION

The use of herbicides to control weeds faces the problem of protecting some crops with low selectivity/ tolerance to some of them. Occasionally some compounds are very aggressive to some particular crops, and therefore, could occur a risk of damaging neighboring highly sensitive crops (Pitina et al., 1986; Strelkov et al., 1997). In addition, inaccuracy and mistakes of operators are possible while applying herbicides. Up to date, some approaches to protect crops from damage from herbicides have been developed, including selection of cultivars, agricultural methods, application of sorbing materials, etc. (Pitina et al., 1986, 1994). One promising approach includes a search for and application of chemical antidotes. Earlier, the possibility to use some pharmaceuticals and plant growth regulators to protect sunflower plants from 2,4-D during their growing season was shown by us (Strelkov et al., 1995a,b, 1997).

The objective of this work was to continue a search for new effective substances to protect crops from herbicides similar to 2,4-D. For this purpose, a number of novel chemical compounds have been synthesized by us, which belong to the derivatives of thieno[2,3-b]pyridines and have the following common formula:



where R = H, CI; X = O, NH, N;  $R^{1}$  = substituted phenyl, alkyl.

The compounds having this type of structure are known as biologically active compounds with a broad spectrum of activity (Litvinov, 1989); therefore, it seemed very useful to study their plant growth-regulating and antidote activity on sunflower seedling and adult plants.

### **MATERIALS AND METHODS**

Germinating sunflower seeds with the embryo root of 2-4 mm in length were placed in the 2,4dichlorophenoxiacetic acid (2,4-D) solution at the concentration of  $10^{-3}$  % for one hour to inhibit the hypocotyls growth by 40-60%. After the herbicide action, the seeds were rinsed with water and put into solutions of the compounds tested for their antidote (safener) activity at the concentrations  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$  % (herbicide + antidote treatment). An hour later, the seeds were washed with water and laid out on the filter paper bands (10 x 75 cm in size), 20 seeds per band. The bands were rolled up and placed into the beakers containing 50 ml of water. The further seed germination happened in the thermostat at 28°C for three days. The solution and rinsing water temperature was 28°C. The seeds from the "herbicide" treatment (comparison standard) were incubated in the solution of 2,4-D at the concentration of  $10^{-3}$  % for one hour and then in water for the following one hour. The seeds from the control treatment were soaked in water for 2 hours.

The experiment included three replications; 20 seeds per replication were used. A protective (antidote) effect was determined by comparing an increase in hypocotyls and root lengths in the herbicide + antidote treatment with the same values in the herbicide treatment (standard).

The antidote field activity was evaluated in the ARRIBPP experimental field located in the central zone of the Krasnodar Region with moderate continental climate conditions. The soil in the field is a super-deep low-humic leached chernozem. The tests were conducted using the following methods: the sunflower plants of the cultivar Flagman, which were at the 10-16 leaf stage, were sprayed with butyl ether of 2,4-dichlorophenoxiacetic acid at the rate of 18 g/ha and, 5 days later, the tested antidote solution was applied at the rate of 200 g/ha by using the working fluid at the rate of 500 l/ha.

The experiment included the following treatments:

- Control – untreated plants;

- Herbicide (standard) – plants treated with herbicide;

- Herbicide + antidote - plants treated with herbicide and antidote.

The experiments were conducted in the 2.8  $\text{m}^2$  plots, with five replications. The plants were harvested with a Xere – 125 combine at the time of full seed ripeness.

An antidote effect was determined as a percentage by calculating the absolute yield gain value against the herbicide standard according to the formula:

$$A_{x} = \frac{A - E}{E} \times 100,$$

 $A_x$  – antidote effect, %;

A – yield in the herbicide + antidote treatment;

E – yield in the herbicide (standard) treatment.

The data obtained were statistically processed using Student's t-test at the probability level P = 0.95.

# RESULTS

Twelve novel compounds derivatives of thieno[2,3-*b*]pyridines were synthesized using conventional methods (Shestopalov et al., 1988). Under the laboratory experiment conditions it was determined that the synthesized compounds had no growth-regulating effect on sunflower seedlings. At the same time, some compounds having an antidote effect were identified (Table 1).

The compounds deploying the most activity during the laboratory experiment were tested under the conditions of a field small-plot experiment. The results are given in Table 2.

						Treatment							
No.	R	Х	$\mathbf{R}^1$	Control A <sup>1</sup>	Standard A	Herbicide + antidote at the below concentrations, %							
INO.						10-2		10-3		10-4		10-5	
				А	A	А	В	Α	В	А	В	А	В
1	Н	NH	2 hromphonyl	<u>65</u>	40	45	113	48	120*	<u>46</u>	115	40	100
1	п	INΠ	2-bromphenyl	110	44	46	105	56	127*	57	130*	36	82
2	CI	NH	2- bromphenyl	<u>65</u>	<u>40</u>	47	<u>118</u> *	44	110	<u>36</u>	90	40	100
				110	44	57	130*	50	114	38	86	41	93
3	Н	NH	3-fluorophenyl	<u>77</u> 115	$\frac{36}{32}$	$\frac{43}{47}$	<u>119*</u>	<u>39</u> 36	100	$\frac{28}{27}$	<u>78</u> 84	<u>36</u> 32	100
5	11						147*		122*				100
4	CI	NH	3- fluorophenyl	<u>74</u>	$\frac{51}{69}$	<u>59</u> 73	<u>116*</u>	<u>57</u>	112	<u>59</u>	<u>116*</u>	<u>55</u>	<u>108</u>
•	CI	1,11	5 indorophenyr	143			106	83	120*	81	117*	72	104
5	Н	Ν	dipropyl	<u>70</u>	<u>46</u>	<u>51</u>	<u>111</u>	<u>46</u>	100	<u>46</u>	100	<u>43</u>	<u>93</u> 87
U	11	.,	aiptopyt	125	61	69	113	63	103	61	100	53	
6	CI	Ν	dipropyl	<u>70</u> 125	<u>46</u>	<u>50</u> 67	109	<u>47</u>	102	<u>49</u>	107	<u>50</u>	109
Ũ	01				61		110	55	90	61	100	57	93
7	Н	NH	2,5-dimethoxy-	<u>73</u>	<u>40</u>	<u>44</u>	<u>110</u>	<u>49</u>	<u>123*</u>	49	<u>123*</u>	<u>44</u>	<u>110</u>
			4- chlorophenyl	116	42	56	133*	54	129*	68	162*	60	143*
8	CI	NH	2,5- dimethoxy-	<u>73</u>	<u>40</u>	<u>41</u>	<u>103</u>	<u>34</u>	<u>85</u>	40	<u>97</u>	46	<u>115</u>
			4- chlorophenyl	125	61	68	111	67	110	59	100	57	93
9	Н	0	benzyl	<u>76</u>	<u>37</u>	49	<u>132*</u>	<u>42</u>	<u>114</u>	<u>42</u>	<u>114</u>	<u>44</u>	<u>119</u>
				120	47	51	109	51	109	38	81	38	81
10	Н	0	allyl	<u>76</u>	$\frac{37}{47}$	$\frac{52}{42}$	<u>141*</u>	$\frac{44}{44}$	<u>119</u>	$\frac{50}{42}$	<u>135*</u>	<u>49</u>	<u>132*</u>
	~			120			89		94		89	44	94
11	CI	0	benzyl	<u>77</u> 91	$\frac{44}{44}$	<u>56</u> 63	<u>127*</u> 11	<u>54</u>	<u>123</u> *	<u>51</u>	<u>116*</u>	<u>53</u>	<u>120*</u>
	ar	0					43*	54	123*	55	125*	60	136*
12	CI	0	allyl	<u>77</u> 91	$\frac{44}{11}$	54	<u>123*</u>	<u>45</u>	102	<u>43</u>	<u>98</u>	$\frac{45}{43}$	102
				91	44	46	105	47	107	41	93	43	98

**Table 1.** Antidote activity of the derivatives of thieno[2,3-*b*]pyridines having a common formula: against 2,4-D in sunflower seedlings (numerator:hypocotyl, denominator:root)

<sup>1</sup> A – average hypocotyl length, mm; B – increase in hypocotyl length compared to the standard, %.; \* Reliable differences.

_	Treatment							
Compound (Number given in	Control (untreated)	Standard (herbicide)	Herbicide + antidote					
the Table 1) –		Seed yield, g/ha		Gain against standard, %				
2	2.83	0.89	1.43	161*				
3	2.83	0.89	1.16	130*				
7	2.04	0.75	1.11	148*				
9	3.30	1.07	1.20	124				
10	3.30	1.07	1.23	126*				
11	3.19	0.94	0.99	105				

Table 2. Antidote activity of the derivatives of thieno[2,3- <i>b</i> ]pyridines applied at the rate of 200 g/ha
against 2,4-D in sunflower plants (field experiment)

\* Reliable differences

### DISCUSSION

As a result of screening novel compounds for their antidote activity against 2,4-D in sunflower, it was determined that a clearly marked and statistically reliable protective effect was produced by the derivatives of thieno[2,3-*b*]pyridines number 2, 3, 7, and 10. They contributed to the negative effect reduction of 2,4-D and increase in yield compared to the standard by 61, 30, 48, and 26 %, respectively (Table 2).

Under the laboratory experiment conditions, it was determined that the tested compounds did not have any growth-stimulating activity in sunflower seedlings; therefore, reduction in the phytotoxicity of 2,4-D could not be caused by its influence. It may be supposed that the herbicide action leveling was caused by one of the mechanisms described in the overview of Pitina et al. (1986).

The results obtained should be considered as the development of previous work and will expand the spectrum of protective means reducing negative effects of herbicides containing 2,4-D as part of their compositions. This is especially important in view of high sensitivity of sunflower to the herbicides of the 2,4-D group and insufficient research done in this field.

The results of the primary screening of novel antidotes (safeners) belonging to a series of thieno[2,3b]pyridines led us to expect that, after adjusting their rates of application and spraying terms, they could be used to reduce negative impacts on 2,4-D on sunflower crops.

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