

Article

Growth-Regulatory Effect of Thiazolyl Acetic Acid Derivatives on *Lepidium sativum* and *Sinapis alba*

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Abstract

The search for new growth-regulating compounds remains a relevant research direction in view of the issue of food security. Previously, a number of thiazolyl acetic acid derivatives have been synthesized, which are promising biologically active compounds according to their physicochemical characteristics. The aim of this work was to study the growth-regulating properties of both previously and newly synthesized thiazolyl acetic acid derivatives using a growth phytotest with *Lepidium sativum* and *Sinapis alba*. This study was carried out under laboratory conditions of phytotesting growth indicators of test plants of the class *Dicotyledones*—*L. sativum* and *S. alba* under the influence of 10 µg/mL, 100 µg/mL, and 1000 µg/mL aqueous solutions of the compounds with a comparative analysis of the action of the active components of Rhizopon™ and herbicide benazolin. It was found that, exhibiting high herbicidal properties at a concentration of 1000 µg/mL (primarily the compound with a benzothiazole fragment), the studied thiazolyl acetic acid derivatives with decreasing concentration (100 µg/mL and 10 µg/mL) reduce phytotoxicity to its complete elimination against *L. sativum* and *S. alba* for the compound 2-[2-(N-tert-butoxycarbonyl)-aminoethyl-1,3thiazol-4-yl]acetic acid (compound 3), as well as against *L. sativum* for the compound 5-phenylthiazol-2-yl acetic acid (compound 5). A weak stimulating effect on the length of the above-ground part of *S. alba* seedlings was recorded for 2-[2-(3,3,3-trifluoropropyl)-1,3thiazol-4-yl]acetic acid (compound 1) and 2-[2-(N-tert-butoxycarbonyl)-aminoethyl-1,3thiazol-4-yl]acetic acid (compound 3) at their concentration of 10 µg/mL; however, an improvement in the vitality index under the action of these compounds was not observed. The results obtained in this study indicate the biological activity of both previously and newly synthesized thiazolyl acetic acid derivatives, namely their growth-regulatory properties, expanding knowledge about promising herbicidal compounds with a possible hormetic effect, which requires further research.

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1. Introduction

The growth-regulatory activity of compounds is particularly noteworthy due to its importance and relevance in terms of food security issues [1–3]. In particular, attention is paid to auxins as plant growth stimulants and herbicides as plant growth inhibitors and to the search for their analogues among newly synthesized compounds [3–5]. Auxins belong to phytohormones, one of the three groups of plant growth biostimulants, and their function is to regulate metabolism and organic processes [6]. Chemically synthesized organic compounds with auxin-like action should be considered as chemical fertilizers. Synthetic hormones (in particular, naphthaleneacetic acid (NAA), 6-benzyladenine, gibberellins, cytokinins, abscisic acid, ethylene, brassinosteroids, and jasmonates), so-called plant growth regulators (PGRs), are widely used in horticulture to increase the production of vegetables and fruits [7]. Recently, the mechanisms of phytohormones control in fruit setting have been investigated, given that their use in horticulture and agriculture allows for the production of seedless fruits and increases the productivity and quality of agricultural crops. Thus, several studies have shown the effect of synthetic auxin (NAA) and gibberellins on improving fruit set and growth, increasing the size and quality of many fruits [8]. However, some studies have shown that residues of PGRs applied to agricultural crops are associated with genotoxicity, hepatotoxicity, and renal toxicity, which pose a significant risk to human health [8]. It is important to consider the application rates, application methods, and safe intervals for each use between application and harvest, which should be defined and approved by international and national authorities to control PGR residues in crops to maintain food safety [8]. In addition, the use of chemically synthesized organic compounds has both direct and indirect environmental impacts (including eutrophication and soil degradation), as well as increased energy consumption associated with their production [6], which should be considered as a negative effect of using such compounds.

Among synthetic compounds, thiazolyl acetic acids deserve attention, some derivatives of which at concentrations from 10 to 1000 µg/mL exhibited growth-regulating (namely growth-stimulating) properties in wheat and peas according to the results of the growth test [9]. In particular, 2-chlorothiazole-4-acetic acid had appreciable activity, whilst activity was also observed with the 2-amino-, 2-methylamino-, and 2-methyl-analogues [9]. In addition, some derivatives of thiazolyl acetic acids (2-(2-aminothiazol-5-yl)acetic acid and 2-[2-(methylamino)-1,3-thiazol-5-yl]acetic acid) and thiazolidine acetic acids (2-(2,4-dioxothiazolidin-5-yl)acetic acid) also have phytotoxic properties against wheat and peas according to the growth test, as shown by Garraway in 1970 [9].

Since the search for new biologically active compounds remains a relevant research direction, we previously synthesized a number of thiazolyl acetic acid derivatives, which, according to their physicochemical characteristics, are promising biologically active compounds [10]. To assess their growth-regulatory properties, this study used a growth phytotest, which is an accessible and simple research method and is used in a number of similar studies [11–13]. In particular, test plants sensitive to the effects are *Lepidium sativum* L. [14–23] and *Sinapis alba* L. [24–29].

The following scientific hypothesis was determined: thiazolyl acetic acid derivatives exhibit concentration-dependent growth-regulatory activity on seedlings of *L. sativum* and *S. alba*, which is structurally and species-specific, which is manifested in the

differences in the effects of individual compounds on the growth parameters and viability of test plants.

Therefore, the aim of this study was to investigate the growth-regulatory properties of both previously and newly synthesized thiazolyl acetic acid derivatives using a growth phytotest with *L. sativum* and *S. alba*.

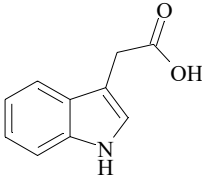
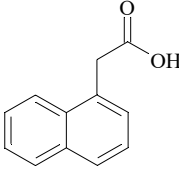
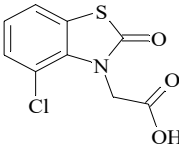
2. Materials and Methods

2.1. Compounds Under Investigation

The study used 1000 µg/mL, 100 µg/mL, and 10 µg/mL aqueous solutions of the compounds: compounds **1–5**—synthesized derivatives of thiazolyl acetic acid in the form of potassium salts of the corresponding acids (synthesis methods are described below); preparation **6** contained 3-indoleacetic acid, 3-indolylbutyric acid, and 1-naphthylacetic acid (from a commercial preparation Rhizopon™ AA 1% Powder (Rhizopon BV, Hazerswoude-Rijndijk, the Netherlands) for rooting plants, a regulator of plant growth and development), which are the active ingredients according to the manufacturer Rhizopon BV (Hazerswoude-Rijndijk, the Netherlands); compound **7** is a post-emergence herbicide benazolin (LGC Limited, Guildford, UK) [30] purchased online. The concentrations indicated (10, 100, and 1000 µg/mL) represent the final concentrations in the growth medium. The structure of the studied compounds is presented in Table 1. Log P was calculated using a free web tool SwissADME (Swiss Institute of Bioinformatics, Molecular Modeling Group, Switzerland) [31].

Table 1. Chemical structures of tested compounds.

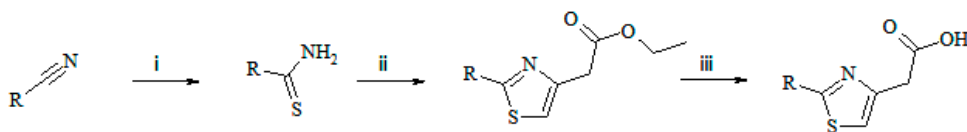
Symbol	Chemical Structure	Name	Log P *
1		2-[2-(3,3,3-trifluoropropyl)-1,3-thiazol-4-yl]acetic acid	2.37
2		2-[2-[1-(2-tert-butoxycarbonyl)piperidin-4-yl]-1,3-thiazol-4-yl]acetic acid	2.21
3		2-[2-(N-tert-butoxycarbonyl)-3-aminoethyl-1,3-thiazol-4-yl]acetic acid	1.62
4		2-(6-bromo-1,3-benzothiazol-2-yl)acetic acid	2.48
5		5-phenylthiazol-2-yl acetic acid	2.19
6		Composition with 3-indoleacetic acid (A), 3-indolylbutyric acid (B), 1-naphthylacetic acid (C)	1.83(A) 1.51(B) 2.33(C)

			
	B		
			
	C		
7		(4-chloro-2-oxo-1,3-benzothiazol-3(2H)-yl)acetic acid (Benazolin)	1.76

* Log P—logarithm of the octanol/water partition coefficient, characterizing the lipophilicity of the compound.

All starting materials for the synthesis of the indicated compounds were provided by Enamine Ltd. and used without further purification. Compounds **1** and **3** were synthesized for the first time, compounds **2**, **4**, **5** were already previously obtained [32–34], and, for some, we adapted other methods of preparation. As a source of auxin, namely indolylbutyric acid, a commercially available preparation Rhizopon™ AA 1% Powder (Rhizopon BV, Hazerswoude-Rijndijk, the Netherlands) was used, from which an alcoholic extract was obtained with subsequent dissolution in water to the appropriate concentration. The solvents were purified according to standard procedures. Column chromatography was performed using Kieselgel Merck 60 (230–400 mesh) as a stationary phase. The yields of the compounds refer to chromatographically and spectroscopically (¹H NMR spectroscopy) homogeneous material. ¹H NMR spectra were recorded at 500 MHz. Chemical shifts are given in ppm relative to the SiMe₄ (¹H) standard as an internal standard. Mass spectra were recorded using an LC-MS instrument with chemical ionization (CI). The spectra of the obtained compounds are given in Supplementary Materials S1.

The synthesis of thiazolyl acetic acids (compounds **1–3**) was carried out according to the general Scheme 1:



Scheme 1. Synthetic route for synthesis of compounds **1–3**. (i) H₂S, Py, TEA, rt, 8–24 h, 37–55%; (ii) ClCH₂COCH₂COOEt, EtOH, 80 °C, 8–12 h, 55–80%; (iii) KOH, H₂O, 100 °C, 1–2 h, 85–95%.

2-[2-(3,3,3-Trifluoropropyl)-1,3thiazol-5-yl]acetic acid (compound **1**) was obtained from 4,4,4-trifluorobutyronitrile. Hydrogen sulfide was bubbled through a solution of 12.3 g (0.1 mol) of 4,4,4-trifluorobutyronitrile in 30 mL of pyridine and 10.1 g (0.1 mol) of triethylamine with stirring at a rate of 1–2 bubbles per second for 24 h at room temperature. The mixture was poured into cold water, and after a certain period of time, the thioamide crystallized from the resulting emulsion as low-melting orange crystals.

The crystals were filtered off with suction, washed several times with cold water, and recrystallized from a mixture of isopropyl alcohol and hexane. Yield: 37%. M.p. 59 °C.

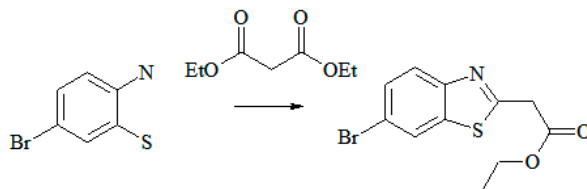
A total of 16.5 g (0.1 mol) of ethyl 4-chloro-3-oxobutanoate was added to a solution of 15.7 g (0.1 mol) of thioamide in 200 mL of ethanol; the mixture was heated under reflux for 12 h, the solvent was distilled off on a rotary evaporator, and a 10% aqueous solution of 0.2 mol of alkali was added to the resulting residue and heated for 2 h at 100 °C under reflux. The mixture was cooled and neutralized with 5% HCl solution to pH 7. The aqueous mixture was evaporated to dryness in a rotary evaporator, the residue was extracted with hot isopropanol, the solvent was evaporated, and the residue was washed with tert-butyl methyl ether, dried, and treated with a solution of hydrogen chloride in dioxane. The precipitate of 2-[2-(3,3,3-trifluoropropyl)-1,3thiazol-4-yl]acetic acid hydrochloride formed was filtered off and recrystallized from isopropanol, forming light gray crystals. Yield: 48%. Mp. 120–122 °C. ¹H NMR (500 MHz, DMSO-d₆): δ = 2.75 (m, 2H), 3.20 (m, 2H), 3.69 (s, 2H), 7.36 (s, 1H), 7.75–9.00 ppm (s, 2H); MS (APCI): m/z (%) = 100, 240 [M+H]⁺.

In a similar manner, thiazolyl acetic acids (compound 2) and (compound 3) were obtained from the corresponding nitriles, but the hydrochlorides of the acid esters after condensation formed crystalline precipitates upon cooling the reaction mixture, and the acids themselves were isolated from the aqueous solution after saponification of the esters by precipitation with a weak HCl solution.

2-[2-[1-(2-Tert-butoxycarbonyl)piperidin-4-yl]-1,3-thiazol-4-yl]acetic acid (compound 2) was synthesized according to the specified method and not according to the original patent [32]: cream-colored crystals. Final yield 42%. M.p. 122–124 °C. ¹H NMR (500 MHz, DMSO-d₆): δ = 1.38 (s, 9H), 1.47 (m, 2H), 1.96 (dd, 2H), 2.75–2.95 (m, 2H), 3.13 (m, 1H), 3.65 (s, 2H), 3.96 (dd, 2H) 7.29 (s, 1H), 12.37 ppm (s, 1H); MS (APCI): m/z (%) = 97.55, 325 [M-H]⁺.

2-[2-(N-Tert-butoxycarbonyl)-2-aminoethyl-1,3thiazol-4-yl]acetic acid (compound 3) was obtained by the above method as a cream-colored crystalline powder. Final yield 39%. M.p. 92–94 °C. ¹H NMR (500 MHz, DMSO-d₆): δ = 1.35 (s, 9H), 3.02 (m, 2H), 3.23 (m, 2H), 3.65 (s, 2H), 6.56–6.95 (m, 1H) 7.27 (s, 1H), 12.38 ppm (s, 1H); MS (APCI): m/z (%) = 100, 287 [M+H]⁺.

2-(6-Bromo-1,3-benzothiazol-2-yl)acetic acid ethyl ester (compound 4) was obtained by an adapted Trapani method [35] from the corresponding 5-bromo-2-aminothiophenol by reacting it with malonic ester in xylene in the presence of p-toluenesulfonic acid (Scheme 2), followed by chromatography of the reaction residue.



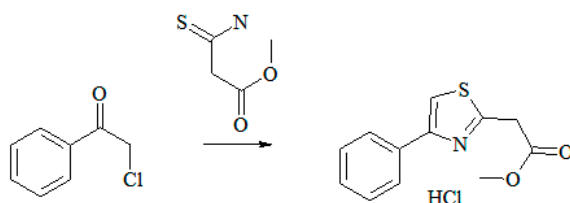
Scheme 2. Synthetic route for synthesis of compound 4.

For the experiment, the obtained ethyl 2-benzothiazolyl acetate is hydrolyzed with an aqueous alkali solution. Ethyl ester of 2-(6-Bromo-1,3-benzothiazol-2-yl)acetic acid (compound 4) is a yellow crystalline powder. Yield: 48%. Mp. 115–117 °C. ¹H NMR (500 MHz, DMSO-d₆): δ = 1.19 (t, 3H), 4.15 (dd, 2H), 4.30, (s, 2H), 7.64 (m, 1H), 7.88(m, 1H) 8.37 ppm (s, 1H); MS (APCI): m/z (%) = 97.79, 300 [M+H]⁺.

When trying to obtain a sample of pure acid from the ester hydrolysate, even under mild conditions, the acid is decarboxylated, as evidenced by the release of gas during

acidification of the hydrolysate, as well as the results of analytical studies. The main product in this case is 6-bromo-2-methyl-1,3-benzothiazole. Mp. 80–84 °C. ^1H NMR (500 MHz, DMSO-d_6): δ = 2.75 (s, 3H), 7.60 (d, 1H), 7.80 (d, 1H), 8.30 (s, 1H); MS (APCI): m/z (%) = 90.75, 228 $[\text{M}+\text{H}]^+$.

2-(4-Phenyl-1,3-thiazol-2-yl)acetic acid (compound 5) was obtained as the hydrochloride of the corresponding methyl ester by the reaction of α -phenacyl chloride with methyl 2-carbamoylthioacetate according to the method of Scherschener [34] (Scheme 3).



Scheme 3. Synthetic route for synthesis of compound 5.

The experiment used the hydrolysate of this ester, obtained by heating the appropriate amounts of ester and alkali with subsequent dilution of the resulting solution of a neutral solution of the acid salt to the required concentration. 2-(4-phenyl-1,3-thiazol-2-yl)acetic acid hydrochloride: light brown crystalline powder. Mp. 150–152 °C. ^1H NMR (500 MHz, DMSO-d_6): δ = 3.66 (s, 3H), 4.23 (s, 2H), 7.31, (m, 1H), 7.40 (m, 2H), 7.91 (m, 2H) 8.87 ppm (s, 1H); MS (APCI): m/z (%) = 98.71, 234 $[\text{M}+\text{H}]^+$.

When obtaining an acid sample by acidification of the alkaline hydrolysate with a weak solution of hydrochloric acid, the sample is partially decarboxylated. That is why the obtained sample contains an admixture of 2-methyl-4-phenyl-1,3-thiazole, which is confirmed by analytical data. Mp. 170–174 °C. ^1H NMR (500 MHz, DMSO-d_6): δ = 4.10 (s, 3H), 7.30 (m, 1H), 7.40 (m, 2H), 7.90 (m, 2H), 8.00 (s, 1H), 12.50 ppm (s, 1H); MS (APCI): m/z (%) = 91.53, 230 $[\text{M}+\text{H}]^+$. Signal of 2-methyl-4-phenyl-1,3-thiazole: MS (APCI): m/z (%) = 8.47, 176 $[\text{M}+\text{H}]^+$.

2.2. Growth Test with *L. sativum* and *S. alba* for Phytotoxicity of Compounds

The growth test was carried out in Petri dishes, using as test plants representatives of the class *Dicotyledones*—*L. sativum* and *S. alba*, the seeds of which were purchased in the online store dr-green.store. In the process of preparing the experiment, the filter paper in the Petri dishes was moistened either with distilled water (control) or with a 10–1000 $\mu\text{g/mL}$ aqueous solution of the corresponding substance (experiment). Next, 10 seeds of the corresponding test plant were placed in each Petri dish and germinated in the dark at a temperature of 23 ± 2 °C, assessing the seed germination energy on the 3rd day from the beginning of the experiment, seed germination and biometric-morphometric indicators (length of roots and above-ground part of seedlings, simplified vitality index (SVI), root/shoot ratio (R/S)) on the 5th day (*L. sativum*) and the 6th day (*S. alba*) from the beginning of the experiment. The following formulas were used [36]:

$$\text{GE} = (\text{N}_1/\text{N}_0) \times 100\%, \quad (1)$$

where GE is germination energy, %; N_1 —number of seeds germinated on the 3rd day; N_0 —number of test seeds.

$$\text{GP} = (\text{N}_t/\text{N}_0) \times 100\%, \quad (2)$$

where GP is germination percentage, %; N_t number of seeds germinated on the 5th (*L. sativum*) or on the 6th (*S. alba*) day; N_0 —number of test seeds.

$$SVI = GP \times LS_i, \quad (3)$$

where SVI is simplified vitality index; GP is germination percentage, %; LS_i —the seedling length at the end of germination (mm).

Based on the obtained data, phytotoxic indices were also calculated: seed germination index (SGI) and root length index (RLI), as described previously [37]. Toxicity scale used [38]:

- −0.25 ≤ SGI or RLI < 0—slight toxicity;
- −0.5 ≤ SGI or RLI < −0.25—moderate toxicity;
- −0.75 ≤ SGI or RLI < −0.5—high toxicity;
- −1 ≤ SGI or RLI < −0.75—extreme toxicity.

2.3. Statistical Analysis of Results

All variants of the research were carried out in triplicate. The arithmetic mean and the error of the arithmetic mean were determined. The significance of the differences was assessed by the ANOVA analysis of variance followed by Dunn's post hoc test. The Past 4.03 software package was used for statistical data processing [39].

3. Results

3.1. Growth Indicators of *L. sativum* Under the Influence of Aqueous Solutions of Thiazolyl Acetic Acid Derivatives

The results of this study of growth indicators of *L. sativum* under the influence of 10–1000 µg/mL aqueous solutions of the studied compounds are given in Figure 1 and Tables 2 and 3.

Table 2. Test indicators of *L. sativum* under the influence of 10–1000 µg/mL aqueous solutions of the studied compounds.

Experiment Option	GE, % Relative to Control	GP, % Relative to Control	LR, % Relative to Control	LAP, % Relative to Control	SVI, % Relative to Control
C1-1000	80 ± 15	93 ± 7	2.0 ± 0.9 *	12.3 ± 1.4 *	5.2 ± 0.5 *
C2-1000	100 ± 0	100 ± 0	7.7 ± 0.7 *	19.4 ± 0.8 *	11.8 ± 0.6 *
C3-1000	100 ± 0	100 ± 0	45.2 ± 1.7 *	92.1 ± 2.4 *	61.8 ± 1.8 *
C4-1000	0*	0*	0*	0*	0*
C5-1000	27 ± 3*	37 ± 7*	5.0 ± 1.0 *	9.9 ± 2.0 *	2.5 ± 0.5 *
C6-1000	0*	0*	0*	0*	0*
C7-1000	97 ± 3	97 ± 3	2.6 ± 0.1 *	7.3 ± 0.3 *	3.9 ± 0.2 *
C1-100	100 ± 0	100 ± 0	14.3 ± 0.6 *	60.1 ± 1.8 *	30.2 ± 0.8 *
C2-100	97 ± 3	97 ± 3	35.6 ± 2.1 *	84.5 ± 3.7 *	50.9 ± 2.3 *
C3-100	97 ± 3	97 ± 3	92.7 ± 5.3	98.0 ± 5.5	92.7 ± 4.9
C4-100	93 ± 3	93 ± 3	13.5 ± 1.4 *	31.8 ± 1.8 *	18.5 ± 1.3 *
C5-100	90 ± 6	93 ± 7	27.8 ± 4.8 *	65.2 ± 4.1 *	38.1 ± 3.8 *
C6-100	90 ± 10	90 ± 10	6.9 ± 0.7 *	11.6 ± 1.0 *	7.8 ± 0.7 *
C7-100	97 ± 3	97 ± 3	14.9 ± 0.9 *	20.8 ± 1.0 *	16.2 ± 0.7 *
C1-10	100 ± 0	100 ± 0	77.3 ± 4.0 *	97.1 ± 3.8	83.1 ± 3.6 *
C2-10	100 ± 0	100 ± 0	61.4 ± 3.4 *	101.9 ± 3.6	73.3 ± 3.1 *
C3-10	100 ± 0	100 ± 0	107.5 ± 3.4 *	104.6 ± 2.7	105.7 ± 3.1 *
C4-10	100 ± 0	100 ± 0	85.4 ± 3.6 *	76.9 ± 1.9 *	83.0 ± 2.8 *
C5-10	93 ± 3	93 ± 3	97.8 ± 3.1	97.1 ± 2.7	90.8 ± 2.2
C6-10	97 ± 3	97 ± 3	25.4 ± 2.0 *	51.6 ± 1.9 *	31.9 ± 1.6 *
C7-10	100 ± 0	100 ± 0	51.9 ± 3.4 *	76.4 ± 4.4 *	59.7 ± 3.1 *

Note: C1–C7 indicate the test compounds in aqueous solutions of 10, 100, or 1000 µg/mL concentration, respectively. GE—germination energy; GP—germination percentage; LR—length of the roots; LAP—length of the above-ground part. * The difference compared with the control is significant at $p \leq 0.05$.

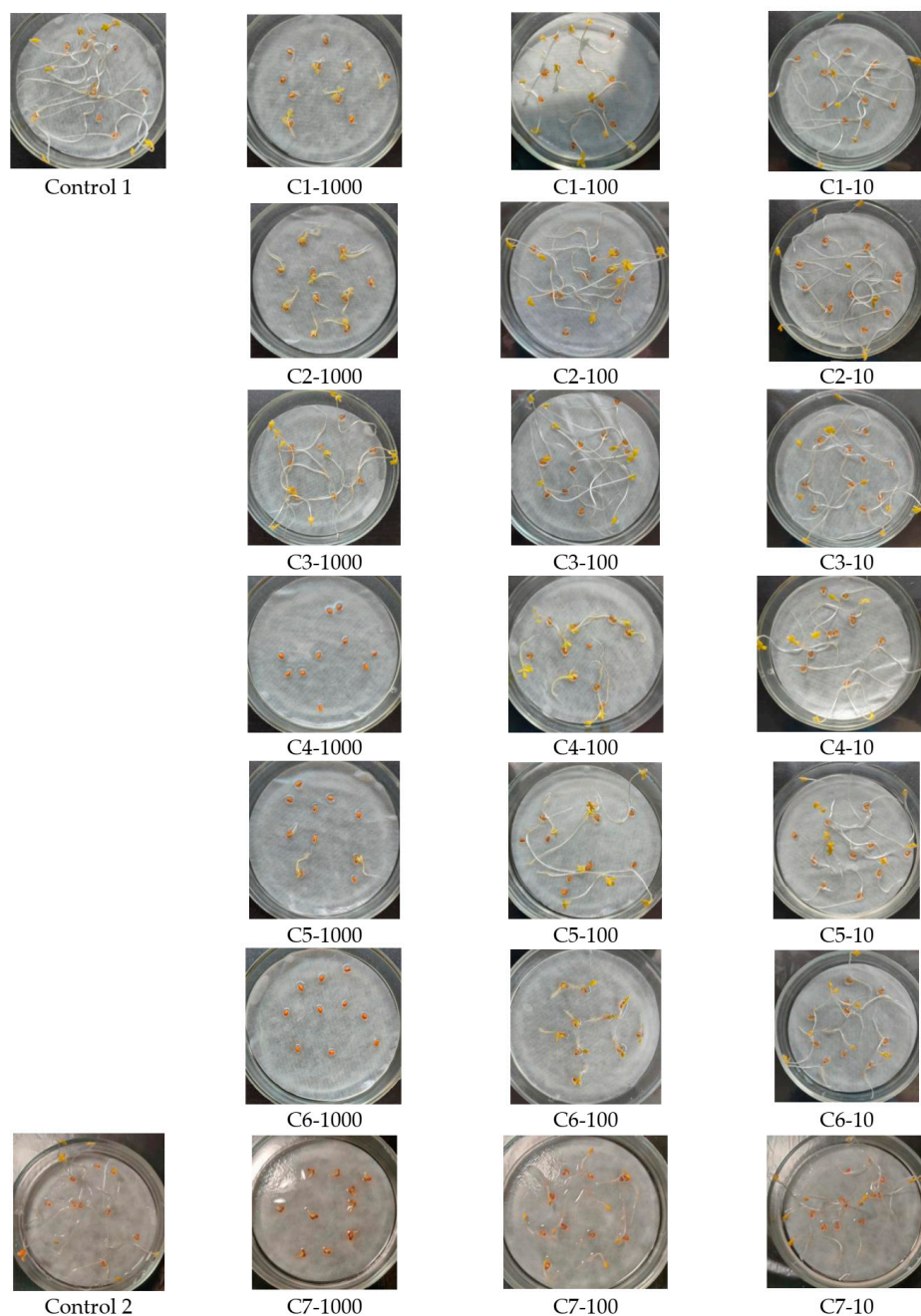


Figure 1. *L. sativum* seeds when treated with the test compounds (5th day of germination). C1–C7 indicate the test compounds in aqueous solutions of 10, 100, or 1000 µg/mL concentration, respectively.

Table 3. Root/shoot ratio of *L. sativum* seedlings under the influence of the studied compounds.

Compound	Compound Concentration, µg/mL	Root/Shoot Ratio
Control 1	0	2.1 ± 0.06
1	1000	0.3 ± 0.04 *
	100	0.5 ± 0.02 *
	10	1.9 ± 0.1
	1000	0.7 ± 0.1 *

	100	0.8 ± 0.05 *
	10	1.5 ± 0.1 *
	1000	0.9 ± 0.03 *
3	100	1.9 ± 0.1
	10	2.5 ± 0.07 *
	1000	0 *
4	100	0.8 ± 0.06 *
	10	2.7 ± 0.1 *
	1000	1.0 ± 0.3 *
5	100	0.8 ± 0.1 *
	10	2.5 ± 0.1 *
	1000	0 *
6	100	1.2 ± 0.1 *
	10	1.2 ± 0.1 *
	0	2.2 ± 0.2
Control 2		
7	1000	0.8 ± 0.06 **
	100	1.6 ± 0.1 **
	10	1.5 ± 0.1 **

* The difference compared with control 1 is significant at $p \leq 0.05$. ** The difference compared with control 2 is significant at $p \leq 0.05$.

According to the results of this study, thiazolyl acetic acid derivatives showed phytotoxic properties in relation to the growth indicators of *L. sativum*, but to varying degrees, depending on the concentration of the substances studied. It was established that the germination energy and germination of *L. sativum* seeds are affected by compounds **4** and **5** and preparation **6** at a concentration of 1000 µg/mL. At the same time, seed germination was not recorded under the action of compound **4** and preparation **6** at a concentration of 1000 µg/mL (Table 2).

Compound **5** at a concentration of 1000 µg/mL statistically significantly reduced the germination energy and germination of seeds compared to the control: by 3.7 times and 2.7 times, respectively (Table 2). At the same time, the length of the roots was significantly less than in the control, by 20.1 times, and the length of the above-ground part—by 10.1 times (Table 2).

Compounds **1**, **2**, and **3** and herbicide benazolin (compound **7**) at a concentration of 1000 µg/mL, although they did not affect the germination energy and seed germination, showed phytotoxic properties in relation to the biometric and morphometric indicators of seedlings. Thus, a statistically significant decrease was noted compared to the control in both the length of the roots of seedlings—by 51.4 times, 13.0 times, 2.2 times, 39.3 times, respectively, and the length of their aerial part—by 8.2 times, 5.2 times, 1.1 times, 13.8 times, respectively (Table 2).

When studying lower concentrations (10–100 µg/mL) of thiazolyl acetic acid derivatives, the absence of a statistically significant effect on the germination energy and seed germination of *L. sativum* was recorded. At the same time, inhibition of the growth of test plant seedlings was observed under the influence of compound **1** (except for its concentration of 10 µg/mL, at which the length of the aerial part remained at the control level), compounds **2**, **4**, **5** (except for their concentration of 10 µg/mL, at which the length of the roots and aerial part remained at the control level), preparation **6**, and compound **7** (herbicide benazolin). Under the influence of compound **3** at a concentration of 100 µg/mL, the length of the roots and aerial part remained at the control level, but, at a concentration of 10 µg/mL, significantly greater root length and total seedling length were noted. The simplified vitality index of *L. sativum* was statistically significantly lower than

the control value under the influence of all studied compounds, except for compound 3 (100 µg/mL and 10 µg/mL) and compound 5 (10 µg/mL), for which the specified index was within the control limits (Table 2).

Analysis of root/shoot ratio of *L. sativum* seedlings under the influence of the studied compounds showed a decrease in this indicator compared to the control for all compounds at concentrations of 100–1000 µg/mL, with the exception of compound 3 (Table 3). Root/shoot ratio of *L. sativum* seedlings under the influence of compound 3 was at the same level as the control. This indicator was also at the same level as the control for compound 1 at a concentration of 10 µg/mL (Table 3). However, the root/shoot ratio of *L. sativum* seedlings was statistically significantly higher than in the control under the influence of compounds 3, 4, and 5 and statistically significantly lower than in the control under the influence of compound 2, preparation 6, and compound 7 (herbicide benazolin) at their concentrations of 10 µg/mL (Table 3).

According to the calculated phytotoxic indices of the effect of 1000 µg/mL aqueous solutions of the studied compounds on *L. sativum* (Table 4), solutions of all the studied compounds are extremely toxic, with the exception of compound 3, which is highly toxic. With a decrease in the concentration of the compounds, the toxicity of their aqueous solutions (according to the calculated phytotoxic indices) also decreases, but not for all compounds—100 µg/mL solutions of compounds 1 and 4, preparation 6, and compound 7 (herbicide benazolin) remain extremely toxic. The 100 µg/mL solutions of compounds 2 and 5 are highly toxic, and the solution of compound 3 is weakly toxic. The 10 µg/mL solutions of compounds 1, 4, and 5 are weakly toxic, compounds 2 and 7 are moderately toxic, preparation 6 is highly toxic, and the solution of compound 3 at a concentration of 10 µg/mL did not show phytotoxicity (Table 4).

Table 4. Phytotoxic indices of the effect of 10–1000 µg/mL aqueous solutions of the studied compounds on *L. sativum*.

Research Option	SGI	RLI	Interpretation of the Results of Phytotest	Comments
Control	0.00	0.00	No toxicity	No inhibition of growth
C1-1000	−0.07	−0.98	Extreme toxicity	Inhibition of growth > 90%
C2-1000	0.00	−0.92	Extreme toxicity	Inhibition of growth > 90%
C3-1000	0.00	−0.55	High toxicity	Inhibition of growth > 50%
C4-1000	−1.00	−1.00	Lethal effect, extreme toxicity	No root growth observed
C5-1000	−0.63	−0.95	Extreme toxicity	Inhibition of growth > 90%
C6-1000	−1.00	−1.00	Lethal effect, extreme toxicity	No root growth observed
C7-1000	−0.03	−0.98	Extreme toxicity	Inhibition of growth > 90%
C1-100	0.00	−0.86	Extreme toxicity	Inhibition of growth > 80%
C2-100	−0.03	−0.64	High toxicity	Inhibition of growth > 60%
C3-100	−0.03	−0.07	Slight toxicity	A slight inhibition of growth
C4-100	−0.07	−0.87	Extreme toxicity	Inhibition of growth > 80%
C5-100	−0.07	−0.72	High toxicity	Inhibition of growth > 70%
C6-100	−0.1	−0.93	Extreme toxicity	Inhibition of growth > 90%
C7-100	−0.03	−0.85	Extreme toxicity	Inhibition of growth > 80%
C1-10	0.00	−0.23	Slight toxicity	A slight inhibition of growth
C2-10	0.00	−0.39	Moderate toxicity	Inhibition of growth > 30%
C3-10	0.00	0.08	No toxicity	No inhibition of growth
C4-10	0.00	−0.15	Slight toxicity	A slight inhibition of growth
C5-10	−0.07	−0.02	Slight toxicity	A slight inhibition of growth
C6-10	−0.03	−0.75	High toxicity	Inhibition of growth > 70%
C7-10	0.00	−0.48	Moderate toxicity	Inhibition of growth > 40%

Note: C1–C7 indicate the test compounds in aqueous solutions of 10, 100, or 1000 µg/mL concentration, respectively.

3.2. Growth Indicators of *S. alba* Under the Influence of Aqueous Solutions of Thiazolyl Acetic Acid Derivatives

The results of this study of growth rates of *S. alba* under the influence of 10–1000 $\mu\text{g/mL}$ aqueous solutions of the studied compounds are given in Figure 2 and Tables 5 and 6.

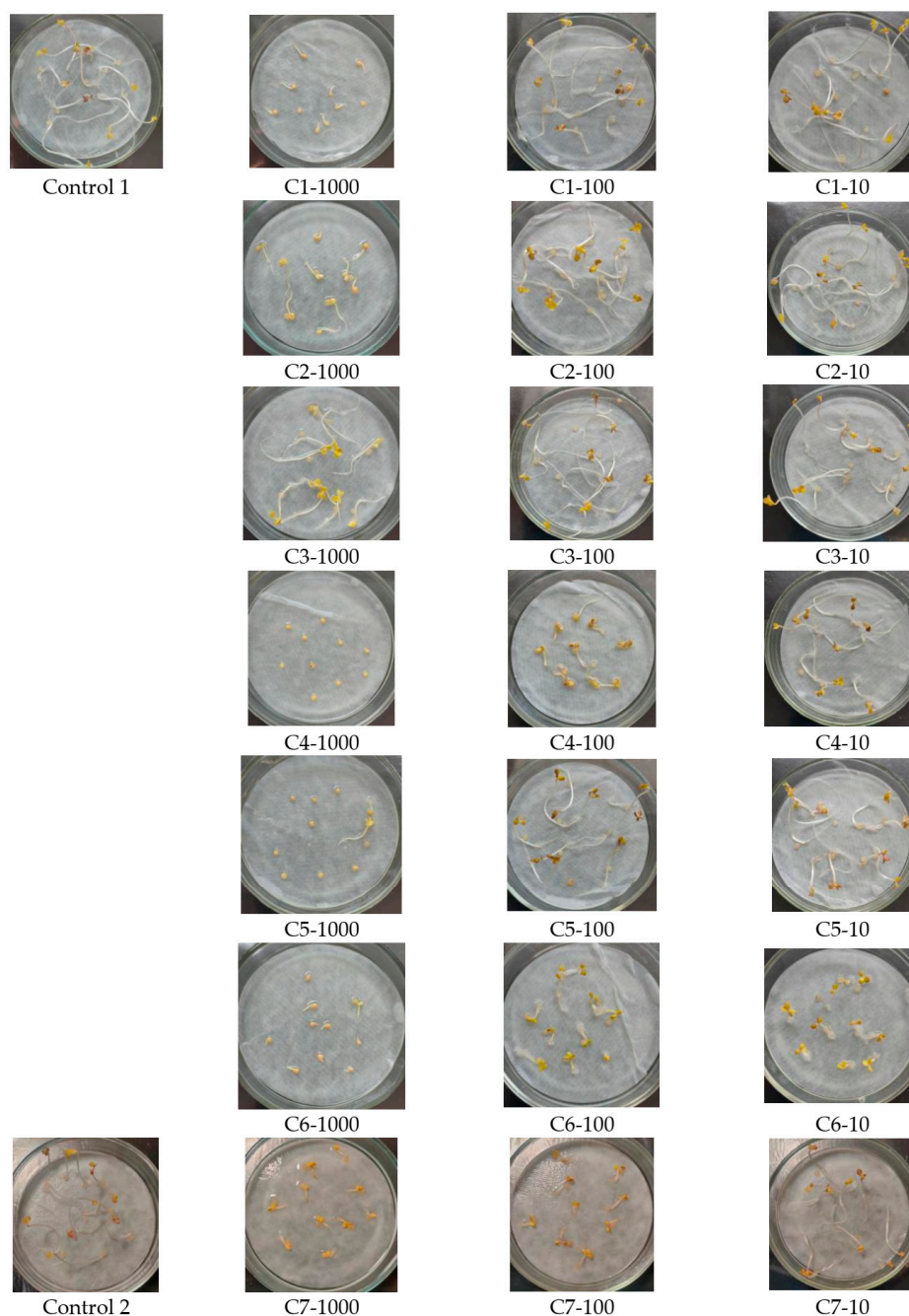


Figure 2. *S. alba* seeds when treated with the test compounds (5th day of germination). C1–C7 indicate the test compounds in aqueous solutions of 10, 100, or 1000 $\mu\text{g/mL}$ concentration, respectively.

Table 5. Test indicators of *S. alba* under the influence of 10–1000 µg/mL aqueous solutions of the studied compounds.

Experiment Option	GE, % Relative to Control	GP, % Relative to Control	LR, % Relative to Control	LAP, % Relative to Control	SVI, % Relative to Control
C1-1000	80 ± 10	83 ± 9	2.5 ± 0.2 *	10.4 ± 1.0 *	4.0 ± 0.3 *
C2-1000	93 ± 3	93 ± 3	5.5 ± 0.5 *	20.5 ± 1.7 *	9.1 ± 0.7 *
C3-1000	100 ± 0	100 ± 0	19.3 ± 1.8 *	55.3 ± 3.7 *	29.5 ± 2.0 *
C4-1000	0*	0*	0 *	0 *	0 *
C5-1000	17 ± 3*	17 ± 3*	4.9 ± 1.0 *	20.3 ± 4.4 *	1.6 ± 0.3 *
C6-1000	80 ± 10	87 ± 13	1.6 ± 0.2 *	5.2 ± 0.5 *	2.3 ± 0.2 *
C7-1000	103 ± 0	103 ± 0	3.3 ± 0.1 *	9.0 ± 0.5 *	5.2 ± 0.2 *
C1-100	97 ± 3	97 ± 3	18.7 ± 1.6 *	92.7 ± 4.9	38.5 ± 0.0 *
C2-100	97 ± 3	97 ± 3	27.0 ± 2.5 *	81.5 ± 3.4 *	41.2 ± 2.4 *
C3-100	100 ± 0	100 ± 0	77.7 ± 4.7 *	105.8 ± 2.9	85.1 ± 3.7 *
C4-100	97 ± 3	100 ± 0	4.0 ± 0.5 *	40.4 ± 3.7 *	14.3 ± 1.2 *
C5-100	93 ± 3	93 ± 3	38.9 ± 4.4 *	98.8 ± 4.6	52.1 ± 3.7 *
C6-100	97 ± 3	97 ± 3	3.8 ± 0.6 *	9.0 ± 1.0 *	5.1 ± 0.6 *
C7-100	93 ± 0	97 ± 3	5.5 ± 0.3 *	15.2 ± 1.9 *	8.3 ± 0.7 *
C1-10	97 ± 3	97 ± 3	36.6 ± 3.6 *	106.8 ± 5.5 *	69.0 ± 4.5 *
C2-10	100 ± 0	100 ± 0	44.3 ± 4.6 *	95.6 ± 4.7 *	74.2 ± 4.8 *
C3-10	100 ± 0	100 ± 0	82.4 ± 6.2	108.6 ± 5.2 *	111.9 ± 5.8
C4-10	93 ± 3	93 ± 3	36.5 ± 4.8 *	87.2 ± 4.7	59.5 ± 4.8 *
C5-10	97 ± 3	97 ± 3	42.7 ± 5.2 *	91.4 ± 5.0	68.5 ± 5.1 *
C6-10	100 ± 0	100 ± 0	4.7 ± 0.4 *	26.4 ± 1.8 *	13.8 ± 1.0 *
C7-10	103 ± 0	103 ± 0	43.7 ± 4.4 *	59.2 ± 3.0 *	50.2 ± 3.6 *

Note: C1–C7 indicate the test compounds in aqueous solutions of 10, 100, or 1000 µg/mL concentration, respectively. GE—germination energy; GP—germination percentage; LR—length of the roots; LAP—length of the above-ground part.* The difference compared with the control is significant at $p \leq 0.05$.

Table 6. Root/shoot ratio of *S. alba* seedlings under the influence of the studied compounds.

Compound	Compound Concentration, µg/mL	Root/Shoot Ratio
Control 1	0	2.5 ± 0.1
1	1000	0.7 ± 0.06 *
	100	0.5 ± 0.03 *
	10	0.8 ± 0.08 *
2	1000	0.8 ± 0.08 *
	100	0.8 ± 0.07 *
	10	1.1 ± 0.1 *
3	1000	0.9 ± 0.06 *
	100	1.7 ± 0.1 *
	10	1.9 ± 0.2 *
4	1000	0 *
	100	0.3 ± 0.03 *
	10	1.0 ± 0.1 *
5	1000	0.7 ± 0.16 *
	100	1.0 ± 0.1 *
	10	1.1 ± 0.1 *
6	1000	0.8 ± 0.09 *

	100	1.1 ± 0.08 *
	10	0.5 ± 0.05 *
Control 2	0	2.4 ± 0.3
	1000	0.8 ± 0.06 **
7	100	1.1 ± 0.1 **
	10	1.6 ± 0.2 **

* The difference compared with the control is significant at $p \leq 0.05$. ** The difference compared with the control 2 is significant at $p \leq 0.05$.

It was found that the effect of 1000 µg/mL aqueous solutions of compounds 1–5 on the growth parameters of *S. alba* is similar to that described above for *L. sativum*. At the same time, no statistically significant changes in the germination energy and seed germination were observed for the studied compounds 1, 2, 3, and 7 (herbicide benazolin) (Table 5). For compound 5, a decrease in these parameters was recorded compared to the control by 5.9 times, which is greater than that observed for the experiment with *L. sativum*. The length of the roots and the above-ground part of *S. alba* seedlings was statistically significantly less than in the control, respectively, by 40.8 times and 9.6 times (compound 1), by 18.2 times and 4.9 times (compound 2), by 5.2 times and 1.8 times (compound 3), and by 20.4 times and 4.9 times (compound 5). As on *L. sativum*, compound 4 also showed herbicidal properties on *S. alba*—under its action, the seeds did not germinate (Table 5).

At the same time, a difference was noted in the manifestation of the action of preparation 6 at a concentration of 1000 µg/mL on *S. alba* seeds compared to the action on *L. sativum* seeds. Unlike *L. sativum*, *S. alba* seeds under the action of preparation 6 germinated, and the germination energy and seed germination were on a par with the control. However, the length of the roots and the length of the above-ground part of the seedlings were statistically significantly less than in the control—63.8 times and 19.3 times, respectively (Table 5).

When treated with compound 7 (herbicide benazolin), germination energy and germination of *S. alba* seeds were (as in the case of *L. sativum*) on par with the control, but root length and above-ground part length were statistically significantly lower compared to the control—30.7 times and 11.2 times, respectively.

The 100 µg/mL aqueous solutions of the compounds did not affect the germination energy and germination of *S. alba* seeds, but they changed the growth indicators of the test plant seedlings in different ways (Table 5). Thus, statistically significant inhibition of root growth was observed compared to the control—5.4 times (compound 1), 3.7 times (compound 2), 1.3 times (compound 3), 25 times (compound 4), 2.6 times (compound 5), 26.3 times (preparation 6), and 18.1 times (compound 7) (Table 5). Also, compounds 2 and 4, preparation 6, and compound 7 statistically significantly inhibited the growth of the above-ground part—1.2 times, 2.5 times, 11.1 times, and 6.6 times, respectively.

The 10 µg/mL aqueous solutions of the compounds did not affect the germination energy and germination of *S. alba* seeds but had a suppressive effect on the growth of seedlings of this plant. Thus, a statistically significant decrease in the length of the roots of seedlings compared to the control was noted under the action of the studied compounds 1 (by 2.7 times), 2 (by 2.3 times), 4 (by 2.7 times), 5, and 7 (by 2.3 times) and preparation 6 (by 21.3 times). Compound 3 did not show a suppressive effect on the root length indicator—the differences compared to the control are statistically insignificant (Table 5). The length of the above-ground part was suppressed under the action of compound 2 (by 1.1 times), preparation 6 (by 3.8 times), and compound 7 (by 1.7 times), and, under the action of compounds 4 and 5, the differences in this indicator compared to the control were statistically insignificant (Table 5). At the same time, under the action of

compounds **1** and **3** at a concentration of 0.001%, a significant stimulation of the growth of the above-ground part by 1.1 times was noted, although, in terms of SVI, compound **1** at this concentration inhibits plant growth, and compound **3** has an SVI at the same level as the control (Table 5).

The R/S ratio of *S. alba* under the influence of all the studied compounds and concentrations was statistically significantly lower than in the control (Table 6). In particular, the lowest values were recorded for compound **4** and preparation **6**. According to the calculated phytotoxic indices of the influence of aqueous solutions of the studied compounds on the growth performance of *S. alba*, all the studied solutions at 1000 µg/mL concentration were extremely toxic; at 100 µg/mL concentration—extremely toxic (compounds **1**, **4**, and **7** and preparation **6**), highly toxic (compounds **2** and **5**) and weakly toxic (compound **3**); at 10 µg/mL concentration—extremely toxic (preparation **6**), highly toxic (compounds **1**, **2**, **4**, **5**, and **7**) and weakly toxic (compound **3**) (Table 7).

Table 7. Phytotoxic indices of the effect of 10–1000 µg/mL aqueous solutions of the studied compounds on *S. alba*. Note: C1–C7 indicate the test compounds in aqueous solutions of 10, 100, or 1000 µg/mL concentration, respectively.

Research Option	SGI	RLI	Interpretation of the Results of Phytotest	Comments
Control	0.00	0.00	No toxicity	No inhibition of growth
C1-1000	−0.17	−0.98	Extreme toxicity	Inhibition of growth > 90%
C2-1000	−0.07	−0.95	Extreme toxicity	Inhibition of growth > 90%
C3-1000	0.00	−0.81	Extreme toxicity	Inhibition of growth > 80%
C4-1000	−1.00	−1.00	Lethal effect, extreme toxicity	No root growth observed
C5-1000	−0.83	−0.95	Extreme toxicity	Inhibition of growth > 90%
C6-1000	−0.13	−0.98	Extreme toxicity	Inhibition of growth > 90%
C7-1000	0.03	−0.97	Extreme toxicity	Inhibition of growth > 90%
C1-100	−0.03	−0.81	Extreme toxicity	Inhibition of growth > 80%
C2-100	−0.03	−0.73	High toxicity	Inhibition of growth > 70%
C3-100	0.00	−0.22	Slight toxicity	A slight inhibition of growth
C4-100	−0.03	−0.96	Extreme toxicity	Inhibition of growth > 90%
C5-100	−0.07	−0.61	High toxicity	Inhibition of growth > 60%
C6-100	−0.03	−0.96	Extreme toxicity	Inhibition of growth > 90%
C7-100	−0.04	−0.95	Extreme toxicity	Inhibition of growth > 90%
C1-10	−0.03	−0.63	High toxicity	Inhibition of growth > 60%
C2-10	0.00	−0.56	High toxicity	Inhibition of growth > 50%
C3-10	0.00	−0.18	Slight toxicity	A slight inhibition of growth
C4-10	−0.07	−0.64	High toxicity	Inhibition of growth > 60%
C5-10	−0.03	−0.57	High toxicity	Inhibition of growth > 50%
C6-10	0.00	−0.95	Extreme toxicity	Inhibition of growth > 90%
C7-10	0.03	−0.56	High toxicity	Inhibition of growth > 50%

Therefore, the results obtained in this study indicate the biological activity of both previously and newly synthesized thiazolyl acetic acid derivatives. Showing high herbicidal properties at a concentration of 1000 µg/mL (primarily the compound with a benzothiazole fragment), the studied thiazolyl acetic acid derivatives with decreasing concentration (100 µg/mL and 10 µg/mL) reduce phytotoxicity to its complete elimination against *L. sativum* and *S. alba* for the compound 2-[2-(N-tert-butoxycarbonyl)-aminoethyl-1,3-thiazol-4-yl]acetic acid (compound **3**) and against *L. sativum* for the compound 5-phenylthiazol-2-yl acetic acid (compound **5**). A stimulating effect on the length of the above-ground part of *S. alba* seedlings was recorded for 2-[2-(3,3,3-trifluoropropyl)-1,3-

thiazol-4-yl]acetic acid (compound 1) and 2-[2-(N-tert-butoxycarbonyl)-aminoethyl-1,3-thiazol-4-yl]acetic acid (compound 3) at their concentration of 10 µg/mL; however, an improvement in the vitality index under the action of these compounds was not observed. Therefore, the results of this study, supplementing the information on thiazolyl acetic acid derivatives as growth-regulating compounds, expand the knowledge about promising herbicidal compounds with a possible hormetic effect.

4. Discussion

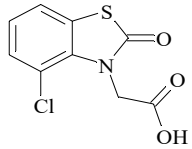
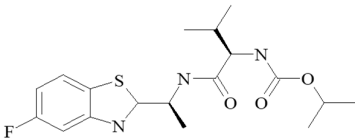
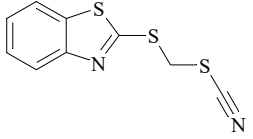
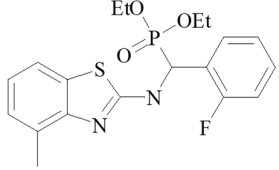
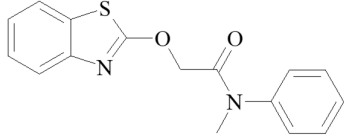
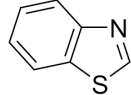
Plant growth, development, and reproduction are regulated, in particular, by phytohormones—auxins, the search for analogues of which among synthesized compounds (both previously and newly synthesized) continues to be a priority area of scientific research. Synthetic auxins cover a wide range of compounds, which includes not only organic acids with an indole nucleus. Their biological activity is due to the presence of a carboxyl group and a planar molecular structure formed by an aromatic or heterocyclic nucleus. In addition, an important role is played by the spatial arrangement of the carboxyl group relative to the planar part of the molecule. If the structure of the molecule does not fully correspond to these parameters but still causes a physiological response in the plant, it can undergo metabolic transformations that bring it closer to the active form [9].

Another important criterion when searching for compounds with potential auxin-like action is the use of chemoinformatic approaches, in particular, assessing compliance with Lipinski's rule for biologically active compounds [40]. Also, important characteristics include lipophilicity, which is determined by the Log P and Log D coefficients [41].

As part of the study of phytohormone-like action, a number of previously synthesized (compounds 2, 4, and 5) and newly synthesized (compounds 1 and 3) thiazolyl acetic acid derivatives were used. Although compounds 2, 4, and 5 were previously synthesized, specific information about their biological properties is missing from the scientific and methodological base available to us. In general, compounds of this class are known to have biological activity as antimicrobial compounds [42] and anti-inflammatory and immunosuppressive compounds [43–45], antioxidant activity [46,47] and cytotoxic activity against A549 lung adenocarcinoma cells [47]. Since information on their biological activity and relevant publications are lacking, the data presented in this work constitute the first publication on the growth-regulatory activity of the studied thiazolyl acetic acid derivatives.

The compounds selected for our study met the chemoinformatic requirements and contained both a carboxyl group and a planar heterocyclic system. In particular, the structure of compound 4 is very close to indolyl acetic acid, a derivative with a benzothiazole fragment, for compounds with which bioactive properties for plants are known (Table 8).

Table 8. Functional benzothiazole derivatives with biological effects on plants.

Chemical Structure	Name	Agrochemicals Group	Reference
	Benazolin	The post-emergence herbicide	[30]
	Benthiavalcicarbisopropyl	The fungicide	[48,49]
	Benthiazole ([(1,3-benzothiazol-2-yl)sulfanyl]methyl thiocyanate)	The fungicide	[50]
	Dufulin	The antiviral agent	[49,51]
	Mefenacet	The systemic herbicide	[49,52]
	Benzothiazole	The natural fungicide	[53]

In general, compounds with a benzothiazole moiety are actively investigated as agrochemicals, in particular as green, eco-friendly compounds for protecting plants against infections [53,54].

Although compound **4** has been synthesized previously, there is no information about its biological activity in the scientific and methodological database available to us. It is known that this compound was used for the synthesis of new benzothiazole sulfones, which were subsequently investigated as potent and selective inhibitors of endothelial lipase [33]. It can be noted that 2-(6-bromo-1,3-benzothiazol-2-yl)acetic acid serves as a key synthetic intermediate for the development of divalent ligand dimers, in particular with a piperazine core, which demonstrate significant potential as dual inhibitors of critical inflammatory targets, including inducible nitric oxide synthase (iNOS) and nuclear factor kappaB (NF-κB) [55]. In addition, structural analogues of this benzothiazolone skeleton have been reported to exhibit both anti-inflammatory and analgesic activity, which for some compounds is comparable to such established drugs as indomethacin and ketorolac [55].

The structure of compound **4** is similar to that of benazoline, which belongs to the auxin herbicides that demonstrate systemic mobility and selective action mainly against dicotyledonous weeds in cereal crops [9]. Our studies have demonstrated significant herbicidal properties of compound **4**—the root length index of test plants *L. sativum* and *S. alba* at a concentration of 100–1000 µg/mL indicated extreme phytotoxicity of the specified compound, and at a concentration of 10 µg/mL—weak toxicity. However, the

simplified vitality index at all tested concentrations recorded significant phytotoxicity of compound 4. Therefore, the new synthesized compound with a benzothiazole fragment (compound 4) exhibits growth inhibitory properties and is promising as a new herbicide. Comparison of its growth inhibitory properties with those of compound 7 (benazolin) showed that compound 4 is more effective at a concentration of 1000 µg/mL than benazolin since it completely inhibits seed germination, while, under the action of benazolin, the seeds germinate. At the same time, when the concentration is reduced to 100 µg/mL and 10 µg/mL, inhibition of the growth of test plants was observed, but to a lesser extent than for benazolin (compound 7). Currently, high activity of commercial preparation flumioxazine has also been shown at concentrations of 10 µg/mL [56]. At the same time, a species-dependent plant response was observed in 50% inhibition of the coleoptile length (EC50 values) to the action of alloxydim (a selective postemergence herbicide) and deallyloxydim: from 1.15 µg/mL (for *Bromus diandrus* L. under the action of Alloxydim-B 1) to 690.53 µg/mL (for *Solanum lycopersicum* L. cv. Marmande under the action of DP1-B 1) [57]. Doses of 25–100 µg/mL were used in the study of the toxicity of carbamate pesticides (carbamoyl, methomyl, carbofuran) in a bioassay with *Vigna mungo* L. [58]. A negative effect on plants was noted for all studied pesticides [58]. However, carbofuran, for which the maximum inhibition of test indicators was noted, at the highest concentration tested did not provide 100% inhibition—germination efficiency, root length, shoot length, plant survival, and tolerance index of *V. mungo* decreased by only 50, 75, 65, 70, and 66%, respectively, compared to the control. A glyphosate concentration of 1.35 µg/mL was effective for 50% inhibition of *S. alba* growth [24]. At the same time, 100% inhibition was not observed at the highest concentration tested (1296 µg/mL) [24]. Since herbicide application occurs in field conditions and is calculated in kg/ha, additional research is needed on effective concentrations of new potential herbicides under field experimental conditions. Larger studies using a set of different weeds, test animals to determine their sensitivity, and various toxicological and ecological assessments of the safety of these compounds, including food safety, are also needed.

Compounds 2 and 3 were included in this experiment to assess the influence of aminoalkyl radicals on the potential auxin-like activity. It was expected that, during metabolism, these compounds would lose their N-protecting groups, which would increase their hydrophilicity [4], facilitating the transition to transport forms and subsequent delivery to target cells. Phytotoxicity of compound 2 was manifested towards *L. sativum* and *S. alba* at all tested concentrations, but for compound 3 only at concentrations of 100–1000 µg/mL. At a concentration of 10 µg/mL of compound 3, its stimulating effect on the root growth and the general level of seedling viability (simplified vitality index) of *L. sativum* was noted, and a stimulating effect on the growth of the above-ground part of *S. alba* seedlings was also noted. Since the stimulating response in one plant trait does not necessarily correlate or coincide with the stimulating response in other plant traits [59], according to Agathokleous et al. [60], this should also apply to the same trait measured for roots and shoots. At low doses of stress, an increase in photosynthetic carbon uptake and an increase in its distribution in roots may be observed. At high doses of stress, a decrease in photosynthetic carbon uptake by stomatal closure may lead to a decrease in root biomass/elongation [60]. The R/S ratio also changes in a dose-dependent manner, which may affect ecological risk assessment and carbon storage estimates [61,62]. The main molecular mechanisms of hormonal response include the interrelationship between cellular signaling pathways, gene regulation, and adaptive processes [63]. Thus, in our study, a dose-dependent response of root/shoot ratio of *L. sativum* was observed under the influence of compound 3: at a concentration of 1000 µg/mL—inhibition of this indicator; at a concentration of 100 µg/mL—no changes compared to the control; at a concentration of 10 µg/mL—a weak stimulation. The ability of chemical and physical

agents to stimulate biological effects at doses below the threshold of toxicity, while causing toxicity at doses above that threshold, is called hormesis. The criteria for proving hormesis in a study are (1) the nature of the study design (e.g., total number of doses, number of doses below the toxic threshold, presence of an adequate control group), (2) the type of endpoints measured, (3) the magnitude and statistical significance of the responses, and (4) the ability to replicate the data [64]. Based on these, we can conclude that the data in our study are insufficient to define the observed results as hormetic. The number of doses of the compounds tested, including those below the toxic threshold, should be increased in future studies.

Compound 1 contains a trifluoropropyl fragment, which, due to the presence of fluorine in the alkyl substituent, significantly increases the value of the logP index, which confirms the thesis that fluorine atoms increase the lipophilicity of compounds [65]. Therefore, it is assumed that such a structure will contribute to better penetration of this molecule through biological membranes. In general, phytotoxic properties were noted for this compound at all tested concentrations regarding root growth and overall viability of seedlings (vitality index) of test plants, although a case of stimulating effect on the growth of the aerial part of *S. alba* was observed at a concentration of 10 µg/mL; however, the root/shoot ratio did not demonstrate a hormetic dose–response.

Compound 5, due to its high Log P. value (2.19), has significant possibilities of penetration through the cell membrane, which may explain its biological activity. In particular, phytotoxic properties regarding the growth indicators of *L. sativum* and *S. alba* were noted for the specified derivative at concentrations of 100–1000 µg/mL. However, at a concentration of 10 µg/mL, all test indicators (*L. sativum*) or the length of the aerial part (*S. alba*) were at the same level as the control. However, it was shown that the R/S ratio of *L. sativum* was statistically significantly higher than in the control.

Currently, there is no information on the ecotoxicological properties of the above-mentioned compounds, including their accumulation, hormonal effects, general mechanism of action and decomposition, interaction with fertilizers, etc., which require further thorough research.

The most studied compounds among those studied are the active components of the active substance of a commercial preparation for plant rooting, a regulator of plant growth and development (preparation 6)—indole-3-acetic acid, 1-naphthylacetic acid, and indole-3-butyric acid, for which growth-regulatory properties are known. In particular, indole-3-acetic acid is the main phytohormone from the auxin group, the homeostasis of which is critically important for ensuring optimal hormonal balance and regulation of plant growth and development. It is involved in the processes of cell division, cell elongation, their differentiation, as well as in the formation of fruits [66,67]. Plants usually synthesize indole-3-acetic acid in small quantities or obtain it from associated microorganisms, since excessive concentrations of this compound negatively affect physiological processes, slowing them down, in particular, inhibiting seed germination and plant growth [68–71]. For example, indole-3-acetic acid, produced by the fungus *Pythium aphanidermatum*, exhibited phytotoxic properties, and, according to the authors, it was the causal substance of Pythium red blight on bentgrass [72]. Also, the phytotoxic properties of indole-3-acetic acid (50 mg/L), produced by the basidiomycetous yeast *Rhodospiridiobolus fluvialis* DMKU-CP293, were demonstrated against the growth of weeds (*Cyperus rotundus* L.) [73]. According to the authors, indole-3-acetic acid has the potential to develop an herbicidal bioproduct to replace chemical herbicides banned in various countries [73]. The phytotoxic effect of elevated concentrations of indole-3-acetic acid is associated with increased ethylene synthesis due to activation of the enzyme aminocyclopropane-1-carboxylic acid, which is stimulated by the accumulation of indole-3-acetic acid. This leads to an “ethylene explosion”, which causes growth disorders and premature aging. In

addition to ethylene, an essential role in the phytotoxic effect of high doses of indole-3-acetic acid is played by excessive formation of abscisic acid [9].

1-Naphthylacetic acid is classified as a pesticide, namely a plant growth regulator [74–76]. 1-Naphthyl acetate is toxic to aquatic organisms, as demonstrated in testing with the aquatic plant *Lemna gibba* (Acute EC₅₀: 5.09–5.61 mg/L), and has pesticidal activity and toxicological relevance [75,77]. At the same time, stimulation of germination and germination rate of *Solanum linnaeanum* seeds after soaking for 24 h in 1-naphthyl acetate at 0.01% and 0.005% concentrations has been shown [78]. The herbicidal activity of 1-naphthylacetic acid was demonstrated against *Oxalis corniculata* L. In particular, a linear response of *O. corniculata* to ethyl ester of 1-naphthylacetic acid was observed for doses up to 5.6 kg/ha (approximately 80% of test plants were damaged in all experiments) and doses of 8.4 and 11.2 kg/ha (99% and 100% of test plants were damaged, respectively). The doses of 1-naphthylacetic acid that controlled *O. corniculata* (5.6 and 11.2 kg/ha) were not phytotoxic to several ornamental species [79]. There are reports that the use of synthetic auxins 1-naphthylacetic acid and 2(1-naphthyl)acetamide after flowering prevents premature fruit drop and thinning. However, when applied in larger amounts, growth inhibition and disruption of proper plant development are observed [80].

Indole-3-butyric acid is a plant growth regulator used to stimulate and accelerate rooting of plant cuttings and reduce transplant shock of non-food ornamental seedlings. Indole-3-butyric acid is also used on fruit and vegetable crops, field crops, and ornamental turf to stimulate the growth and development of flowers and fruits and to increase yield. Indole-3-butyric acid is classified as a biochemical pesticide because it is similar in structure and function to the natural plant growth hormone indole-3-acetic acid [81]. 3-Indolylbutyric acid stimulated germination of soybean seeds (*Glycine max* (L.) Merr.) of the Pella variety “86” without pretreatment (without soaking) in the concentration range from approximately 0.001% to 0.0001% [82]. However, treatment with concentrations above 0.001% inhibited germination. Thus, when using a 1% solution, germination of *G. max* seeds was completely inhibited [82]. Our study shows the phytotoxic properties of a commercial preparation with the components indole-3-acetic acid, 1-naphthylacetic acid, and indole-3-butyric acid (preparation 6) at all concentrations used, which indicates the herbicidal properties of this preparation.

Compound 7 is the herbicide benazolin [83], which is classified as a Category III (slightly hazardous) compound by the WHO Classification [30]. Its use is currently not approved, i.e., effectively banned, in the European Union [84]. Benazolin is known for its effective growth-inhibiting properties against a number of plants both in the field (in particular, against common cocklebur [85], and in laboratory conditions (in particular, when using wild mustard (*Brassica kaber* (DC.) L. C. Wheeler var. *pinnatifida* (Stokes) L. C. Wheeler), turnip rape (*Brassica campestris* L. ‘Echo’), and rape (*Brassica napus* L. ‘Target’) as test plants [86]. According to Schafer and Stobbe [86], based on the determined ED₅₀, wild mustard was more sensitive to foliar feeding with benazolin than turnip (19 times) and rapeseed (32 times). The authors explain the sensitivity of wild mustard by the features of the leaf surface, which led to high spray retention and rapid penetration of benazolin [86]. It is reported that benazolin, applied alone, rarely killed broadleaf weeds [87]. Also, compared to natural 3-indoleacetic acid, benazolin is approximately 100 times less active [87]. Our results confirm the high growth-inhibitory properties of benazolin (compound 7) against *L. sativum* and *S. alba*, but they are indeed lower than the similar properties of preparation 6, one of the active components of which is 3-indoleacetic acid.

5. Conclusions

Thus, the growth-regulatory activity of both previously and newly synthesized thiazolyl acetic acid derivatives was established, which depended on the concentration, chemical structure, and lipophilicity of the corresponding compound. A tendency was observed to decrease the growth-inhibitory activity of all the studied compounds with a decrease in their concentration and lipophilicity. At the same time, the lowest phytotoxicity was shown by compound **3** (2-[2-(N-tert-butoxycarbonyl)-3-aminoethyl-1,3thiazol-4-yl]acetic acid) and the highest by preparation **6**, which is a commercial preparation for plant rooting, a regulator of plant growth and development, and contains indole-3-acetic acid, 1-naphthylacetic acid, and indole-3-butyric acid as active ingredients. All the compounds tested are potential herbicides and show signs of a biphasic dose–response relationship, but further detailed studies are needed, including possible hormesis properties. However, a clear answer can be obtained by studying the physiological parameters of test plants exposed to concentrations lower than those used in this study. A promising direction for further research is the assessment of the growth-regulatory activity of these synthesized thiazolyl acetic acid derivatives at concentrations lower than 10 µg/mL, as well as the cyto- and genotoxicity of these compounds in the *Allium*-test using *Allium cepa* L.—a representative of the class *Monocotyledones*.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ijpb17030014/s1>, Figures S1: Spectra of the obtained compounds.

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Abbreviations

The following abbreviations are used in this manuscript:

GE	germination energy
GP	germination percentage
<i>L. sativum</i>	<i>Lepidium sativum</i>
LR	length of the roots
LAP	length of the above-ground part
NAA	naphthaleneacetic acid
PGRs	plant growth regulators
RLI	root length index
R/S	root/shoot ratio
<i>S. alba</i>	<i>Sinapis alba</i>
SGI	seed germination index
SVI	simplified vitality index
<i>V. mungo</i>	<i>Vigna mungo</i>

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