PERIÓDICO TCHÊ QUÍMICA
ARTIGO ORIGINAL

USO DE NOVOS COMPOSTOS DA SÉRIE QUINOLINA COMO ESTIMULANTES EFICAZES DOS PROCESSOS DE CRESCIMENTO

USE OF NEW COMPOUNDS OF THE QUINOLINE SERIES AS EFFECTIVE STIMULANTS OF GROWTH PROCESSES

ИСПОЛЬЗОВАНИЕ НОВЫХ СОЕДИНЕНИЙ ХИНОЛИНОВОГО РЯДА КАК ЭФФЕКТИВНЫХ СТИМУЛЯТОРОВ РОСТОВЫХ ПРОЦЕССОВ

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RESUMO

Os resultados de um estudo da ação de compostos da fórmula geral: 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1,2-di-hidroquinolina e 1-alquil-2,2,4-trimetil-6 -aminocarbotioil-1,2,3,4-tetra-hidroquinolina. Os estimulantes de crescimento mais eficazes dos compostos das séries 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1,2-di-hidroquinolina e 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1, Foram reveladas 2,3,4-tetrahidroquinolina para rododendro amarelo (Rhododendron luteum) e rododendro Ledebur (Rhododendron ledebourii). As mudas de rododendro foram contadas para estudar a germinação em laboratório e plantadas em caixotes em terreno fechado, aos 21 dias após o início do experimento. Foi estabelecido que os produtos químicos sintetizados causam estímulo ao crescimento de espécies do gênero Rhododendron em comparação com as preparações comerciais existentes. A eficiência do uso de soluções de compostos das séries 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1,2-di-hidroquinolina e 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1,2,3,4-tetrahidroquinolina e suas concentrações. É divulgado um método de utilização de compostos desta série como estimulantes do crescimento, que permite aumentar a germinação de espécies do gênero Rhododendron de 20 para 50%, aumentar a altura de mudas de Rhododendron luteum de 18 para 63% e Rhododendron ledebourii de 33 para 183%. As dihidroquinolinas são mais eficazes para espécies do gênero Rhododendron. Os compostos contendo um substituinte di-hidro-6-quinolinil estimulam o crescimento dessas plantas. A especificidade da ação dos estimulantes do crescimento é observada. A conveniência de usar compostos da série quinolina para a produção de material de plantio de plantas ornamentais para paisagismo é mostrada. Sugere-se a atividade auxina de compostos da fórmula geral: 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1,2-di-hidroquinolina e 1-alquil-2,2,4-trimetil-6-aminocarbotioil -1,2,3,4-tetra-hidroquinolina. Supõe-se que os compostos das séries 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1,2-di-hidroquinolina e 1-alquil-2,2,4-trimetil-6-aminocarbotioil-1,2, A 3,4-tetrahidroquinolina pode ter atividade de proteção ao estresse para espécies do gênero Rhododendron. Os materiais do artigo são de valor prático para biólogos, ecologistas e cultivadores de plantas.

Palavras-chave: *estimuladores de crescimento, processos de crescimento, compostos orgânicos sintetizados, plantas ornamentais*.

ABSTRACT

The results of a study of the action of compounds of the general formula: 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline are presented. The most effective growth stimulants from compounds of the series 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline for yellow rhododendron (*Rhododendron luteum*) and Ledebur rhododendron (*Rhododendron ledebourii*) were revealed. *Rhododendron* seedlings were counted to study laboratory germination and planted in crates in closed ground on 21 days after the start of the experiment. It was established that the synthesized chemicals cause stimulation of the growth of species of the genus *Rhododendron* in comparison with existing commercial preparations. The efficiency of using solutions of compounds of the series 1-alkyl-2,2,4-trimethyl-6-

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aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline and their concentrations. A method of using compounds of this series as growth stimulants is disclosed, which allows increasing seed germination of species of the genus *Rhododendron* from 20 to 50%, increasing the height of *Rhododendron luteum* seedlings from 18 to 63%, and *Rhododendron ledebourii* from 33 to 183 %. Dihydroquinolines are most effective for species of the genus *Rhododendron*. Compounds containing a dihydro-6-quinolinyl substituent stimulate the growth of these plants. The specificity of the action of growth stimulants is noted. The expediency of using quinoline series compounds for the production of planting material of ornamental plants for landscaping is shown. It is suggested the auxin activity of compounds of the general formula: 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline. It is assumed that compounds of the series 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline may have the stress-protective activity for species of the genus *Rhododendron*. The materials of the article are of practical value for biologists, ecologists, plant growers.

Keywords: *growth stimulators, growth processes, synthesized organic compounds, ornamental plants*.

АННОТАЦИЯ

Представлены результаты исследования действия соединений общей формулы: 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2-дигидрохинолин и 1-алкил-2,2,4-триметил-6 -аминокарботиоил-1,2,3,4-тетрагидрохинолин. Выявлены наиболее эффективные стимуляторы роста из соединений ряда 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2-дигидрохинолина и 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2,3,4-тетрагидрохинолина для рододендрона желтого (*Rhododendron luteum*) и рододендрона Ледебура (*Rhododendron ledebourii*). Проростки рододендрона подсчитывали для изучения лабораторной всхожести и высаживали в ящики в закрытом грунте на 21 день после начала эксперимента. Установлено, что синтезированные химические вещества вызывают стимуляцию роста видов рода *Rhododendron* по сравнению с существующими коммерческими препаратами. Эффективность использования растворов соединений ряда 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2-дигидрохинолина и 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2,3,4-тетрагидрохинолина и их концентрации. Раскрыт способ использования соединений этой серии в качестве стимуляторов роста, который позволяет увеличить всхожесть семян видов рода *Rhododendron* с 20 до 50%, увеличить высоту сеянцев *Rhododendron luteum* с 18 до 63%, а *Rhododendron ledebourii* с 33 до 183%. Таким образом, дигидрохинолины наиболее эффективны для видов рода *Rhododendron*. Соединения, содержащие дигидро-6-хинолинильный заместитель, стимулируют рост этих растений. Отмечена специфичность действия стимуляторов роста. Показана целесообразность использования соединений серии хинолин для производства посадочного материала декоративных растений для ландшафтного дизайна. Предполагается ауксиновая активность соединений общей формулы: 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2-дигидрохинолин и 1-алкил-2,2,4-триметил-6-аминокарботиоил -1,2,3,4-тетрагидрохинолин. Предполагается, что соединения ряда 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2-дигидрохинолина и 1-алкил-2,2,4-триметил-6-аминокарботиоил-1,2, 3,4-тетрагидрохинолин может обладать стресс-защитной активностью для видов рода *Rhododendron*. Материалы статьи представляют практическую ценность для биологов, экологов, растениеводов.

Ключевые слова: *стимуляторы роста, ростовые процессы, синтезированные органические соединения, декоративные растения*

1. INTRODUCTION

Maintenance of seed quality is mandatory for the sale of seed as well as for assuring the required plant population and final yields to end-user (Sudhakar *et al*., 2016). It is possible to increase seed germination and the quality of plants obtained from them using growth regulators (Bashmakov *et al*., 2012). Seed lots are evaluated based on their germination capabilities and vigor (Sudhakar *et al*., 2016). In the physiological sense, germination begins with seed water uptake and ends with the initiation of elongation by the embryonic axis, usually the radicle (Welbaum *et al*., 1998). However, many tests used to evaluate seed physiological characteristics require time and skilled laboratory, making it a costly process (Neverova, 2004; Vetchinnikova, 2004; Kalaev *et al*., 2006; Takahashi *et al*., 2006, 2007; Bukharina, 2011; Gar'kova *et al*., 2011; Popov *et al*., 2011; Yakymchuk, 2015; Lapshina *et al*., 2016; Sudhakar *et al*., 2016; Baranova, Kalaev, 2017). Models have been developed to predict germination based on thermal time, hydrotime,

and combined hydrothermal time (Welbaum *et al*., 1998). These population-based models indicate that the timing of germination is closely tied to physiologically determined temperature and water potential thresholds for radicle emergence, which vary among individual seeds in a population (Welbaum *et al*., 1998). The tests of the germination capability and the height of the seedlings are used in modern research (Fedorova, Shunelko, 2003; Vetchinnikova, 2004; Ivanov, 2011; Lyanguzova, 2011; Moiseeva *et al*., 2012a,b; Bome *et al*., 2015; Opalko, Opalko, 2015; Kuzemko, 2016; Fachi *et al*., 2019).

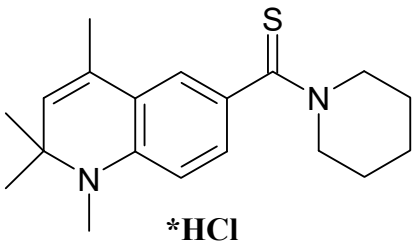
Currently, an active search is underway for regulators of growth processes among new synthesized organic substances that could have a stronger positive effect compared to existing commercial preparations. Hydroquinoline derivatives with wide biological activity are essential heterocyclic compounds for the synthesis of organic and medical chemistry (Mohammed *et al*., 1992; Shmyreva, 2000; Abadi, Brun, 2003; Saudi *et al*., 2003; Abdel-Gawad *et al*., 2005; Shujiang *et al*., 2005; Williamson, Ward 2005; Denmark, Venkatraman, 2006; Trivedi *et al*., 2008; Litvinov, 2009; Mosalam *et al.*, 2011a,b; Azizian *et al*., 2014; Shikhaliev *et al*., 2014; Ghoneim, Assy, 2015). It seems relevant to reveal the species-specific reactions of seedlings of herbaceous and woody plants to seed pretreatment with synthesized organic compounds, the effect of aftereffect of seed treatment, and the influence of the substitute base compound.

The purpose of the study was to study the effects of the synthesized organic compounds of the series 1-alkyl-2,2,4-trimethyl-6-amino carbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline at growth indicators (by which we meant seed germination and plant height) of *Rhododendron Iedebourii* and *Rhododendron luteum.*

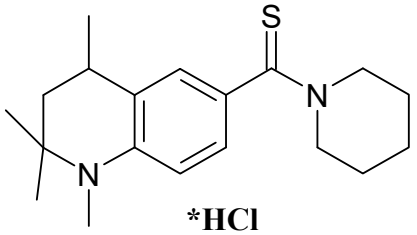
2. MATERIALS AND METHODS

Seeds were treated with compounds synthesized at the Department of Organic Chemistry of the Voronezh State University according to the methods developed by the staff, which are described in the literature (Manahelohe *et al.*, 2015a,b). Below is a general scheme for the synthesis of organic compounds of the series 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2 3,4-tetrahydroquinoline (Fig. 1).

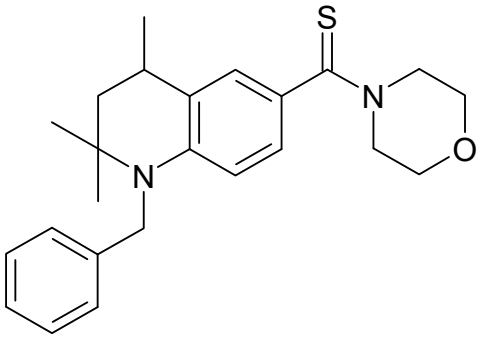
A mixture of the corresponding hydroquinoline carboxaldehyde (1 mmol), amine (1.33 mmol), and elemental sulfur (1.33 mmol) in dimethylformamide (2 ml) was heated under reflux until the completion of the reaction (the control by the thin layer chromatography). After cooling, the reaction mass was poured into 5 ml of ice water with vigorous stirring. The solidified after grinding, and the precipitate was filtered, washed with water, and recrystallized from 75% ethanol. Non-hardening thiocarboxamides were treated with a double excess of hot 2M hydrochloric acid, filtered and recrystallized from ethanol.



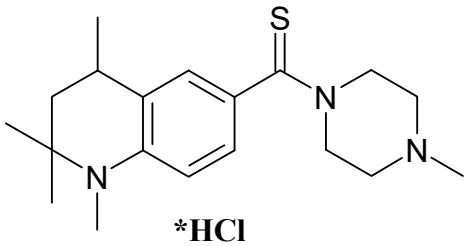
1,2,2,4-tetramethyl-6-(1-piperidinylcarbothioyl)-1,2-dihydroquinoline hydrochloride (compound 1);



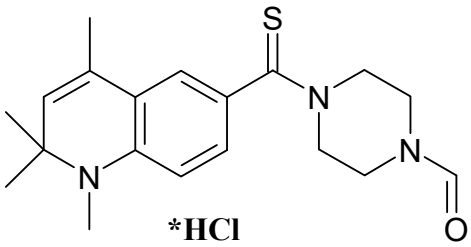
1,2,2,4-tetramethyl-6-(1-piperidinylcarbothioyl)-1,2,3,4-tetrahydroquinoline hydrochloride (compound 2);



1-benzyl-2,2,4-trimethyl-6-(4-morpholinylcarbothioyl)-1,2,3,4-tetrahydroquinoline (compound 3);



1,2,2,4-tetramethyl-6-[(4-methyl-1-pipera zinyl)carbothioyl]-1,2,3,4-tetrahydroquinoline hydrochloride (compound 4);



4-[(1,2,2,4-tetramethyl-1,2-dihydro-6-quino linyl)carbothioyl]-1-piperazinylcarbaldehyde hydro chloride (compound 5).

To identify the biological effects of the synthesized organic compounds, morphometric parameters of perennial woody plants: Ledebour rhododendron (*Rhododendron ledebourii* Pojark.) and yellow rhododendron (*Rhodododeron luteum* Sweet.) (Alexandrova, 2003; Baranova *et al*., 2018; Burmenko *et al*., 2018a,b).

The seeds of the test plants were kept in aqueous solutions of the above chemical compounds at concentrations of 0.01%, 0.05% and 0.1% for 18 hours. As a traditional stimulator, the commercial preparation Epin-Extra (Russian produced by NNPP NEST M) in a working concentration according to the instructions for use - 0.05%. The control seeds were soaked in tap water. The experiment was carried out in triplicate (100 seeds in each). Seeds were germinated under laboratory conditions at a constant temperature of 22 ° C. The germination of seeds and the determination of the germination was carried out according to GOST 13056.6-97. The laboratory germination of seeds was determined as the ratio of the number of germinated seeds to the total number of seeds and was expressed in%, according to the recommendations (GOST 13056.6-97). *Rhododendron* seedlings were counted to study laboratory germination and planted in crates in closed ground on 21 days after the start of the experiment. The height of the seedlings was measured using a ruler.

Computer statistical processing was performed using the Stadia software package. The procedures for grouping data and their processing were described in the work of A. P. Kulaichev (2006). The seed germination in the control and experimental variants was compared according to the criterion of frequency agreement using Z-statistics. The comparison of mean values was carried out using Student's t-test. The influence of the chemical treatment factor at different concentrations on growth rates was determined using a two-way analysis of variance.

3. RESULTS AND DISCUSSION:

The results of the influence of tested chemical compounds on the germination of *Rhododendron* seeds are presented in Table 1-2.

The seed germination of Ledebour rhododendron (*Rhododendron ledebourii*) and yellow rhododendron (*Rhododendron luteum*) increase all tested chemical compounds at the concentration of 0.1%. For *Rh. ledebourii* compound 1 is the most effective and for *Rh. luteum* also compound 5 at concentrations 0.01%, 0.05% and 0.1%. A positive effect (stimulation) is observed when treating the seeds of the *Rhododendron* species with compounds 1, 3-5 in all tested concentrations (0.01%, 0.05%, and 0.1%). The germination of Ledebur rhododendron seeds under the influence of synthesized organic substances at the indicated concentrations (0.01%, 0.05%, and 0.1%) was increased from 24.3 to 54% for yellow rhododendron - from 21.4 to 56.2%.

The height of the seedlings of species of the genus *Rhododendron* grown from seeds treated by synthesized chemical compounds is presented in Tables 3-4. Compounds 1 and 5 at concentrations of 0.01%, 0.05%, and 0.1% is shown the most significant stimulating effect. All tested substances are effective at concentrations of 0.05% and 0.1%. The height of Ledebur rhododendron seedlings under the influence of synthesized organic compounds was risen from 33.3 to 183.3%, for yellow rhododendron - from 18.2 to 63.6%.

The influence of the “chemical compound treatment” and “concentration” factors was evaluated by the results of the analysis of variance, which showed a significant effect on the height of seedlings *Rh. ledebourii* ($P < 0.05$), *Rh. luteum* ($P < 0.05$).

Mild and moderate stress activates the body's defenses. The use of various growth stimulants that can protect the plant and reduce the harmful effects of heavy metals on the body is based on this mechanism. For example, the effect of the synthetic growth regulator of the cytokinin type of action (cytodef) and heavy metal ions: Pb^{2+}, Sr^{2+}, Zn^{2+} and Ni^{2+} on the rate of generation of superoxide anion radical, the intensity of lipid peroxidation and the content of carotenoids in the leaves of 7-day-old cucumber plants (Cucumis sativus L., cultivar Graceful) was studied. The use of a synthetic growth regulator of the cytokinin type of action (cytodef) in some cases reduced the toxicity of heavy metals (Pb^{2+}, Sr^{2+}, $Zn^{2+,}$ and Ni^{2+}), which was manifested in partial or complete removal of the negative effect of metals on oxidative processes and an increase in the concentration of antioxidants (carotenoids) (Bashmakov *et al*., 2012). The use of some biological growth regulators allows one to obtain a crop with a lower content of lead and cadmium ions (Titov *et al*., 2011).

The results of this work are consistent with earlier studies by R. G. Gafurov and co-workers on carbon N- and O-benzyl-containing compounds that have a bright auxin activity (Gafurov, Makhmutova, 2003, 2005). In this regard, it is assumed that compounds of the series 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroqui noline and 1-alkyl-2,2,4-trimethyl-6-aminocarbo thioyl-1,2,3 may have the stress-protective activity for species of the genus *Rhododendron*.

4. CONCLUSIONS:

Thus, the greatest effect on increasing the germination of seeds of species of the genus Rhododendron was produced by the synthesized organic compounds of the 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline at a concentration of 0.1%. Dihydroquinolines or compounds containing a dihydro-6-quinolinyl substituent are most effective. All of the compounds under consideration show a clear tendency to increase seed germination with increasing concentration. All tested substances exhibit a stimulating effect at the studied concentrations and increase the height of seedlings of species of the genus *Rhododendron* in comparison with the control. Synthesized chemical compounds of the series 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2-dihydroquinoline and 1-alkyl-2,2,4-trimethyl-6-aminocarbothioyl-1,2,3,4-tetrahydroquinoline cause the growth increase of species of the genus *Rhododendron* compared to existing commercial preparations, such as Epin-Extra, and it is advisable to use them as growth stimulators for the production of planting material.

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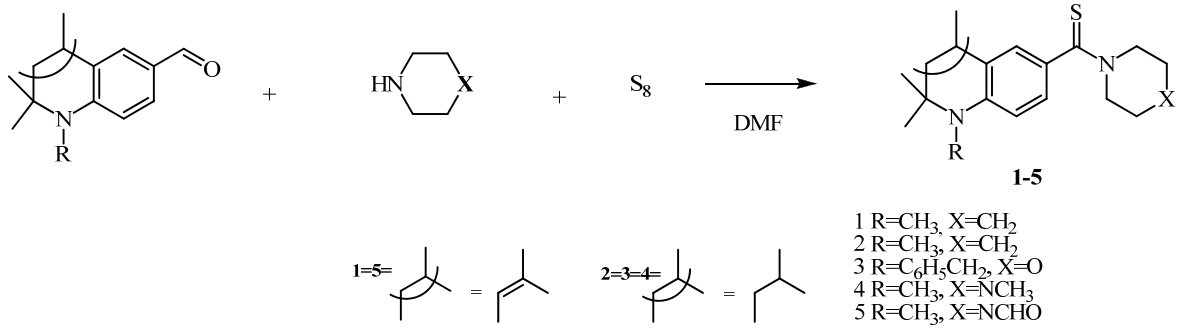

Figure 1. *The general scheme for the synthesis of 2,2,4-tetramethylhydroquinolin-6-ylcarbothioamides 1-5.*

Table 1. *The seed germination (in%) of Ledebur rhododendron treated with synthesized organic compounds*

Concentration	Control group, %	Epin group, %	compound 1	compound 2	compound 3	compound 4	compound 5
0,01%	41.1	43.3	52.8**[2]	42.2	51.1*[1]	52.2**[2]	47.8*[1]
0,05%			58.6**[2]	45.7	57.6**[2]	58.9**[2]	53.5*[1]
0,1%			63.3**[2]	55.4*[1]	64.4**[2]	61.7**[2]	58.2**[2]

Note for Table 1-4:

** – differences with the control group are reliable (p<0.05)*

** – differences with the control group are reliable (p<0.01)*

** – differences with the control group are reliable (p<0.001)*

[1] - differences with the Epin group are reliable (p<0.05);

[2] - differences with the Epin group are reliable (p<0.01);

[3] - differences with the Epin group are reliable (p<0.01);

1,2,2,4-tetramethyl-6-(1-piperidinylcarbothioyl)-1,2-dihydroquinoline hydrochloride (compound 1);
1,2,2,4-tetramethyl-6-(1-piperidinylcarbothioyl) -1,2,3,4-tetrahydroquinoline hydrochloride (compound 2);
1-benzyl-2,2,4-trimethyl-6-(4-morpholinylcarbothioyl)-1,2,3,4-tetrahydroquinoline (compound 3);
1,2,2,4-tetramethyl-6-[(4-methyl-1-piperazinyl)carbothioyl]-1,2,3,4-tetrahydroquinoline hydrochloride (compound 4);
4-[(1,2,2,4-tetramethyl-1,2-dihydro-6-quinolinyl)carbothioyl]-1-piperazinylcarbaldehyde hydrochloride (compound 5).

Table 2. *The seed germination (in %) of yellow rhododendron treated with synthesized organic compounds*

Concentration	Control group, %	Epin group, %	compound 1	compound 2	compound 3	compound 4	compound 5
0,01%	52.3	58.4	68.1*[1]	54.2	68.6**[2]	57.8	72.2**[2]
0,05%			76.5**[2]	58.7*	72.4**[2]	63.5*[1]	78.4**[2]
0,1%			80.4**[2]	64.8*[1]	76.3**[2]	68.2**[2]	81.7**[2]

Table 3. *The height (in cm) of Rhododendron ledebourii seedlings 21 days after the start of the experiment*

Concentration	Control group, %	Epin group, %	compound 1	compound 2	compound 3	compound 4	compound 5
0.01 %	0.6±0.02	0.7±0.02*	1.4±0.04**[3]	0.8±0.03**	0.6±0.02[1]	0.7±0.02*	1.3±0.03**[3]
0.05 %			1.5±0.04**[3]	0.9±0.02**[3]	0.7±0.02*	0.7±0.02*	1.3±0.03**[3]
0.1 %			1.7±0.04**[3]	0.9±0.03**[3]	0.9±0.02**[3]	0.8±0.03**	1.4±0.02**[3]

Table 4. *The height (in cm) of Rhododendron luteum seedlings 21 days after the start of the experiment*

Concentration	Control group, %	Epin Extra group, %	compound 1	compound 2	compound 3	compound 4	compound 5
0.01 %	1.1±0.03	1.2±0.02*	1.6±0.04**[3]	1.5±0.02**[3]	1.4±0.02**[3]	1.3±0.02**[1]	1.6±0.03**[3]
0.05 %			1.7±0.03**[3]	1.6±0.02**[3]	1.5±0.02*	1.4±0.02**[2]	1.6±0.03**[3]
0.1 %			1.8±0.03**[3]	1.7±0.03**[3]	1.6±0.03**[3]	1.5±0.03**[3]	1.7±0.04**[3]