BIOCHEMISTRY AND BIOTECHNOLOGY

БИОХИМИЯ И БИОТЕХНОЛОГИЯ

ISSN 2686-7575 (Online)

https://doi.org/10.32362/2410-6593-2022-17-5-394-409

UDC 577.151.042; 546.23

RESEARCH ARTICLE

Thiol-dependent mechanisms of selenium-containing preparations and thiolylfluanide effect on electrolytes leaching and peroxidase activity in *Zea mays* L.

Pavel A. Poluboyarinov[1,✉], Natalia V. Shchetinina[1], Inessa Ya. Moiseeva[1], Nadezhda I. Mikulyak[1], Nadezhda A. Golubkina[2], Alexander P. Kaplun[3]

[1]Penza State University, Penza, 440026 Russia
[2]Federal Scientific Center of Vegetable Production, VNIISSOK, Moscow oblast, 143072 Russia
[3]MIREA – Russian Technological University (M.V. Lomonosov Institute of Fine Chemical Technologies), Moscow, 119571 Russia
[✉]Corresponding author, e-mail: poluboyarinovpavel@yandex.ru

Abstract

Objectives. *While organic and inorganic derivatives of selenium like thiol poisons are known to activate enzymes in cells of different organisms, the mechanism of enzyme activity induction is poorly studied. Therefore, the aim of the study was to investigate the effect of selenium compounds on peroxidase activity induction in maize tissues.*

Methods. *Mechanism of sulfhydryl groups blocking in selenium derivatives was studied on maize in comparison with fungicide tolylfluanid—a typical thiol poison. Electrolytes leakage was determined using conductometry and capillary electrophoresis, protein fractions—by the Ermakov–Durinina method, protein concentration—according to Bradford protein essay, and peroxidase activity—by the Boyarkin method.*

Results. *Diacetophenolylselenide (DAPS-25) was shown to react with SH-groups similarly with tolylfluanid fungicide. DAPS-25 increased K^+ and NH_4^+ leakage by 58 and 14 times, while appropriate increases for tolylfluanid were 4.4 and 1.5 times as compared to control. Increased*

total protein content—especially albumins—was due to electrolyte leakage from maize cells. DAPS-25 increased albumins concentration by 2.4–4.5 times, and tolylfluanid application by 2 times. Similar increase of peroxidase activity in maize roots and sprouts as a result of DAPS-25 (by 63% and 112%) and tolylfluanid (by 73% and 63%) application indicates close mechanism of their effect. Under DAPS-25 loading L-cysteine decreases peroxidase activity, which records the removal of SH-groups blockage. A less intensive effect was registered for sodium selenite and L-selenocystin, also capable of reacting with SH-groups. L-cysteine supplementation to DAPS-25 solution decreases selenium concentration in maize, indicating the decrease of selenium bioavailability.

Conclusions. *The results indicated that selenium containing compounds react with SH-groups of maize cells increasing electrolytes leakage, protein content and especially albumins resulting in the increase of peroxidase activity.*

Keywords: *diacetophenonyl selenide, tolylfluanid, Zea mays, peroxidase, electrolytes, proteins*

For citation: Poluboyarinov P.A., Shchetinina N.V., Moiseeva I.Ya., Mikulyak N.I., Golubkina N.A., Kaplun A.P. Thiol-dependent mechanisms of selenium-containing preparations and thiolylfluanide effect on electrolytes leaching and peroxidase activity in *Zea mays* L. *Tonk. Khim. Tekhnol. = Fine Chem. Technol*. 2022;17(5):394–409 (Russ., Eng.). https://doi.org/10.32362/2410-6593-2022-17-5-394-409

НАУЧНАЯ СТАТЬЯ

Тиолзависимые механизмы действия селеносодержащих препаратов и толилфлуанида на истечение электролитов и активность пероксидазы в растениях кукурузы (*Zea mays* L.)

П.А. Полубояринов[1,✉], Н.И. Щетинина[1], И.Я. Моисеева[1], Н.И. Микуляк[1], Н.А. Голубкина[2], А.П. Каплун[3]

[1]Пензенский государственный университет, Пенза, 440026 Россия
[2]Федеральный научный центр овощеводства, ВНИИССОК, Московская обл., 143086 Россия
[3]МИРЭА – Российский технологический университет (Институт тонких химических технологий им. М.В. Ломоносова), Москва, 119571 Россия
✉ *Автор для переписки, e-mail: poluboyarinovpavel@yandex.ru*

Аннотация

Цели. *Неорганические и органические соединения селена, как и ряд других тиоловых ядов, активируют ферменты в клетках разных организмов, однако механизм индукции ферментативной активности малоизучен, в связи с этим целью настоящей работы стало изучение механизма влияния соединений селена на индукцию активности фермента пероксидазы в тканях растений кукурузы.*

Методы. *Механизм блокирования сульфгидрильных групп (SH-групп) соединений селена исследовали на растениях кукурузы в сравнении с фунгицидом толилфлуанидом – классическим тиоловым ядом. Истечение электролитов определяли методом кондуктометрии и капиллярного электрофореза, фракции белков по методу Ермакова–Дурыниной, их концентрацию по Брэдфорду, активность пероксидазы по методу Бояркина.*

Результаты. *Было установлено, что диацетофенонилселенид (ДАФС-25) взаимодействовал с SH-групами, как и фунгицид толилфуанид, который является классическим органическим тиоловым ядом. ДАФС-25 стимулирует истечение катионов калия и аммония в 58 и 14 раз, а толилфлуанид в 4.4 и 1.5 раз в сравнении с контролем. Истечение электролитов из клеток растений кукурузы приводит к увеличению концентрации общего белка и особенно альбуминов. Концентрация альбуминов с ДАФС-25 возрастала в 2.4–4.5 раза, а с толилфлуанидом – в 2 раза. ДАФС-25 активировал фермент пероксидазу в корнях и надземной части кукурузы на 63% и 112%, а толилфлуанид на 73% и 63%, что говорит о схожем механизме их действия. L-цистеин снижает активность пероксидазы от действия ДАФС-25, т.е. снимает блокирование SH-групп. Слабее активируют пероксидазу Na_2SeO_3 и L-селеноцистин, которые также взаимодействуют с SH-группами. Содержание селена в растениях кукурузы уменьшается при добавлении L-цистеина в раствор с ДАФС-25, что говорит о снижении его поступления в растения.*

Выводы. *Исследования показали, что селенсодержащие вещества взаимодействуют с SH-группами клеток растений кукурузы, усиливая истечение электролитов и повышая концентрацию белков в тканях, особенно альбуминов, а, следовательно, увеличивая активность фермента пероксидазы.*

Ключевые слова: *диацетофенонилселенид, толилфлуанид, кукуруза, пероксидаза, электролиты, белки*

Для цитирования: Полубояринов П.А., Щетинина Н.И., Моисеева И.Я., Микуляк Н.И., Голубкина Н.А., Каплун А.П. Тиолзависимые механизмы действия селеносодержащих препаратов и толилфлуанида на истечение электролитов и активность пероксидазы в растениях кукурузы (*Zea mays* L.). *Тонкие химические технологии*. 2022;17(5):394–409. https://doi.org/10.32362/2410-6593-2022-17-5-394-409

INTRODUCTION

In recent years, the catalytic functions of the trace element selenium, which forms the active selenol sites of antioxidant enzymes—in the first place, four selenium-dependent glutathione peroxidases, selenium-containing peptides and proteins—have been widely studied [1].

Inorganic salts of selenium (sodium selenate and selenite) and organic selenium compounds: ebselen, 2-phenylbenzoselenazol-1,2-3(2n)-one)[2], selenopyran, 9-phenyl-sym-nona-hydro-10-selenaanthracene[1], diacetophenonyl selenide (DAPS-25), 1,5-diphenyl-3-selenapentadione-1,5 [3], (**I**), have an activating effect on a number of enzymes: catalase, peroxidase, superoxide dismutase, glutathione peroxidase (GPx) in plants [4–7], bacteria [8], insects [9], crustaceans [10], farm animals and birds [11, 12]. It should be especially noted that out of 27 organic selenium compounds and their 16 sulfur-containing analogs, the highest activity of phase **II** enzymes—quinone reductase (EC 1.6.5.5) and glutathione-S-transferase (EC 2.5.1.18)—was induced by 9 selenium-containing compounds: dimethyl diselenide, dibenzyl diselenide, diphenyl diselenide, benzyl selenol, benzene selenic acid, ebselen, 2,5-diphenyl selenophen, triphenylselenonium chloride, i.e., mainly those drugs that interact with sulfhydryl groups of mouse hepatoma cells (Hepa-1c1c7) with the formation of selenosulfide bonds [13]. However, the mechanisms of metabolism of organoselenium xenobiotics in biological media and their effect on the induction of enzyme activity are not well understood. It is known that at high concentrations, inorganic selenium compounds: selenite, sodium selenate, selenium oxide, act as thiol poisons to block the sulfhydryl groups of proteins [14, 15]. Such poisons acting in this way also include certain heavy metals: mercury, cadmium, and lead.

[1] Blinokhvatov A.F. *9-R-sim-nonahydro-10-oxa (chalcogen) anthracene and 9-R-sim-octahydro-10-oxonium (chalcogenonia) anthracene salts*. Dr. Sci. Thesis (Chem.). Saratov: SGU; 1993.

A relationship between electrolyte leakage in wheat root cell membrane damage by mercury chloride ($HgCI_2$) was shown to involve an increase in the concentration of malondialdehyde (MDA), along with activation of catalase, superoxide dismutase, peroxidase, and ascorbate peroxidase [16]. In contrast to plants not treated with selenium, where the level of enzyme activity is lower, rapeseed plants treated with sodium selenite demonstrated an increase in the activity of catalase and ascorbate peroxidase under stress and drought conditions [17].

The method of inhibitors is widely used to determine the mechanism of action of various drugs. The classic thiol poison is tolylfluanid (**IV**) (fungicide Euparen Multi 500 g/kg), which does not contain selenium. Regarding the mechanisms of action, it is known that it nonspecifically inhibits biochemical processes in which enzymes and coenzymes containing sulfhydryl groups and thiol-containing cellular components take part [18]. Like all thiol poisons, it increases the permeability of cell membranes and promotes the "leakage" of potassium ions from the cell [19].

The mechanism of increased activity of enzymes may be due to the synthesis of *de novo* isoenzymes, a change in the conformation of the enzyme molecule or prosthetic group under the influence of an inhibitor, or the catalytic effect of the trace element selenium on selenium-dependent enzymes. However, antioxidant defense enzymes (catalase, peroxidase, superoxide dismutase), which utilize peroxides and free radicals, do not belong to selenium-dependent enzymes. In most scientific studies, there is a relationship between the action of thiol poisons—heavy metal ions, selenium preparations—and the induction of the activity of various enzymes. This may be due to the leakage of electrolytes, i.e., modification of ion channels, aquaporins, and lead to an increase in protein concentration in the biomass, and, as a result, an increase in enzyme activity.

In connection with the above, the aim of the present study is to study the mechanism of the effect of selenium compounds on the induction of peroxidase enzyme activity in corn seedlings (*Zea mays* L.).

MATERIALS AND METHODS

Reagents and equipment

The following reagents were used in the work: hydrogen peroxide 30%, benzidine, L-cysteine hydrochloride, acetone (*Vekton*, Russia), DAPS-25 (*Sulfat*, Russia), tolylfluanid—Euparen Multi fungicide (*BASF*, Germany). The organoselenium xenobiotic DAPS-25 and tolylfluanid were dissolved in acetone and added to the Knop's solution[2]. Sodium selenite and L-selenocystin were dissolved in 0.1 M HCI (*Vekton*, Russia). Solvents—acetone (chemically pure) and hydrochloric acid (chemically pure) (*Vekton*, Russia)—were added to the control variants.

Determination of the electrical conductivity of distilled water and solutions was carried out on the conductometer Expert-002-2-6 (*AnalitPromPribor*, Russia) according to GOST 6709-72[3].

Determination of inorganic cations in water was carried out according to the M 01-31-2011[4] method using a Capel 105M capillary electrophoresis system (*LUMEX Group of Companies*, Russia).

Peroxidase activity was determined using a KFK-3 photometer (*ZOMZ*, Russia).

The study of the anatomy of corn root cells was carried out under a Levenhuk D320L microscope (*Levenhuk*, Russia).

Germination of corn seeds

Seeds of corn (*Zea mays* L.) varieties *Krasnodarsky 291 AMV* (*Gavrish*, Russia) and *Utrennyaya Pesnya* (*Gavrish*, Russia) were germinated for 3 days in a thermostat at a temperature of 25–26°C [20]. For experiments, seedlings with a root length of 1–2 cm were used. The roots of control seedlings were immersed in a Knop's solution or distilled water through a perforated plastic plate, while the experimental seedlings were immersed in a solution with the addition of preparations. The roots of the seedlings were kept either in the Knop's solution or distilled water during the entire time of the experiment (3 days).

To determine protein fractions (albumins, globulins, prolamins, and glutelins) and peroxidase activity, unseparated corn roots were immersed in Knop's solutions containing selenium-containing preparations and tolylfluanid in various concentrations for 3 days. Next, the seedling samples were divided into roots and aerial parts (hereinafter referred to as seedlings), crushed, ground, and centrifuged. Proteins were extracted according to the Ermakov–Durynina method [21]. The content of individual protein fractions was determined by the Bradford method [22]. The control was corn

[2] Chesnokov V.A., Bazyrina E.N., Bushueva T.M., Il'inskaya N.L. *Growing plants without soil*. Leningrad: Izd. Leningrad. Univ.; 1960. 170 p.

[3] GOST 6709-72. Interstate Standard. Distilled water. Specifications. Moscow: Standartinform; 2010.

[4] https://www.lumex.ru/complete_solutions/11ar03_01_02_1.php. Accessed April 18, 2020.

seedlings whose roots were in the Knop's solution without the addition of biologically active substances.

Peroxidase activity was determined by the Boyarkin method at a wavelength of 610 nm. This method is based on measuring the time during which a certain optical density is reached in an experimental solution (E = 0.250). The change in optical density for 1 s per 1 g of raw tissue was calculated. Benzidine was used as a substrate, the oxidation of which results in the formation of a blue compound [23].

The presence of elemental selenium was determined by a qualitative reaction according to Feigley and West [24]. The total selenium content in the roots and seedlings of corn was determined by the fluorimetric method with diaminonaphthalene.[5]

Statistical analysis was carried out using the Duncan test and the computer statistical program Excel.

RESULTS AND DISCUSSION

Influence of DAPS-25 and tolylfluanid on the outflow of electrolytes from the cells of the roots of corn plants

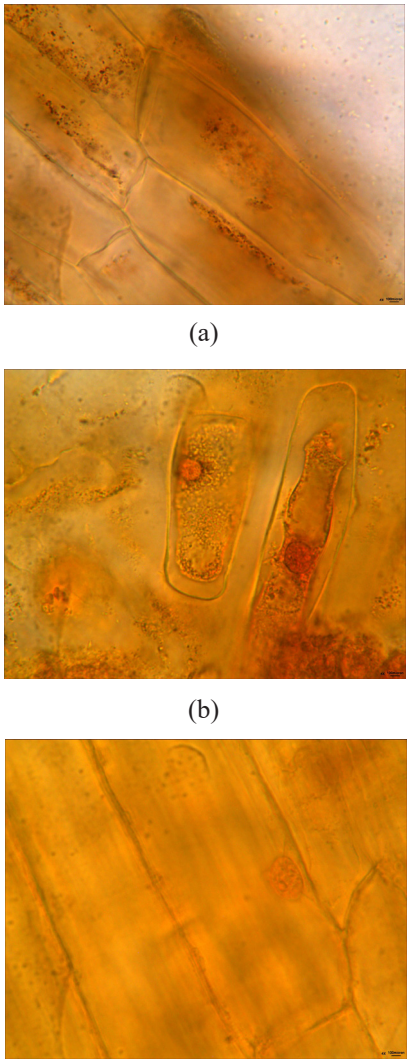
When DAPS-25 is added to the Knop's solution, a reaction occurs on the roots of corn seedlings with the formation of a red modification of elemental selenium (Fig. 1a). The formation of elemental selenium granules and strong plasmolysis revealed under microscopic examination indicates an increase in the permeability of cell membranes and the outflow of electrolytes from root cells. An increase in the permeability of cell membranes is characteristic of some thiol poisons [19].

Plasmolysis of maize root cells was also noted in the variant with tolylfluanid (Fig. 1b). Thus, the separation of the protoplast from the cell wall of the corn root is related to the presence of thiol poison in the Knop's solution.

Thiol poisons can disrupt the functioning of potassium channels [19] to cause the outflow of electrolytes from cells. To determine the outflow of electrolytes from root cells, distilled water was used as a nutrient solution instead of Knop's solution (Table 1).

Thus, according to Table 1, it can be judged that DAPS-25 promotes the outflow of electrolytes from root cells, increasing the permeability of cell membranes, causing plasmolysis. Determination of cations by capillary electrophoresis showed the presence of ammonium, potassium, sodium, magnesium and calcium ions (Table 2).

Analysis of electropherogram data and those given in Table 2 indicates that DAPS-25 stimulates the outflow from root cells mainly of potassium cations, as well as ammonium cations, whose similarity in terms of ionic radius to potassium ions [25] indicates a probable modification of the potassium ion channels of DAPS-25. Residues of the amino acid cysteine contained in potassium ion channels and aquaporins [26] increase sensitivity to the effects of thiol poisons such as mercury [27] and silver [28] ions, as well as to subsequent blocking of ion channels.



(a)

(b)

(c)

Fig. 1. Maize roots with 100× magnification: (a) DAPS-25 in Knop's solution (0.025 mg Se/L, 0.16 mM/L), (b) tolylfluanide (0.16 mM/L), (c) control.

[5] MUK 4.1.033-95. *Methods of control. Chemical factors. Determination of selenium in food. Methodical instructions*. Moscow: Inform.-izd. Tsentr Goskomsanepidemnadzora Rossii; 1995.

Table 1. Electrical conductivity of solution from roots of maize, *Krasnodarsky 291 AMV* (μS/cm^2)*

Days	Control, μS/cm	DAPS-25, 0.025 mg Se/L, μS/cm
3	2.13 ± 0.17 a	2.04 ± 0.14 a
4	13.61 ± 0.54 b	70.24 ± 3.51 b
6	12.97 ± 0.65 b	265.20 ± 26.52 c

*Values in columns with the same letters are not statistically different according to Duncan's test with a significance value of $p < 0.05$.

Table 2. Cations of solutions from roots of maize, *Krasnodarsky 291 AMV* (mg/L)*

Variants	Cations				
	NH_4^+	K^+	Na^+	Mg^{2+}	Ca^{2+}
Control	0.34 ± 0.01 a	3.57 ± 0.04 a	1.82 ± 0.04 a	0.37 ± 0.01 a	0.96 ± 0.013 a
DAPS-25	19.72 ± 0.78 b	52.17 ± 1.56 b	4.69 ± 0.15 b	7.22 ± 0.02 b	4.84 ± 0.17 b
Multiplicity of increase in the expiration of cations, DAPS-25, times	58.0	14.6	2.6	19.5	5.0

*Values in columns with different letters are significantly different at $p < 0.001$.

The outflow of electrolytes from the root cells occurred similarly in the experiment with another variety of corn with the addition of DAPS-25 and tolylfluanid (Table 3).

The outflow of electrolytes in this experiment was most active in the variant with DAPS-25 and to a much lesser extent in the variant with tolylfluanid. Capillary electrophoresis analysis also demonstrated the presence of ammonium, potassium, sodium, magnesium and calcium ions (Table 4).

The outflow of ammonium ions from the cells of corn roots is 42 and 1.5 times higher than the control in the variants with DAPS-25 and tolylfluanid, while the outflow of potassium ions is 16.7 and 4.4 times higher, respectively. The outflow of sodium and calcium ions is 3.6 and 1.9 times higher in the

Table 3. Electrical conductivity of solution from roots of maize, *Utrennyaya Pesnya* (μS/cm^2)*

Days	Control	DAPS-25, 0.025 mg Se/L, 0.16 mmol/L	Tolylfluanid, 0.16 mmol/L
3	2.047 ± 0.08	1.890 ± 0.1	1.789 ± 0.05
6	6.12 ± 0.36	101.7 ± 6.1	21.79 ± 1.1

*Values with the same indices do not differ statistically according to the Duncan's test at $p < 0.05$.

Table 4. Electrolyte cations of solution from roots of maize, *Utrennyaya Pesnya* (mg/L)*

Variants	Cations				
	NH_4^+	K^+	Na^+	Mg^{2+}	Ca^{2+}
Control	0.164 ± 0.01 a	1.16 ± 0.04 a	0.268 ± 0.04 a	0.41 ± 0.01 a	1.76 ± 0.01 a
DAPS-25	6.90 ± 0.78 b	19.36 ± 1.56 b	0.96 ± 0.15 b	3.58 ± 0.02 b	3.39 ± 0.17 b
Tolylfluanid	0.25 ± 0.03 c	5.10 ± 0.15 c	0.56 ± 0.01 c	0.77 ± 0.02 c	2.26 ± 0.05 c
Multiplicity increase in the expiration of cations, DAPS-25/tolylfluanid, times	42.0/1.52	16.7/4.4	3.56/2.0	8.7/1.88	1.9/1.3

*Values in columns with different letters are statistically different according to Duncan's test at $p < 0.05$.

variants with DAPS-25 and tolylfluanid. The concentration of magnesium ions in the solution is 8.7 and 1.9 times higher in the variants with DAPS-25 and tolylfluanid compared to the control. In general, tolylfluanid is more ion channel selective than DAPS-25 and promotes efflux mainly of potassium cations. The absence of protein in the studied solutions indicates that the cell walls of the plant roots have remained intact.

In our studies, DAPS-25 (**I**) interacts with reduced glutathione and L-cysteine to form elemental selenium and acetophenone (**II**) [29–31]. As a result of the first reaction, acetophenone and S-(acetophenylselenyl) cysteine (**III**) are formed (Fig. 2). This selenosulfide compound (**III**) is detected by high performance liquid chromatography. A similar substance—S-(acetophenylselenyl)glutathione—is formed by the interaction of reduced glutathione and DAPS-25.

It is possible that DAPS-25 interacts with cysteine residues in aquaporins and potassium channels, increasing the water permeability of corn root cell membranes (Fig. 3a).

The outflow of electrolytes from plant cells and their plasmolysis upon the addition of

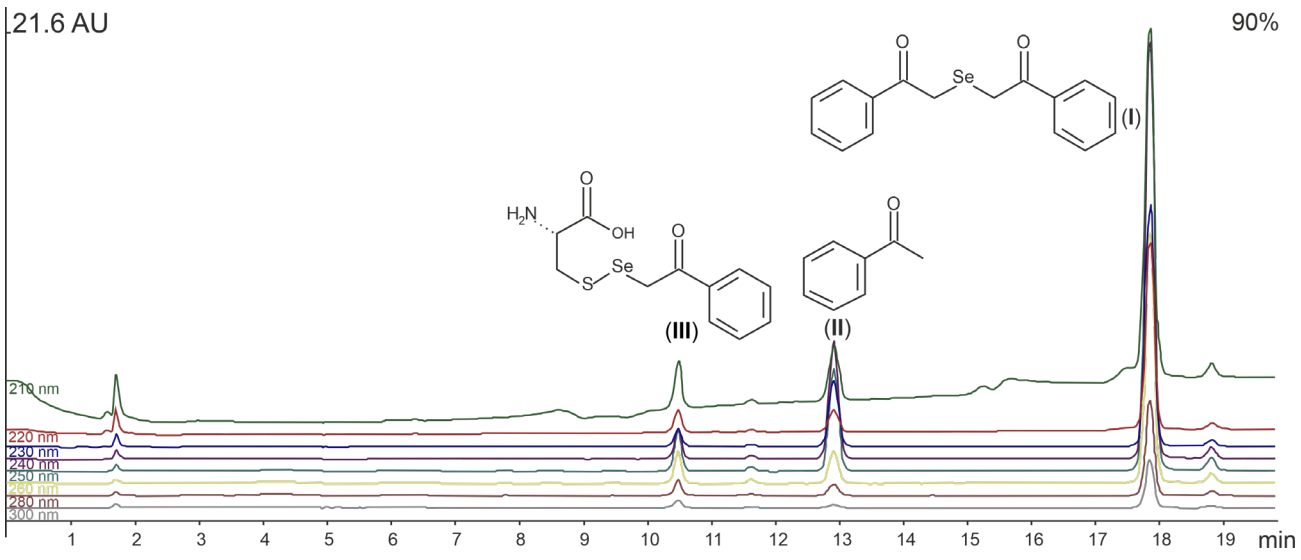


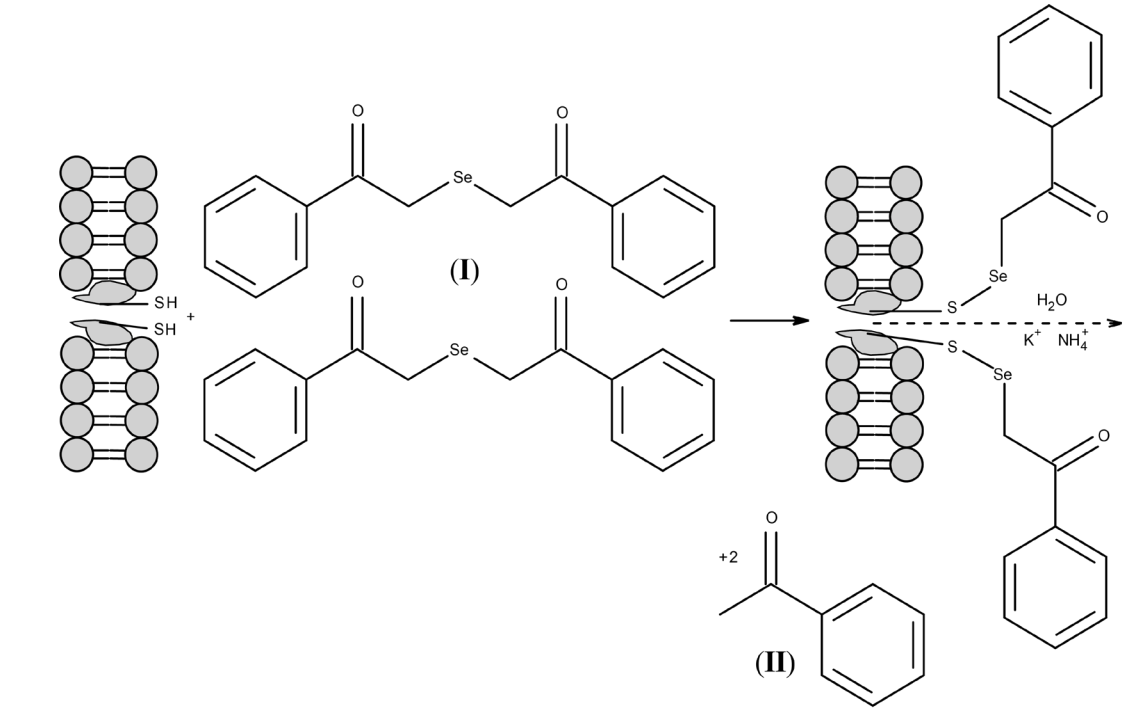
Fig. 2. Chromatogram of a reaction mixture obtained in DAPS-25 and cysteine interaction (molar ratio 1:1, pH 7.0).

tolylfluanid (**IV**) additionally indicates the general mechanism of action of both substances in the modification of ion channels (Fig. 3b).

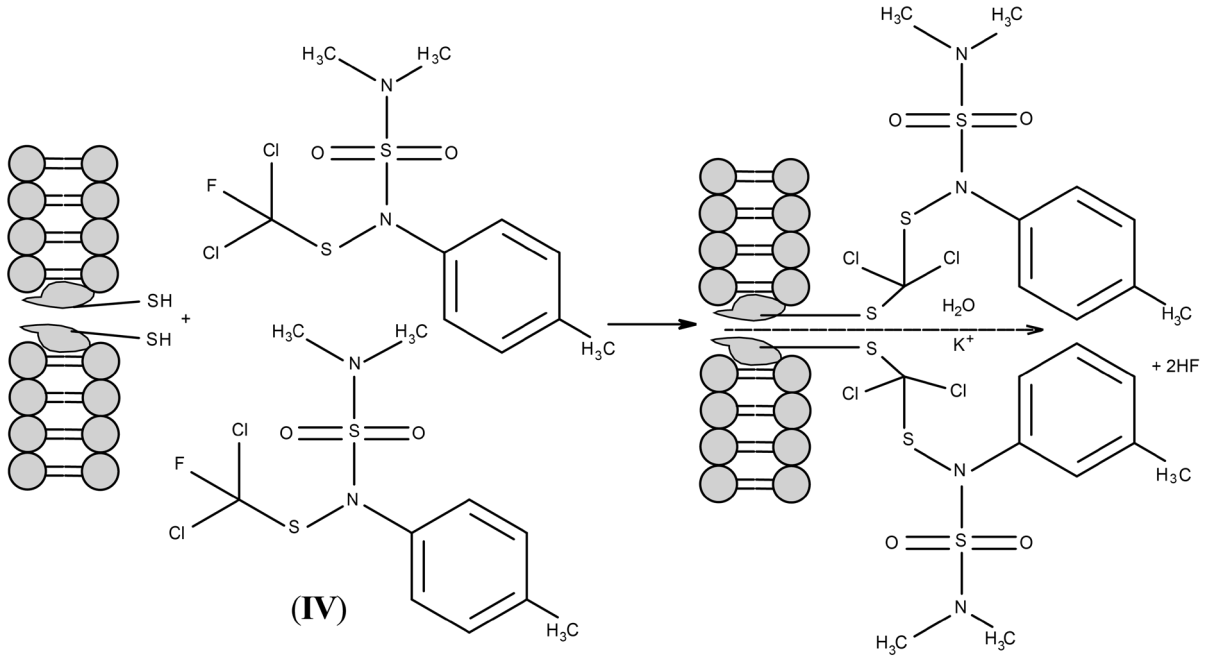
Influence of DAPS-25 and tolylfluanid on the content and fractions of proteins in corn plants

With the loss of electrolytes and dehydration of the body, an increase in the concentration of proteins and, first of all, albumins is observed [32]. It is known that the total protein of plants includes albumins and prolamins—mainly low molecular weight, water-soluble and alcohol-soluble proteins, as well as globulins—proteins soluble in salt solutions. The last group of so-called storage high-molecular proteins are alkali-soluble proteins—glutelins.

The outflow of electrolytes from the cells of corn plants causes their dehydration and increases the concentration of proteins in them (Fig. 4).

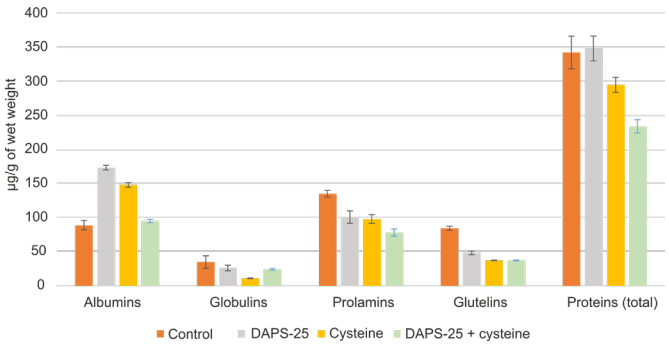


(a)

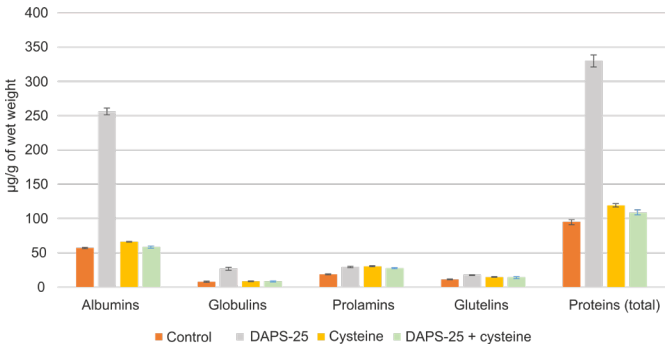


(b)

Fig. 3. Interaction of DAPS-25 (a) and tolylfluanide (b) with sulfhydryl groups in ionic channels of maize cells.

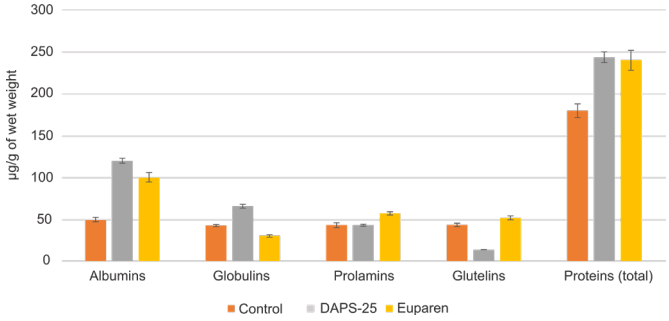


(a)

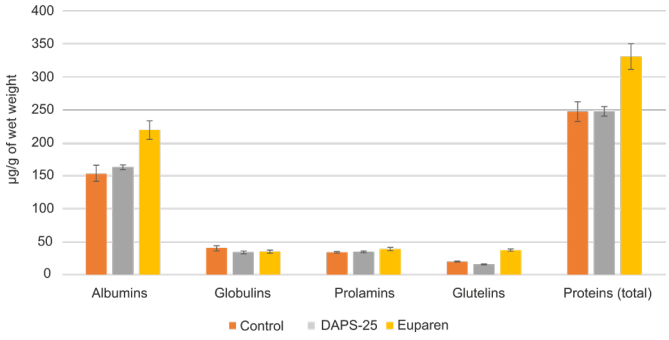


(b)

Fig. 4. Effect of DAPS-25, cysteine, and their mixture on quantitative composition of protein fractions in roots (a) and sprouts (b) of maize seedlings (*Krasnodarsky 291 AMV*).



(a)



(b)

Fig. 5. Effect of DAPS-25 and tolylfluanide on quantitative composition of protein fractions in roots (a) and sprouts (b) of maize seedlings (*Utrennyaya Pesnya*).

DAPS-25 increased the content of albumins in the aerial part by 4.5 times, globulins by 3.5 times, prolamins and glutelins by 1.5 times, and total protein by 3.5 times. Apparently, DAPS-25 causes dehydration of corn root cells due to the loss of electrolytes, which leads to an increase in the concentration of proteins. In another experiment, with tolylfluanid and DAPS-25, there was also an increase in the albumin fraction and the concentration of total protein in the roots and aerial parts of corn seedlings (Fig. 5).

As in the previous study, the content of albumin in the roots in the variant with DAPS-25 increased by 2.4 times, with tolylfluanid by 2 times. In the aerial part, the content of albumins changed less significantly: in the variant with DAPS-25 it increased by 6%, with tolylfluanid by 1.4 times. The concentration of other protein fractions changes less significantly.

Thus, in the variants with thiol poisons—DAPS-25 and tolylfluanid—the content of the albumin fraction and total protein increased both in the roots and in the above-ground mass of plants, which indicates their dehydration.

The antidote of thiol poisons is the amino acid L-cysteine, which contains a sulfhydryl group. The addition of L-cysteine to a Knop's solution containing DAPS-25 showed that the content of the albumin fraction and total protein in corn plants differed from the control by no more than 10–20%. L-cysteine leveled the effect of DAPS-25 (Fig. 5), i.e., was its antidote.

Effect of DAPS-25 and tolylfluanid on peroxidase activity in corn plants

An increase in the protein content in plant tissues due to the loss of electrolytes under the influence of thiol poisons should also lead to a higher enzyme protein content, and, as a result, an increase in their activity. DAPS-25 had a significant effect on peroxidase activity in both roots and seedlings of corn (Figs. 6a and 6b).

DAPS-25 sharply stimulated the activity of the enzyme in almost all concentrations. The most significant increase in peroxidase activity was observed on the first day under the action of the highest concentration of DAPS-25, 0.025 mg Se/L (63% in the roots and 112% in the aerial part), a less significant increase was observed at a concentration

of 0.0025 mg Se/L (29% in the roots and 57% in the aerial part). At the conclusion of the experiment, DAPS-25 at a concentration of 0.00025 mg Se/L had a stimulating effect on peroxidase activity in the variant with roots, 29% (Fig. 7a), but a weakly inhibitory effect in seedlings, 8.6% (Fig. 7b). In the control, during the experiment, peroxidase activity in seedlings changed little, but slightly increased in the roots.

Similarly to the other maize variety, an increase in peroxidase activity in the variant with DAPS-25 was noted as compared to the control (Figs. 7c and 7d). In corn roots, peroxidase activity in the variant with tolylfluanid is 73% higher, while with DAPS-25, it is 36% higher than the control. In the aerial part variant at the beginning of the experiment, peroxidase activity is higher with tolylfluanid by 60%, while at the end of the experiment in the variant with DAPS-25 it is 95% higher. Thus, tolylfluanid, having a similar mechanism of action to that of DAPS-25, increases the activity of peroxidase.

It is known that thiol-dependent redox mechanisms can modulate the activity of the adenosine triphosphate-dependent K^+ channel in the pancreatic beta cell [33]. Oxidation of sulfhydryl groups with mercury-containing thimerosal and 2,2'-dithio-bis-(5-nitropyridine) (DTBNP) at micromolar concentrations causes rapid blocking of the channel, which is reversible by thiols, dithiothreitol and cysteine. Moreover, an excess of thiols restores the functioning of aquaporins blocked by ions of mercury, silver, and other heavy metals [26–28]. Apparently, DAPS-25, interacting with sulfhydryl groups, blocks ion channels, leading to the outflow of electrolytes from the cell (Tables 2 and 4) and consequent increase in protein concentration (Figs. 5 and 6) and activity peroxidase (Fig. 7). Accordingly, an excess of L-cysteine should restore the functioning of ion channels to prevent the outflow of electrolytes from the cell, reducing the concentration of proteins almost to control values along with the peroxidase activity.

In our study, the amino acid L-cysteine reduces the activity of peroxidase both in the roots and in the aerial parts of corn (Figs. 7a and 7b).

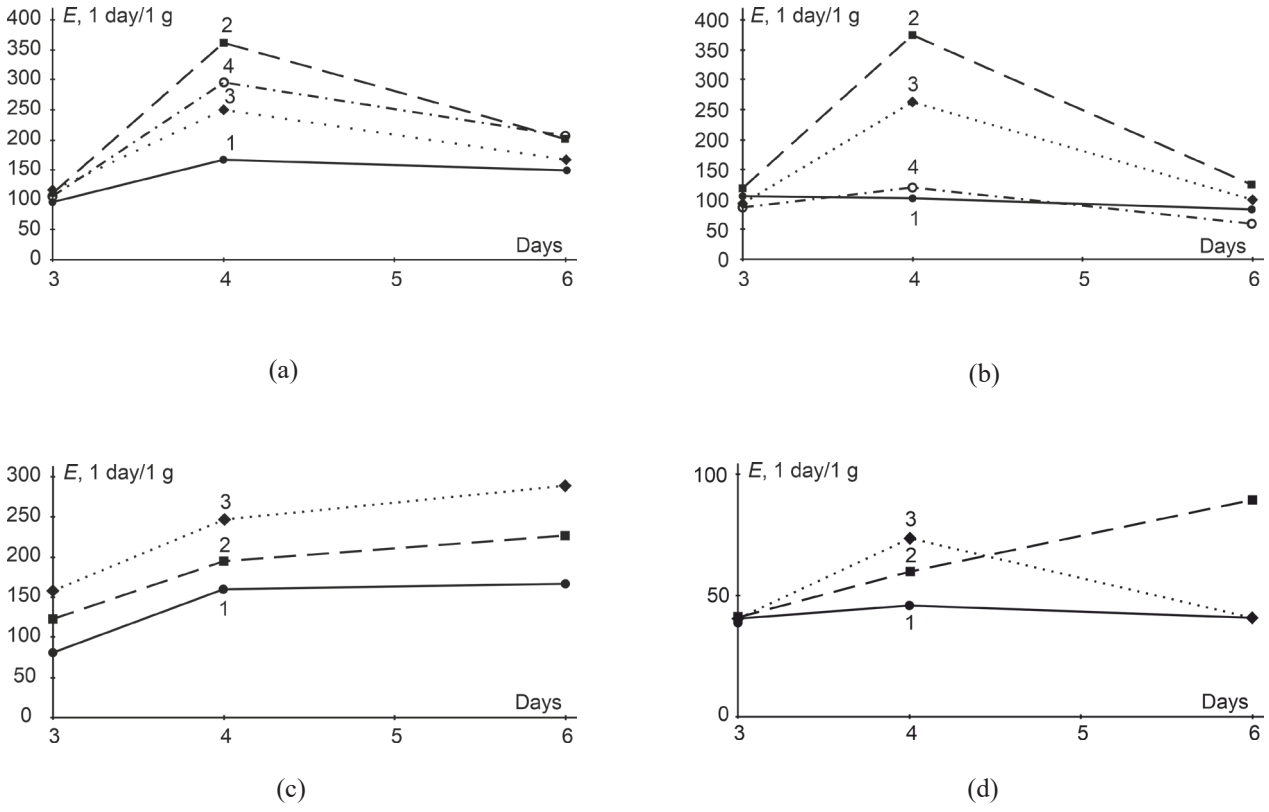


Fig. 6. Effect of DAPS-25 on peroxidase activity in roots (a) and sprouts (b) on maize seedlings (*Krasnodarsky 291 AMV*). 1 – Control; 2 – 0.025 mg Se/L; 3 – 0.0025 mg Se/L; 4 – 0.00025 mg Se/L. Effect of DAPS-24 and tolylfluanides on peroxidase activity in roots (c) and sprouts (d) of maize seedlings (*Utrennyaya Pesnya*). 1 – Control; 2 – DAPS-25 (0.025 mg Se/L); 3 – tolylfluanide. The ordinate is the change in optical density (E_{610}); the abscissa axis is the processing time, starting from 3 days from the moment of the beginning of the corn germination.

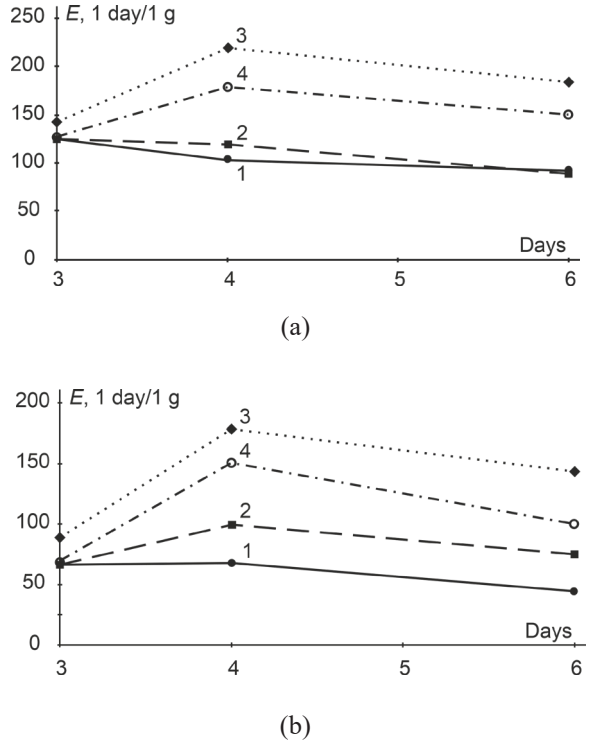


Fig. 7. Changes in peroxidase activity in roots (a) and sprouts (b) of maize seedlings treated with DAPS-25 and L-cysteine. The ordinate is the change in optical density (E_{610}); the abscissa axis is the processing time, starting from 3 days from the moment of the beginning of the corn germination. 1 – Control; 2 – 0.1% L-cysteine; 3 – 0.025 mg Se/L DAPS-25; 4 – 0.025 mg Se/L DAPS-25 + 0.1% L-cysteine.

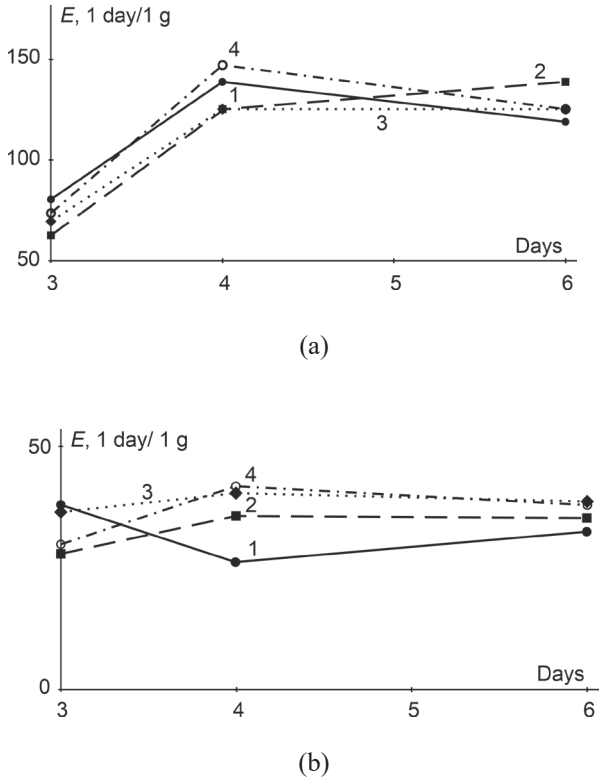


Fig. 8. Effect of sodium selenite Na_2SeO_3 on peroxidase activity in roots (a) and sprouts (b) of maize seedlings. The ordinate is the change in optical density (E_{610}); the abscissa axis is the processing time, starting from 3 days from the moment of the beginning of the corn germination. 1 – Control; 2 – 0.025 mg Se/L; 3 – 0.0025 mg Se/L; 4 – 0.00025 mg Se/L.

In this experiment, peroxidase showed the highest activity on the first day in the variant with DAPS-25 at a concentration of 0.025 mg Se/L; this was true both of the roots and the aerial parts (exceeding the control by 69% and 129%, respectively). In a mixture of DAPS-25 (0.025 mg Se/L) with L-cysteine (0.1%), there was a significant decrease in peroxidase activity to 42% and 79% in comparison with the variant where only DAPS-25 was added. A decrease in peroxidase activity indicates a decrease in the blocking effect of DAPS-25 on ion channels in maize plant cells to reduce electrolyte outflow and lower protein concentration, including the peroxidase enzyme.

A similar, but much weaker effect on the increase in peroxidase activity is exerted by an inorganic salt of selenium, sodium selenite, in the roots (Fig. 8a) and aboveground parts of corn plants (Fig. 8b), which also interacts with sulfhydryl groups like DAPS-25 to form selenodisulfides [34].

In general, starting from the highest (0.025 mg Se/L) and low concentrations (0.00025 mg Se/L), all concentrations of sodium selenite slightly stimulated peroxidase activity in the roots; this effect was closer towards the end of the experiment and somewhat stronger in the aerial part of corn seedlings. It is likely that the relatively weak stimulation of peroxidase activity is associated with the difficulty of transporting the negatively charged selenite ion into the cell interior. For example, thimerosal, which is poorly permeable to membranes, inhibits channel activity only when applied to the intracellular surface of the plasma membrane. On the contrary, DTBNP, which is a lipophilic substance, causes potassium channel blocking and, as a result, membrane potential depolarization even when applied extracellularly [35].

In the experiment with the amino acid L-selenocystin, which also interacts with sulfhydryl groups, peroxidase-like activity was increased by 8.8–30.3% both in the roots and in the aerial part of the plant throughout the entire experiment (Fig. 9.).

The lowest concentration of L-selenocystin (0.00025 mg Se/L) weakly stimulates peroxidase activity in the roots and aerial parts of corn seedlings.

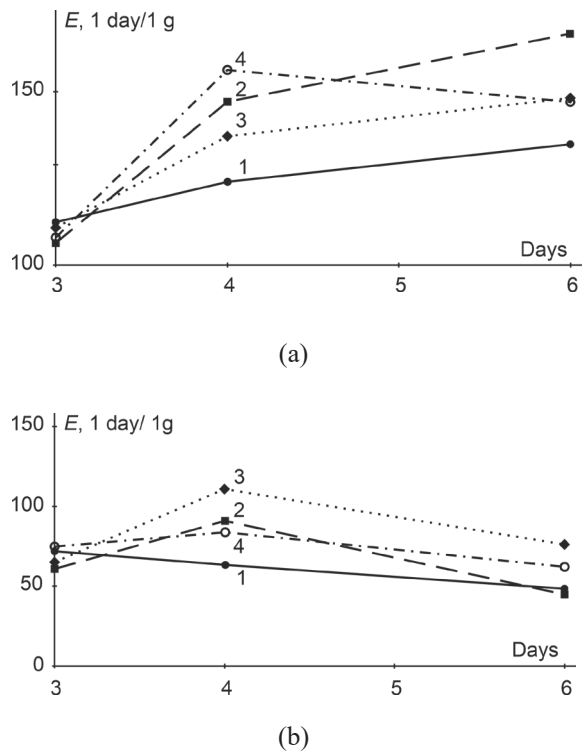


Fig. 9. Effect of L-selenocystine (Sec) on peroxidase activity in roots (a) and sprouts (b) of maize seedlings. The ordinate is the change in optical density (E_{610}); the abscissa axis is the processing time, starting from 3 days from the moment of the beginning of the corn germination. 1 – Control; 2 – 0.025 mg Se/L; 3 – 0.0025 mg Se/L; 4 – 0.00025 mg Se/L.

A more significant increase in peroxidase activity is observed under the action of an average concentration (0.0025 mg Se/L) and to a lesser extent under the action of a high concentration (0.025 mg Se/L) in the aerial part of corn seedlings.

The data obtained demonstrate a similar relationship between the increase in peroxidase activity in selenite- and L-selenocystin-treated corn seedlings. Evidently, the amino acid L-selenocystin enters the cell more easily due to being a less polar compound than selenite; by interacting with the sulfhydryl groups of the cell, it causes a stronger induction of peroxidase activity compared to the inorganic selenium salt.

The total selenium content in the roots of corn seedlings also depends on the presence of thiols in the solution. It is maximum in the variant with DAPS-25 and significantly lower in the variant of combined use of DAPS-25 and L-cysteine (Table 5).

A decrease in the total selenium content indicates a decrease in the intake of DAPS-25 into the plant due to the presence of exogenous sulfhydryl groups of L-cysteine in solution, but not in the tissues of the roots of corn seedlings, which also confirms the effect of the sulfur-containing amino acid as an antidote for thiol poisons.

CONCLUSIONS

The conducted studies showed that the thiol-dependent redox mechanisms of action of DAPS-25 and the organic thiol poison tolylfluanid increase the water permeability of corn root cell membranes, which leads to electrolyte leakage. The action of thiol poisons leads to plasmolysis of maize plant cells and an increase in the concentration of proteins, primarily albumins. An increase in the content of proteins in plant biomass leads to an increase in the concentration of the enzyme and consequent increase in peroxidase activity. The addition of a thiol, L-cystine, to a solution containing DAPS-25 leads to a decrease in the concentration of proteins in plant biomass and a decrease in peroxidase activity. While sodium selenite and L-selenocystin interact with sulfhydryl groups of peroxidase cells to increase peroxidase activity in a similar manner to lipophilic DAPS-25 and tolylfluanid, the effect is much weaker.

Authors' contributions

P.A. Poluboyarinov, N.V. Shchetinina, N.A. Golubkina – conducting the experiments;

P.A. Poluboyarinov, I.Ya. Moiseeva, N.I. Mikulyak – writing the text of the article and the analysis of the obtained results;

N.A. Golubkina, A.P. Kaplun, I.Ya. Moiseeva – scientific editing;

P.A. Poluboyarinov, A.P. Kaplun – idea of the study and general management.

The authors declare no obvious and potential conflicts of interest related to the publication of this article.

Table 5. Selenium content in roots and sprouts of maize seedlings (μg/kg of dry weight)

Plant part	Control	DAPS-25 0.025 mg Se/L	DAPS-25 0.025 mg Se/L + cysteine, 0.1%
Roots	40 ± 3 a	19300 ± 428 c	4853 ± 167 e
Sprouts	53 ± 4 b	5099 ± 278 d	4812 ± 135 e

REFERENCES

1. Behn D., Weiss-Nowak C., Kalcklösch M., Westphal C., Gessner H., Kyriakopoulos A. Studies on the distribution and characteristics of new mammalian selenium-containing proteins. *Analyst*. 1995;120(3):823–825. https://doi.org/10.1039/an9952000823

2. Sies H. Ebselen, a selenoorganic compound as glutathione peroxidase mimic. *Free Radic. Biol. Med.* 1993;14(3):313–323. https://doi.org/10.1016/0891-5849(93)90028-s

3. Drevko B.I., Antipov V.A., Zhukov O.I., *et al*. *Means for the treatment and prevention of diseases caused by selenium deficiency in the body of farm animals and birds*: RF Pat. 2051681. Publ. 10.01.1996. (in Russ.).

4. Usubova E.Z., Zhizhaev A.M., Mironov P.V. Effect of selenium on physiological parameters and efficiency of bean (*Phaseolus vulgaris* L.). *Fundamental'nye issledovaniya = Fundamental Research*. 2012;(3):257–260 (in Russ.).

5. Poluboyarinov P.A., Golubkina N.A. Investigation of the biochemical function of selenium and its influence on the content of protein fractions and peroxidase activity in maize seedlings. *Russ. J. Plant Physiol*. 2015;62(3):367–374. https://doi.org/10.1134/S1021443715030164

6. Castillo-Godina R.G., Foroughbakhch-Pournavab R., Benavides-Mendoza A. Effect of selenium on elemental concentration and antioxidant enzymatic activity of tomato plants. *J. Agr. Sci. Tech*. 2016;18(1):233–244.

7. Huang C., Qin N., Sun L., Yu M., Hu W., Qi Z. Selenium improves physiological parameters and alleviates oxidative stress in strawberry seedlings under low-temperature stress. *Int. J. Mol. Sci*. 2018;19(7):1900–1913. https://doi.org/10.3390/ijms19071913

8. Bebien M., Lagniel G., Garin J., Touati D., Vermeglio A., Labarre J. Involvement of superoxide dismutases in the response of *Escherichia coli* to selenium oxides. *J. Bacteriol.* 2002;184(6):1556–1564. https://doi.org/10.1128/jb.184.6.1556-1564.2002

9. Strogov V.V., Rodionova T.N. Influence of selenium on the functional state and economic parameters of honeybee colonies. *Vestnik veterinarii*. 2011;59(4):150–152 (in Russ.).

10. Wang H.W., Cai D.B., Xiao G.H., Zhao C.L., Wang Z.H., Xu H.M., Guan Y.Q. Effects of selenium on the activity of antioxidant enzymes in the shrimp, *Neocaridina heteropoda*. *The Israeli Journal of Aquaculture – Bamidgeh*. 2009;61(4):322–332.

11. Boryaev G.I., Gavryushina I.V., Fedorov Yu.N. Biochemical and physiological status of lambs in early postnatal ontogenesis against the background of selenium compounds injections to ewe in yean. *Sel'skokhozyaistvennaya biologiya = Agricultural Biology*. 2010;45 (2):65–70 (in Russ.).

12. Dzobo K., Naik Y.S. Effect of selenium on cadmium-induced oxidative stress and esterase activity in rat organs. *South Afr. J. Sci.* 2013;109(5–6):1–8. https://doi.org/10.1590/sajs.2013/965

13. Xiao H., Parkin K.L. Induction of phase II enzyme activity by various selenium compounds. *Nutr. Cancer*. 2006;55(2):210–223. https://doi.org/10.1207/s15327914nc5502_13

14. Filov V.A. Bandman A.L. Volkova N.V. Grekhova T.D. *Vrednye khimicheskie veshchestva. Neorganicheskie soedineniya elementov V–VIII grupp* (*Harmful Chemical Substances. Inorganic Compounds of Elements of V–VIII groups*). Leningrad: Khimiya; 1989. P. 263–282 (in Russ.).

СПИСОК ЛИТЕРАТУРЫ

1. Behn D., Weiss-Nowak C., Kalcklösch M., Westphal C., Gessner H., Kyriakopoulos A. Studies on the distribution and characteristics of new mammalian selenium-containing proteins. *Analyst.* 1995;120(3):823–825. https://doi.org/10.1039/an9952000823

2. Sies H. Ebselen, a selenoorganic compound as glutathione peroxidase mimic. *Free Radic. Biol. Med.* 1993;14(3):313–323. https://doi.org/10.1016/0891-5849(93)90028-s

3. Древко Б.И., Антипов В.А., Жуков О.И. и др. *Средство для лечения и профилактики болезней, вызываемых недостаточностью селена в организме сельскохозяйственных животных и птиц*: пат. 2051681 РФ. Заявка № 93045743/15, заявл. 24.09.1993; опубл. 10.01.1996.

4. Усубова Е.З., Жижаев А.М., Миронов П.В. Влияние селена на физиологические показатели и продуктивность фасоли сорта «сакса» (*Phaseolus vulgaris* L.). *Фундаментальные исследования*. 2012;(3):257–260.

5. Полубояринов П.А., Голубкина Н.А. Изучение биохимической функции селена и его влияние на содержание белковых фракций и активность пероксидазы в проростках кукурузы. *Физиология растений.* 2015;62(3):396–403. https://doi.org/10.7868/S0015330315030161

6. Castillo-Godina R.G., Foroughbakhch-Pournavab R., Benavides-Mendoza A. Effect of selenium on elemental concentration and antioxidant enzymatic activity of tomato plants. *J. Agr. Sci. Tech.* 2016;18(1):233–244.

7. Huang C., Qin N., Sun L., Yu M., Hu W., Qi Z. Selenium improves physiological parameters and alleviates oxidative stress in strawberry seedlings under low-temperature stress. *Int. J. Mol. Sci*. 2018;19(7):1900–1913. https://doi.org/10.3390/ijms19071913

8. Bebien M., Lagniel G., Garin J., Touati D., Vermeglio A., Labarre J. Involvement of superoxide dismutases in the response of *Escherichia coli* to selenium oxides. *J. Bacteriol.* 2002;184(6):1556–1564. https://doi.org/10.1128/jb.184.6.1556-1564.2002

9. Строгов В.В., Родионова Т.Н. Влияние селена на функциональное состояние и хозяйственно-полезные качества пчелиных семей. *Вестник ветеринарии.* 2011;59(4):150–152.

10. Wang H.W., Cai D.B., Xiao G.H., Zhao C.L., Wang Z.H., Xu H.M., Guan Y.Q. Effects of selenium on the activity of antioxidant enzymes in the shrimp, *Neocaridina heteropoda*. *The Israeli Journal of Aquaculture – Bamidgeh.* 2009;61(4):322–332.

11. Боряев Г.И., Гаврюшина И.В., Федоров Ю.Н. Биохимический и физиологический статус ягнят в раннем постнатальном онтогенезе на фоне инъекций соединений селена суягным овцематкам. *Сельскохозяйственная биология.* 2010;45(2):65–70.

12. Dzobo K., Naik Y.S. Effect of selenium on cadmium-induced oxidative stress and esterase activity in rat organs. *South Afr. J. Sci.* 2013;109(5–6):1–8. https://doi.org/10.1590/sajs.2013/965

13. Xiao H., Parkin K.L. Induction of phase II enzyme activity by various selenium compounds. *Nutr. Cancer*. 2006;55(2):210–223. https://doi.org/10.1207/s15327914nc5502_13

14. Филов В.А. Бандман А.Л. Волкова Н.В. Грехова Т.Д. *Вредные химические вещества. Неорганические соединения элементов V–VIII групп*. Химия: Ленинград; 1989. С. 263–282.

15. Avtsin A.P., Zhavoronkov A.A., Rish M.A., Strochkova L.S. *Mikroelementozy cheloveka* (*Human Microelementoses*). Moscow: Meditsina; 1991. P. 196–231 (in Russ.).

16. Sahu G.K., Upadhyay S., Sahoo B.B. Mercury induced phytotoxicity and oxidative stress in wheat (*Triticum aestivum* L.) plants. *Physiol. Mol. Biol. Plants*. 2012;18(1):21–31. https://doi.org/10.1007/s12298-011-0090-6

17. Sofo A., Scopa A., Nuzzaci M., Vitti A. Ascorbate peroxidase and catalase activities and their genetic regulation in plants subjected to drought and salinity stresses. *Int. J. Mol. Sci*. 2015;16(6):13561–13578. https://doi.org/10.3390/ijms160613561

18. Golyshin N.M. *Fungitsidy* (*Fungicides*). Moscow: Kolos; 1993. 318 p. (in Russ.).

19. Yoshida M., Yokimoto M. Effects of fungicides on channels in the fungal membrane. *Pesticide Biochemistry and Physiology*. 1993;47(3):171–177. https://doi.org/10.1006/pest.1993.1076

20. Dudka I.A., Vasser S.P. *Metody eksperimental'noi mikologii* (*Experimental mycology methods*). Kiev: Naukova Dumka; 1982. 550 p. (in Russ.).

21. Mineev V.G., Sychev V.G., Amel'yanchik O.A., Bolysheva T.N., Gomonova N.F., Durynina E.P., Egorov B.C., Egorova E.V., Edemskaya N.L., Karpova E.A., Prizhukova V.G. *Praktikum po agrokhimii* (*Practical work on agrochemistry*). Moscow: MGU; 2001. 689 p. (in Russ.).

22. Bradford M.M. A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding. *Anal. Biochem*. 1976;72(1–2):248–254. https://doi.org/10.1006/abio.1976.9999

23. Gavrilenko V.F., Ladygina M.E., Khandobina L.M. *Bol'shoi praktikum po fiziologii rastenii. Fotosintez. Dykhanie* (*A Large Workshop on Plant Physiology. Photosynthesis. Breath*). Moscow: Vysshaya shkola; 1975. 392 p. (in Russ.).

24. Nazarenko I.I., Ermakov A.N. *Analiticheskaya khimiya selena i tellura* (*Analytical Chemistry of Selenium and Tellurium*). Moscow: Nauka; 1971. 248 p. (in Russ.).

25. Ugai Ya.A. *Neorganicheskaya khimiya* (*Inorganic Chemistry*). Moscow: Vysshaya shkola; 1989. 463 p. (in Russ.).

26. Bienert G.P., Cavez D., Besserer A., Berny M.C., Gilis D., Rooman M., Chaumont F. A conserved cysteine residue is involved in disulfide bond formation between plant plasma membrane aquaporin monomers. *Biochem. J.* 2012;445(1):101–111. https://doi.org/10.1042/bj20111704

27. Frick A., Järvå M., Ekvall M., Uzdavinys P., Nyblom M., Törnroth-Horsefield S. Mercury increases water permeability of a plant aquaporin through a non-cysteine-related mechanism. *Biochem. J.* 2013;454(3):491–499. https://doi.org/10.1042/bj20130377

28. Sadok W., Sinclair T.R. Transpiration response of 'slow-wilting' and commercial soybean (*Glycine max* (L.) Merr.) genotypes to three aquaporin inhibitors. *J. Exp. Bot.* 2010;61(3):821–829. https://doi.org/10.1093/jxb/erp350

29. Poluboyarinov P.A., Vikhreva V.A., Leshchenko P.P., Aripovsky A.N., Likhachev A.N. Formation of elementary selenium decay of molecules of selenium-organic preparation DAFS-25 under influence of growing micella of mushrooms. *Vestnik Moskovskogo Universiteta. Seriya 16. Biologiya.* 2009;16(4):33–37 (in Russ.).

30. Poluboyarinov P.A., Leshchenko P.P. A qualitative reaction for cysteine, reduced glutathione and diacetophenonyl selenide. *J. Anal. Chem*. 2013;68(11):949–952. https://doi.org/10.1134/S1061934813110105

15. Авцин А.П., Жаворонков А.А., Риш М.А., Строчкова Л.С. *Микроэлементозы человека*. М.: Медицина; 1991. С. 196–231.

16. Sahu G.K., Upadhyay S., Sahoo B.B. Mercury induced phytotoxicity and oxidative stress in wheat (*Triticum aestivum* L.) plants. *Physiol. Mol. Biol. Plants*. 2012;18(1):21–31. https://doi.org/10.1007/s12298-011-0090-6

17. Sofo A., Scopa A., Nuzzaci M., Vitti A. Ascorbate peroxidase and catalase activities and their genetic regulation in plants subjected to drought and salinity stresses. *Int. J. Mol. Sci.* 2015;16(6):13561–13578. https://doi.org/10.3390/ijms160613561

18. Голышин Н.М. *Фунгициды*. М.: Колос; 1993. 318 с.

19. Yoshida M., Yokimoto M. Effects of fungicides on channels in the fungal membrane. *Pesticide Biochemistry and Physiology*. 1993;47(3):171–177. https://doi.org/10.1006/pest.1993.1076

20. Дудка И.А., Вассер С.П. *Методы экспериментальной микологии*. Киев: Наукова Думка; 1982. 550 с.

21. Минеев В.Г., Сычев В.Г., Амельянчик О.А., Болышева Т.Н., Гомонова Н.Ф., Дурынина Е.П., Егоров В.С., Егорова Е.В., Едемская Н.Л., Карпова Е.А., Прижукова В.Г. *Практикум по агрохимии*. М.: МГУ; 2001. 689 с.

22. Bradford M.M. A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding. *Anal. Biochem*. 1976;72(1–2):248–254. https://doi.org/10.1006/abio.1976.9999

23. Гавриленко В.Ф., Ладыгина М.Е., Хандобина Л.М. *Большой практикум по физиологии растений. Фотосинтез. Дыхание*. М.: Высшая школа; 1975. 392 с.

24. Назаренко И.И., Ермаков А.Н. *Аналитическая химия селена и теллура*. М.: Наука; 1971. 248 с.

25. Угай Я.А. *Неорганическая химия*. М.: Высшая школа; 1989. 463 с.

26. Bienert G.P., Cavez D., Besserer A., Berny M.C., Gilis D., Rooman M., Chaumont F. A conserved cysteine residue is involved in disulfide bond formation between plant plasma membrane aquaporin monomers. *Biochem. J.* 2012;445(1):101–111. https://doi.org/10.1042/bj20111704

27. Frick A., Järvå M., Ekvall M., Uzdavinys P., Nyblom M., Törnroth-Horsefield S. Mercury increases water permeability of a plant aquaporin through a non-cysteine-related mechanism. *Biochem. J*. 2013;454(3):491–499. https://doi.org/10.1042/bj20130377

28. Sadok W., Sinclair T.R. Transpiration response of 'slow-wilting' and commercial soybean (*Glycine max* (L.) Merr.) genotypes to three aquaporin inhibitors. *J. Exp. Bot.* 2010;61(3):821–829. https://doi.org/10.1093/jxb/erp350

29. Полубояринов П.А., Вихрева В.А., Лещенко П.П., Ариповский А.Н., Лихачев А.Н. Образование элементарного селена при распаде молекулы селенорганического препарата ДАФС-25 под влиянием растущего мицелия грибов. *Вестник Московского университета. Серия 16. Биология*. 2009;16(4):33–37.

30. Полубояринов П.А., Лещенко П.П. Качественная реакция на цистеин, восстановленный глутатион и диацетофенонилселенид. *Журн. аналит. химии*. 2013;68(11):1063. https://doi.org/10.7868/S0044450213110108

31. Полубояринов П.А., Лещенко П.П., Моисеева И.Я., Колесникова С.Г., Эпштейн Н.Б. Механизм реакции элиминирования селена в диацетофенонилселениде под действием восстановленного глутатиона. *Журн. аналит. химии*. 2017;72(7):633–638. https://doi.org/10.7868/S0044450217070118

[Original Russian Text: Poluboyarinov P.A., Leshchenko P.P. A qualitative reaction for cysteine, reduced glutathione and diacetophenonyl selenide. *Zhurnal Analiticheskoi Khimii.* 2013;68(11):1063–1066 (in Russ.). https://doi.org/10.7868/S0044450213110108]

31. Poluboyarinov P.A., Leshchenko P.P., Moiseeva I.Ya., Kolesnikova S.G., Epshtein N.B. Mechanism of the reaction of selenium elimination in diacetophenonyl selenide under the action of reduced glutathione. *J. Anal. Chem.* 2017;72(7):739–744. https://doi.org/10.1134/S1061934817070103

[Original Russian Text: Poluboyarinov P.A., Leshchenko P.P., Moiseeva I.Ya., Kolesnikova S.G., Epshtein N.B. Mechanism of the reaction of selenium elimination in diacetophenonyl selenide under the action of reduced glutathione. *Zhurnal Analiticheskoi Khimii.* 2017;72(7):633–638 (in Russ.). https://doi.org/10.7868/S0044450217070118]

32. Busher J.T. Serum Albumin and Globulin. In: Walker H.K., Hall W.D., Hurst J.W. (Eds.). *Clinical Methods: The History, Physical, and Laboratory Examinations*: 3rd ed. Boston: Butterworths; 1990. Chapter 101. ISBN 978-0409900774.

33. Islam M.S., Berggren P.O., Larsson O. Sulfhydryl oxidation induces rapid and reversible closure of the ATP-regulated K^+ channel in the pancreatic β-cell. *FEBS Lett*. 1993;319(1–2):128–132. https://doi.org/10.1016/0014-5793(93)80051-u

34. Poluboyarinov P.A., Elistratov D.G., Shvets V.I. Metabolism and mechanism of toxicity of selenium-containing drugs supplements used for optimizing human selenium status. *Tonk. Khim. Tekhnol. = Fine Chem. Technol.* 2019;14(1):5–24 (in Russ.). https://doi.org/10.32362/2410-6593-2019-14-1-5-24

32. Busher J.T. Serum Albumin and Globulin. In: Walker H.K., Hall W.D., Hurst J.W. (Eds.). *Clinical Methods: The History, Physical, and Laboratory Examinations*: 3rd ed. Boston: Butterworths; 1990. Chapter 101. ISBN 978-0409900774.

33. Islam M.S., Berggren P.O., Larsson O. Sulfhydryl oxidation induces rapid and reversible closure of the ATP-regulated K^+ channel in the pancreatic β-cell. *FEBS Lett*. 1993;319(1–2):128–132. https://doi.org/10.1016/0014-5793(93)80051-u

34. Полубояринов П.А., Елистратов Д.Г., Швец В.И. Метаболизм и механизм токсичности селенсодержащих препаратов, используемых для коррекции дефицита микроэлемента селена. *Тонкие химические технологии*. 2019;14(1):5–24. https://doi.org/10.32362/2410-6593-2019-14-1-5-24

About the authors:

Pavel A. Poluboyarinov, Cand. Sci. (Agricul.), Associate Professor, Department of General and Clinical Pharmacology, Penza State University (40, Krasnaya ul., Penza, 440026, Russia). E-mail: poluboyarinovpavel@yandex.ru. Scopus Author ID 55913331500, RSCI SPIN-code 1855-6069, https://orcid.org/0000-0001-9870-0272

Natalia V. Shchetinina, Cand. Sci. (Biol.), Associate Professor, Department of Human Physiology, Penza State University (40, Krasnaya ul., Penza, 440026, Russia). E-mail: singl71@list.ru. Scopus Author ID 6603851588, RSCI SPIN-code 1027-6691, https://orcid.org/0000-0002-0076-2553

Inessa Ya. Moiseeva, Dr. Sci. (Med.), Dean of the Faculty of Medicine, Penza State University (40, Krasnaya ul., Penza, 440026, Russia). E-mail: moiseeva_pharm@mail.ru. Scopus Author ID 7004249589, RSCI SPIN-code 9607-0306, https://orcid.org/0000-0003-1168-2871

Nadezhda I. Mikulyak, Dr. Sci. (Med.), Head of the Department of Human Physiology, Penza State University (40, Krasnaya ul., Penza, 440026, Russia). E-mail: normphys@mail.ru. Scopus Author ID 55904922500, ResearcherID S-7843-2016, RSCI SPIN-code 5278-7302, https://orcid.org/0000-0001-8473-5781

Nadezhda A. Golubkina, Dr. Sci. (Agricul.), Chief Researcher, Laboratory and Analytical Center, Federal Scientific Center of Vegetable Production (14, Selektsionnaya ul., VNIISSOK, Odintsovo urban district, Moscow oblast, 143080, Russia). E-mail: segolubkina45@gmail.com. Scopus Author ID 7004449622, ResearcherID AAV-1695-2020, RSCI SPIN-code 9284-3454, https://orcid.org/0000-0003-1803-9168

Alexander P. Kaplun, Dr. Sci. (Chem.), Professor, N.A. Preobrazhensky Department of Chemistry and Technology of Biologically Active Compounds, Medicinal and Organic Chemistry, M.V. Lomonosov Institute of Fine Chemical Technologies, MIREA – Russian Technological University (86, Vernadskogo pr., Moscow, 119571, Russia). E-mail: alexander.p.kaplun@gmail.com. Scopus Author ID 7006433250, RSCI SPIN-code 5856-0218, https://orcid.org/0000-0002-5600-8648

Об авторах:

Полубояринов Павел Аркадьевич, к.с.-х.н., доцент кафедры «Общая и клиническая фармакология» ФГБОУ ВО «Пензенский государственный университет» (440026, Россия, г. Пенза, ул. Красная, д. 40). E-mail: poluboyarinovpavel@yandex.ru. Scopus Author ID 55913331500, SPIN-код РИНЦ 1855-6069, https://orcid.org/0000-0001-9870-0272

Щетинина Наталья Викторовна, к.б.н., доцент кафедры «Физиология человека» ФГБОУ ВО «Пензенский государственный университет» (440026, Россия, г. Пенза, ул. Красная, д. 40). E-mail: singl71@list.ru. Scopus Author ID 6603851588, SPIN-код РИНЦ 1027-6691, https://orcid.org/0000-0002-0076-2553

Моисеева Инесса Яковлевна, д.м.н., декан лечебного факультета ФГБОУ ВО «Пензенский государственный университет» (440026, Россия, г. Пенза, ул. Красная, д. 40). E-mail: moiseeva_pharm@mail.ru. Scopus Author ID 7004249589, SPIN-код РИНЦ 9607-0306, https://orcid.org/0000-0003-1168-2871

Микуляк Надежда Ивановна, д.м.н., заведующий кафедрой «Физиология человека» ФГБОУ ВО «Пензенский государственный университет» (440026, Россия, г. Пенза, ул. Красная, д. 40). E-mail: normphys@mail.ru. Scopus Author ID 55904922500, ResearcherID S-7843-2016, SPIN-код РИНЦ 5278-7302, https://orcid.org/0000-0001-8473-5781

Голубкина Надежда Александровна, д.с.-х.н., главный научный сотрудник лабораторно-аналитического центра ФГБНУ «Федеральный научный центр овощеводства» (143080, Россия, Московская обл., Одинцовский городской округ, поселок ВНИИССОК, ул. Селекционная, д. 14). E-mail: segolubkina45@gmail.com. Scopus Author ID 7004449622, ResearcherID AAV-1695-2020, SPIN-код РИНЦ 9284-3454, https://orcid.org/0000-0003-1803-9168

Каплун Александр Петрович, д.х.н., профессор кафедры химии и технологии биологически активных соединений, медицинской и органической химии им. Н.А. Преображенского Института тонких химических технологий им. М.В. Ломоносова ФГБОУ ВО «МИРЭА – Российский технологический университет» (119571, Россия, Москва, пр-т Вернадского, д. 86). E-mail: alexander.p.kaplun@gmail.com. Scopus Author ID 7006433250, SPIN-код РИНЦ 5856-0218, https://orcid.org/0000-0002-5600-8648

The article was submitted: February 04, 2022; approved after reviewing: March 30, 2022; accepted for publication: September 26, 2022.

Translated from Russian into English by H. Moshkov
Edited for English language and spelling by Thomas Beavitt