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Coordination compounds and chemical compositions with antioxidant properties

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Abstract. In the paper there are presented the main results that argue the antioxidant effect of BACC and some chemical compositions on plants. The anti-stress action of the new preparations - Conimid, Difecoden, Fludisec, Polyel, Galmet and Thiogalmet, is provided by increasing the antioxidant protection capacity due to the decrease of the content of malondialdehyde, intensification of the activity of antioxidant enzymes, increase in the content of non-enzymatic antioxidants with low molecular mass. The possibilities of optimizing the resistance of plants to oxidative stress, caused by drought, and stabilization of plant productivity are promising. The biological performance of plants pre-treated with BACC and antioxidant preparations are more fully realized under both optimal moisture and moderate drought conditions.

Keywords: biologically active coordination compounds, antioxidant chemical compositions, enzymatic and non-enzymatic system of antioxidant protection, resistance, productivity.

Compuşi coordinativi şi compoziţii chimice cu proprietăţi antioxidante

Rezumat. În lucrare sunt prezentate principalele rezultate care argumentează efectul antioxidant al compuşilor coordinativi biologic activi (CCBA) şi unele compoziţii chimice asupra plantelor. Acţiunea anti-stres a noilor preparate - Conimid, Difecoden, Fludisec, Poliel, Galmet şi Tiogalmet, este asigurată prin creşterea capacităţii de protecţie antioxidantă datorită scăderii conţinutului di-aldehidei malonice, intensificării activităţii enzimelor antioxidante, creşterii conţinutului de antioxidanţi non-enzimatici cu masă moleculară mică. Posibilităţile de optimizare a rezistenţei plantelor la stresul oxidativ, cauzate de secetă şi stabilizarea productivităţii plantelor sunt promiţătoare. Performanţele biologice ale plantelor pre-tratate cu CCBA şi preparate antioxidante sunt realizate mai complet, atât în condiţii optime de umiditate, cât şi în condiţii de secetă moderată.

Cuvinte-cheie: compuşi coordinativi biologic activi, compoziţii chimice antioxidante, sistem enzimatic şi neenzimatic de protecţie antioxidantă, rezistenţă, productivitate.

1. Introduction

It has become an axiom the affirmation that one of the reactions of plants to the action of stress factors, including drought, is the intensification of reactive oxygen species (ROS) formation, which, depending on their concentration, have the role of signalling and activating protective mechanisms or induction of oxidative stress and destruction of cellular structures [1, 2]. Under normal conditions, ROS in cells are involved in metabolism, participate in the synthesis of some substances (phytohormones, physiologically active substances), in immunity reactions, in the inactivation of toxic substances, in the processes of cell division, in the annihilation of affected structures etc. Active oxygen compounds are formed continuously throughout the entire ontogenesis of plants, but in adverse environmental conditions, their formation intensifies and oxidative stress becomes a priority. Under optimal conditions, antioxidant enzymes and metabolites neutralize ROS, minimizing oxidative destruction. ROS, generated during drought, induce chlorophyll degradation in chloroplasts, causes stomatal closure, stop photosynthesis and reduce plant productivity [3, 4]. The key mechanisms, related to the adequate response to the unfavourable fluctuation of humidity and the establishment of drought conditions, are mechanisms coupled with the self-regulation of the formation and neutralization of ROS by activating the antioxidant potential, with the intensification of the synthesis of compounds with regulatory and protective functions. Avoidance of over-accumulation of ROS in cells is ensured by enzymatic and non-enzymatic antioxidant protection systems, which include antioxidant enzymes and low molecular weight compounds with antioxidant properties. A possibility to increase the productivity and quality of agricultural crops is the use of physiologically active substances (PhAS) with antioxidant properties [5, 6, 7]. In this sense, the coordination compounds which possess antioxidant properties deserve attention [8].

In recent years it has been shown that exogenous antioxidants can be used to increase the tolerance of plants to stress factors. The existence of a positive correlation between the exogenous administration of many PhAS, antioxidant protection and the formation of plant drought tolerance is known [3,6,9]. It is considered that the intensification of the activity of antioxidant enzymes increases the tolerance of plants to oxidative stress, conditioned by different unfavourable factors, through a more efficient elimination of ROS. Enzymatic decomposition and with the participation of low molecular mass compounds (ascorbic acid, glutathione, α-tocopherol) protect the plant from excessive ROS production.

Based on the above, one of the objectives of the investigations for several years consisted in the elucidation of the properties of new coordination compounds to increase the activity of antioxidant protection enzymes and to reduce the impact of oxidative stress, caused by unfavourable conditions in the external environment.

2. Materials and Methods

Zea mays L., *Phaseolus vulgaris* L., *Glycine max* Merr. (L.), as well as *garlic Allium sativum* L. plants, pre-treated with solutions of BACC - Difecoden, Conimid, Fludisec, and chemical compositions Polyel, Galmet and Thiogalmet, synthesized in the Laboratory of Coordination Chemistry of the Institute of Chemistry within the Moldova State University, served as objects of study. The testing of the effect of the new preparations on the antioxidant protection systems of plants was carried out in the laboratories, the Vegetation Complex and in the fields of the Institute of Genetics, Physiology and Plant Protection of the MSU on small plots according to the requirements of the State Centre for the testing and approval of fertilizer products and plant improvers. In the experiments, the seeds were embedded with the respective solutions before sowing, and foliar treated during the vegetative growth of the plants.

The molecular and crystal structure of the coordination compounds was carried out in the Institute of Applied Physics of MSU at the Nonius Kappa CCD diffractometer (MoKα radiation, graphite monochromator, ω-2θ scan) [12]. The IR spectra were recorded on the FT-IR spectrometer Perkin-Elmer Spectrum instrument in Nujol in a range of 4000-400 cm^{-1} and in the attenuated total reflectance (ATP) mode in a range 4000-650 cm^{-1}, and their interpretation was carried out using the sources: [15,16, 17].

The estimation of the adaptive changes of the enzymatic system of antioxidant protection was carried out by comparing the degree of intensification of the activity of antioxidant enzymes in the leaves of control plants and those pre-treated with BACC and exposed to the action of oxidative stress, caused by the action of moderate drought [6]. The effect of plant pre-treatment on the indices that characterize the intensity of oxidative destruction (content of malondialdehyde - MDA) and the activity of antioxidant defence enzymes (superoxide dismutase - SOD, catalase - CAT, ascorbate peroxidase - APX, glutathione peroxidase - GLPX, glutathione reductase - GLR) were studied. SOD activity was determined by the inhibition of nitroblue tetrazolium photochemical reduction assay, described in detail by Becana M., Aparicio-Tejo P.M., Irigoyen J.J., Sanchez-Diaz M. [18]. The incubation medium contains K-Na-phosphate buffer (60 mmol, pH 7.8), methionine (13 mmol), riboflavin (2 μmol), nitroblue tetrazolium (63 μmol), EDTA (0.1 mmol) and 100 μL of extract. The reaction runs for 10 minutes at light intensity of 15W fluorescent lamps. Samples incubated in the dark served as controls. Enzyme activity that inhibits 50% of the nitroblue tetrazolium photo-reduction is considered as a conventional unit of

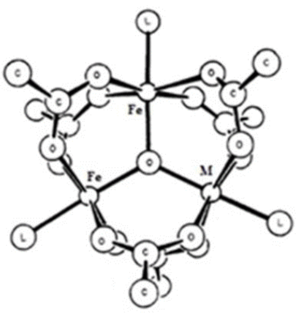
SOD activity. CAT activity was estimated by the method of Chance B. and Machly A. [19] by spectrophotometric determination at λ 240 nm of H_2O_2 decomposition; APX – by monitoring the oxidation rate of ascorbate at λ 290 nm [20]; GLR - by reducing oxidized glutathione in the presence of $NADP^+H$ [21]. Homogenization of plant material and extraction – as described in [17]. The activity of the antioxidant enzymes was expressed in mmol of oxidized substrate and was estimated as a percentage of the enzymes' activity in leaves of the control plants.

The effect of PhAS on plants was concluded by identifying differences in physiological and biochemical parameters. The results were statistically analyzed using the "Statistic 7" software package for computers.

3. Results and Discussion

a) *Characteristics of BACC*, chemical compositions *and obtaining methods*

Syntheses of coordination compounds and chemical compositions or carried out in the Laboratory of Coordination Chemistry of the Institute of Chemistry of the MSU. Two types of coordination compounds (BACC) were obtained and investigated: clusters of the "μ3-oxo" class (Figure 1) [10, 11] and complexes from the "dioximate" class of metals (Figures 2 and 3) [12].



$[Fe^{III}{}_2M^{II}O(CH_3COO)_6L_3]$ (L=H_2O, 3-$CONH_2$-Py, 3-$CON(C_2H_5)_2$-Py, 3-, 4-$COOC_2H_5$-Py

M=Fe^{III}, L=nicotinamide (**Trifenamid**);
M=Fe^{III}, L=N,N-dietilnicotinamide (**Trifeden**);
M=Co^{II}, L= N,N-dietilnicotinamide (**Difecoden**);
M=Mn^{II}, L=N,N-dietilnicotinamide (**Difemanden**)

Figure 1. General structure of "μ3-oxo" class clusters.

The chemical composition, spectral and structural properties of the chemical products were determined using the following methods: elemental analysis, IR spectroscopy and single crystal X-ray diffraction. It should be noted that the Fludisec preparation consists of 3 complexes in different molecular ratios, which differ from each other by the axial component of the complexes: a) Seu-Seu, b) Seu-SeSeu and c) Seu-SeSe (Figure 4).

The structure of the coordination compound Fludisec was established by the single crystal X-ray diffraction method [12].

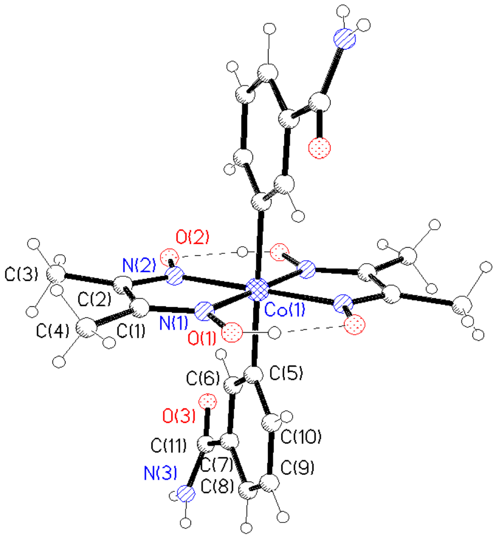


Figure 2. Complex cation structure in $[Co(DH)_2(Nia)_2][BF_4]\cdot 2H_2O$ compound

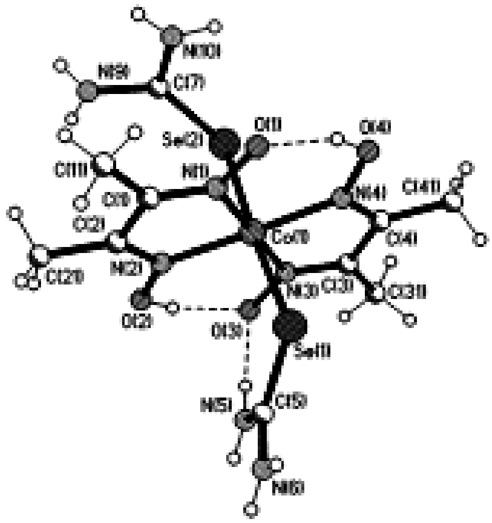
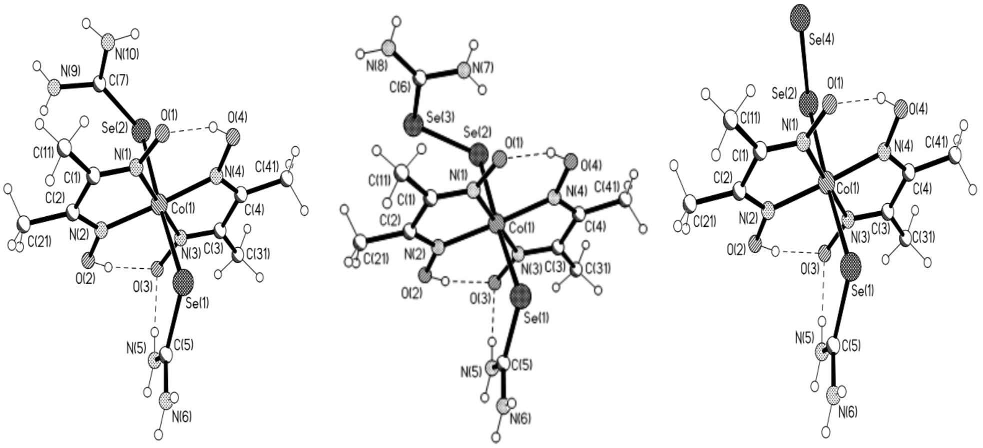


Figure 3. Cation structure $[Co(DH)_2(Seu)_2]^+$ in $[Co(DmgH)_2(Seu)_{1.4}(Se\text{-}Seu)_{0.5}(Se_2)_{0.1}][BF_4]$ ("**Fludisec**") compound

Difecoden complex – with the chemical formula $[Fe_2^{III}Co^{II}O(CH_3COO)_6(DENA)_3]\cdot H_2O$ is obtained by substituting coordinated water molecules in the initial complex with the ligand having the nitrogen atom as donor (DENA). The complex $[Fe_2^{III}Co^{II}O(CH_3COO)_6(H_2O)_3]\cdot 2H_2O$ with a mass of 2 g was suspended in 40 mL of acetone. 2 mL of diethylnicotinamide (DENA) was added to the obtained suspension. The reaction mixture is heated to 50°C until the initial complex is completely dissolved. The solution is filtered and left at room temperature for the acetone to evaporate. As a result, a light brown colored substance was formed, which is separated by filtration, washed 3-4 times with diethyl ether in a volume of 30 mL and air-dried. 2.2 g of final product is obtained.

The coordination compound, conventionally called Conimide, represents the nitrate of trans-bis(dimethylglyoxymato)bis(nicotinamide)cobalt(III) dihydrate, with the chemical formula $[Co(DmgH)_2(PP)_2]NO_3\cdot 2H_2O$, in which: DmgH – monoanion of dimethylglyoxime (CH_3-C(=NOH)-C(=NO-)-CH_3); PP – vitamin PP (nicotinic acid amide, 3-$CONH_2$-C_5H_4N), having the crude formula $C_{20}H_{30}CoN_9O_{11}$ and a molecular mass equal to 631,445. The compound was obtained from the mixture of 0.29g (0.001 mol)



a) b) c)

Figure 4. Structure of $[Co(DmgH)_2(Seu)_{1.4}(Se\text{-}Seu)_{0.5}(Se_2)_{0.1}][BF_4]$ (“Fludisec”) compound: a) $[Co(DmgH)_2(Seu)_2]^+$; b) $[Co(DmgH)_2(Seu)(Se\text{-}Seu)]^+$; c) $[Co(DmgH)_2(Seu)(Se_2)]^+$.

$Co(NO_3)_2{\cdot}6H_2O$, 0.23g (0.002 mol) dimethylglyoxime in 100 mL of water: methanol mixture in a 1:1 volume ratio. The reaction mixture was heated in a water bath at a temperature of 50-60°C until the complete dissolution of the dimethylglyoxime. 0.24g (0.002 mol) of nicotinamide dissolved in 50 mL of methanol is added to the obtained solution, after oxidizing with oxygen in the air for 30 minutes. As a result, a light tan crystalline product is formed with a yield of 70%. The substance is soluble in water, methanol, ethanol and insoluble in diethyl ether. The IR spectrum shows the absorption bands that characterize trans-dimethylglyoximates of cobalt(III) with nicotinamide: $\nu_{as}(NH_2)$ 3379 cm^{-1}, $\nu_s(NH_2)$ 3203 cm^{-1}, ν(C=O) 1694 and 1674 cm^{-1}, $\delta(NH_2)$ 1604 cm^{-1}, $\delta_{as}(CH_3)$ 1446 cm^{-1}, $\delta_s(CH_3)$ 1384 cm^{-1}, ν_{as}(NO) 1234 cm^{-1}, ν_s(NO) 1093 cm^{-1}, δ $(CH_{arom.})$ in plane 1135 and 1067 cm^{-1}, $\delta(CH_{arom.})$ out of plane 755 cm^{-1}.

Fludisec is an ionic coordination compound of selenium tetrafluoroborate-[bis(dimethylglyoxymato)-$(selenocarbamide)_{1.4}$-$(selenium\text{-}selenocarbamide)_{0.45}$-$(selenium\text{-}selenium)_{0.15}$cobalt(III)] with the chemical formula $[Co(DH)_2Seu_{1.4}Se\text{-}Seu_{0.45}Se\text{-}Seu_{0.15}]BF_4$, in which two monodeprotonated DH^-/$DmgH^-$ ligands were coordinated to the complex generator atom, where DH_2/$DmgH_2$ is the dimethylglyoxime molecule, Seu – selenocarbamide molecule, and Se-Seu – a neutral carbamide molecule containing two Se atoms. To obtain 0.34 g (0.001 mol) of $Co(BF_4)_2{\cdot}6H_2O$ in 30 mL of water, 0.23 g

(0.002 mol) of dimethylglyoxime in 40 mL of methanol and 0.25 g (0.002 mol) of selenourea in 30 mL of methanol were added. The obtained solution was heated for 10 minutes in the water bath in a graphite crucible at ~70°C. Crystals of the same color precipitated from the dark-brown solution upon slow evaporation (yield ~32%). The compound is soluble in alcohols, partially in water. In the IR spectrum, the characteristic absorption bands of the $Co(DmgH)_2$ fragment are present, cm^{-1}: $\nu_{as}(CH_3)$=2928, $\nu_s(CH_3)$=2871,ν_{as}(C=N)=1546, $\delta_{as}as(CH_3)$=1461, $\delta_s(CH_3)$=1376,ν_{as}(N=O)=1237, ν_s(C=N)=1285, ν_s(N=O)=1083, γ(OH)=972, δ(CNO)=730, ν_{as}(Co-N)=507 and ν_s(Co-N)=428. For the $[BF_4]^-$ ions in the outer sphere, the bands $\nu_{as}(BF_4)$=1084, $\nu_s(BF_4)$=761, δ(F–B–F)=524 cm^{-1} can be assigned.

The crystal structure of $[Co(DmgH)_2Seu_{(1+0.4)}Se\text{-}Seu_{0.45}Se\text{-}Se_{0.15}]BF_4$ was determined by the X-ray analysis method in the X-calibre diffractometer equipped with a CCD detector at room temperature. Crystallographic data indicate triclinic syngony, symmetry space group P-1, unit cell parameters: a=7.9163(9), b=11.679(2), c=13.433(3) Å, α=64.50(2), β=75.31 (1), γ=82.05(1)°, V=1083.8(3) $Å^3$, the number of independent structural units Z=2, ρ(calc.)=1.906 g/cm^3 for the composition $C_{10}H_{22}BCoF_4N_8O_4Se_2$. The structure was determined by direct methods, and the coordinates of the basic (non-hydrogen) atoms were specified by the least squares method in the anisotropic variant within the SHELX-97 program complexes.

The preparation, called **Polyel**, is a light-brown chemical composition, hygroscopic, well soluble in water, soluble in alcohols, stable over time and in light. The composition contains thiourea, coordination compounds with biological activity, macro- and microelements in the following composition of active ingredients, %: thiourea - 50.00; $Mg(NO_3)_2{\cdot}6H_2O$ - 20.12; $Ca(NO_3){\cdot}24H_2O$ - 14.51; potassium salicylate -11.43; $Mn(CH_3COO)_2{\cdot}4H_2O$ - 0.55; $[Co(DmgH)_2(SeUrea)_2]BF_4{\cdot}2H_2O$ - 1.73; $[Fe_3O(CH_3COO)_6(H_2O)_3]NO_3{\cdot}3H_2O$ - 0.69; $[Co(DmgH)_2(Nia)_2]BF_4{\cdot}2H_2O$ - 0.36; $Zn(NO_3)_2{\cdot}6H_2O$ - 0.26; $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ - 0.19; $(HOC_6H_4COO)_2Cu{\cdot}4H_2O$ - 0.16.

The coordination compounds of iron(III) and cobalt(III) were obtained according to the following protocols: $[Fe_3O(CH_3COO)_6(H_2O)_3]NO_3{\cdot}3H_2O$, $[Co(DmgH)_2(Nia)_2]BF_4{\cdot}2H_2O$ - according [8], $[Co(DmgH)_2(Se\text{-}Urea)_2]BF_4{\cdot}2H_2O$ [12], where DmgH – dimethylglyoximate monoanion, Nia – nicotinamide (vitamin PP). The starting substances for the synthesis of coordination compounds and other components of the Polyel preparation were purchased from SIGMA-ALDRICH and used without further purification.

Thiogalmet is a solid, powdery substance of light-brown colour, stable at room temperature, well soluble in water. It was obtained by mixing two parts (m/m) of thiourea with one part of the known biologically active preparation Galmet. The calculated content of bioactive components in Thiogalmet, %: thiourea – 66.66; gallate anion ($(OH)_3C_6H_2COO^-$) – 21.52; K^+ - 1.63; Mg^{2+} - 0.97; Mo(VI) – 0.99; NH_4^+ - 1.07; total nitrogen – 25.36.

The IR spectrum of the Thiogalmet composition is characterized by the presence of several absorption bands of different intensity, the knowledge of which will allow the use of the spectrum as a benchmark when obtaining the respective composition repeatedly. IR (ν, cm^{-1}): 3623w, 3361m, 3251s, 3163s, 3083m, 2989s, 2686m, 2647w, 1680w, 1607m, 1539v.s, 1456s, 1399v.s, 1366v.s, 1345v.s, 1317sh, 1276s , 1262s, 1220w, 1201s, 1096m, 1082m, 1055s, 1044s, 965w, 890sh, 876m, 836w, 800m, 792m, 773m, 748m, 729s, 672m, 631s, 488v.s, 467s, 412w (v.s – very strong, s – strong, m – medium, w – weak, v.w – very weak, sh – shoulder).

b) *Arguing the antioxidant properties of the newly synthesized BACC and chemical compositions*

It is known that the resistance of plants to unfavourable conditions consists of a complex of protective mechanisms - physiological, biochemical, anatomical-morphological, oriented towards maintaining the internal environment of the organism at a relatively constant level, a necessary condition for the normal realization of the growth and development program each species and variety of plants encoded in the genetic apparatus. Those physiologically active substances, including BACC, which under suboptimal environmental conditions have a positive impact on these mechanisms, can be considered tolerance inducers. Much of the damage caused by drought is associated with oxidative damage at the cellular level as a result of excessive ROS formation caused by cell dehydration. Logically, it is correct to assume that the property of plants to control and maintain at a certain level the ROS content is directly correlated with their resistance to the action of unfavourable factors.

It has been demonstrated that some coordination compounds and some chemical compositions possess the property of protecting plant cells from the destruction of cellular structures by reactive oxygen species. It was established (Table 1), that BACC **Conimid** $[Co(DmgH)_2(PP)_2]NO_3{\cdot}2H_2O$ and **Difecoden** $[Fe_2CoO(CH_3COO)_6(DENA)_3]{\cdot}H_2O$, differ in antioxidant protection capacity.

Treatment of seeds and foliage of *Phaseolus vulgaris*, L plants with Conimid and Difecoden significantly reduces the formation of malondialdehyde - the end product of the oxidative destruction of phospholipids, and intensifies the activity of antioxidant protection enzymes. The obtained data demonstrate that the new preparation, - Conimid, has a significantly stronger antioxidant effect compared to Difecoden. The treatment of seeds and foliage with Conimid reduces the formation of malondialdehyde by 32.87%

Table 1. The content of malondialdehyde and the activity of antioxidant enzymes in the leaves of plants pre-treated with Difecoden and Conimid

Variant	**MDA**, μmol · g-1 fr. m. *		**SOD**, conv. un. · g-1 fr. m.		**APX**, mmol · g-1 fr. m.		**CAT**, mmol · g-1 fr. m.	
	M ± m	Δ, %	M ± m	Δ, %	M ± m	Δ, %	M ± m	Δ, %
Control	15.9 ± 0.8		145.7 ± 2.2		3.1 ± 0.1		2.10 ± 0.05	
Difecoden	12.4 ± 0.6	-21.8	154.5 ± 1.9	6.0	4.7 ± 0.2	52.1	3.06 ± 0.06	45.7
Conimid	10.7 ± 0.4	-32.8	165.6 ± 0.9	13.6	5.3 ± 0.3	61.7	3.12 ± 0.09	48.6

fr. m. * - fresh mass

compared to the content of malondialdehyde in the leaves of control plants and by 14.15% compared to plants treated with Difecoden. The activity of the antioxidant enzymes SOD, APX and CAT under the influence of this BACC increases compared to the control by 13.6; 61.7 and 48.6 % respectively. Enhancing the antioxidant protection capacity of plants ensures the stabilization of the complex of assimilatory pigments and reduces the oxidative destruction of chlorophyll (Table 2). Pre-treating the plants with the respective compounds protect the assimilatory pigments from oxidative destruction. The plants pre-treated with Difecoden and, especially, with Conimid, are characterized by an assimilative apparatus with a significantly higher content of assimilative pigments compared to the control plants.

Table 2. Effect of Difecoden and Conimid on content of assimilatory pigments ($mg·dm^{-2}$) in leaves

Variant	**Chlorophyll *a***		**Chlorophyll *b***		**Carotenoids**		**Cl *a* + Cl *b***	
	M ± m	Δ, % C	M ± m	Δ, % C	M ± m	Δ, % C	M ± m	Δ, % C
Control C	1.441 ± 0.002		0.601 ± 0.003		0.424 ± 0.001		2.091 ± 0.002	
Difecoden	1.910 ± 0.002	32.6	0.902 ± 0.003	38.5	0.621 ± 0.001	47.6	2.802 ± 0.001	34.0
Conimid	2.320 ± 0.001	61.8	1.043 ± 0.005	59.7	0.715 ± 0.001	70.1	3.373 ± 0.001	61.2

Carbon assimilation processes in *Phaseolus vulgaris* plants pre-treated with Conimid prevailed over the control by 40.4 and 8.3 percent. Plant productivity in moderate drought conditions in pre-treated plants exceeded the productivity value of control plants in the same humidity conditions by 30.2%.

Therefore, BACC Difecoden and Conimid, show antioxidant properties, and the pre-treated plants possess a significantly higher antioxidant protection capacity compared to control plants, with a positive impact on plant growth and productivity.

Currently, one of the important objectives of modern agriculture is to obtain production with an increased content of microelements and vitamins with a protective function from reactive oxygen species, which cause oxidative stress both in the body of plants and animals, including humans. Special attention is paid to products with a high selenium content due to its importance in the food chain. The organic form of selenium, obtained by the human body from vegetable products, is considered more active and useful. It has been demonstrated that selenium in small concentrations conditions the amplification of the adaptive potential of plants, diminishes the negative action of drought, stabilizes the surface of the assimilation apparatus, reduces the fall of flower buds and contributes to the activation of growth processes during the repair period after the improvement of humidity conditions [13].

The ionic coordinating compound Fludisec, which has selenium in its composition $[Co(DH)_2(Seu)_{1.4}(Se\text{-}Seu)_{0.5}(Se_2)_{0.1}][BF_4]$, has the property of stimulating the growth processes of garlic seedlings already at the initial stages of ontogenesis. It has antioxidant properties, significantly increases the activity of antioxidant protection enzymes, the content of photosynthetic pigments and the productivity of garlic plants (Table 3). The character of the changes in the content of malondialdehyde and the activity of antioxidant protection enzymes in the treated plants confirms the effect of reducing the oxidative stress induced by selenium.

Antioxidant action of selenium is manifested by the tendency to normalize these parameters; malondialdehyde values decreased significantly not only compared to those of untreated plants. The optimization of the antioxidant protection capacity provided by BACC Fludisec has a positive impact on the functional state of the plant's consequence of drought-caused oxidative stress is abundant generation of singlet oxygen, destruction of chloroplasts and decrease in the content of assimilatory pigments in leaves. According to our data [12], the supplementation of garlic plants with Se by treating the foliar apparatus with Fludisec caused an increase in content of assimilatory pigments, rate of photosynthesis and plant productivity. Selenium content in leaves and bulbs of the plants

Table 3. Malondialdehyde content and activity of antioxidant defence enzymes in garlic (*Allium sativum* L.) leaves and bulbs

Parameter	**Control**	**Fludisec 0,00001%**	
	M ± m	M ± m	Δ, %
In leaves			
MDA, µmol · g^{-1} fr. m.	32.35 ± 0.38	25.52 ± 0.36	-21.11
SOD, conv. un. · g^{-1} fr. m.	62.81 ± 0.73	78.39 ± 0.47	24.80
CAT, mmol · g^{-1} fr. m.	1.30 ± 0.01	1.94 ± 0.04	4.23
APX, mmol · g^{-1} fr. m.	8.43 ± 0.13	12.44 ± 0.35	47.57
GlR, mmol · g^{-1} fr. m.	172.81 ± 2.08	118.30 ± 2.12	38.46
GlPX, mmol · g^{-1} fr. m.	85.44 ± 1.94	217.01 ± 3.64	25.56
In bulbs			
MDA, µmol · g^{-1} fr. m.	16.18 ± 0.20	12.11 ± 0.19	-25.15
SOD, conv. un. · g^{-1} fr. m.	52.81 ± 0.77	70.14 ± 0.52	32.82
CAT, mmol · g^{-1} fr. m.	2.14 ± 0.01	2.98 ± 0.05	39.25
APX, mmol · g^{-1} fr. m.	7.16 ± 0.10	11.31 ± 0.02	57.96
GlR, mmol · g^{-1} fr. m.	182.84 ± 2.95	227.01 ± 3.89	24.16
GlPX, mmol · g^{-1} fr. m.	95.15 ± 2.31	120.21 ± 2.05	26.34

pre-treated with Fludisec exceeds the respective control values by about 19 and 49% (Table 4).

Maximum effect of increasing selenium content in both leaves and bulbs were recorded in plants treated with Fludisec. Biomass accumulation of the plants pre-treated with Fludisec was significantly higher compared to the control plants. The effect of plant mass increasing is respectively 6.87 and 21.20%. Average bulb mass exceeded control values by 7.47 and 22.20 percent respectively. Plant treating with the new preparation provided a 22.18% increase in production compared to the control. Supplementation of garlic plants

Table 4. Effect of garlic treatment on selenium content in leaves and bulbs ($\mu g \cdot kg^{-1}$ fr. m.)

Organ	**Control**	**Fludisec 0,00001%**	
	M ± m	M ± m	Δ, % Control
In leaves	74.0 ± 1.8	88.0 ± 1.9	18.92
In bulbs	47.0 ± 0.7	70.0 ± 1.1	48.94

(*Allium sativum* L.) with selenium by treating them with Fludisec increases tolerance to oxidative stress caused by drought.

A number of new chemical compositions also have been found to possess significant antioxidant properties. Plants treated with **Polyel** possess a significantly higher capacity of antioxidant protection compared to the plants treated with thiourea and, in particular, with those from the control group (Table 5).

Seed and leaf treatment of corn and soybean plants during vegetative growth with complex preparation **Polyel** ensures the increase of plants' resistance to drought, stabilizes productivity under fluctuating environmental conditions by 24.1% higher than in the control plants and by 13.8% higher than the plants treated with thiourea.

So, new chemical composition Polyel has a genuine influence on the antioxidant protection capacity of plants both under favourable conditions and under drought conditions.

It has been proven with certainty that the compositions **Galmet** and **Thiogalmet** possesses antioxidant properties and its use for the pre-treatment of plants in optimal humidity conditions ensures an improvement of the red-ox status by activating antioxidant enzymes and reducing the content of MDA (Table 6).

MDA content in plants pre-treated with Thiourea, Galmet and Thiogalmet under moderate drought conditions was maintained at a lower level by 7.79; 18.63 and 15.31% in corn and with 14.40; 13.08 and 22.02% in soybean, compared to the index values of untreated and drought-exposed control plants. MDA content in plants pre-treated with thiourea and Thiogalmet under moisture deficiency exceeded the MDA levels of control plants under optimal moisture by 28.93 and 18.42% in corn and by 29.93 and 15.36% - in soybean plants, which represents a significantly lower degree of MDA content modification than in untreated plants but exposed to drought-caused oxidative stress. Activity of antioxidant enzymes under optimal humidity increases in corn and soybean plants by 9.31 and 8.89 percent under the influence of thiourea and by 24.1 and 14.4 respectively when pre-treated with Galmet. Under these conditions, overall enzyme activity in corn and soybean plants

Table 5. Influence of plant treatment with PhAS on antioxidant defence capacity of *Glycine max (L.) Merr plants. 'Deia'* variety under drought conditions

Parameter	Control	Thiourea		Polyel	
	M ± m	M ± m	Δ, % M	M ± m	Δ, % M
MDA, µmol · g^{-1} fr. m.	17.4 ± 0.3* 28.5 ± 0.2**	16.0 ± 0.2 18.9 ± 0.4		14.8 ± 0.3 17.6 ± 0.5	
SOD, conv. un. · g^{-1} fr. m.	68.2 ± 0.6 81.7 ± 1.4	74.5 ± 0.1 96.5 ± 1.6	18.1	82.3 ± 2.1 109.6 ± 1.2	34.3
CAT, mmol · g^{-1} fr. m.	6.5 ± 0.1 8.1 ± 0.2	7.3 ± 0.2 9.3 ± 0.1	14.4	7.5 ± 0,2 13.9 ± 0.4	70.4
APX, mmol · g^{-1} fr. m.	8.3 ± 0.1 13.1 ± 0.3	10.9 ± 0.3 17.8 ± 0.4	35.7	13.7 ± 0.2 20.3 ± 0.5	55.1
GPX, mmol · g^{-1} fr. m.	51.8 ± 0.9 68.8 ± 0.5	60.6 ±1.3 76.0 ± 2.1	10.5	62.8 ± 1.1 78.7 ±1.4	14.4
GwPX, mmol · g^{-1} fr. m.	39.3 ± 0.6 66.4 ± 0.9	58.1 ± 0.8 93.8 ± 2.1	41.3	59.8 ± 1.3 120.5 ± 2.6	81.6
GR, mmol · g^{-1} fr. m.	121.4 ± 1.8 152.4 ± 2.7	132.3 ± 3.8 173.1 ± 5.2	13.6	148.8 ± 4.3 176.7 ± 3.5	15.9

*- control optimum 70% TWC; **- control drought 30% TWC

increased by 27.5 and 16.9% respectively compared to the index values of control plants. The beneficial physiological effect of Thiogalmet is also confirmed by the higher levels of assimilation and growth process in plants (Table 6). The intensity of photosynthesis in soybean and corn plants pre-treated with Thiogalmet constitutes an increase of 54.5 and 62.0%, respectively, compared to the value of carbon dioxide assimilation recorded in the control plants. Under insufficient moisture, the intensity of photosynthesis of the plants pre-treated with Thiogalmet was 2-fold higher compared to the control plants, exposed to drought. As a result of these changes, the efficiency of water use in assimilation process

Table 6. Antioxidant protection capacity and CO_2 assimilation process of plants pre-treated with Thiogalmet and exposed to moderate drought

Variants		Control	Thiourea	Galmet	Thiogalmet
Indices		M ± m	M ± m	M ± m	M ± m
***Zea mays*, L. cv. P458**					
MDA, $\mu mol \cdot g^{-1}$ fr. m.	*optimum*	33.7 ± 0.2	31.4 ± 0.1	26.8 ± 0.1	24.9±0.1
	drought	47.1 ± 0.9	43.4 ± 0,2	39.9 ± 0.2	39.8±0.1
Total enzymatic activity	*optimum*	145.4 ± 8.4	158.9 ± 6.8	180.5 ± 6.7	185.4±9.9
	drought	210.2±6.6	249.0 ± 6.7	280.5 ± 6.7	300.3±5.0
Assimilation, mmol $CO_2 \cdot m^{-2} \cdot h^{-1}$	*optimum*	5.0 ± 0.5	6.5 ± 0.2	7.6 ± 0.2	8.1±0.3
	drought	1.9 ± 0.4	2.90 ± 0.09	2.8 ± 0.2	3.7±0.3
***Glycine max (Merr)*, L., 'Nadejda' variety**					
MDA, $\mu mol \cdot g^{-1}$ fr. m.	*optimum*	32.9 ± 0.1	25.4 ± 0.06	26.2 ± 0.1	24.7±0.7
	drought	49.9 ± 0.4	42.70 ± 0.04	43.4 ± 0.1	37.9±0.1
Total enzymatic activity	*optimum*	203.7 ± 6.5	221.9 ± 6.5	232.5 ± 6.6	238.1±6.8
	drought	291.2 ± 5.3	326.4 ± 6.9	339.4 ±6.9	356.2±9.6
Assimilation, mmol $CO_2 \cdot m^{-2} \cdot h^{-1}$	*optimum*	5.2 ± 0.2	7.0 ± 0.2	7.2 ± 0.5	7.9±0.3
	drought	1.2 ± 0.2	2.1 ± 0.1	2.5 ± 0.1	2.80±0.16

in plants pre-treated with Thiogalmet was higher by 72.8% compared to control plants under same humidity conditions [14]. The intensification of carbon dioxide assimilation processes conditions a significant increase in plant growth and productivity. Plant pre-treatment with Thiogalmet caused an increase in growth of soybean and corn plants under optimal humidity conditions by 5.6 and 14.6% compared to the control plants. Under conditions of insufficient moisture, soybean plants pre-treated with Thiogalmet were 17.8% taller than control plants exposed to drought. The productivity of soybean and corn plants pre-treated with the new composition was higher by 21.9 and 25.6% under optimal moisture and by 35.6 and 48.3% - under moderate moisture deficiency. The biological performance and productivity potential of soybean and corn plants pre-treated with Thiogalmet are more thoroughly fulfilled under both optimal moisture and moderate drought conditions.

4. Conclusions

(1) Changing the chemical composition by substituting coordinated water molecules in ”μ_3-oxo” type complexes $[M^{III}_3O(CH_3COO)_6\,(H_2O)_3]NO_3$, $[M^{III}_2M^{II}O(CH_3COO)_6\,(H_2O)_3]$, as well as by the variation of ligands on axial coordinates in ”dioximate” type compounds with biologically active ligands such as nicotinamide (vitamin PP), N,N-diethylnicotinamide (cordiamine), selenourea leads to obtaining coordination compounds with pronounced antioxidant properties.

(2) The coordination compounds Conimid, Difecoden, Fludisec and the chemical compositions Polyel, Galmet and Thiogalmet possess properties of antioxidant substances, and can be used to protect plants from oxidative stress, caused by unfavourable environment, in particular, by drought.

(3) Plant tolerance to adverse conditions of external environment can be enhanced by pre-treating seed prior to sowing and plants during vegetative growth with BACC solutions and chemical compositions with antioxidant properties.

(4) The anti-stress action of the new preparations - Conimid, Difecoden, Fludisec, Polyel, Galmet and Thiogalmet, is provided by increasing the antioxidant protection capacity due to the decrease of the content of malondialdehyde, intensification of the activity of antioxidant enzymes.

(5) Plants pre-treated with BACC have a higher antioxidant protection capacity compared to untreated plants.

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References

[1] Bhattacharjee, S. *Journal of Botany*, 2012, 22 p.
[2] Mittler, R. *Trends in Plant Science*, 2002, 7 (9), 405 – 410
[3] Asada, K. *Plant Physiol.*, 2006, 141 (2), 391-396

[4] Wang, W.H.; Yi, X.Q.; Han, A.D.; Liu, T.W. ; Chen, J. ; Wu, F.H.; Dong, X.J.; He, J.X.; Pei, Z.M.; Zheng, H.L. *Journal of Exp. Botany*, 2012, 63 (1), 177 – 190

[5] Foyer, C.; Shigeoka, S. *Plant Physiol.*, 2011, 155, 93 -100

[6] Ştefîrţă, A.; Brînză, L.; Vrabie, V.; Aluchi, N. *Fiziologia stresului, adaptării şi rezistenţei la secetă a plantelor de cultură*. Tipografia: ASM, Chişinău, Republica Moldova, 2017, 372 p.

[7] Munné-Bosch, S.; Queval, G.; Foyer, C. *Plant Physiol.*, 2013, 161, 5-19

[8] Coropceanu, E., Ciloci, A., Ştefîrţă, A., Bulhac, I. Study of useful properties of some coordination compounds containing oxime ligands, *Academica Greifswald*, Germany, 2020, 266 p.

[9] Ştefîrţă, A.; Bulhac, I.; Coropceanu, E.; Brînză, L. Polyel–compound with antioxidant properties. *Journal of Applied Life Sciences and Environment* (JALSE), 2021, Volume LIV, 2 (186),146-155

[10] Turtă, K.; Shova S.; Spatar, F.; Mazus, M.; MalinovskII, T. *Journal of Struct. Chem.*, 1994, 35, 248–255

[11] Sato, T.; Ambe, F. *Acta Cryst.*, 1996, C52, 3005-3007

[12] Coropceanu, E.; Bulhac, I.; Shtefyrtse, A.; Botnar, V.; Melenchuk, M.; Kuligin, E.; Bourosh, P. Russ. *Journal of Coord. Chem.*, 2017, 43 (3), 164 – 171

[13] Ştefîrţă, A.; Botnari, V.; Brînză, L.; Bulhac, I.; Coropceanu, E.; Bouroş, P.; Chilinciuc Al. *Acta Chemica*, Iaşi, 2017, 252, p. 208 -231

[14] Ştefîrţă, A.; Bulhac, I.; Cocu, M.; Brînză, L.; Zubarev, V. *International Journal of Advanced Research* (IJAR), 2022, 10 (4), p. 1109-1119

[15] Nacano Y.; Asada K. *Plant Cell Physiol.*, 1981, 22, 867-880

[16] Schadle, M.; Bassham *J. Plant Physiol.*, 1977, 59, 1011-1012

[17] Keshavkant, S.; Naithani, S. *Acta Physiol. Plant.*, 2001, 23 (4), 457-466

[18] M. Becana; P. M. Aparicio-Tejo; J. J. Irigoyen; M. Sanchez-Diaz *Plant Physiol.*, 1986, 82, 1169-1171

[19] Chance, B.; Machly, A. Assay of catalases and peroxidises. In *Methods in Enzymology*, S. P. Colowick and N. O. Kaplan Eds.; Acad. Press, N.Y., USA, 1955, Volume 2, pp. 764-775

[20] Nacano, Y.; Asada K. *Plant Cell Physiol*., 1981, 22, 867-880

[21] Schadle, M.; Bassham *J. Plant Physiol.*, 1977, 59, 1011-1012

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