

ЎЗБЕКИСТОН РЕСПУБЛИКАСИ
ОЛИЙ ВА ЎРТА МАХСУС ТАЪЛИМ ВАЗИРЛИГИ

ФАРҒОНА ДАВЛАТ УНИВЕРСИТЕТИ

**FarDU.
ILMIY
XABARLAR-**

1995 йилдан нашр этилади
Йилда 6 марта чиқади

5-2021

**НАУЧНЫЙ
ВЕСТНИК.
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Издаётся с 1995 года
Выходит 6 раз в год

Муассис: Фарғона давлат университети.

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Босишга рухсат этилди:

Қоғоз бичими: - 60×84 1/8

Босма табоғи:

Офсет босма: Офсет қоғози.

Адади: 50 нусха

Буюртма №

ФарДУ нусха кўпайтириш бўлимида чоп этилди.

Манзил: 150100, Фарғона ш., Мураббийлар кўчаси, 19-уй.

**Фарғона,
2021.**

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1-(2-КАРБОКСИФЕНИЛ)-1'-N-МЕТИЛ ОКСИФЕРРОЦЕНИЛ ТИОАМИД СИНТЕЗИ ВА УНИНГ БИОСТИМУЛЯТОРЛИК ХОССАЛАРИ

СИНТЕЗ 1-(2-КАРБОКСИФЕНИЛ)-1'-N-МЕТИЛ ОКСИФЕРРОЦЕНИЛ ТИОАМИДА И БИОСТИМУЛЯТОРНЫЕ СВОЙСТВА

SYNTHESIS OF 1-(2-CARBOXYPHENYL)-1'-N-METHYL OXYFERROCENYL THIOAMIDE AND BIOSTIMULATORY PROPERTIES

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Аннотация

Мақолада о-ферроценилбензой кислотаси, о-ферроценилбензой кислотасининг метилолтиомочевина билан ҳосиласи, унинг сувда эрувчан калийли ва натрийли тузлари синтези ҳамда уларнинг биологик фаолликларини ўрганиш бўйича маълумотлар келтирилган.

Аннотация

В статье представлены данные по изучению о-ферроценилбензойной кислоты, производного о-ферроценилбензойной кислоты с метилолтиомочевинной, синтезу ее водорастворимых солей калия и натрия, а также их биологической активности.

Annotation

The article presents data on the study of o-ferrocenylbenzoic acid, a derivative of o-ferrocenylbenzoic acid with methylolthiourea, its synthesis of water-soluble potassium and sodium salts, as well as their biological activity.

Таянч сўз ва иборалар: ферроцен, дициклопентадиенил, о-ферроценилбензой кислотаси, ферроценкарбон кислотаси, монометилолтиомочевина, диэтил эфир, 1-(2-карбокисфенил)-1'-N-метилоксиферроценилтиоамид.

Ключевые слова и выражения: ферроцен, дициклопентадиенил, о-ферроценилбензойная кислота, ферроценкарбоновая кислота, монометилолтиомочевина, диэтиловый эфир, 1-(2-карбокисфенил)-1'-N-метилоксиферроценилтиоамид.

Key words and expressions: ferrocene, dicyclopentadienyl, o-ferrocenylbenzoic acid, ferrocene carboxylic acid, monomethylolthiourea, diethyl ether, 1-(2-carboxyphenyl)-1'-N-methyloxyferrocenylthioamide.

Introduction. Today, as a result of population growth in the world, there is a sharp increase in demand for agricultural products, which are the basis of food production. The introduction of new types of biologically active substances that accelerate plant growth and increase their productivity plays an important role in solving problems in this area.

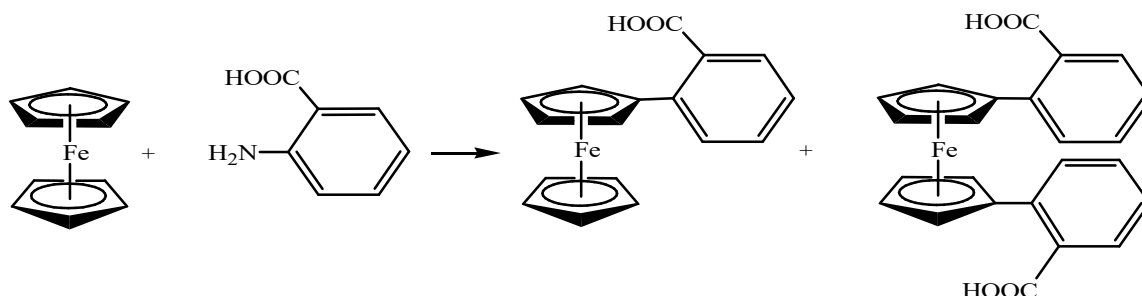
A number of countries focus on the creation and introduction of new types of environmentally friendly biologically active substances that effectively affect the growth, vegetation and yield of agricultural crops in agriculture.

To date, many new compounds with high biological activity based on ferrocene have been synthesized, which are used in agriculture, pharmaceuticals and in a number of areas of the national economy.

The literature describes the synthesis of a number of new biologically active compounds based on ferrocene [1,2,3]. These literature sources provide information about the activity of ferrocene-containing compounds due to the ferrocene core.

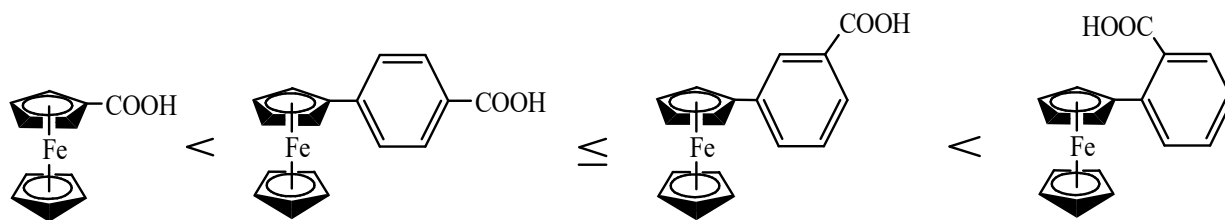
The compounds used as biostimulants should be well soluble in water and have a stable composition in this medium. The solution of these problems requires the creation of new methods for the synthesis of substances. A number of scientists are conducting research on the synthesis of ferrocene derivatives with these properties.

In 1955, a group of scientists led by Academician A.N. Nesmeyanov managed to synthesize o-ferrocenyl benzoic acid [4]:

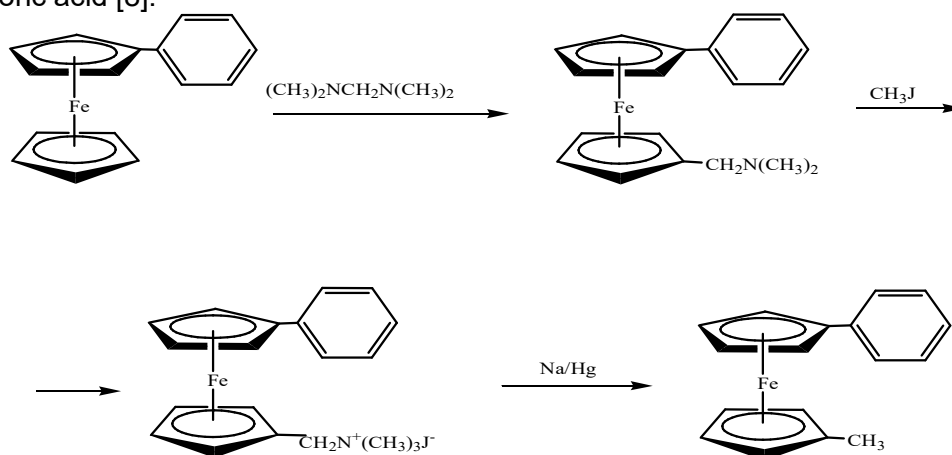


The same reactions were carried out with m - and p-aminobenzoic acids and the corresponding compounds were obtained. As a result of the reaction, mainly monoferrocenyl benzoic acid is formed. Small amounts of heteroannular diacids are also formed as by-products. The reaction is mainly carried out in an acetic acid medium. A number of scientists have proved that it can be carried out in acetone, water-ether and halocarbon media [5, 6]. Scientists have studied the acidic properties of ferrocenyl benzoic acids by the chronopotentiometric method [7; p.632].

o-Ferrocenyl benzoic acid exhibits stronger acidic properties compared to m- and p-ferrocenyl benzoic acids, m- and p-ferrocenyl benzoic acids are equally strong acids. These are acids that are several times stronger than ferrocenecarboxylic acid. The acidity increases as follows:



Nesmeyanov A.N., Perevalova E.G., Gubin S.P. and other scientists comprehensively studied the reactions of aminomethylation, sulfonation and nitration of phenylferrocene. The process of aminomethylation of phenylferrocene was carried out in the presence of tetramethylaminomethane and phosphoric acid [8].

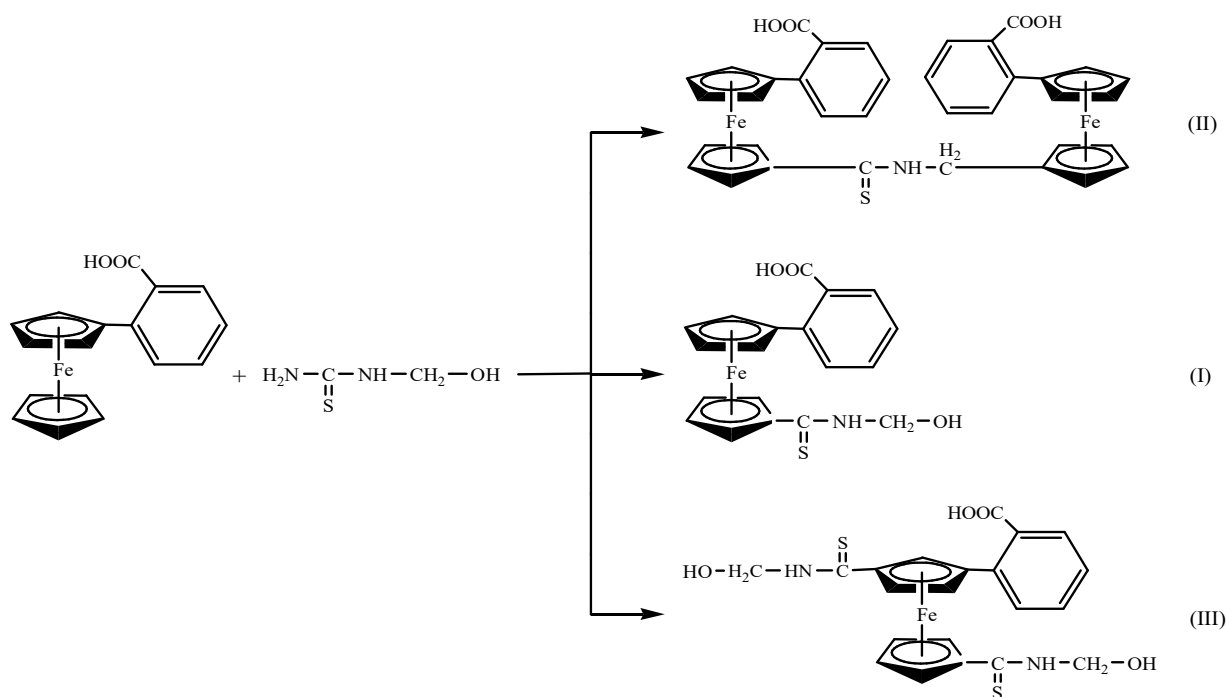


Although many ferrocene derivatives have been synthesized, only a small number of them have been implemented in practice. In particular, a small number of ferrocene compounds used in practice as biologically active substances requires accelerated research in this area [9].

КИМЁ

Analyzing the above and other scientific studies, we synthesized a new ferrocene derivative, 1-(2-carboxyphenyl)-1'-N-methoxyferrocenylthioamide.

Experimental part. Synthesis of 1-(2-carboxyphenyl)-1'-N-methoxyferrocenylthioamide. 100 ml of distilled water, 100 g of ice, 0.92 g of monomethylolthiourea and 10 ml of concentrated hydrochloric acid are poured into a round-bottomed flask with a volume of 500 ml. The flask containing the mixture was equipped with an auto mixer and placed on an ice bath. 2.3 g of sodium nitrite solution dissolved in 50 ml of water was added to the mixture drop by drop, while stirring for 1 hour. Then the ice bath was replaced with a water bath. 3.06 g of o-ferrocenyl benzoic acid was dissolved in 100 ml of diethyl ether and added to the reaction mixture. The mixture was stirred at 34-35 °C for 3 hours. At the end of the reaction, the ether and water extracts were separated. The water part was washed with diethyl ether. We collected essential extracts and washed them with water. Then a 2 % solution of sodium hydroxide was added. The alkaline part was separated and a 5 % solution of hydrochloric acid was added. At the same time, a reddish-brown precipitate was formed. The precipitate was separated by filtration. The reaction was carried out according to the following scheme:



Results. As a result of the reaction, mainly substance (I) 98.7% is formed, as a by-product substance (II) is formed in very small amounts of 0.3%, substance (III) 1%.

When analyzed by IR spectroscopy, 1-(2-carboxyphenyl)-1'-N-methoxyferrocenylthioamide formed by the reaction of o-ferrocenyl benzoic acid with monomethylolthiourea shows that the light absorption at 1020 cm^{-1} and 1110 cm^{-1} is the result of the presence of substituted cyclopentadienyl rings in the ferrocene residue. The absorption line at 1490 cm^{-1} indicates the presence of deformation-vibrational OH – groups.

To increase the biological activity of 1-(2-carboxyphenyl)-1'-N-methoxyferrocenylthioamide, its potassium and sodium salts were obtained. The biostimulating properties of the synthesized salts were tested in the laboratory during wheat germination. The experiments were carried out by one of the most common methods – the Kalinkevich method. The seeds were treated with equal volumes of solutions of various compounds synthesized at different concentrations. Distilled water was used as a control experiment, and a solution of the widely used biologically active substance UNUM was used as a standard. The results of the experiments are presented in Table 1.

Table 1

Results of laboratory studies of the effect of potassium and sodium salts of 1-(2-carboxyphenyl)-1'-N-methyloxperrocenylothioamide on wheat germination

№	Name of the drug	Concentration of solutions, %	Energy of entry, %			Germination rate, %		
			average value	deviation		average value	deviation	
				Control	standard		control	standard
1	Water (control)	-	83	-	-4	88	-	-3
2	Sodium salt of a derivative of o-ferrocenyl benzoic acid with monomethylolthiourea	0.1	85	+7	+4	90	+5	+3
		0.01	88	+10	+7	92	+7	+5
		0.001	91	+13	+10	93	+8	+6
3	Potassium salt of a derivative of o-ferrocenyl benzoic acid with monomethylolthiourea	0.1	84	+6	+4	91	+5	+4
		0.01	85	+7	+4	93	+7	+5
		0.001	86	+8	+4	98	+12	+7
4	Output (standard)	0.1	85	+7	+	89	+4	+2
		0.01	87	+9	+2	91	+6	+5
		0.001	89	+11	+8	93	+8	+6

Analysis of the results of laboratory studies presented in the table showed that a 0.001% solution of the potassium salt of o-ferrocenyl benzoimomethylolthiourea most effectively affected the germination of wheat. A 0.001% aqueous solution of the potassium salt of an o-ferrocenyl benzoic acid derivative with monomethylolthiourea, which showed good biostimulating properties in laboratory conditions, was tested in field conditions in 2020 on 5 hectares of a wheat field at the Ferghana Research and Experimental Station. For the experiment, the wheat variety "Thunder" was chosen at the Ferghana Experimental Station at the FRES. Wheat was soaked in a solution of 0.001% aqueous solution of potassium salt of a derivative of o-ferrocenyl benzoic acid with monomethylolthiourea. At the same time, seeds soaked in water were sown for comparison (control). The germination of wheat, its growth, the number of seedlings, height, and the number of ears were regularly calculated. Wheat yield was determined by counting ears of wheat per 1 m².

In the grain field of agriculture, scientific research is being conducted in a number of areas. The goal of scientists conducting research in this area is to contribute to the economy of our country by increasing the yield of wheat, which is the national treasure of our people. Wheat is one of the most economically important crops among agricultural crops.

Without iron, chlorophyll is not produced in plants. Iron is part of the enzymes that synthesize green pigments. Therefore, this element is directly related to the process of photosynthesis in plants. This is due to the fact that this element is contained in ferrioxin, which stores iron, which is involved in plant photosynthesis. Another function of iron is to regulate the oxidation and reduction of complex organic compounds in plants.

The results of the experiment showed that the germination rate of ears treated with different biostimulants and drugs differs. On November 25, the number of wheat germination in the control variant was 330, the number of germination in variant 2 was 366, the number of germination in variant 3 was 375, the number of germination in variant 4 was 352. As of April 25, the number of ear formations was 100 in option 1, 111 in option 2, 113 in option 3 and 106 in option 4. As of June 15, when calculating the number of ears per 1m², these figures were 747 in the control version, 829 in the 2nd version, 849 in the 3rd version and 797 in the 4th version. The wheat yield as of June 15 was 73 c / ha in the control variant, 81 c / ha in the 2nd variant, 83 c / ha in the 3rd variant and 78 c / ha in the 4th variant. The results are presented in table 2.

Table 2

Results of the study of the effect of potassium and sodium salts of
1-(2-carboxyphenyl)-1'-N-methyloxyperrocenylthioamide on wheat germination

№	Experience options	Normative ratios of mineral fertilizers (N, P, K), kg / ar			Number of germinations	Ear formation	The number of ears per 1 m ²	Wheat yield c / ar
		N	P	K				
1	Water (control)	180	126	90	330	100	747	73
2	Sodium salt of 1-(2-carboxyphenyl)-1'-N-methyloxyperrocenylthioamide	180	126	90	366	111	829	81
3	Potassium salt of 1-(2-carboxyphenyl)-1'-N-methyloxyperrocenylthioamide	180	126	90	375	113	849	83
4	Output (standard)	180	126	90	352	106	797	78

Conclusion. The analysis of the results showed that in the variant treated with the potassium salt of the o-ferrocenyl benzoic acid derivative with monomethylolthiourea, it was 10 c / ar compared with the control, compared with the sodium salt of the o-ferrocenyl benzoic acid derivative with monomethylolthiourea, it was higher by 4 c / ar, compared with the UNUM preparation, it was higher by 5 c / ar.

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