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PROSPECTS FOR OBTAINING BIOSTIMULANTS BASED ON FERROCENE

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Abstract
The article provides information on the production of ferrocene and biologically active compounds synthesized on its basis, their physicochemical properties, practical significance, and influence on the growth, development and yield of plants. Data on the synthesis of o-ferrocenyl benzoic acid, its structure and chemical composition are also provided.
Keywords: ferrocene, biologically active compound, cyclopentadienyl ring, ferrocene core, biostimulator, bioclay, ferroceron, ferrostimulator, aromaticity, organometallic compound, o-aminobenzoic acid, DMFA, acetone, diethyl ether, methanol, heptane, hexane, IR spectroscopy, mass spectrometry.

Introduction

Certainly! Here's an introduction for an article titled "Prospects for Obtaining Biostimulants Based on Ferrocene":

In the ever-evolving landscape of agricultural science, the quest for innovative solutions to enhance crop yield and quality has led researchers to explore unconventional avenues. Among these, the utilization of ferrocene, a compound known for its unique properties, emerges as a promising frontier in the development of biostimulants. This article delves into the prospects and potential applications of obtaining biostimulants based on ferrocene, aiming to unravel the scientific advancements and practical implications in the realm of agriculture. As we navigate the challenges of sustainable food production, understanding the biochemical intricacies and agricultural benefits of ferrocene-based biostimulants presents an exciting opportunity to revolutionize modern farming practices. Join us in this exploration of the untapped potential and future possibilities that lie within the realm of ferrocene-derived biostimulants, as we embark on a journey toward sustainable and resilient agriculture.

Literature review

The possibility of synthesizing new biologically active compounds based on ferrocene is reported in many works of literature [1,2,3] and was thoroughly studied on a scientific basis. It is noted in the literature that compounds containing ferrocene in their molecule can show strong biological activity due to the unique molecular structure of the ferrocenyl nucleus. One of the reasons for the low implementation of substances obtained based on ferrocene compounds as biologically active compounds is the lack of water-soluble stable ferrocene compounds and the complexity of their production methods. A compound used as a biologically active substance should first of all be water-soluble and stable compound in an aqueous environment. The synthesis of such substances requires solving specific problems [4,5].

In the 1980s in Andijan, the scientific centre studying the properties of ferrocene was operating under the leadership of I.R. Askarov. 16 of them received relevant references confirming that they are physiologically active substances synthesized for the first time in the world, and copyright certificates for these substances. 1989 for the fact that "Ferrostimulyator-1", "Ferrostimulyator-2", and "Ferrostimulyator-3" bio-stimulants, which increase seed germination, increase productivity, and ensure early ripening in agriculture, gave positive results in laboratory tests and confirmed their positive properties in field conditions. I.R. Askarov and Sh. M. Kirgizov were awarded the title of Inventor.

Several new "Ferand" and "FerandMI" for the treatment and prevention of anaemia for medical use, several chemical preparations such as "Ferask" for the treatment of colds (inflammation), and use in surgery of parenchymatous organs it is noteworthy that bio glues such as "Siakrin AP-1" and "Siakrin AndMos" recommended for Currently, the compounds synthesized based on ferrocene and put into practice include the sodium salt of o-carboxy benzoyl ferrocene (Ferroseron) synthesized by A.N.Nesmeyanov and a group of scientists, the sodium salt of p-ferrocenyl phenol (Ferrand) synthesized by I.R.Askarov and his students, potassium salt (ferrostimulator-1), other aromatic derivatives (ferrostimulator-2, ferrostimulator-3) can be used as an example [6].

The biostimulatory property of compounds is the process of accelerating their growth and development by positively affecting cells, tissues and organisms. There are several methods of studying the biostimulatory properties of compounds, and the biological activity of synthesized compounds is determined by testing them in animals and plants [7].

Several new types of biologically active compounds are being synthesized and put into practice at the "Scientific Laboratory of Commodity Chemistry and Folk Medicine" established at Andijan State University. These biostimulants contain ferrocenyl group-preserving biologically active substances. The newly synthesized biostimulants accelerate the growth of plants, especially cotton and wheat, and at the same time have an effective effect on seed germination and development. It has also been proven that it has a positive effect on

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significantly increasing productivity [8,9,10,11]. As a result of scientific research conducted by M. Khojimatov, derivatives of ferrocene and methylolurea and ferrocene and thiourea were obtained. The biological activity of synthesized compounds was tested in scientific laboratories on seed germination and cotton vegetation and productivity in fields [12].

As a result of scientific research carried out by N. Tolakov, methods of obtaining acetylferrocene, ferrocene carbonic acid, some water-soluble salts of ferrocene carbonic acid, the water-soluble potassium salt of o-carboxy benzoyl ferrocene have been implemented. The biological activities of the synthesized new compounds were tested. The drug MAXIT-1 was created from compounds with high biostimulating properties, and the biostimulating activity of the drug was first tested in a scientific laboratory. After the laboratory tests gave positive results, the properties of the biostimulator were tested in the field [13].

F.S. Abdugapparov studied the structure and biological activity of complex esters synthesized based on amygdalin and ferrocenbenzoic acids and their influence on seed germination and productivity. A biostimulator named "AsXA-1" was created based on the obtained new compound. Low-concentration solutions of this drug have been found to show high biological activity [14].

Q.Q.Otakhonov carried out scientific research on the synthesis and classification of biostimulants based on thiomochevine derivatives of ferrocenylbenzoic acids. In his work, the researcher mainly synthesized derivatives of p-ferrocenyl benzoic acid with mono-methylolthiomochevine, dimethylthiomochevine, methyloldithiomochevine, thiomochevine. Sodium and potassium salts of synthesized p-ferrocenyl benzoic acid and thiourea derivatives have been found to have a positive effect on seed germination. Among them, "ASHOAK", which has the highest biostimulatory activity, is explained by the fact that it has a positive effect on the germination, development and yield of cotton in field practice on a large scale [15].

Experimental part

Synthesis of o-Ferrocenylbenzoic acid. To a solution of 1.4 g (10 mmol) of o-aminobenzoic acid in 25 ml of water, add 3 ml of concentrated hydrochloric acid to a solution of 0.7 g (10 mmol) of $NaNO_2$ in 10 ml of water dropwise while stirring in an ice bath at -5 ℃ it was cold. After the addition was complete, the mixture was stirred for 30 min at a temperature below 5 ℃. Then, a solution of 1 g (5.4 mmol) of ferrocene in 50 mL of diethyl ether was added to the mixture, stirred at -5 ℃ for 30 minutes and left to stir overnight at room temperature. The organic phase was separated from the mixture, and the aqueous phase was washed twice with 50 ml of diethyl ether. All organic phases were combined and washed 3 times with 50 mL of water. Then it was extracted 3 times with 50 ml of 5% NaOH, and 5% HCl solution was added to the extract until pH=3. The resulting brown precipitate was filtered off, washed with water until neutral, and dried in vacuo. The obtained substrate was recrystallized in benzene and 0.9 g of o-ferrocenylbenzoic acid (52%) was obtained. Ts=124-126 ℃.

o-the synthesis of ferrocenyl benzoic acid was carried out according to the following scheme according to the diazotization reaction:

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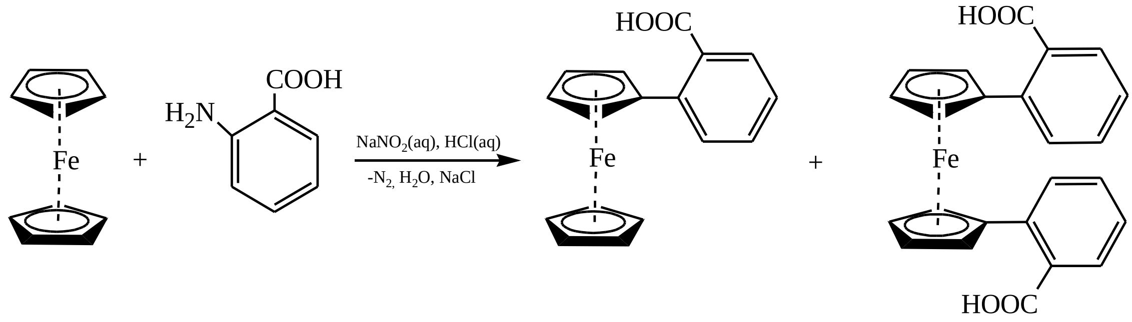

(A) (B)

The reaction products (A, B) were isolated. o-Ferrocenylbenzoic acid is well soluble in DMFA, acetone, diethyl ether, and methanol. Slightly soluble in ethanol, heptane, and hexane. It does not dissolve in water. ts=120-121 °C. Calculated for $C_{17}H_{14}O_2Fe$: Fe 18.3%; determined: Fe 17.96%.

The equivalent molar mass was calculated: as 306.112 g/eq; determined: as 305.94 g/eq (titrant KOH, eq point pH=9.5).

Mass spectrum. 307.0141 m/z ($C_5H_5FeC_5H_4C_6H_4COOH$ +, 100%), 306.0069 m/z ($C_5H_5FeC_5H_4C_6H_4COO$ +, 45.56%), 308.0171 m/z ($C_5H_5FeC_5H_4C_6H_4COOH_2$+, 16.78%), 305.0184 m/z ($C_5H_4FeC_5H_4C_6H_4COO$ +, 3.45%).

IR spectrum. Benzene ring: 750 cm^{-1}, 780 cm^{-1} and 1015 cm^{-1} (rSN), 1460 cm^{-1}, 1535 cm^{-1} (weak intensive, bSH), 680 cm^{-1} and 1030 cm^{-1} (dSSS), 1605 cm^{-1} (nSC), 3180-3280 cm^{-1} (broadband nSH). Substituted cyclopentadienyl ring: 800 cm^{-1}, 820 cm^{-1} (weak intensity, rSN), 1055 cm^{-1}, 1240 cm^{-1} and 1415 cm^{-1} (bSH), 920 cm^{-1} (dSSS), 1105 cm^{-1} (nSC). Unsubstituted cyclopentadienyl ring: 890 cm^{-1} (dSSS), 1020 cm^{-1} (bSH), 1125 cm^{-1} (nSC). Carboxyl group: 660 cm^{-1} (dSO2), 1280 cm^{-1} (dSOH), 1685 cm^{-1} (nC=O), 3300-3600 cm^{-1} (broad, nOH).

Synthesis of 1-(2-carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide.

Synthesis of o-ferrocenylbenzoic acid derivative -1-(2-carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide with dimethylolurea was carried out according to the synthesis of o-ferrocenylbenzoic acid. For this, 2.64 g (0.02 mol) of methylenedimourea was used and 3.65 ml of concentrated hydrochloric acid, and 6.12 g of o-ferrocenyl benzoic dissolved in 200 ml of diethyl ether were added. The yield of the obtained product is 4,545 g (52% relative to o-ferrocenylbenzoic acid). Ts=179-180 °C.

Determined: Fe 13.30 %, calculated: Fe 114.194 %. Gross formula: C20H19O4N3Fe.

IR spectrum (n, cm-1): 746 (Cp), 1560 (C=O), 1600 (COOH), 3448 (OH); (δ, cm^{-1}): 660 (Cp), 1232 (CNH), 1284 (C_6H_4), 1560 cm^{-1}.

Mass spectrum: (m/z) 273 [-OOCC$_6$H$_4$Fe], 421 [HOOCC$_6$H$_4$FcC(O)NH CH$_2$NHC(O)NH$_2$].

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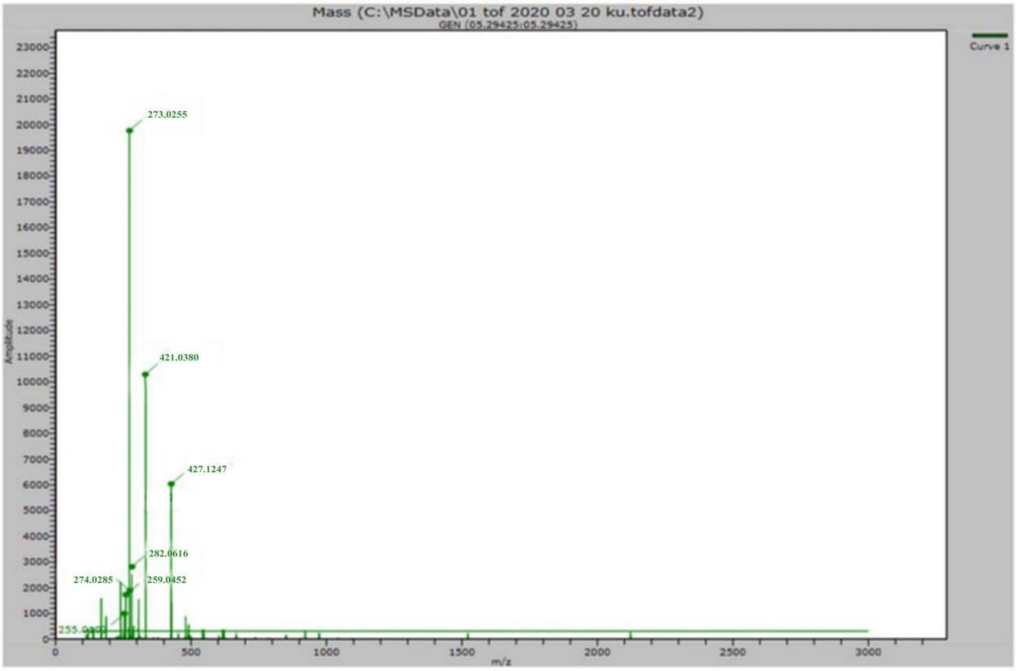

Figure 1. Mass spectrum of 1-(2-carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide

Results and discussion

Using Gaussian 98 program DFT/B3LYP method 6-21G basis, optimized structures of all possible isomers, Hartree energies (EHart) were calculated and differences (DE) were determined to energetically justify the structure of the reaction products between o-ferrocenylbenzoic acid and monomethylolurea (Table 1). The optimized structures of the isomers that can be formed as a result of the diazotization reaction of o-Ferrocenylbenzoic acid with monomethylolurea are presented in the following scheme:

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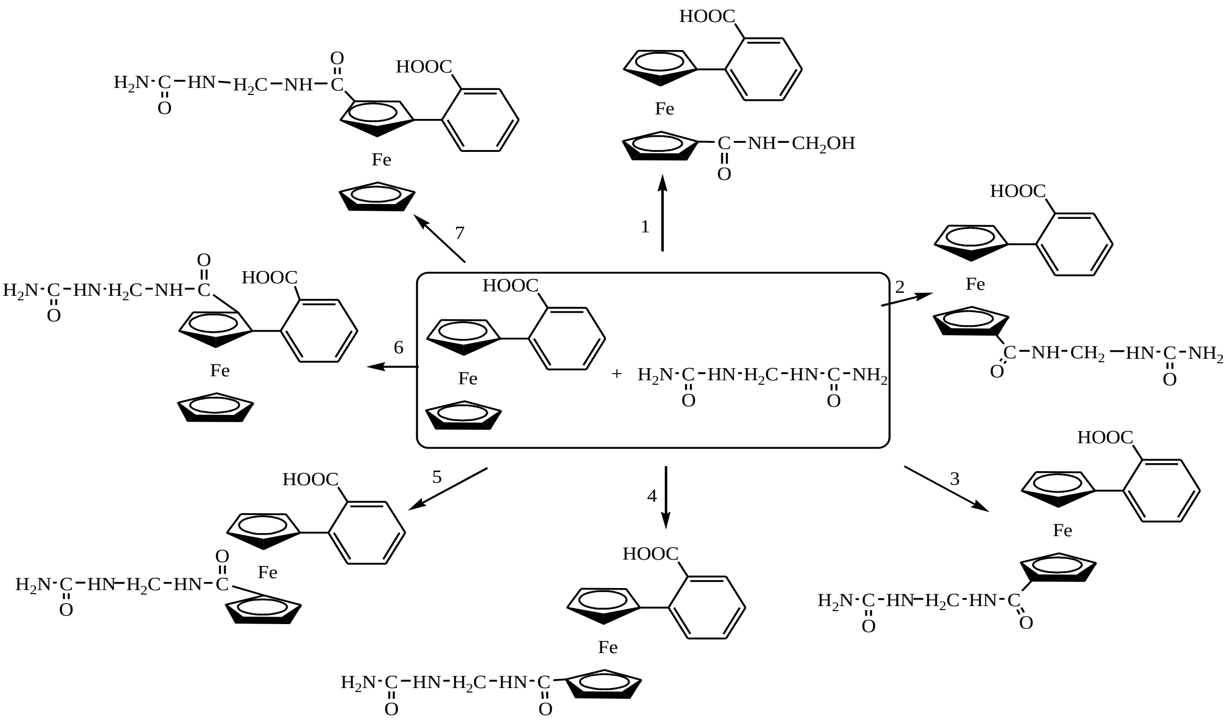

Table 1. Hartree energies of possible isomers of 1-(2-carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide.

Substance	Isomers	EHart, kJ/mol	DE, (kJ)	Dipole moment, D
1-(2-Carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide	1	-2341.6560	0.0327	3.0372
	2	-2341.6761	0.0126	5.4198
	3	-2341.6732	0.0155	3.8567
	4	-2341.6729	0.0158	3.1966
	5	-2341.6887	0	7.3983
1-(2-Carboxyphenyl)-2-N-Ferrocenylamidemethanecarboxamide	6	-2341.6664	0.0223	5.6105
1-(2-Carboxyphenyl)-3-N-Ferrocenylamidemethanecarboxamide	7	-2341.6694	0.0193	4.8199

It can be seen from Table 1 that among the products formed as a result of the reaction of o-ferrocenyl benzoic acid with ethylenediamine, 5 products were proved to be energetically stable.

o-The main peak in the mass spectrum of 1-(2-carboxyphenyl)-1'-N-ferrocenyl amide methanecarboxamide formed as a result of the reaction of ferrocenylbenzoic acid with methylene urea (Fig. 1) was found to belong to the molecular ions of the reaction products (Table 2).

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Table 2. Mass spectrometric parameters of 1-(2-carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide

No	Ion	*m/z*	Relative intensity, %
1	[-OOCC6H4Fe]	273	87±1
2	[$HOOCC_6H_4FcC(O)NHCH_2NHC(O)NH_2$]	421	47±1

It can be seen from Figure 1 and Table 2 that it belongs to the molecular ion characteristic of 1-(2-carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide
[$HOOCC_6H_4FcC(O)NHCH_2NHC(O)NH_2$
]) with a relative intensity of 47±1%. can be seen.

Conclusions

Iron is of particular importance in the vital activity of a living organism. Iron accelerates the assimilation of some macro- and microelements in plants. Lack of iron in plants leads to negative consequences, for example, the occurrence of chlorosis, which leads to a violation of the formation of chlorophyll in the leaves and a decrease in the activity of photosynthesis. Effective use of iron-containing drugs such as 1-(2-carboxyphenyl)-1'-N-ferrocenylamidemethanecarboxamide in agriculture can prevent plant diseases, increase productivity, and thereby satisfy the population's need for food and non-food goods. will give.

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