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SYNTHESIS OF 1`-CARBOXFERROCENYL THIOCARBOXAMIDE

СИНТЕЗ 1`-КАРБОКСФЕРРОЦЕНИЛ ТИОКАРБОКСАМИДА

1`-KARBOKSIFERROTSENIL TIOKARBOKSAMID SINTEZI

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Annotatsiya

Ushbu maqolada ferrotsen asosida yangi biologik faol birkimalar sintez qilish mumkinligi, molekulasida ferrotsen saqlovchi birikmalar ferrotsenil yadrosining o‘ziga xos molekulyar tuzilishi evasiga kuchli biologik faollikni namoyon qilishi keltirib o‘tilgan. Ferrotsenkarbon kislotasining tiomochevina va uning hosilalarini bilan birikmalarini sintez qilish va ularni amaliyotga joriy etish bo‘yicha amalga oshirilgan ishlar yoritilgan. Ushbu reaksiya diazotirlash usuli bo‘yicha olib borildi. Sintez qilib olingan birkmani suyuqlanish temperaturasi SMP10 asbobida, IQ-spektrlari Perkin Elmer Spektrum IR spektrometrida qayd etilgan. Reaksiya mahsulotining individualligi yupqa qatlam xromatagrafiyasi usuli bilan tekshirildi va kalonkali xromotografiya yordamida ajratib olindi. Asosiy modda 1`-karboksiferrotsenil tiokarboksamidning chiqish unumi 98 % ni tashkil qilib birikmaning tuzilishi IQ-spektrlar yordamida o‘rganildi. Olingan IQ-spektr ma’lumotlari bilan mass-spektrometriya natijalari bilan tasdiqlandi.

Аннотация

В данной работе обсуждается возможность синтеза новых биологически активных соединений на основе ферроцена, в которых ферроценсодержащие соединения в молекуле проявляют сильную биологическую активность за счет специфического молекулярного строения ферроценильного ядра. Описаны работы по синтезу соединений ферроценкарбоновой кислоты с тиомочевиной и ее производными и их применению на практике. Эту реакцию проводили диазотированием. Температуру разжижения синтезированного соединения регистрировали на приборе SMP10, ИК-спектры – на ИК-спектрометре Perkin Elmer Spectrum. Индивидуальность продукта реакции исследовали с помощью тонкослойной хроматографии и выделяли с помощью колоночной хроматографии. Выход основного вещества 1'-карбоксиферроценилтиокарбоксамида составил 98%, строение соединения изучено с помощью ИК-спектров. Полученные ИК-спектральные данные подтверждены результатами масс-спектрометрии.

Abstract

This paper discusses the possibility of synthesizing new biologically active compounds based on ferrocene, in which ferrocene-containing compounds in the molecule exhibit strong biological activity due to the specific molecular structure of the ferrocenyl nucleus. The work on the synthesis of ferrocencarboxylic acid compounds with thiourea and its derivatives and their application in practice is described. This reaction was performed by diazotization. The liquefaction temperature of the synthesized compound was recorded on the SMP10 instrument, and the IR spectra were recorded on the Perkin Elmer Spectrum IR spectrometer. The individuality of the reaction product was examined by thin-layer chromatography and isolated using columnar chromatography. The yield of the main substance 1`-carboxyferrocenyl thiocarboxamide was 98% and the structure of the compound was studied using IR spectra. The obtained IR-spectral data were confirmed by the results of mass spectrometry.

Kalit so‘zlar: *Ferrotsen, biostimulyator, tiomochevina, ferrotsenkarbon kislota, diazotirlash, MAKSIT-1, ADUMAX-1, xloroz, geteroannulyar, deformatsion tebranish.*

Ключевые слова: *Ферроцен, биостимулятор, тиомочевина, ферроценкарбоновая кислота, диазотирование, MAKSIT-1, ADUMAX-1, хлороз, гетерокольцевой, деформационная вибрация.*

Key words: *Ferrocene, biostimulant, thiourea, ferrocenecarboxylic acid, diazotization, MAKSIT-1, ADUMAX-1, chlorosis, heteroannular, deformation vibration.*

INTRODUCTION

At present, there is no branch of the national economy that does not include chemistry. For example, polyethylene pipes used in the national economy, organic fertilizers increase crop yields, drugs that protect plants from diseases and various pests, biostimulants that have a positive effect on plant growth and development, and other chemicals. The importance of ferrocene and ferrocene-based derivatives in the production of such biologically active substances is incomparable.

LITERATURE ANALYSIS AND METHODS

Both biotic and abiotic factors affect the quality and quantity of agricultural products. Abiotic factors include soil composition, excessive salinity, acidity, high and low temperatures, drought, pollution, moisture, rain, wind or ultraviolet radiation. Stress caused by negative stimuli can significantly reduce productivity because plants respond by using their energy reserves to deal with stress instead of focusing on productivity.

Biotic factors include various bacteria, fungi or viruses that cause many plant diseases. These factors can not only reduce yields, but also lead to the loss of the entire crop. In modern agriculture, to prevent this, the priority task is to stimulate plant growth and increase yields, the use of plant protection products, rational and technical and technological innovations that do not have a negative impact on the environment, and the search for alternative methods of environmentally friendly farming. One of these methods is the use of biostimulants [1]

Biostimulants are a group of natural substances that reduce dependence on chemical fertilizers, increase plant productivity and nutrient uptake. One of the important factors in the widespread use of biostimulants in agriculture is their organic origin and environmental friendliness. Biostimulants are a way to improve return on investment and satisfy consumer demand.

Thiourea (thiocarbamide) is a sulfur-containing analogue of urea and has a pronounced biological activity. In agriculture, thiourea can be used as a fertilizer and plant growth promoter or as a seed germination promoter for some plants.

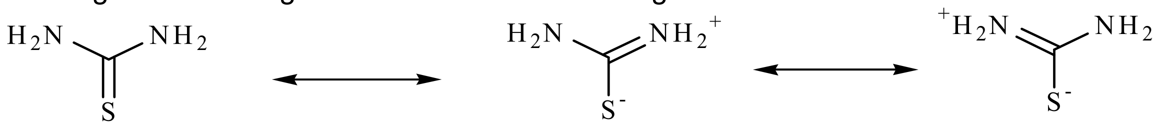
Just as urea is synthesized from ammonia and carbon dioxide, thiourea can be synthesized by reacting ammonia and carbon disulfide.

$$CS_2 + 2NH_3 \rightarrow CS(NH_2)_2 + H_2S$$

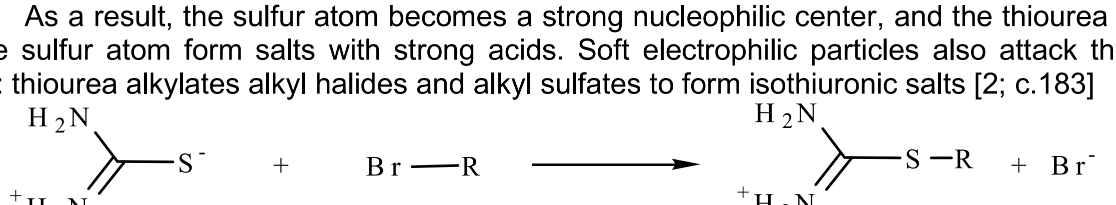
Thiourea is also obtained by the interaction of H2S, ammonium sulfide or alkali metal sulfides with calcium cyanamide in aqueous solutions.

$$CaCN_2 + (NH_4)_2S + 2H_2O \rightarrow CS(NH_2)_2 + Ca(OH)_2 + 2NH_3$$

The structure of the thiourea molecule can be represented by the canonical form of thiamide and the form of thioimid, a mesomer with a negative charge on the sulfur atom and a positive charge on the nitrogen atoms of the amidine fragment:



As a result, the sulfur atom becomes a strong nucleophilic center, and the thiourea protons at the sulfur atom form salts with strong acids. Soft electrophilic particles also attack the sulfur atom: thiourea alkylates alkyl halides and alkyl sulfates to form isothiuronic salts [2; c.183]



Thiourea and its derivatives are widely used in various industries: thiols, dyes, synthesis of synthetic resins, pharmaceuticals, separation of paraffins, used as a reagent for the photometric determination of Bi, Os, Re, Ru. Many urea derivatives have valuable pharmacological properties and are therefore used as antituberculous, antitumor, anti-inflammatory, antipyretic, analgesic, antimicrobial, antiulcer, and other therapeutically active substances [3].

The use of thiourea in agriculture is due to its rapid action on pathogenic microflora, in addition, this substance can completely cure onions and potatoes. Thiourea is actively used in agriculture as a valuable inorganic fertilizer and fungicide.

Potassium, calcium, magnesium and iron are essential for normal plant growth and development. Iron ions act as catalysts for the formation of chlorophyll molecules. This element is part of the enzymes catalase, peroxidase, cytochrome oxidase, which are involved in redox reactions. Iron deficiency can lead to yellowing of the leaves and chlorosis. Iron-containing biostimulants are involved in the period from seed germination to maturation and have a positive effect.

It has been studied that new biologically active compounds can be synthesized on the basis of ferrocene, and ferrocene-containing compounds in the molecule exhibit strong biological activity due to the specific molecular structure of the ferrocenyl core.

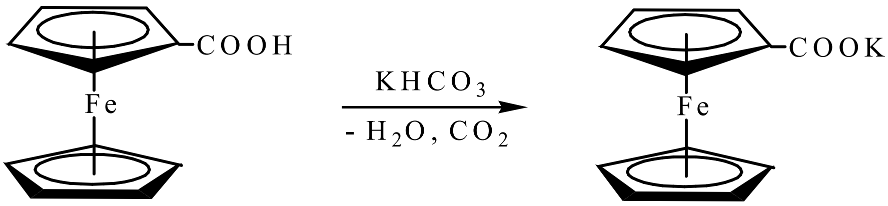
The properties of synthesized biologically active compounds based on water-soluble aromatic and aliphatic derivatives of ferrocenecarboxylic acid and ferrocene, which have a positive effect on early germination, growth, development, yield and maturation of seeds and wheat, have been well studied.

Interest in ferrocene carboxylic acids increased significantly after the discovery of important properties. In the treatment of various diseases that can be caused by metabolic disorders, its water-soluble derivatives have shown their effectiveness in increasing crop yields [5].

It is allowed to use in practice ferrostimulators synthesized on the basis of ferrocene by scientists of the chemical faculty of Andijan State University, preparations MAXIT-1, ADUMAKS-1 as biostimulants that have a positive effect on germination, growth, development and productivity [6] .

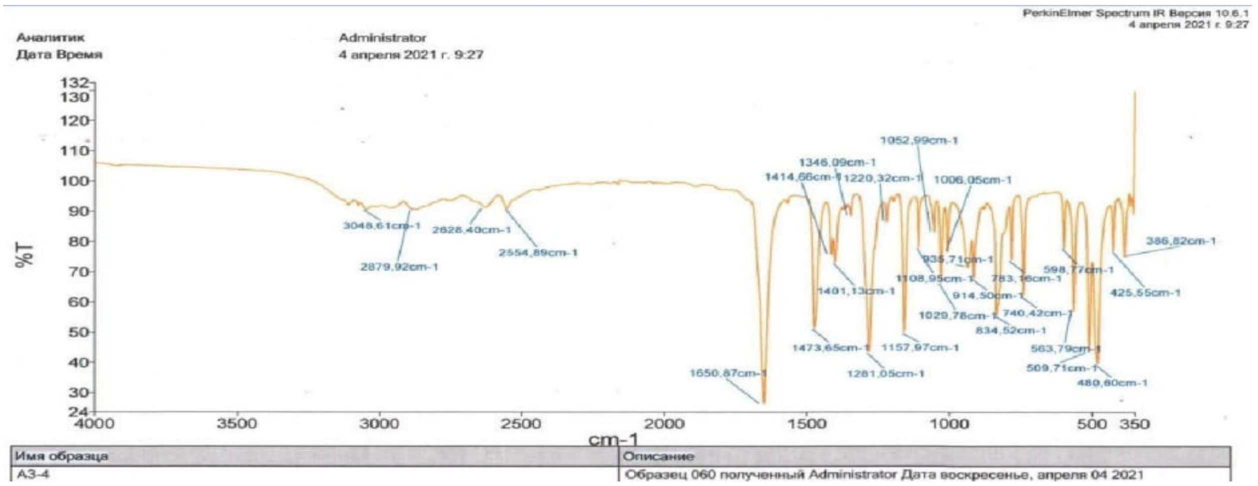
The technology of using the biostimulator MAXIT-1, synthesized on the basis of ferrocenecarboxylic acid, has been introduced on more than 160 hectares of cotton fields in Andijan region.

The potassium salt of ferrocenecarboxylic acid has a positive effect on the prevention of chlorosis, which can occur as a result of depletion of iron reserves in the plant body, early seed germination and precocity and high yield [7].

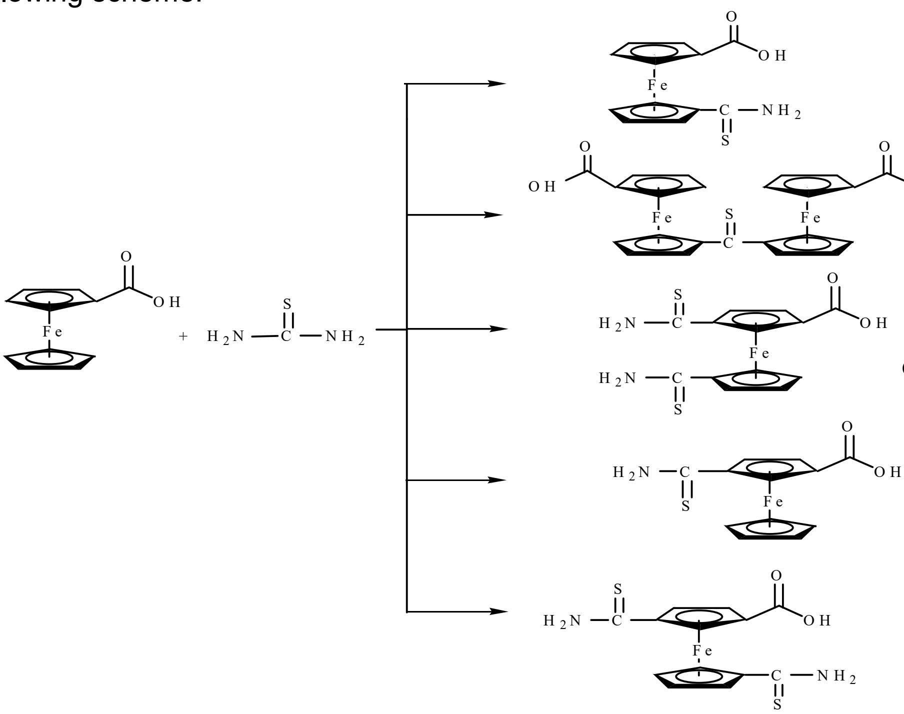


RESULTS AND DISCUSSION

The positive effect of thiourea and ferrocenecarboxylic acid on plants has been studied and analyzed. Based on the foregoing, we carried out the reaction of ferrocenecarboxylic acid with thiourea. The reaction was carried out by diazotization. The identity of the reaction product was examined by thin layer chromatography and isolated by column chromatography. The yield of the basic substance 1`-carboxyferrocenylthiocarboxamide was 98%. The structure of the synthesized compound was studied using IR spectra. The absorption lines in the region of 1158 and 1029 cm^{-1} of the IR spectrum belong to the heteroannular diasubstituted ferrocenyl group, the absorption lines in the region of 914 cm^{-1} are due to the presence of a pentadiene ring substituted in the ferrocene residue, the absorption line in the region of 935 cm-1 is deformed by the deforming OH- , the absorption line at 1269 cm^{-1} indicates the presence of -C(S), and the absorption line in the region of 3428 cm^{-1} indicates the presence of valence-oscillating -NH-groups [8; 127-215]



Based on the analysis of IR spectra, it was found that this reaction proceeds according to the following scheme:



The obtained IR spectral data are confirmed by the results of mass spectrometric analysis. The structure of the ions formed in the mass spectrum (Figure 1) and their m/z values are shown in Table 1 below.

Table 1

Mass spectrometric parameters of 1'-carboxyferrocenylthiocarboxamide

№	Formula	m/z	Relative intensity, %
1	$(C_5H_4)_2FcCO+ H^+$	213	100%
2	$[(C_5H_4)_2FeCOCS]_2$ $2H^+$	514	50%
3	$(C_5H_4)C_5H_5FeCOOH$	230	42%
4	$(C_5H_5)_2Fc+ H^+$	185	25%

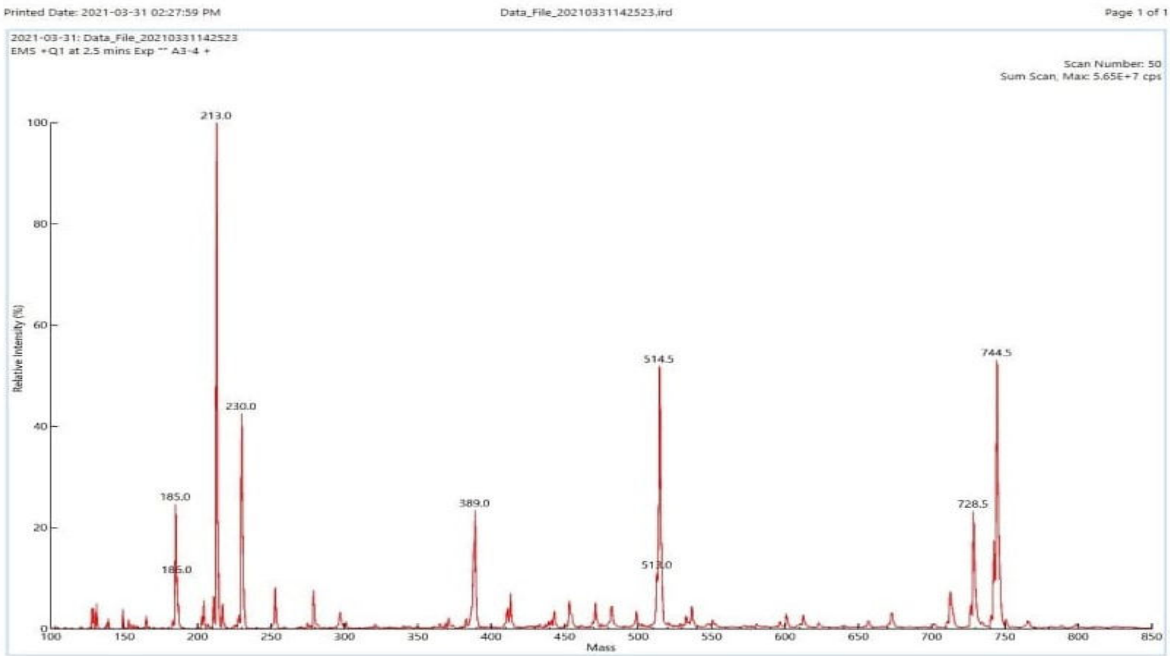


Figure 1. Mass spectrum of 1'-carboxyferrocenylthiocarboxamide.

EXPERIMENTAL PART

The liquefaction temperature was determined on an SMP10 instrument (Germany). IR spectra were recorded on a PerkinElmer Spectrum IR spectrometer (version 10.6.1), mass spectra were recorded on a Sum Scan Mac 5.65E +7 cps mass spectrometer.

Reaction of ferrocenecarboxylic acid with thiourea

0.76 g (0.01 mol) of thiourea, 20 ml of distilled water, 10 g of ice, 1 ml of 35% concentrated hydrochloric acid are placed in a 500 ml flask with three round necks, cooled to -50°C. With stirring in the flask, 20 ml of an aqueous solution of 1.1 g of sodium nitrite was added dropwise over 20 min through a dropping funnel. After diazotization was completed, a nitrating agent (0.02 g of urea dissolved in 2 ml of water and 0.04 g of sodium acetate solution dissolved in 4 ml of water) was added to the reaction mixture in a flask to cleave excess HNO_2. During diazotization, temperature and pH were kept constant. The process of diazotization was carried out at a temperature of -50°C at pH=1. The ice bath was then replaced with a water bath and the addition funnel was replaced with a reflux condenser. To the reaction mixture was added 2.3 g of ferrocenecarboxylic acid dissolved in 50 ml of diethyl ether.

The reaction mixture was heated on a water bath by stirring at 33–340°C for 3–4 h. At the end of the reaction, the mixture was poured into a separating funnel and the aqueous part was separated from the ether part. The aqueous portion was washed 3 times with diethyl ether. The ether part was separated and washed 3 times with water. The ether layers were added and treated with 5% sodium hydroxide solution. The alkaline part was neutralized with 7% hydrochloric acid solution. The result is an orange precipitate. The precipitate was filtered off and dried at room temperature.

The reaction yield is 50% of theory. The resulting yellow substance is readily soluble in organic solvents, moderately in water. Tm = 195°C. The empirical formula is $C_{12}H_{11}O_2NSFe$.

As by-products, 0.75%, 0.3%, 0.45%, 0.5% of substances II, III, IV and V are isolated in the form of ferrocenecarboxylic acids.

Water-soluble salts of the synthesized compound can be used as promising biostimulants in agricultural production.

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