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SYNTHESIS OF COMPLEX COMPOUNDS OF IONS OF SOME d-ELEMENTS WITH QUERCETIN AND RUTIN AND ASSESSMENT OF THEIR STABILITY CONSTANTS

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Abstract. In this work, the synthesis of iron (Fe(II)), cobalt (Co(II)) and zinc (Zn(II)) ion complexes with flavonoids quercetin and rutin was studied and their stability constants at different pH values were estimated. The synthesis of the complexes was carried out under spectrophotometric control , and the stability constants were determined by the isomolar series method. The results showed that the stability of the complexes depends on the acidity of the medium, with the highest values of the stability constants being recorded for quercetin complexes with Fe(II) at neutral pH. The data obtained indicate the prospects for using these complexes in medicine and agricultural technology, in particular for targeted drug delivery and antioxidant therapy.

Keywords: flavonoids, quercetin, rutin, ion metals, iron, cobalt, constant resistance, spectrophotometry, pH.

Ba’zi d-elementlar ionlarining kversetin va rutin bilan komplekslari sintezi va ularning barqarorlik konstantalarini baholash

Annotatsiya. Ishda temir (Fe(II)), kobalt (Co(II)) va rux (Zn(II)) ionlari komplekslarining kversetin va rutin flavonoidlari bilan sintezi o‘rganilib, ularning barqarorlik konstantalari turli pH da baholandi. Komplekslarning sintezi spektrofotometrik nazorat ostida amalga oshirildi va barqarorlik konstantalari izomolyar ketma-ketlik usuli bilan aniqlandi. Komplekslanish jarayonida kuzatilgan spektral o‘zgarishlar metall ionlarining flavonoidlarning gidroksil guruhlari bilan muvofiqlashtirilganligini ko‘rsatadi. Natijalar shuni ko‘rsatdiki, komplekslarning barqarorligi muhitning kislotaligiga bog‘liq bo‘lib, barqarorlik konstantalarining eng yuqori qiymatlari neytral pH da Fe (II) bilan kversetin komplekslari uchun qayd etilgan. Olingan ma’lumotlar ushbu komplekslarni tibbiyot va qishloq xo‘jaligi texnologiyasida, xususan, dori-darmonlarni maqsadli etkazib berish va antioksidant terapiyada qo‘llash mumkinligini ko‘rsatdi.

Kalit so‘zlar: flavonoidlar, kversetin, rutin, metall ionlari, temir, kobalt, barqarorlik konstantalari, spektrofotometriya, pH.

Синтез комплексных соединений ионов некоторых d-элементов с кверцетином и рутином и оценка их констант устойчивости

Аннотация. В данной работе синтезированы комплексы ионов железа Fe(II), кобальта Co(II) и цинка Zn(II) с флавоноидами кверцетином и рутином, а также проведена оценка их констант устойчивости при различных значениях pH. Синтез комплексов был осуществлен под контролем спектрофотометрии, а константы устойчивости определены методом изомолярных серий. Спектральные изменения,

наблюдаемые при комплексообразовании, указывают на координацию ионов металлов с гидроксильными группами флавоноидов. Результаты показали, что стабильность комплексов зависит от кислотности среды, при этом наибольшие значения констант устойчивости были зарегистрированы для комплексов кверцетина с Fe(II) при нейтральном pH. Полученные данные указывают на перспективность использования данных комплексов в медицине и агротехнике, в частности для целевой доставки лекарственных средств и антиоксидантной терапии.

Ключевые слова: флавоноиды, кверцетин, рутин, ионы металлов, железо, кобальт, константы устойчивости, спектрофотометрия, pH.

Introduction. Flavonoids such as quercetin and rutin are important biologically active compounds that exhibit a wide range of beneficial properties, including antioxidant, anti-inflammatory and antibacterial activity [1-3]. Studies of their interaction with metal ions, in particular d-elements such as iron, cobalt and zinc, allow the creation of new complex compounds with improved biological properties, which expands the possibilities of their application in medicine and agricultural technology [4-12].

Complexes of metal ions with flavonoids can find application in the creation of targeted drug delivery systems, antioxidant preparations, and to increase plant resistance to various diseases. However, for their successful application, it is important to evaluate their stability under various conditions, since this directly affects the effectiveness and safety of these compounds. Studying the stability constants of such complexes will allow a deeper understanding of their behavior in biological and natural systems and develop optimal conditions for their use [4-6].

Complexes of flavonoids with metal ions have long been the subject of intensive research due to their potential biological and pharmacological properties. Quercetin and rutin, as representatives of flavonoids, have been studied for their interaction with various metals, including iron, copper, zinc, cobalt and other d-elements. Studies have shown that such complexes have antioxidant, anti-inflammatory, antimicrobial properties, and can also stabilize metal ions, preventing their oxidation [10-12].

Many studies have focused on the synthesis of metal complexes with quercetin and rutin , their structural characterization, and the study of the mechanisms of formation of these complexes [7]. Researchers have studied the influence of various factors, such as pH of the medium, concentration of reagents, and temperature, on the formation and stability of these complexes. Spectrophotometry and spectroscopy methods have become one of the main tools for assessing the stability constants of complexes, which allows for an accurate assessment of their stability and application potential [11,12].

However, despite significant progress in the study of metal-flavonoid complexes, open questions remain regarding their application in specific biological and agricultural systems. Further studies are needed to assess the toxicity, bioavailability, and mechanisms of action of these complexes at cellular and molecular levels, as well as to develop methods for their targeted delivery.

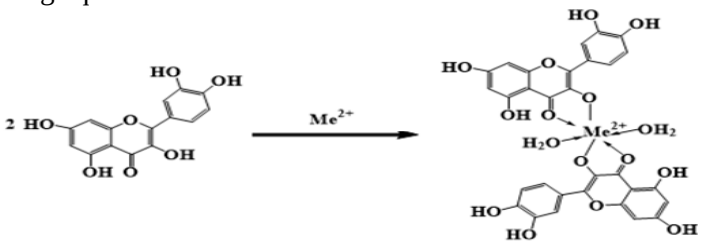
The aim of this study is to synthesize complex compounds of iron (Fe(II)), cobalt (Co(II)) and zinc (Zn(II)) ions with flavonoids quercetin and rutin , as well as to evaluate their stability constants at different pH values.

Materials and methods of research. The following chemical reagents and materials were used to conduct the experiments: Quercetin dihydrate ($C_{15}H_{10}O_7$ $2H_2O$, 99.8%) ; Rutin ($C_{27}H_{30}O_{16}$, 99%) ; Iron(II) sulfate hexahydrate ($FeSO_4$ $7H_2O$, 99%) ; Cobalt(II) chloride hexahydrate ($CoCl_2$ $6H_2O$, 99%) ; Zinc(II) sulfate heptahydrate ($ZnSO_4$ $7H_2O$, 99%) ; Methanol (CH_3OH, 99.9%) ; Distilled water.

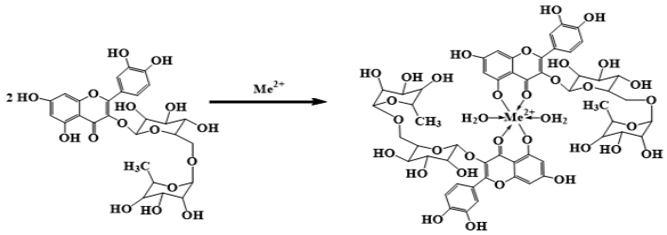
Equipment: UV spectrophotometer (T80+ UV/VIS) for measuring the optical density of solutions and analytical balance (AUY120) for precise weighing of reagents.

Synthesis method of complex compounds. For the synthesis of quercetin and rutin complexes with iron, cobalt and zinc ions, solutions of the starting materials with a concentration of 0.0001 mol/l were prepared. The synthesis reactions were carried out in different pH media (2.0, 4.0,

6.0, 7.0, 9.0) to study the effect of acidity on the stability of the complexes. The solutions of metals and flavonoids were mixed in equimolar quantities to form complexes. The reactions proceed according to the following equations:



Complexation reaction quercetin with Me (II) cations (Me = Fe $^{2+}$, Co $^{2+}$, Zn $^{2+}$).



Complexation reaction of rutin with Me (II) cations (Me = Fe $^{2+}$, Co $^{2+}$, Zn $^{2+}$).

The isomolar series method was used to assess the stability of the complexes. The optical densities of the solutions were measured at wavelengths of 273 nm and 402 nm using 1 cm thick quartz cuvettes.

Usually, along with the stability constants, the molar absorption coefficient of the complex compound is also determined, which is calculated using the following formula:

$$\varepsilon_{ij} = \sqrt{\frac{A_i \cdot (A_j)^2 - A_j \cdot (A_i)^2}{A_j \cdot C_{Mi} \cdot C_{Ri} - A_i \cdot C_{Mj} \cdot C_{Rj}}},$$

where $\varepsilon_{ij}$is the molar absorption coefficient of the complex; C_{Mi} , C_{Mj} , C_{Ri} , C_{Rj} are the initial concentrations of metal ions (M) and ligands (R) in solutions; A_i and A_j are the optical densities of the same solutions.

Based on the average value of the molar absorption coefficient and optical density , the stability constant of the studied complex compound (β_K') was calculated using the formula:

$$\beta_K' = \frac{A/\varepsilon_K}{\left(C_R - \frac{A}{\varepsilon_K}\right) \cdot \left(C_M - \frac{A}{\varepsilon_K}\right)}.$$

Results and discussion . As a result of the experiments, complexes of iron (Fe(II)), cobalt (Co(II)) and zinc (Zn(II)) ions with quercetin and rutin were synthesized. To assess their stability, spectrophotometric measurements were carried out at different pH values (2.0, 4.0, 6.0, 7.0, 9.0), and molar absorption coefficients were calculated, on the basis of which the stability constants of the complexes were calculated (Table 1).

Table 1

Stability constants of complexes in different environments (273 nm and 402 nm)

p H	Quercetin complex with Fe(II) (273 nm)	Quercetin complex with Fe(II) (402 nm)	Quercetin complex with Co(II) (402 nm)	Rutin complex with Fe(II) (402 nm)	Rutin complex with Co(II) (402 nm)
2.0	$2.1\,1 \cdot 10^{-3}$	$2.0\,9 \cdot 10^{-3}$	-	-	-
4.0	$3.1\,5 \cdot 10^{-3}$	$2.6\,2 \cdot 10^{-3}$	-	-	-
6.0	$2.2\,3 \cdot 10^{-3}$	$2.2\,6 \cdot 10^{-3}$	-	-	-
7.0	$1.93 \cdot 10^{-3}$	$2.03 \cdot 10^{-3}$	$1.21 \cdot 10^{-3}$	$1.23 \cdot 10^{-3}$	$1.42 \cdot 10^{-3}$
9.0	$2.08 \cdot 10^{-3}$	$2.78 \cdot 10^{-3}$	-	-	-

For quercetin complexes with Fe(II), an increase in the stability constants is observed with an increase in pH from 2.0 to 4.0. This may be due to the fact that at lower pH values, protons compete with Fe(II) ions for coordination sites on the quercetin molecule, which reduces the stability of the

complex. A slight decrease in the stability constants at pH 6.0 and 7.0 may indicate deprotonation of the hydroxyl groups of quercetin, which changes its coordination properties. Differences in the stability constants obtained at different wavelengths (273 nm and 402 nm) due to different sensitivity of the method to the formation of complexes of different compositions or different electron transitions in the resulting complexes.

Solutions of metals and flavonoids are mixed in equimolar amounts. It is important to note that complexes with different stoichiometry (e.g., 1:1, 1:2, 2:1) can be formed in the solution, and the use of equimolar amounts alone may not allow for a complete study of all possible complexes. The general equations of quercetin complexation reactions and rutin with Me(II) cations are given. The method is used to assess the stability of complexes and is based on measuring the optical density of solutions at different ratios of components at a constant total concentration. The optical densities of the solutions were measured at wavelengths of 273 nm and 402 nm. The choice of these wavelengths is probably based on the spectral characteristics of quercetin and rutin and their complexes. A formula for calculating the molar absorption coefficient of a complex compound is given. This is an important parameter necessary for calculating stability constants. In the presented method for the synthesis of complex compounds of d-element ions (Fe^{2+}, Co^{2+}, Zn^{2+})

Analysis of results. It is evident from the data in Table 1 that the stability of the complexes depends on the acidity of the medium. For example, for the quercetin complex with Fe(II) ions, stability increases at pH 4.0, which indicates the presence of stronger interactions in acidic media. At pH 7.0, the stability constants decrease slightly, but remain high, which indicates the potential for using these complexes in neutral biological conditions.

Complexes of vercetin and rutin with Co(II) ions showed slightly lower stability compared to Fe(II), which may be due to differences in the electronic structure of metal ions. Complexes of rutin with Fe(II) also demonstrated high stability constants at neutral pH, which makes them promising for biomedical applications.

The obtained data show that flavonoid complexes with Fe(II) and Co(II) ions can be used to develop targeted drug delivery systems where high stability in neutral or slightly acidic environments is required. Quercetin complexes with iron can also find application as antioxidant agents to protect cells from oxidative stress.

Thus, the conducted study demonstrated that complexes of d-element ions with quercetin and rutin have significant stability, especially in neutral and slightly acidic environments. This opens up prospects for their use in medicine, for example, in active substance delivery systems or as antioxidant drugs. In general, the obtained values of stability constants are in the range of 10^{-3}, which indicates a relatively low stability of the studied complexes in aqueous solutions. This should be taken into account when developing pharmaceuticals and dietary supplements containing flavonoids and metals. To increase the stability of the complexes, one can consider using organic solvents, modifying the structure of flavonoids, or introducing additional ligands that promote stabilization.

Particular attention was paid to determining the optimal pH values for the stability of the complexes. The highest stability constants were recorded for quercetin and rutin complexes with iron ions (Fe(II)) at pH 4.0 and 7.0. This result indicates the highest stability of these complexes in slightly acidic and neutral environments, which is especially important for the development of applications in biological systems, where pH is usually in these ranges. This indicates the prospects for using these complexes in medical applications, where stability under physiological conditions is of paramount importance.

Quercetin complexes with Fe(II) demonstrated high stability constants, which makes them promising candidates for medical applications. High stability under physiological conditions (pH around 7.0) opens up opportunities for using these complexes in targeted drug delivery systems and antioxidant therapeutics. Iron ions in the complex can have a synergistic effect with the antioxidant properties of quercetin, enhancing the therapeutic effect. In addition, the controlled release of iron ions from the complex can be used to treat iron deficiency conditions, offering a new approach to the treatment of this common disease.

Despite the significant results obtained in the study, it is important to note the importance of further research to better understand the properties of the synthesized complexes. Key areas of future research should be determining the stoichiometry of the complexes, studying their structure using spectroscopic methods and X-ray structural analysis, and assessing their biological activity in vitro and

in vivo. In addition, it is necessary to carefully study the toxicity of the complexes for various types of cells and organisms to ensure their safety and suitability for medical use. Overall, this study has made a significant contribution to the understanding of the interactions of flavonoids with metal ions, opening up prospects for the development of new therapeutic agents and bioactive materials.

Conclusions.

1. Fe(II)), cobalt (Co(II)) and zinc (Zn(II)) ions with quercetin and rutin were successfully synthesized and studied at different pH values.
2. Spectrophotometric study showed that the stability of the complexes depends on the acidity of the medium. The highest values of stability constants were recorded for complexes of quercetin and rutin with iron ions (Fe(II)) at pH 4.0 and 7.0, indicating their potential for use in biological and neutral environments.
3. Quercetin complexes with Fe(II) have demonstrated high stability constants, making them potential candidates for medical applications, particularly in targeted drug delivery systems and antioxidant therapeutics.

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