SYNTHESIS, CRYSTAL STRUCTURE AND RESEARCH OPPORTUNITIES OF 2,4-DIACETYL-3-(3'-NITROPHENYL)-5-HYDROXY-5-METHYLCYCLOHEXANONE

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Abstract. On the base of 3-nitrobenzaldehyde and acetylacetone 2,4-diacetyl-3-(3'-nitrophenyl)-5-hydroxy-5-methylcyclohexanone was synthesized. The crystal structure of the reagent was set by XRD. The crystals are triclinic: $a=8,1300(8)$, $b=8,8135(9)$, $c=13,6189(14)$ Å, $\alpha=99,088(2)°$, $\beta=92,825(2)°$, $\gamma=104,969(2)°$, $V=926,74(16)$ Å^3, space group, $P2_1/m$, $Z=2$. XRD results showed that the crystal structure of the reagent corresponds to enol form. The complexation of the reagent with iron (III) ions in the presence of 1,10-phenanthroline investigated and highly selective method of determination for the direct determination of trace iron in the strawberry and apricot developed.

1.   Introduction

Organic reagents containing OH-groups are widely used to determine the number of metal ions including iron ions (III) (Savvin & Guryeva, 2003; Ivanov & Mamedova 2006; Upor, 1985). The high sensitivity and selectivity towards ions of some transition metals causes the need for investigation of the analytical capabilities of other members of these reagents.

The aim of this work is synthesis of 2,4-diacetyl-3-(3'-nitrophenyl)-5-hydroxy-5-methylcyclohexanone, studyng its crystal structure and complexation with iron(III) ion in the presence of 1,10-phenanthroline.

2.   Experimental part

Synthesis of the reagent. Reagent is prepared from 3-nitrobenzaldehyde and acetylacetone at a molar ratio of 1:2, respectively, in the presence of piperidine as catalyst: a flat-bottomed 50 ml flask equipped with a dropping funnel and a stirrer was charged with 7,5565 g (0,05mol) of 3-nitrobenzaldehyde, 10,00 g (0,1 mol) of freshly distilled acetylacetone and 20 ml of ethanol and stirred until a homogeneous mixture. Then while stirring is added dropwise 2 ml of piperidine and 5 ml of ethanol, the mixture was left at room temperature for three days. The precipitated colorless crystal filtered, washed with cold ethanol. 10,5 g (63%), m.p.202-203ºC (methanol), (Rajanarendar *et al.,* 2006) m.p. 203° C.

Reagent's synthesis scheme is shown below:
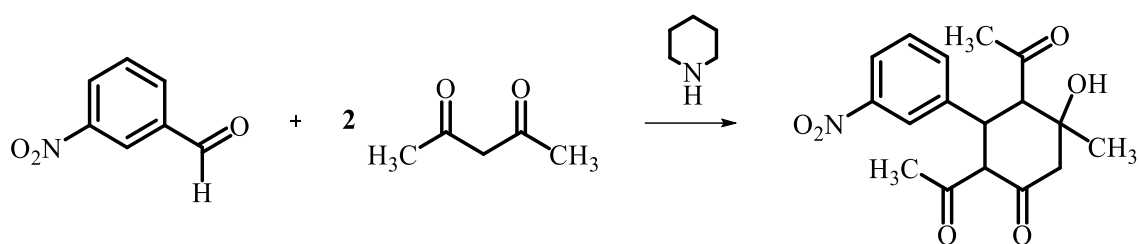
As the compound contains in its structure 1,3-dioxofragment, the presence of keto-enol tautomerism is possible, which can be represented by the following formulas:

keto form   **enol form**
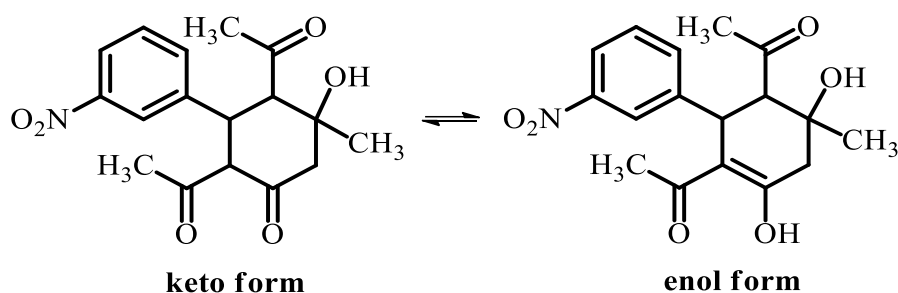
Strong electron withdrawing groups (NO$_2$) in the benzene ring can affect the keto-enol tautomerism, whereby one of the forms may be predominant.

3. Results and discussions

XRD of the reagent. Taking into account the above, X-ray diffraction have been used for establishing the structure of the reagent. Single crystals for X-ray diffraction were obtained by twice crystallization of compound from methanol. It was established that the reagent's crystal structure corresponds to the enol form. X-ray diffraction study was carried out on a diffractometer Brucker SMART APEX II CCD (MoK$_\alpha$ radiation, graphite monochromator, φ- and ω- scan). 10657 diffraction reflections are measured, θ$_{max}$=28°. Intensity of symmetrically equivalent reflections were averaged. As a result of averaging, 4468 independent diffraction reflections with R(int)=0,0146, which have been used for decryption and refinement of the crystal structure, are turned out. The crystals are triclinic: a=8,1300 (8), b=8,8135 (9), c=13,6189 (14) Å, α=99,088 (2)°, β=92,825 (2)°, γ=104,969 (2)°, V=926,74 (16) Å^3, space group, P2$_1$/m, Z=2. The structure was decrypted by direct methods and refined by least squares methods on F^2 in the anisotropic approximation for non-hydrogen atoms. The hydrogen atoms, which are involved in intramolecular and intermolecular hydrogen bonds OH ... O is found from the electron density difference map and refined in the isotropic approximation. The coordinates of the remaining hydrogen atoms are geometrically calculated and specified in the model of "rider". For a molecule of methanol (atoms O(7), O(7'), C(18), C(18') which is crystallizing with ligand molecule (HL), two crystallographic sites with occupancy of 0,766 (9) and 0,224 (9) are identified. The final values of divergence factors: R$_1$=0,0503 and *w*R$_2$=0,1498 (for 3429 diffraction reflections with I> 2σ (I)), R$_1$=0,0641 and *w*R$_2$=0,1582 for the entire set of independent diffraction reflections. All calculations were performed using SHELXTL complex programs (Sheldrick, 2008).

The structure is registered in the Cambridge Structural Database (CCDC) under the number 1528190 (HL) and is available at: ccdc.cam.ac.uk/getstructures.
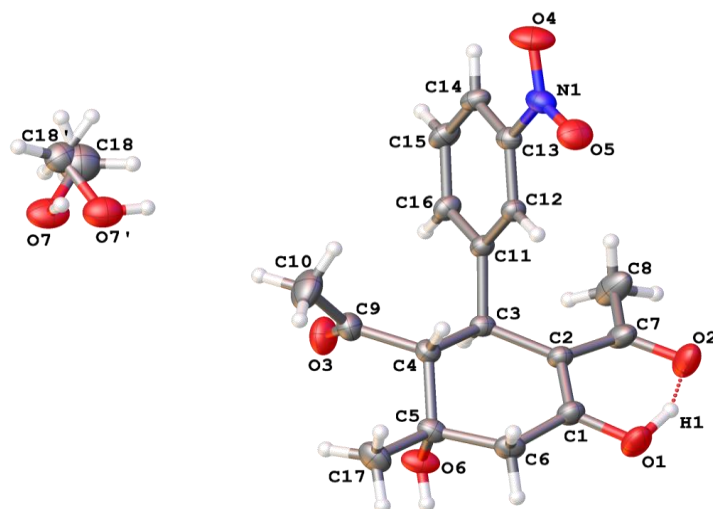

Figure 1. The structure of the HL molecule with the numbering of non-hydrogen atoms

Complex formation of iron(III) with the reagent in the presence of 1,10-phenanthroline. In the reaction of iron(III) with a reagent (R) a colored complex in an acidic environment at pH 1,0-7,0 is formed. Absorption spectra of the reagent and its complex with iron(III) is shown in Fig. 2. Absorbance of the reagent is maximum at 253 nm (curve 1), and its complex with iron(III) at 460 nm (curve 2).
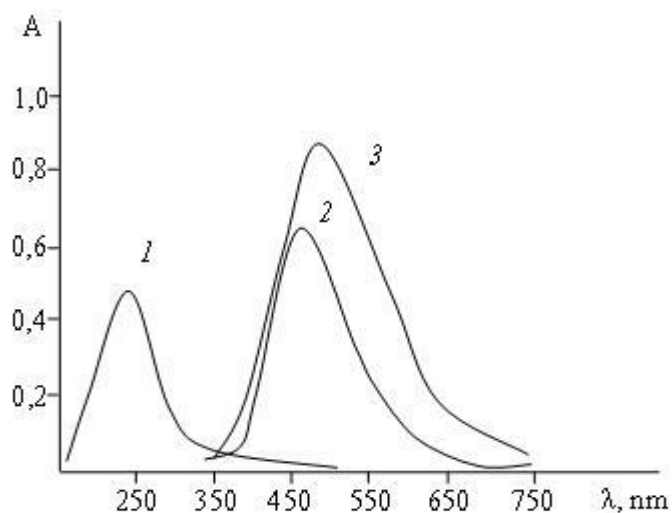

Figure 2. The absorption spectra of complexes of iron(III) at the optimal pH:
1 - R, 2 - Fe(III)-R, 3 - Fe(III)-R-Phen
C_{Fe}=8,0·10^{-4} M, C_R=2,0·10^{-4} M, C_{Phen}=2,0·10^{-4}M, Lambda-40, ℓ=1,0 sм

The study of dependence of optical density on pH of the solution showed that the yield of the complex Fe(III)-R is maximal at pH 4,5-5,0 (Fig. 3, curve 1). In the presence of 1,10-phenanthroline (Phen) ternary complex Fe(III)-R-Phen is formed,

while there is a bathochromic shift in the absorption spectrum and its maximum output is shifted into the acidic environment compared to binary complex Fe(III)-R. The absorption of the complex Fe(III)-R-Phen maximum at 478 nm (Fig. 2, curve 3) and its maximum yield is observed at pH 2,6 to 3,0 (Fig. 3, curve 2).

The effect of the concentration of the reactants, temperature and time on the formation of the binary and mixed-ligand complexes of iron(III) was studied. Fe(III)-R complex output is maximal at a concentration of reagent $2,0 \cdot 10^{-4}$ M and Fe(III)-R-Phen complex at $1,8 \cdot 10^{-4}$ M of reagent and $2,0 \cdot 10^{-4}$ M of 1,10-phenanthroline. It is found that the multiple molar excess of reagent and 1,10-phenanthroline does not affect the optical density of the complexes. Complexes are formed immediately after mixing solutions and differ in stability. Thus, if the complex Fe(III)-R is stable for 2 hours and heating to 60^0C, the complex of Fe(III)-R-Phen is stable for more than aday and more stable when heated to 80^0C.
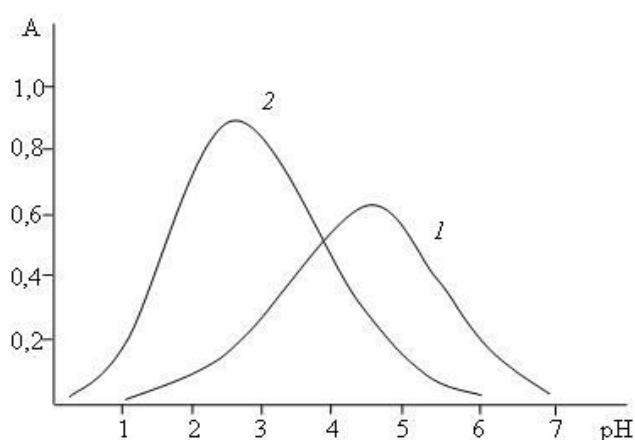

Figure 3. Effect of pH on the light absorption of iron complexes (III) in λ_{max}:
1 - Fe (III) -R, 2 - Fe (III) -Phen
$C_{Fe}=8,0 \cdot 10^{-4}$ M, $C_R=2,0 \cdot 10^{-4}$ M, $C_{Phen}=2,0 \cdot 10^{-4}$M,
Lambda-40, $\ell=1,0$ см

The ratio of components in the composition of the resulting colored complexes established by methods of isomolar series, the relative yield of Starik-Barbanel and shift the equilibrium (Bulatov & Kalinkin, 1986). All methods are shown that the ratio of the components in binary complex - 1:2 and in ternary complexes - 1:2:2. By the Astakhov method the number of protons displaces upon complexation is determined, the ratio of components in the complexes and confirmed (Astakhov *et al.,* 1961).

By the method of intersection of the curves stoichiometry and stability constant of the sameligand complex of Fe(III)-R are defined. The results obtained by these methods are confirmed while determining the stoichiometry and found that lgβ=9,32±0,21. Considering the molar ratio of the components in a mixed-ligand complex of Fe(III)-R-Phen, its stability constant is determined, and found that in the presence of 1,10-phenanthroline the stability of the complex rises more than six orders of magnitude: lgβ=15,44±0,29.

The calibration curve was linear over the concentration range of iron(III) 0,36-4,48 mkg/ml for the complex Fe(III)-R and 0,22-5,60 mkg/ml for the complex Fe(III)-R-Phen respectively. The molar absorbance coefficients, as well as other chemical-analytical characteristics of complexes are given in table. 1. It is seen that in the presence of 1,10-phenanthroline molar light absorption coefficient rises.

Table 1. Chemical-analytical characteristics of complex iron(III) with 2,4-diacetyl-3-(3'-nitrophenyl)-5-hydroxy-5-methylcyclohexanone.

Complex	pH_{opt}	$\lambda_{макс}$, нм	$\Delta\lambda$, nm	$\varepsilon\cdot10^3$ (at λ_{max})	$lg\beta$	Ratio of components	Interval calibration curve, mcg / ml
Fe-R	4,5-5,0	460	207	$0,82\pm0,02$	$9,32\pm0,21$	1:2	0,36-4,48
Fe-R-Phen	2,6-3,0	478	225	$1,10\pm0,03$	$15,44\pm0,29$	1:2:2	0,22-5,60

Study of the effect of foreign ions on the determination of iron showed that in the presence of 1,10-phenanthroline significantly increases the selectivity of the reaction. It is found that the determination of iron(III) in the form of a mixed-ligand complex of Fe(III)-R-Phen do not interfere 5000-fold amounts of alkali, alkaline-earth and rare-earth metals; 2000 fold - Cu(II), Co(II), Zn(II), Ni(II), Cd(II), Mg(II), Mn(II), Pb(II), Cr(III); 1000 fold - Al(III), Ga(III), In(III), Bi(III), Sb(III), Th(IV), U(VI); 400 fold - Ti(IV), V(V), Nb(V), Ta(V), F⁻, HPO_4^{2-}, $C_2O_4^{2-}$; 70 fold - Zr(IV), Hf(IV), Mo(VI) and W(VI).

The developed method is applied for the direct determination of trace iron in the strawberry and apricot.

The method of analysis. A portion of the sample of fruit weighing 200g after drying was placed in a graphite cup, burned in a muffle furnace at 600-700ºC until complete decomposition of organic substances. The resulting ash is dissolved in a mixture of 15 ml of HCl and 5 ml of HNO_3 in a glassy cup and treated three times with 5 ml HCl at 70-80ºC until complete distillation of nitrogen oxides. Then the mixture was dissolved in distilled water, filtered in a 100 ml flask and dilute to the mark. An aliquot (5,0-10,0ml) of this solution was transferred into a volumetric flask of 25 ml, 2,25ml of $2,0\cdot10^{-3}$M of reagent solution, 2,5 ml of $2,0\cdot10^{-3}$M solution of 1,10-phenanthroline were added and dilute to the mark by acetate-ammonia buffer pH 3,0. The optical density of the solution is measured with a spectrophotometer "Lambda-40" at $\lambda=478$ nm on the background of water in a cell with the thickness of light absorbing layer $\ell=1,0$ cm. The content of iron is found by preconstructed calibration curve. The results are shown in Table 2 and compared with the analysis data of Atomic Absorption Spectrometry (AAS).

Table 2. Results of the determination of iron in fruits (n=5; p=0,95)

Analyzed object	Found Fe, mg/ kg		S_r	
	R-Phen	AAS	R-Phen	AAS
Strawberry	$0,976\pm0,040$	$0,970\pm0,046$	0,036	0,041
Apricot	$0,592\pm0,027$	$0,586\pm0,032$	0,040	0,048

4.   Conclusion

2,4-Diacetyl-3-(3'-nitrophenyl)-5-hydroxy-5-methylcyclohexanone on the base of 3-nitrobenzaldehyde and acetylacetone was synthesized. The crystal structure of the reagent was set by XRD and the complexation of the reagent with iron (III) ions in the presence of 1,10-phenanthroline investigated. Highly selective method of determination for the direct determination of trace iron in the strawberry and apricot was developed.

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