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Formation of humic substances in the reaction of *D*-glucose with *p*-toluidine in anhydrous ethanol

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Abstract: *The aim of the study was to investigate the processes of formation and structural group composition of the products formed during the reaction of D-glucose with p-toluidine in anhydrous ethanol using electronic and vibrational spectroscopy methods. The evolution of the profiles of the electronic spectra of working solutions shows the formation of a chromophore system: clear peaks at 380 and 440 nm are already present at a reaction time of 60 min. The appearance of an additional maximum at 520 nm (90, 120 min) likely corresponds to the formation of chromophores in condensed structures, as confirmed by a decrease in the values of the* E_4/E_6 *indices over time. The dynamics of the transformation of structural elements is also clearly seen in the analysis of IR spectra: as the reactions proceed, the CH aliphatic component of the structure decreases, while the aromatisation and functionalisation of products by chromophore groups increases. For products obtained between 90 and 120 min, a clear band at 1656* cm^{-1}*, attributed to stretching vibrations of multiple bonds in conjugated C=C–C=O systems and azomethine fragments, indicates the of condensation reactions. In the spectra of insoluble solid products fractionated by water, the intensity of the bands at 1656 and 1190* cm^{-1} *is significantly reduced; this is possibly due to the transfer of some of the coloured low molecular weight products to the aqueous phase. A comparison of the IR Fourier transform spectra of the final solid products with the spectra of natural and synthetic humic-like substances indicates their similar structural group composition. The intensity of the bands at 1620, 1508 and 815* cm^{-1} *indicates a significant contribution of the aromatic component to the structure of the products of water-insoluble fractions; the water-soluble fractions mainly include aliphatic oxygen-containing structures resulting from the oxidative destruction of the initial carbohydrate. The synthesised products seem promising as convenient plant growth regulators with controlled release of the active substance.*

Keywords: *D-glucose, p-toluidine, humic substances, ethanol media, spectroscopy*

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Образование гуминоподобных веществ в реакции *D*-глюкозы с *п*-толуидином в безводном этаноле

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Резюме: *Целью исследования являлось изучение процессов образования и структурно-группового состава продуктов взаимодействия D-глюкозы с п-толуидином в среде безводного этанола методами электронной и колебательной спектроскопии. Эволюция профилей электронных спектров рабочих растворов показывает формирование хромофорной системы: четкие пики при 380 и 440 нм регистрируются уже при продолжительности реакции 60 мин. Появление дополнительного максимума при 520 нм (90, 120 мин), вероятно, отвечает образованию хромофоров конденсированных структур, что подтверждается уменьшением значений индексов* E_4/E_6 *со временем. Динамика трансформации структурных элементов также отчетливо прослеживается при анализе ИК-спектров: по мере протекания реакций СН-алифатическая составляющая структуры уменьшается, при этом увеличивается ароматизация и функционализация продуктов хромофорными группами. Для продуктов, полученных в течение 90 и 120 мин термостатирования, в спектрах* *фиксируется четкая полоса при 1656 см$^{-1}$, относимая к валентным колебаниям кратных связей в сопряженных системах C=C–C=O и азометиновых фрагментах, что указывает на протекание реакций конденсации. В спектрах фракционированных водой нерастворимых твердых продуктов интенсивность полос при 1656 и 1190 см$^{-1}$ существенно снижается, возможно, за счет перехода части окрашенных низкомолекулярных продуктов в водную фазу. Сопоставление характера ИК-Фурье-спектров конечных твердых продуктов со спектрами природных и синтетических гуминоподобных веществ показывает их сходный структурно-групповой состав. Интенсивность полос при 1620, 1508 и 815 см$^{-1}$ свидетельствует о существенном вкладе ароматической составляющей в структуру продуктов водонерастворимых фракций, при этом в состав водорастворимых фракций входят в основном алифатические кислородсодержащие структуры, образующиеся в результате окислительной деструкции исходного углевода. Синтезированные продукты представляются перспективными в качестве доступных регуляторов роста растений с контролируемым выделением активного вещества.*

Ключевые слова: *D-глюкоза, п-толуидин, гуминовоподобные вещества, этанольные среды, спектроскопия*

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INTRODUCTION

Synthetic analogues of natural compounds are important products of modern chemistry and chemical technology. One of the most accessible and widely studied are humic acids and humic substances, whose synthetic structural reproduction became possible in the middle of the 20th century [1, 2]. The interest in synthetic analogues of humic substances is driven by the need to obtain preparations that have valuable properties [3, 4]. Thanks to the established and proven practically-significant properties of humic substances, various methods for their preparation, as well as the relationship between their structure and properties are currently being intensively studied. To date, both chemical [3, 4] and biochemical [5] methods for producing synthetic analogues of humins have been developed. Humic substances are known to display a wide range of known properties (antioxidant, antiviral, surface-active), and can be used as plant growth regulators [3, 5]. These factors, as well as new works in the field of developed surface materials and nanostructures [6, 7] suggest the potential for further developments in the search for new reaction systems for synthesis. Particular attention in this case is given to systems based on simple carbohydrates [3, 6, 7], presenting themselves as reactive and available substrates. Notably, synthetic humins based on monosaccharides were obtained under conditions of acid catalysis, the structure of which is represented by furan or furanic-aliphatic polymers [3, 4], distinguishing them from natural humic substances. The introduction of an active component of aromatic nature into the reaction system opens up additional possibilities for the synthesis of the target products [7], in which the solvent effect plays an important role. The solubility of carbohydrates in ethanol-water solutions decreases significantly with an increase in the proportion of alcohol, which can shift the amino-carbonyl interactions in such systems into the partially heterogeneous category. In this case, process dynamics, which are determined by the desorption rate of products from the surface of the carbohydrate, for the most part do not depend on the nucleophilicity of the amine [8], expanding the possibilities of the classical Maillard reaction with the participation of aromatic amines [9]. In connection with the stated purpose of the present study, processes of formation and structural group composition of the products of the interaction of D-glucose with *p*-toluidine in anhydrous ethanol were examined.

EXPERIMENTAL

The synthesis of the target products was carried out in anhydrous (99.9 %) ethanol ("Merck") in the system *D*-glucose – *p*-toluidine of equimolar composition (0.002 mol) and heated in a three-necked flask with water heating and reflux at a thermostat temperature of 70 °C for a predetermined time. The absorption spectra of diluted samples selected during the processes (0.1 ml in 5 ml of solvent) were recorded in quartz cuvettes (l = 1 cm) on an SF-2000 spectrophotometer (OKB SPECTR, St. Petersburg, Russia) at a wavelength range of 300–700 nm with a step of 5 nm. At the end of the measurement processes, the solvent was removed and the products, presenting themselves as black-brown substances, were washed with anhydrous ether and dried. Some of the products were fractionated with water. IR Fourier spectra of solid products were recorded in the transmission format in KBr pellets (1:250) on an FSM 2201 IR Fourier transform spectrometer (Infraspek LLC, St. Petersburg, Russia) in the wavelength range of 500–4000 cm^{-1} having a spectral resolution of 4 cm^{-1} with 40 scans. The initial spectra were processed in the FSpec and PeakFit software programs. The second derivative spectra were obtained as a result of numerical differentiation using smoothing by a fourth-order polynomial in windows up to 15 points. No fewer than three experiments were carried out.

RESULTS AND DISCUSSION

The direct determination of the structure of humic substances is greatly complicated by the compositional heterofunctionality and large number of combinations of structural units [10, 11]. In this case, IR spectroscopy, being a non-destructive method, provides fairly complete information about the set of basic atomic groups, as well as their mutual structural combination [12]. The dynamics of the transformation of structural elements can be clearly seen in the frequency analysis (Fig. 1):

– as the target processes proceed, a clear peak appears at 1190 cm^{-1} ($\nu_{C\text{-}O\text{-}C}$ + $\nu_{C\text{-}O\text{-}N}$ [13]), whose intensity increases with time;

– for products obtained at 90 and 120 min incubation, a fixed band at 1656 cm^{-1} is attributable to the stretching vibrations of multiple bonds in conjugated system C=C–C=O, indicating the condensation reaction [2].

Fractionation of final solid products with water allows the water-insoluble fractions to be isolated in the form of brown powders, in the spectra of which the main bands remain unchanged in time (Fig. 2, spectra 1, 2), while the band intensities at 1656 and 1190 cm^{-1} decline. The latter may indicate the transition of some of the soluble coloured products to the aqueous phase, which, according to the authors of the publication [13], correlates with an increase in the band in the region of 1660 cm^{-1} and a decrease in the colour intensity of water-soluble fractions.

The nature of the vibrational spectra is a fairly reliable criterion for assigning the structure of products to a certain group of natural substances [2, 3, 5]. The assignment of the main bands in the IR Fourier transform spectra of solid products isolated from reaction systems shows the following structural group composition (see Fig. 2): 1720 cm^{-1} ($\nu_{C=O}$, shoulder), 1190, 1215, 1270 cm^{-1} ($\nu_{CAr\text{-}OH}$, $\nu_{C\text{-}OH}$, $\nu_{C\text{-}O\text{-}C}$), 3400–3200 cm $^{-1}$ ($\nu_{O\text{-}H,\ N\text{-}H}$), aromatic system: 1508, 1580, 1622 см$^{-1}$ ($\nu_{C=C}$), 815 см$^{-1}$ ($\gamma_{=C\text{-}H}$), 3030 cm^{-1} ($\nu_{=C\text{-}H}$), as well as the limiting aliphatic constituent: 1000–1100 cm^{-1} (ν_{CO} + δ_{CO} + ν_{CC} + ν^{as}_{ring}), 2855, 2922, 2950 cm^{-1} ($\nu_{C\text{-}H}$). The presence of intense bands at 1508 and 815 cm^{-1}, as well as signals at 3030 cm^{-1} indicates the contribution of the uncondensed aromatic component characteristic of natural humic substances in the structure of products [10], which distinguishes them from previously synthesised carbonisation products [9]. Similar bands of corresponding intensity were observed by other authors in the IR spectra of natural and synthetic humic-like substances [1–8, 11, 14], indicating their structural similarity with the products we isolated.

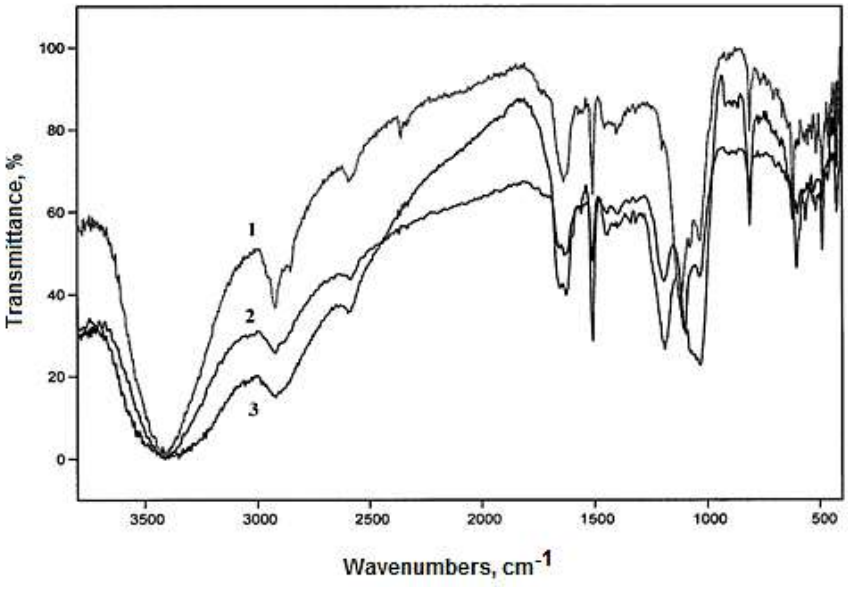

Fig. 1. IR-Fourier transform spectra of solid products isolated from reaction systems with different temperature control durations, min: 1 – 60; 2 – 90; 3 – 120

Рис. 1. ИК-Фурье спектры твердых продуктов, выделенных из реакционных систем при различной продолжительности термостатирования, мин: 1 – 60; 2 – 90; 3 – 120

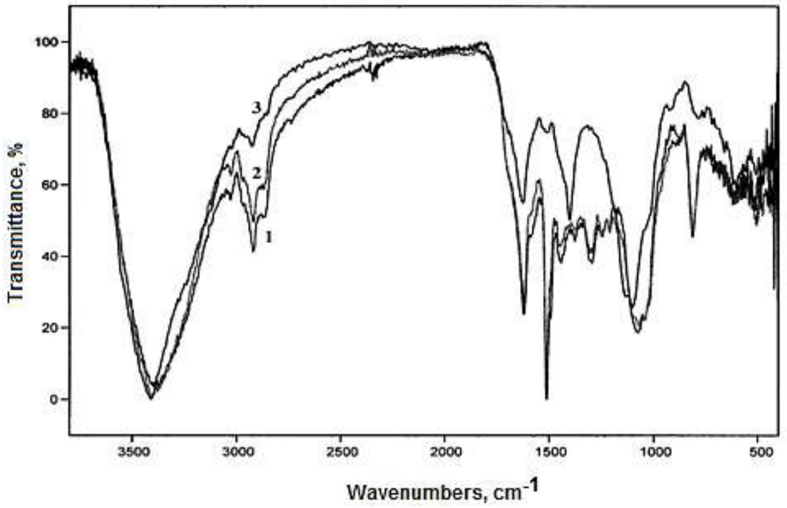

Fig. 2. IR-Fourier transform spectra of solid water-insoluble products isolated from reaction systems at different durations of temperature control, min: 1 – 60; 2 – 120; 3 – product of water-soluble fraction (120 min)

Рис. 2. ИК-Фурье спектры твердых водонерастворимых продуктов, выделенных из реакционных систем при различной продолжительности термостатирования, мин: 1 – 60; 2 – 120; 3 – продукт водорастворимой фракции (120 мин)

The electronic absorption spectra of the working solutions under the accepted experimental conditions are shown in Fig. 3. When analysing the nature of the profiles of their spectra, absorption in the entire wavelength range and increased optical density values are noted; this was not previously observed when using dried alcohol (98 %) as a solvent in the reaction of *D*-glucose with *p*-toluidine [9]. In addition, visual observations show the presence of an insoluble part of the carbohydrate that passes into the solution only at the end of the measurements.

The evolution of the profiles of the electronic spectra of working solutions shows the formation of a chromophore system: clear peaks at 380 and 440 nm are already present at a reaction time of 60 min. The appearance of an additional maximum at 520 nm (90, 120 min) probably corresponds to the formation of chromophores of condensed structures. Similar spectra are charac-

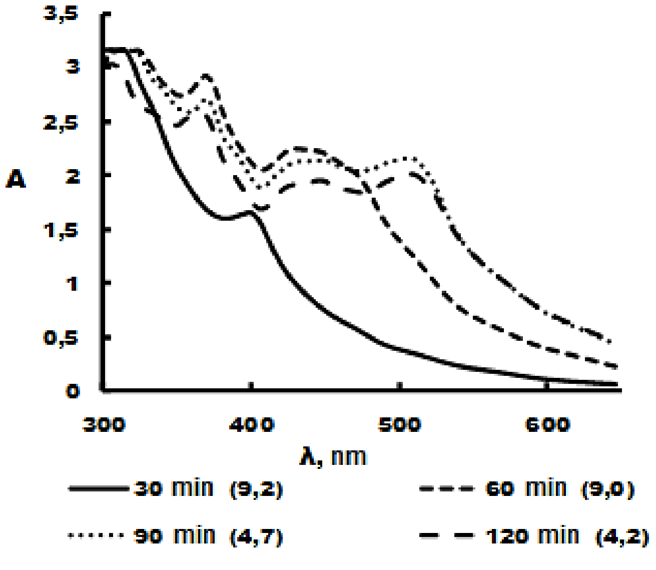

Fig. 3. Absorption spectra of process solutions and condensed products (values of E_4/E_6 indices are in brackets)

Рис. 3. Спектры поглощения рабочих растворов при различной продолжительности термостатирования (в скобках указаны значения индексов E_4/E_6)

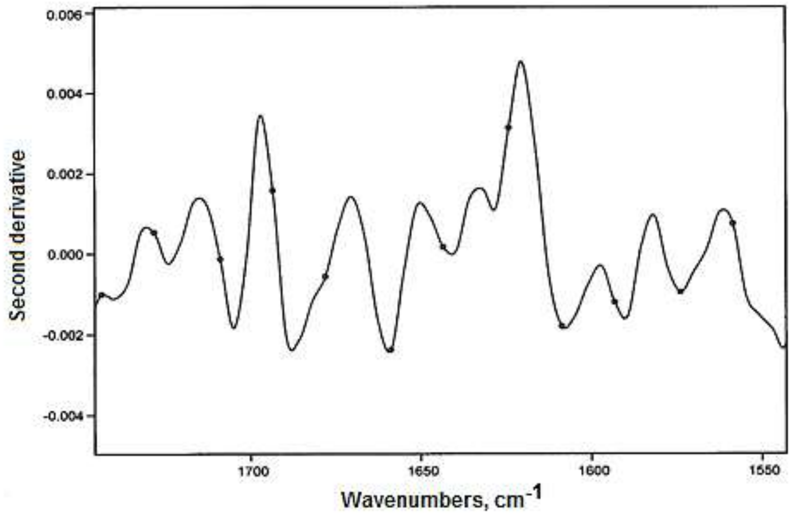

Fig. 4. IR-Fourier transform spectra second derivative of solid water-soluble product

Рис. 4. Вторая производная ИК-Фурье спектра твердого продукта водорастворимой фракции

teristic of πelectron systems of aromatic phenolic and quinoid structures [4], which is consistent with the vibrational spectroscopy data analysed above. A comparison of the indices E_4/E_6 calculated from the absorption values at λ = 465 and 650 nm [5, 10] confirms this conclusion: the particularly sharp decrease in the index values from 60 to 90 min of temperature control indicates the formation of condensed conjugate and aromatic structures or intermolecular donor-acceptor complexes with charge transfer [10].

The decrease in the optical density of the solutions with a thermostating time of 120 min is probably caused by the precipitation of some products due to an increase in molecular weight and a decrease in solubility in the reaction medium. Thus, the chromophore system of the final products, which includes three absorption maxima (380, 440 and 520 nm), begins to form by 60 min: this is represented by a combination of the aromatic component of the structure with oxygen- and nitrogen-containing functional groups.

Removing the solvent from the water-soluble fraction allows a yellow solid residue to be isolated whose IR-Fourier transform spectrum differs from the spectra of the products of water-insoluble fractions (see Fig. 2, spectrum 3). In particular, the intensity of the “aromatic” bands of 815 and 1508 cm^{-1} is significantly reduced; the clear peak appearing at 1404 cm^{-1} probably corresponds to the vibrations of C(O)OH, OH, and CH [2, 3, 10]. Signals at 1656 and 1190 cm^{-1} are not clearly recorded due to merging with wide bands with maxima at 1625 and 1137 cm^{-1}. Twice-repeated differentiation of the IR-Fourier transform spectrum band in the interval 1800–1550 cm^{-1} allows the peak to be divided at 1625 cm^{-1} into several bands (Fig. 4), the most intense of which are at 1620 and 1705 cm^{1} ($\nu_{C=C}$ + $\nu_{C=O}$). Less intense bands (1584, 1645, 1670, 1720 cm^{-1}) can also be attributed to functionalised oxygen fragments [15].

It can be assumed that the composition of water-soluble fractions consists mainly of aliphatic oxygen-containing structures formed as a result of oxidative degradation of the initial carbohydrate [14, 16, 17]; some of the bonds can be hydrolytically cleaved during fractionation [13].

The synthesised products have a number of important properties that are practically significant for their use as plant growth stimulants; in particular, the aromatic component. The authors of [12] showed that the growth-regulating activity of humic substances corresponds to an increase in their aromaticity. Other publications report the effectiveness of Schiff's aromatic bases on the yield of a number of agricultural crops [18, 19]. There has been growing interest in systems that are stable under natural conditions with controlled release of active substances [20]. For this reason, we are currently conducting studies to investigate the dynamics of fractionation of synthesised products, as well as vegetative experiments on test cultures in the Udmurt Republic.

Further studies are planned in the direction of studying the nature of the action of synthesised products on individual phases of plant development, as well as studies of their ecotoxicity and biodegradability. In the future, we also plan to develop a technological scheme that allows the process of synthesising growth regulators to be scaled up for industrial production.

CONCLUSIONS

Electronic and vibrational spectroscopy methods were used to study the formational and structural dynamics of products in the reaction of *D*-glucose with *p*-toluidine in anhydrous ethanol. The implementation of amino-carbonyl reactions of carbohydrates in non-aqueous alcoholic solutions can result in their significant intensification, allowing the procural of fractionated products structurally similar to substances of the humic class. The combination of the aromatic component of the structure with hydrolytically labile oxygen- and nitrogen-containing functional groups determines the biological activity during the growing season, which determines the prospect of using the synthesised products as available plant growth regulators with controlled release of the active substance.

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Contribution

Igor S. Cherepanov and Polina S. Kryukova carried out the experimental work, analyzed the experimental results and prepared the text of the manuscript. Igor S. Cherepanov and Polina S. Kryukova have equal author's rights and bear equal responsibility for plagiarism.

Conflict of interests

The authors declare no conflict of interests regarding the publication of this article.

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