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SYNTHETIC FULVIC ACIDS FROM TANNIN

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Abstract

This research introduces a new, simple and effective method of producing synthetic fulvic acids from tannin. The synthesis is based on the reaction of tannin oxidation by pure oxygen in a highly alkaline environment. The conversion of fulvates to the acid was achieved by passing the resulting mixture through a cation-exchange column in the H-form. The resulting dark-brown product solution has a pH = 2. A complex study of the physicochemical and spectroscopic properties of the obtained product using the methods of elemental analysis, ultraviolet-visible, infra red and electron paramagnetic resonance spectroscopy, scanning electron microscopy, X-ray diffraction showed the similarity of the obtained product to natural fulvic acids. Synthetic fulvic acids are advantageous over natural humic substances due to their reproducible properties as a result of their strict synthesis conditions. This significantly expands the scope of their application, in particular in medicine, where one of the prerequisites is the standardization of properties.

Keywords: tannin; fulvic acid; synthetic humic substances.

СИНТЕТИЧНІ ФУЛЬВОКИСЛОТИ З ТАНІНУ

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Анотація

Дослідження представляє новий, простий і ефективний метод отримання синтетичних фульвокислот з таніну. Синтез заснований на реакції окиснення таніну чистим киснем в сильно лужному середовищі. Комплексне дослідження фізико-хімічних і спектроскопічних властивостей отриманого продукту з використанням методів елементного аналізу, спектроскопії в УФ-, видимій та ІЧ- областях, електронного парамагнітного резонансу, скануючої електронної мікроскопії, рентгеноструктурного аналізу, показало схожість отриманого продукту з природними фульвокислотами. Синтетичні фульвокислоти мають перевагу над природними гуміновими речовинами завдяки їх відтворюваним властивостям в результаті строгого контролю умов синтезу. Це значно розширює області їх застосування, зокрема в медицині, де однією з обов'язкових умов є стандартизація властивостей.

Ключові слова: танін; фульвокислоти; синтетичні гумінові речовини.

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СИНТЕТИЧЕСКИЕ ФУЛЬВОКИСЛОТЫ ИЗ ТАНИНА

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Аннотация

Исследование представляет новый, простой и эффективный метод получения синтетических фульвокислот из танина. Синтез основан на реакции окисления танина чистым кислородом в сильно щелочной среде. Комплексное исследование физико-химических и спектроскопических свойств полученного продукта с использованием методов элементного анализа, спектроскопии в УФ, видимой и ИК областях, электронного парамагнитного резонанса, сканирующей электронной микроскопии, рентгеноструктурного анализа показало сходство полученного продукта с природными фульвокислотами. Синтетические фульвокислоты имеют преимущество перед природными гуминовыми веществами благодаря их воспроизводимым свойствам в результате строгого контроля условий синтеза. Это значительно расширяет области их применения, в частности в медицине, где одним из обязательных условий является стандартизация свойств.

Ключевые слова: танин; фульвокислоты; синтетические гуминовые вещества.

Introduction

Humic substances (HSs) are complex systems of macromolecular organic compounds of natural origin, which are polyfunctional structures of aromatic, alicyclic and heterocyclic nature, substituted by alkyl chains with different functional groups [1; 2]. The complexity of the structure of humic substances is caused by various factors and conditions of their formation, as well as significant effects on the composition and properties of HSs have ways of extracting them from natural objects [2]. Fulvic acid (FA) is a fraction of HSs soluble in alkalis and acids.

At present, there is no single answer to the question about the mechanisms of formation of HS in the environment. Existing models can be divided into two groups. The first includes models that assume the formation of biopolymers (precursors of HS) during secondary metabolism. Their further degradation upon entering the environment leads to the formation of HS [3]. The second group consists of models that provide a two-step process of HS formation: the first stage consists of the complete decomposition of biopolymers into simple monomers, and the second process is their polymerization with the formation dark-colored compounds of high molecular weight [4]. It should be noted that both predicted pathways of HS formation are not mutually exclusive. In both cases, the formation of the polymer is believed to occur as a result of the recombination of the radicals formed by the oxidation of the substituted phenols and hydroquinones.

The idea of obtaining synthetic analogues of natural HS originated in the early 20th century [5; 6]. At least three arguments can be made in favor of developing such research: 1) chemical synthesis will allow better understanding of natural processes; 2) there is a problem of creating standard HS samples of certain composition and properties; 3) production of synthetic analogues of natural HSs under strictly controlled conditions will provide a product with reproducible properties. This will expand the field of use, particularly in medicine, veterinary medicine and agriculture.

Methods of obtaining synthetic humic substances known today are based on the oxidation reactions of various phenolic compounds by different oxidants. The precursors used nowadays to obtain synthetic HS are hydroquinone, pyrogallol [7], D-glucose with p-toluidine [8], gallic acid [9], hematoxylin [10], catechol and glycine [11], 3,4-dihydroxytoluene, 3,4-dihydroxyphenylacetic acid, caffeic acid, hydrocaffeic acid, chlorogenic acid, adrenaline gentisinic acid [12], amino acids [13], protocatechuic acid [14]. The authors of [15] have greatly expanded the range of starting materials that can be used to produce synthetic HSs. The oxidants in the existing methods are pure oxygen, air, Ag_2O, $NaIO_4$, H_2O_2, $K_2S_2O_8$, and enzymes [7–16]. The use of toxic substances as oxidizing agents limits the scope of the final product or requires a multi-stage and cost-effective cleaning. Some researchers have tried to reproduce the natural conditions of formation of HSs, but a significant disadvantage of this method is the long duration of the process [17]. The melanoidin reaction, or the Maillard reaction, named after its first researcher, is also one of the possible ways of forming model HSs [18]. The melanoidin reaction is based on the interaction of reducing sugars with amino acids.

It should be noted that the elemental composition, functional and structural properties, sizes of macromolecules of synthetic HS may be different depending on the choice of precursors and variation of synthesis conditions.

The main disadvantages of the known methods of obtaining synthetic humic substances today are the use of toxic substances in the synthesis, large number of stagesand duration of the process, the lack of conformity of the properties of the resulting product to natural humic substances. Therefore, the development of new, technologically simple and efficient methods for the production of synthetic analogues of natural humic substances from fundamentally new starting materials is an urgent and promising task, both theoretically and practically.

The promising precursors for the production of synthetic humic substances are tannins. Therefore, the purpose of this work was to develop a method for producing synthetic fulvic acids from tannin and complex study of the properties of the resulting product.

Experimental part

The reagents used for all analyses in this research were of analytical grade and the purchases were made directly from Merck, Germany. Milli-Q system (Millipore) was used to prepare deionized water (18.2 MΩ/cm resistivity) for the preparation of aqueous solutions.

For preparation of the synthetic FA 3.3 g of tannin was put into a plastic beaker and carefully placed in a 2 L flask. 80 ml of 1 M NaOH solution and 20 ml of distilled water were added to the reaction flask. The air was forced out of the system with pure oxygen. The mechanical shaking of the reaction flask was then enabled. As a result, the reagents were mixed and the oxidation process began. The reaction was monitored volumetrically. The process was considered complete when oxygen consumption had virtually ceased. Under these conditions, this happened within 2 hours. The resulting dark brown mixture was passed through a cation exchange column in H-form. The separation of the eluate began with the appearance of a brown color of the solution emerging from the column, and was completed by changing its color to light yellow. The resulting fraction was heated at 80 °C for 20 minutes to remove carbonic acid.

The elemental composition of synthetic FA was investigated on a Carlo Erba 1106 CHN-analyzer. UV-visible spectra of synthetic FA from tannin were recorded on a Lambda 35 Perkin Elmer UV-visible spectrophotometer in the range of 320–500 nm. 0.1 ml solution of synthetic FA was diluted to 25 ml in the UV-visible experiments. The FT-IR spectra of synthetic FA from tannin were recorded by the Perkin-Elmer spectrometer (SpectrumGX) with a resolution of 2 cm^{-1} over a scan range 4000–500 cm^{-1} using KBr pellet method. The X-ray diffraction pattern of synthetic FA from tannin were recorded by powder method on a DRON-2 X-ray diffractometer (LOMO, Russia) with FeKα radiation (λ_{Fe} = 0.19360 nm) in the angle range 2θ = 20–120°, at a scanning speed of 0.01°/s. For this, synthetic fulvic acid was dried at 80 °C. The resulting powder was mixed with a PVA water emulsion and applied to an organic glass plate to provide a thin and smooth layer. Studies of the morphology of surface of the synthetic FA were performed on a SEM-100 scanning electron microscope.

Total acidity (carboxylic and phenolic groups) was determined by the baryta method, while the carboxylic acidity is determined by the Ca-acetate method [2]. The concentration of phenolic groups was calculated by subtracting the carboxylic group content from the total acidity.

The reducing capacities of synthetic FA were determined as reported in [19]. Three solutions were prepared for the measurements: solution ***A*** with a concentration of synthetic FA 50 mg/l and $K_3Fe(CN)_6$ concentration of 0.25 mmol/l; a blank solution ***B*** with a concentration of $K_3Fe(CN)_6$ 0.25 mmol/l, and a blank solution ***C*** with a concentration of synthetic FA 50 mg/l. All solutions were prepared on buffer pH = 11, which was prepared by dissolving 6.21 g of boric acid with 4.00 g of sodium hydroxide and 3.70 g of potassium chloride in 1000 ml of distilled water. The resulting solutions were left in the dark for 24 hours at room temperature. Then the optical density of all solutions was measured at 420 nm using Lambda 35 Perkin Elmer UV-visible spectrophotometer. The decrease in optical density ΔA due to the reduction of $K_3Fe(CN)_6$ was determined, according to the formula:

$$\Delta A = A\,(B) + A\,(C) - A\,(A), \qquad (1)$$

where A (A), A (B), A (C) is the optical density of solutions A, B, C. The amount of recovered potassium hexacyanoferrate (III) Δn ($K_3Fe(CN)_6$) was calculated by the value of ΔA from the calibration graph and determined the recovery capacity by the formula:

$$\text{reducing capacity (mmol/g)} = \frac{\Delta n(K_3Fe(CN)_6)}{m_{FA}}, \qquad (2)$$

where Δn($K_3Fe(CN)_6$) is the amount of reductions $K_3Fe(CN)_6$, mmol; and mFA is the mass of FA in the solution, g.

EPR spectra of the synthetic FA were measured using a 2 mm quartz tube. To calculate the spin content in the sample, a spin standard $CuCl_2 \cdot H_2O$ was used. EPR experiment was carried out using a

Bruker ESP 300 E spectrometer operating in the X-band and equipped with 100 kHz field modulation.

Results and discussion

Tannins are a group of phenolic compounds of plant origin that contain a large number of OH groups. The molecular weight of tannins is in the range of 500–3000 [20]. Tannins are an amorphous light yellow powder with a slight peculiar odor, a tart taste, soluble in water, ethanol and glycerol. Tannins are found in bark, wood, leaves, fruits (sometimes seeds, roots, tubers) of many plants – oak, chestnut, acacia, spruce, larch, canine, eucalyptus, tea, cocoa, pomegranate, cherry, persimmon, horseradish sumah, quebra, and others. In the industry, tannins are used for tanning leather and fur, preparing ink, etching textile fibers, giving a variety of drinks a tart and viscous taste, and as a food coloring (E181). In medicine, tannins are used as binders, antidotes (for the poisoning of lead salts, mercury, etc.), anti-diarrhea, hemostatic and hemorrhoids [21]. The choice of tannin as a precursor in synthesis analogs FA is due to the fact that its molecule, in addition to phenolic aromatic nuclei, also contains a carbohydrate moiety that is always present in fulvic acid molecules (Fig. 1).

Oxidation of tannin by molecular oxygen in a highly alkaline environment allows obtaining a product that more fully reproduces the structure and physicochemical properties of natural fulvic acids. The oxidation process was carried out at room temperature and normal atmospheric pressure. In the process of synthesis, the color of the solution varied from marsh-green to yellow-brown. The process was monitored volumetrically, that is, by measuring the volume of oxygen consumed in the reaction. Under these conditions, the reaction is completed within 2 hours. The pH of the solution at the end of the synthesis was 13. Conducting the process in a highly alkaline medium accelerates the oxidation process and reduces the total synthesis time. In order to translate the obtained fulvates into the acid state, the mixture was passed through a cation exchange column in H-form. In this process, the sodium (Na^+) cations were replaced with the hydrogen (H^+) cations, so at the outlet of the column the synthetic fulvic acids were received. The resulting solution of synthetic fulvic acids has a pH = 2. The solubility of this product at any pH value is one of the confirmation that fulvic acids was obtained, and not humic acids, which precipitate at pH < 2. To confirm the similarity of the structure and properties of the resulting product with natural fulvic acids, a comparison of the elemental composition, spectra in the IR, UV and visible regions was performed.

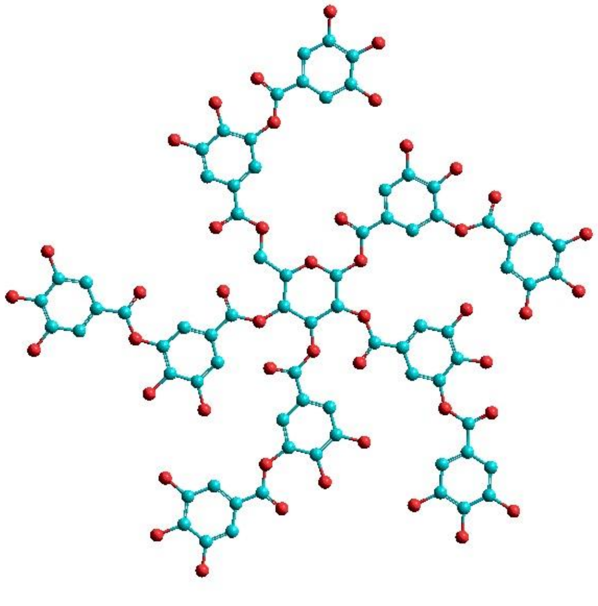

Fig. 1. Ball-and-stick model of the typical structure of hydrolyzed tannin

Elemental analysis showed that the synthesized synthetic fulvic acid contains Carbon, Hydrogen and Oxygen (Table 1), which is in complete agreement with those obtained for fulvic acids extracted from natural sources [2].

Table 1

Elemental composition of tannin, synthetic fulvic acids and natural humic substances

Substances	C	H	O
Tannin	53.66±0.10	3.08±0.10	43.26±0.20
Synthetic FA from tannin	45.72±0.20	2.67±0.20	51.61±0.30
Natural HSs [2]	36.68–47.25	4.03–5.04	46.50–55.81

However, the percentage composition of synthetic FA, directly established in the analysis, does not give a clear idea of the role of individual elements in the construction of molecules. To clarify this role, the H/C and O/C atomic ratios were calculated, showing how many hydrogen atoms and Oxygen atoms per Carbon atom (Table 2). The magnitudes of the H/C atomic ratios make it possible to conclude the ratio of aliphatic and aromatic structures in the synthetic FA molecules. Comparative analysis of the H/C atomic ratio for tannin and synthetic fulvic acids indicates that the overall ratio of aliphatic and aromatic structures in the synthetic FA molecule is maintained, while the number of oxygen-containing groups increased slightly compared to the parent compound. This is indicated by the O/C atomic ratios for tannin and synthetic fulvic acids.

Table 2

The atomic ratios H/C and O/C for tannin and synthetic fulvic acids

Substances	H/C	O/C
Tannin	0.69	0.60
Synthetic FA from tannin	0.70	0.85
Natural HSs [2]	0.69–1.43	0.6–1.5

UV-Visible spectroscopy is another technique which can provide useful information on the composition and origin of HSs [22–24]. In the visible and ultraviolet regions of the spectrum, the synthetic fulvic acids obtained give a continuous spectrum without pronounced highs or lows, which falls into the long wave region (Fig. 2).

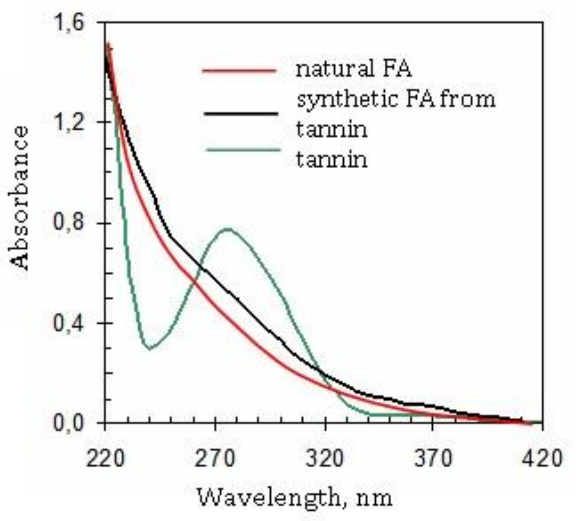

Fig. 2. Absorption spectra of the tannin, synthetic FA from tannin and natural FA

The maximum at 280 nm that occurred in the tannin spectrum disappears on the spectrum of synthetic fulvic acids. The comparison of the spectra in the ultraviolet and visible regions for synthetic and natural FAs demonstrates their similarity, which is a confirmation of the spectral properties and structure of the obtained products with natural materials [22; 24].

Comparing the IR spectra of synthetic (Fig. 3) and natural fulvic acids, we can conclude that their chemical structure is the same.

In particular, the broad absorption band of about 3440 cm^{-1} is due to the valence vibrations of the hydroxyl groups. The bands in the region 2960–2840 cm^{-1} indicate the presence of methylene groups in the synthetic fulvic acids. While the absence of a strong absorption band at 720 cm^{-1} indicates a small length of carbon chains; no more than 4 carbon atoms. The absorption band at 1710 cm^{-1} is characteristic of carboxyl groups. Three bands of about 1610, 1494 and 1450 cm^{-1} are characteristic of aromatic ring oscillations. Peaks at 1210 cm^{-1} correspond to the fluctuations of the C–O bonds of carboxyl and phenol groups, and in the range of 1025-1066 cm^{-1} to the fluctuations of the C-O bonds of the alcohol groups.

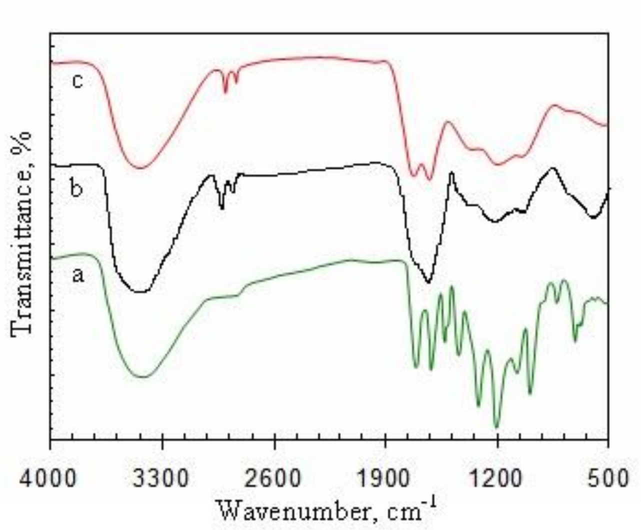

Fig. 3. FTIR spectra of tannin (a), synthetic FA from tannin (b), natural FA (c)

According to X-ray diffraction analysis, synthetic fulvic acids have no crystalline structure (Fig. 4), which is typical of natural humic substances [2].

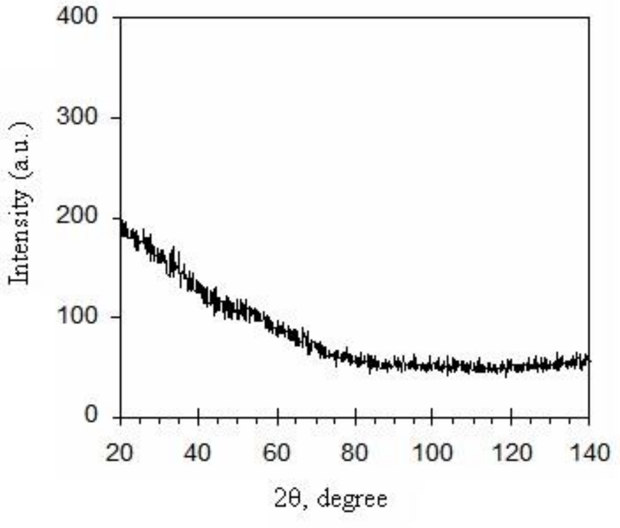

Fig. 4. XRD patterns of the synthetic FA from tannin

The surface relief of synthetic FA obtained from tannin was examined by scanning electron microscopy. The resulting images show the same type of powder was obtained (Fig. 5).

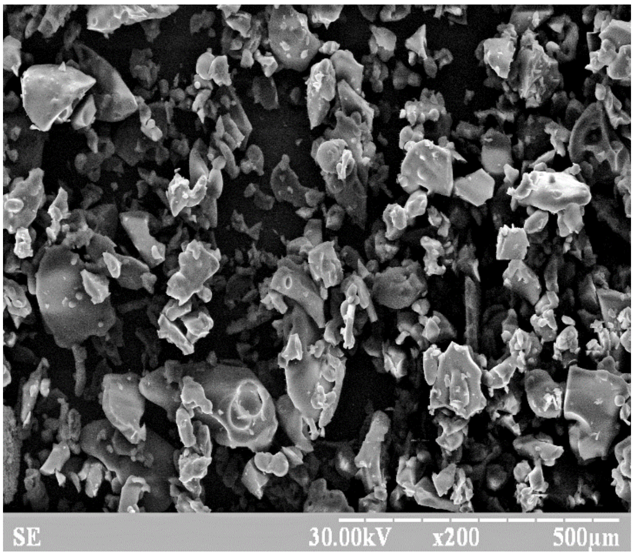

Fig. 5. SEM image of synthetic FA from tannin

Both natural and synthetic FAs contain a large number of functional groups, among which are the carboxylic and phenol groups that determine the acid and ion-exchange properties of FA. Since FAs form low-soluble salts with alkaline earth metals, this property is used in traditional methods of determining acid groups in synthetic FA samples by reactions with barium hydroxide and calcium acetate. To estimate the number of groups that reacted after precipitation of fulvates in the barite method, excess $Ba(OH)_2$ is titrated with HCl, and in Ca-acetate, the amount of acetic acid released by the reaction is determined. The content of phenol groups in the structure of synthetic FA was determined by the difference between the total acidic groups and carboxylic acid. The results obtained for synthetic FAs from tannin compared to natural HSs are shown in Table 3.

Table 3

The content of carboxyl and phenol groups in the structure of synthetic FA compared with natural HSs

Humic substances	Σ(ArOH+COOH), mmol/g	– COOH, mmol/g	ArOH, mmol/g
Synthetic FA from tannin	7.1±0.3	5.2±0.2	1.9±0.1
Natural HSs [2]	5.3–13.4	2.7–10.1	1.9–7.4

The important characteristic of HSs is their redox capabilities, which characterize the redox capacity. Redox capacity is defined as the amount of oxidizer (or reductant) that is reduced (or oxidized) by interaction with the HSs, normalized to their mass. The method proposed by Matiesen [19], whose essence is to reduce $K_3Fe(CN)_6$ to $K_4Fe(CN)_6$ in the presence of HSs, is widely used to determine the reduction capacity of HSs. A number of factors make $K_3Fe(CN)_6$ a fairly convenient reagent for determining the redox capacity of HSs [19]: 1) $K_3Fe(CN)_6$ has a stable redox potential (0.543 V) over a wide pH range (4 to 11). This allows to obtain comparable results of the recovery capacity at different pH of the reaction mixture; 2) the difference in the absorption spectra of the $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ solutions allows them to be photometrically determined in a compatible presence by measuring the optical density at the maximum absorption of $K_3Fe(CN)_6$ at 420 nm (at a given $K_4Fe(CN)_6$ absorption wavelength is very small); 3) high stability of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ prevents the occurrence of adverse reactions such as ligand exchange with HSs. The mechanism of oxidative dimerization of di- and polyphenols induced by an alkaline solution of ferrocyanide was investigated by authors in ref. [25].

The value of redox capacities of the synthetic FA from tannin is equal 4.4 ± 0.2 mmol/g, which is in the range characteristic of natural humic substances from soil, peat and freshwater (1.09 to 6.5 mmol/g) [25].

EPR spectroscopy has been used to measure the free radical content of synthetic FA. The calculated spin density is $4.5 \cdot 10^{17}$ spin/g, the half-width of the line is 3.5 Gauss with $g = 2.0034$. This data agrees with previously reported g-values for fulvic acid from soil and is consistent with semiquinones being the primary organic radicals [1; 25]. The EPR spectrum of synthetic FA from tannin is shown in Fig. 6.

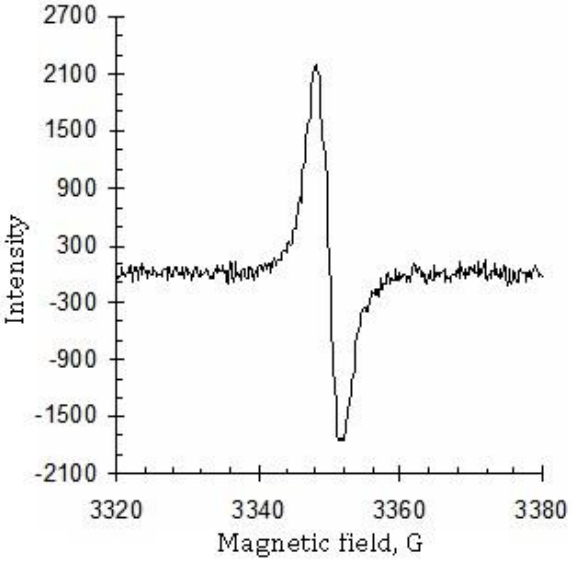

Fig. 6. EPR spectra of synthetic fulvic acid from tannin

Moreover, the concept of the formation of fulvic acids from tannin is further supported by the fact that natural fulvic acids and polymers synthesized by oxidation of tannin are closely related in their chemical properties. In particular, solubility in water under all pH conditions, the formation of precipitates with heavy metals, the formation of complexes with cationic dyes, anodic migration in an electric field.

Conclusion

The development of a novel approach for the preparation of synthetic FA from tannin using molecular oxygen in alkaline solution was carried out. Comparative analysis of the elemental composition and spectral characteristics of synthetic fulvic acids obtained from tannin with natural FA allowed to ascertain their similarity. The content of basic acid groups in the structure of synthetic FA and their reduction capacity are calculated. In particular, the content of carboxyl groups is 5.2±0.2 mmol/g, and the phenolic groups 1.9±0.1 mmol/g; the reduction capacity is 4.4 ± 0.2 mmol/g. X-ray diffraction analysis of synthetic fulvic acids indicated their amorphous nature. The EPR spectrum of the synthetic FA from tannin shows a sharp, narrow single line resonance at g = 2.0034 with line width of 3.5 Gauss and concentration of paramagnetic centers $4.5 \cdot 10^{17}$ spin/g. SEM images of the dried preparations of synthetic fulvic acids show the uniformity of the obtained powder particles. Synthetic FA has an advantage over natural humic substances due to their reproducible properties because of their strict synthesis conditions.

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Bibliography

[1] Gomes de Melo B. A. Humic acids: Structural properties and multiple functionalities for novel technological developments / B. A. Gomes de Melo, F. L. Motta, M. H. Santana // Mater Sci Eng C. – 2016. – Vol. 62. – P. 967–974.

[2] Rigobello E.S. Comparative characterization of humic substances extracted from freshwater and peat of different apparent molecular sizes / E.S. Rigobello, S.X. Campos, E.M. Vieira // Rev. Amb. Água. – 2017. – Vol. 12. – P. 774–785.

[3] Biophysico-Chemical Processes Involving Natural Nonliving Organic Matter in Environmental Systems / N. Senesi, B. Xing, P.M. Huang Eds. – John Wiley & Sons, Inc., 2009. – 904 p.

[4] Kulikowska D. Kinetics of organic matter removal and humification progress during sewage sludge composting / D. Kulikowska // Waste Management. – 2016. – Vol. 49. – P. 196–203.

[5] Eller W. Studien über huminsäuren. IV. Darstellung und eigenschaften künstlicher und natürlicher huminsäuren / W. Eller // Liebigs Ann. Chem. – 1923. – Vol. 431. – P. 133–161.

[6] Welte E. Über synthesehuminsäuren (Oxydationsmessungen) / E. Welte, M. Schatz, W. Ziechmann // Naturwiss. – 1910. – Vol. 41 (9). – P. 213–214.

[7] Cataldo F. On the structure of macromolecules obtained by oxidative polymerization of polyhydroxyphenols and quinines / F. Cataldo // Polym. Int. – 1998. – Vol. 46. – P. 263–268.

[8] Cherepanov I. S. Formation of humic substances in the reaction of D-glucose with p-toluidine in anhydrous ethanol / I.S. Cherepanov, P.S. Kryukova // Proceedings of universities. Applied chemistry and biotechnology. – 2020. – Vol. 10, No. 2. – P. 188–195.

[9] Synthesis and properties of model humic substances derived from gallic acid / D. Sławińska, K. Polewski, P. Rolewski, J. Sławiński // Int. Agrophys. – 2007. – Vol. 21. – P. 199–208.

[10] Litvin V.A. Synthesis and properties of synthetic fulvic acid derived from hematoxylin / V.A. Litvin, B.F. Minaev, G.V. Baryshnikov // J. Mol. Struct. – 2015. – Vol. 1086. – P. 25–33.

[11] Yang T. The copper complexation ability of a synthetic humic-like acid formed by an abiotic humification process and the effect of experimental factors on its copper complexation ability / T. Yang, M. E. Hodson // Environmental Science and Pollution Research. – 2018. – Vol. 25. – P.15873–15884.

[12] Hänninen K.I. Synthesis and characterization of humic acid-like polymers / K.I. Hänninen, R. Klöcking, B. Helbig // Sci. Total Environ. – 1987. – Vol. 62. – P. 201–210.

[13] Synthesis of amino-phenolic humic-like substances and comparison with natural aquatic humic acids: A multi-analytical techniques approach / A.-V. Jung, C. Frochot, S. Parant [et al.] // Org. Geochem. – 2005. – Vol. 36. – P. 1252–1271.

[14] Giannakopoulos E. A humic-acid-like polycondensate produced with no use of catalyst / E. Giannakopoulos, M. Drosos, Y. Deligiannakis // J. Colloid Interface Sci. – 2009. – Vol. 336. – P. 59–66.

[15] Пат. 5945446 США, Process for Preparing Synthetic Soil-Extract Materials and Medicaments Based Thereon / Laub R. J. (США); заявник та патентовласник Laub R. J. (США); заявл. 10.02.1997; опубл. 31.08.99.

[16] Synthesis of humic-like acid from biomass pretreatment liquor: Quantitative appraisal of electron transferring capacity and metal-binding potential / X. Wang, A. Muhmood, R. Dong, S. Wu // Journal of Cleaner Production. – 2020. – Vol. 255. – P. 120243.

[17] Ziechmann W. Über modellreaktionen zur bildung synthetischer huminsäuren. 2. Die synthese von huminsäuren im neutralen milieu / W. Ziechmann // Brennstoff-Chem. – 1960. – Vol. 41. – P. 334.

[18] Ikan R. Characterization of natu-ral and synthetic humic substances (melanoidins) by stable carbon and nitrogen isotope measurements and elemental composition / R. Ikan, T. Dorsey, I. R. Kaplan // Anal. Chim. Acta. – 1990. – Vol. 232. – P. 11.

[19] Matthiessen A. Determining the redox capacity of humic substances / A. Matthiessen // Vom Wasser. – 1995. – Vol. 84. – P. 229–235.

[20] Tannins extraction: A key point for their valorization and cleaner production / P. Hoyos-Martinez, J. Merle, J. Labidi, F.C. Bouhtoury // J. Clean. Prod. – 2019. – Vol. 206. – P. 1138–1155.

[21] Tannins: Extraction from Plants / Aires A. (Ed.). – 2019. – UK, London: IntechOpen. – 136 p.

[22] Spectroscopic characterization of humic and fulvic acids in soil aggregates, Brazil / W. Machadoa, J. C. Franchini, M. de Fátima Guimarães, J.T. Filho // Heliyon. – 2020. – Vol. 6(6). – P. e04078.

[23] Synergistic Extraction and Characterization of Fulvic Acid by Microwave and Hydrogen Peroxide–Glacial Acetic Acid to Oxidize Low-Rank Lignite / Y. Zhang, G. Gong, H. Zheng [et al.] // ACS Omega. – 2020. – Vol. 5, № 12. – P. 6389–6394.

[24] Quantitative and qualitative characterisation of humic products with spectral parameters / E. Filcheva, M. Hristova, P. Nikolova [et al.] // J. Soils Sediments. – 2018. – Vol. 18. – P. 2863–2867.

[25] Struyk, Z. Redox properties of standard humic acids / Z. Struyk, G. Sposito // Geoderma 2001. – Vol. 102. – P. 329–346.

References

[1] Gomes de Melo, B. A., Motta, F. L., Santana, M. H. (2016). Humic acids: Structural properties and multiple functionalities for novel technological developments. Mater Sci Eng C., 62, 967–974. https://doi.org/10.1016/j.msec.2015.12.001

[2] Rigobello, E.S., Campos, S.X., Vieira, E.M. (2017). Comparative characterization of humic substances extracted from freshwater and peat of different apparent molecular sizes. *Rev. Amb. Água*., *12*, 774–785. https://doi.org/10.4136/ambi-agua.2022

[3] Senesi, N., Xing, B., Huang, P.M. (Eds.). (2009). Biophysico-Chemical Processes Involving Natural Nonliving Organic Matter in Environmental Systems. John Wiley & Sons, Inc.

[4] Kulikowska, D. (2016). Kinetics of organic matter removal and humification progress during sewage sludge composting. *Waste Management*, *49*, 196–203. https://doi.org/10.1016/j.wasman.2016.01.005

[5] Eller, W. (1923). Studien über huminsäuren. IV. Darstellung und eigenschaften künstlicher und natürlicher huminsäuren. *Liebigs Ann. Chem*., *431*, 133–161. https://doi.org/10.1002/jlac.19234310108

[6] Welte, E., Schatz, M., Ziechmann W. (1910). Über synthesehuminsäuren (Oxydationsmessungen) *Naturwiss*, *41* (9), 213–214. https://doi.org/10.1007/BF00623027

[7] Cataldo, F. (1998). On the structure of macromolecules obtained by oxidative polymerization of polyhydroxyphenols and quinines. *Polym. Int*., *46*, 263–268. https://doi.org/10.1002/(SICI)1097-0126(199808)46:4<263::AID-PI983>3.0.CO;2-0

[8] Cherepanov, I. S., Kryukova, P. S. (2020). Formation of humic substances in the reaction of D-glucose with p-toluidine in anhydrous ethanol. *Proceedings of universities. Applied chemistry and biotechnology*, *10* (2), 188–195. https://doi.org/10.21285/2227-2925-2020-10-2-188-195

[9] Sławińska, D., Polewski, K., Rolewski, P., Sławiński, J. (2007). Synthesis and properties of model humic substances derived from gallic acid. *Int. Agrophys*, 21, 199–208. https://doi.org/10.1007/s11356-018-1836-2

[10] Litvin, V.A., Minaev, B.F., Baryshnikov, G.V. (2015). Synthesis and properties of synthetic fulvic acid derived from hematoxylin. *J. Mol. Struct*., *1086*, 25–33. https://doi.org/10.1016/j.molstruc.2014.12.091

[11] Yang, T., Hodson, M. E. (2018). The copper complexation ability of a synthetic humic-like acid formed by an abiotic humification process and the effect of experimental factors on its copper complexation ability. *Environmental Science and Pollution Research*, *25*, 15873–15884.

[12] Hänninen, K.I., Klöcking, R., Helbig, B. (1987). Synthesis and characterization of humic acid-like polymers. *Sci. Total Environ*., *62*, 201–210. https://doi.org/10.1016/0048-9697(87)90502-X

[13] Jung, A.-V., Frochot, C., Parant, S., Lartiges, B.S., Selve, C., Viriot, M.-L., Bersillon, J.-L. (2005). Synthesis of amino-phenolic humic-like substances and comparison with natural aquatic humic acids: A multi-analytical techniques approach. *Org. Geochem*., *36*, 1252–1271. https://doi.org/10.1016/j.orggeochem.2005.04.004

[14] Giannakopoulos, E., Drosos, M., Deligiannakis, Y. (2009). A humic-acid-like polycondensate produced with no use of catalyst. *J. Colloid Interface Sci*., *336*, 59–66. https://doi.org/10.1016/j.jcis.2009.03.037

[15] Laub, R.J. (1999). US Patent No. 5945446. Newport Beach, Calif.: US.

[16] Wang, X., Muhmood, A., Dong, R., Wu, S. (2020). Synthesis of humic-like acid from biomass pretreatment liquor: Quantitative appraisal of electron transferring capacity and metal-binding potential. *Journal of Cleaner Production*, *255*, 120243.

[17] Ziechmann, W. (1960). Über modellreaktionen zur bildung synthetischer huminsäuren. 2. Die synthese von huminsäuren im neutralen milieu. *Brennstoff-Chem*., *41*, 334.

[18] Ikan, R., Dorsey, T., Kaplan, I. R. (1990). Characterization of natural and synthetic humic substances (melanoidins) by stable carbon and nitrogen isotope measurements and elemental composition. *Anal. Chim. Acta*, *232*, 11. https://doi.org/10.1016/j.orggeochem.2009.10.002

[19] Matthiessen, A. (1995). Determining the redox capacity of humic substances *Vom Wasser*., *84*, 229–235.

[20] Hoyos-Martinez, P., Merle, J., Labidi, J., Bouhtoury F.C. (2019). Tannins extraction: A key point for their

valorization and cleaner production. *J. Clean. Prod*., *206*, 1138–1155. https://doi.org/10.1016/j.jclepro.2018.09.243

[21] Aires, A. (Ed.). (2019). Tannins: Extraction from Plants. UK, London: IntechOpen.

[22] Machadoa, W., Franchini, J. C., de Fátima Guimarães, M, Filho, J.T. (2020) Spectroscopic characterization of humic and fulvic acids in soil aggregates, Brazil. *Heliyon*, *6*(6), e04078. https://doi.org/10.1016/j.heliyon.2020.e04078

[23] Zhang, Y., Gong, G., Zheng, H., Yuan, X., Xu L. (2020). Synergistic Extraction and Characterization of Fulvic Acid by Microwave and Hydrogen Peroxide–Glacial Acetic Acid to Oxidize Low-Rank Lignite. *ACS Omega*, *5*(12), 6389–6394. https://doi.org/10.1021/acsomega.9b03796

[24] Filcheva, E., Hristova, M., Nikolova, P., Popova, T., Chakalov, K., Savov, V. (2018). Quantitative and qualitative characterisation of humic products with spectral parameters. *J. Soils Sediments*, *18*, 2863–2867. https://doi.org/10.1007/s11368-018-2021-4

[25] Struyk, Z., Sposito, G. (2001). Redox properties of standard humic acids. *Geoderma*, 102, 329–346. https://doi.org/10.1016/S0016-7061(01)00040-4