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Structural-Group Composition and Biological Activity of Humic Acids Obtained from Brown Coals of Russia and Mongolia

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Abstract—The biological activity of humic preparations in the form of sodium and potassium humates was investigated depending on the structural group parameters of humic acids (HAs): the degree of aromaticity (f_a), a hydrophilic–hydrophobic parameter (f_{hh}), and a parameter reflecting the ratio between aromatic and aliphatic fragments in the organic matter of HAs ($f_{ar/al}$). Native and modified HAs isolated from peat and brown coals of Russia and Mongolia, the composition of which was characterized using proximate and ultimate analysis and ^{13}C NMR (CP MAS) spectroscopy, were used as preparations. It was established that modification by destructive alkylation and the subsequent bitumen removal changed the structural-group composition of HAs, increased the degree of aromaticity, and led to an increase in their biological activity.

Keywords: humic acids, structural parameters, biological activity

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INTRODUCTION

Humic substances are a special class of natural compounds formed from the residues of dead organisms with the selection and accumulation of structures resistant to biodegradation. Their annual growth on the planet [1] varies from 0.6 to 2.5 × 10^9 t. They are present in soils, waters, and solid fossil fuels. Low-rank solid fossil fuels contain considerable amounts of humic substances, which are characterized by nonstoichiometric composition, irregularity, structural heterogeneity, and polydispersity [2]. Despite the long history of research, the structure of humic substances is currently considered only hypothetically.

The reason for interest in humic substances is caused by a variety of their specific properties, which open up the possibility of their wide practical applications in many areas. Along with many functions, such as accumulative, transport, and protective ones, humic substances also perform regulatory and physiological functions [1]. The regulatory function primarily includes the formation of soil structure and water-physical properties and, as a consequence, the thermal regime of soil.

The treatment of soil with humates extracted from coal by treating with alkali solutions increases its moisture saturation, which is important for sandy soils whose water-holding capacity increases by a factor of more than 10 under the action of humates. The use of humic preparations as ameliorants is based on the same principles. The humates of potassium, sodium, and ammonium have a significant positive effect on the water-physical and physicochemical properties of the soil. They increase the moisture capacity of light soils (on average, by 30%) facilitating the formation of an agronomically valuable lumpy granular structure, improve the porosity and water permeability of heavy soils preventing the formation of cracks and crusts, regulate ion-exchange reactions between soil and aqueous solutions, and affect the buffer capacity of soils to maintain a natural pH level even with an excessive intake of acidic or alkaline agents. An important task is the restoration of soil fertility and the prevention of desertification.

Humic substances increase plant resistance to adverse environmental factors: excessive doses of mineral fertilizers, high or low temperatures, chemical plant protection products, radiation, etc. [1]. Stimulating effects of humic substances in small doses on the development of plants and on their absorption of nitrogen from mineral fertilizers were noted [3–7]. Large doses of humates (above 0.1%) inhibit the development of plants. The physiological functions include the effects of humic substances on various organisms. With the use of humates in agriculture, an increase in the yields of grain, fodder, and vegetable crops by an average of 10–30%, an increase in seed germination and growth, and an improvement in plant metabolism were noted: the absorption of mineral substances and root formation increased.

Humic acids (HAs) are the most mobile and reactive portion of humic substances; this fraction is soluble in alkalis and insoluble in acids (at $pH < 2$). HAs in water-soluble forms take an active part in the redox processes of cells: they are, on the one hand, a source of activated oxygen and, on the other hand, hydrogen acceptors [8].

Based on experimental studies, Apraksina et al. [9] failed to detect the direct dependence of the biological activity of HAs on the concentration of carboxyl and phenolic hydroxyls in them. On the other hand, Kukharenko [10] supposed that their biological activity is determined by the ability to participate in redox reactions in plant cells and the enhancement of these processes according to the Bach–Paladin–Sainte-Djördi theory. Kukharenko [10] noted that biological activity depends on the concentrations of free radicals, quinoid groups, and phenolic hydroxyls. Less biologically active HAs are characterized by a lower concentration of quinoid groups. The HAs of brown coal and oxidized coal contained 1.8–5.5 mg-equiv/g carboxyl groups, 0–6.0 mg-equiv/g phenolic hydroxyls, and 0.6–4.0 mg-equiv/g quinoid groups [10]. Experiments with the use of humic preparations for cereals (oats and wheat) showed directly proportional relationships between the biological activity of HAs and not only f_a but also other structural group parameters, such as the hydrophilic-hydrophobic parameter f_{hh} and the parameter reflecting the ratio of aromatic and aliphatic fragments in the organic matter of HAs (aromaticity/aliphaticity) $f_{ar/al}$ [11].

Biological activity was also tested with a number of natural and modified humic substances obtained from various sources [12] and evaluated in terms of changes in the root structure using tomato and maize as examples. For the modification, the reactions of hydrolysis, reduction, methyl alkylation, and elimination of alkyl fragments were used. It was found that humic substances oxidized with potassium permanganate and methyl alkylated were most effective. It was hypothesized that the hydrophobic domain of humic substances contains biologically active molecules like auxins. Upon contact with organic acids coming from the root, the hydrophobic shell is broken and the biologically active components are released.

Thus, the use of humic preparations makes it possible to improve the structure of soil and to increase the yield of plants and their resistance to negative environmental factors. Despite the great experience of using humic preparations as plant growth stimulants, there is currently no consensus on the active factor (or a combination of factors) and the mechanism of biological stimulation of plants and soil microorganisms by HAs and relationships with their properties. HAs have common structural principles, but they are different in composition over a wide range depending on the nature of the original substance. In this context, it is necessary to carry out systematic fundamental research aimed at obtaining the structure–property relationships between the elemental and structural-group compositions, structures, and physicochemical characteristics of humic substances and the presence of biological activity in humic substances.

The aim of this work was to determine the physicochemical characteristics of a number of coals and HAs, to select the structural-group composition factors of HAs related to biological activity, and to substantiate the characteristics of HAs for the subsequent selection of raw materials and the production of physiologically active preparations.

EXPERIMENTAL

A number of humus brown coals from the Baganuur (BAG) and Shivee-Ovoo (ShO) deposits (Mongolia), brown coal from the Tisul'skoe deposit in the Kansk-Achinsk Basin (BUTS) and its naturally oxidized form (BUTSO), the Tyul'ganskoe (BUT) and Mayachnoe (BUM) deposits in Southern Ural (Russia), and peat from the Krapivinskoe deposit in Kemerovo oblast (TK) were used in this study. Humic acids were obtained from sodium (HumNa) or potassium (HumK) humates by precipitation from solution upon the addition of hydrochloric acid [13]. A number of humic acids were obtained from coal samples successively alkylated with alcohols and debituminized (HAAs) in accordance with published procedures [14–16].

Table 1. Proximate and ultimate analysis data for the test samples, wt %

Sample	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$(O + N + S)^{daf}$ (by difference)	H/C (atomic)	$(HA)_t^{daf}$
BAG	–	26.3	52.6	67.5	4.4	28.1	0.78	31.2
HumNa BAG	6.9	17.9	–	60.5	3.8	35.7	0.75	52.8
ShO	–	31.6	52.2	70.5	4.4	25.1	0.75	34.0
HumNa ShO	16.2	24.8	–	66.8	4.5	28.7	0.81	58.9
BUTS	8.3	10.3	48.3	61.4	5.0	33.5	0.98	22.1
HA HumK BUTS	5.0	4.0	–	60.8	4.2	35.0	0.83	–
HA HumNa BUTS	3.8	1.9	–	59.8	3.5	36.7	0.70	–
BUTSO	10.0	43.5	80.3	69.3	6.0	24.7	1.04	60.9
HA HumK BUTSO	4.6	17.0	–	46.2	3.2	50.6	0.83	–
HA HumNa BUTSO	10.6	10.9	–	59.7	6.2	34.0	1.25	–
BUT	6.5	23.5	67.3	66.2	7.0	26.8	1.27	39.1
HA HumNa BUT	3.63	7.57	–	62.9	5.82	31.3	1.11	–
BUM	5.3	20.0	63.6	58.6	6.8	34.6	1.39	73.5
HA HumNa BUM	–	–	–	57.3	7.4	35.3	1.55	–
TK	11.2	12.3	72.6	46.8	5.9	47.3	1.51	32.4
HA HumNa TK	–	–	–	45.1	5.5	49.4	1.46	–

W^a is analytical moisture; A^d is ash content on a dry sample basis; V^{daf} is the volatile content; C, H, O, N, and S are carbon, hydrogen, oxygen, nitrogen, and sulfur contents, respectively; $(HA)_t^{daf}$ is the yield of free humic acids; and *daf* is the dry ash-free state of a sample.

Table 2. Concentrations of active oxygen-containing groups in the humic acids of coals from the Baganuur and Shivee-Ovoo deposits

Sample	Acid group concentration, mg-equiv/g			Quinoid groups, mg-equiv/g
	carboxyl groups	phenolic hydroxyls	total	
HumNa BAG	4.33	3.42	7.75	2.75
HumNa ShO	5.13	3.52	8.65	3.17

The test samples of sodium and potassium humates were produced from brown coal and its naturally oxidized form. The starting lignites and humate samples were characterized by proximate, ultimate, and functional-group analyses (Tables 1 and 2).

Barite and acetate methods were used to determine the total acidic (carboxyl and hydroxyl) groups and the concentration of carboxyl groups, respectively [17]. The concentration of hydroxyl groups was determined as a difference between the total acidic groups and carboxyl groups.

The concentration of quinoid groups was determined by the reduction of them with tin(II) chloride in an alkaline solution with the subsequent titration of its excess with a solution of potassium dichromate [18]. The concentrations of functional groups were calculated with consideration for the results of blank experiments.

To establish structure–property relationships, tests were performed to determine the biological activity of HAs in the form of potassium and sodium humates (concentration, 0.02%) obtained from both the initial coal and peat samples and the samples modified by sequential alkylation and debitumination.

In the experiments, Novosibirsk 89 and Iren wheat varieties and a Smak radish variety were used in accordance with published procedures [19, 20] and the State Standards GOST 12038-84 and GOST 54221-2010 [21, 22]. The seeds were germinated at a constant temperature of 20°C in the dark in special germinator trays between the layers of moistened filter paper. The biological activity of HAs and HAAs was determined based on an increase in the length of wheat roots Δ_1 (excess over control, %) and the value of phytoactivity index (PI) (% of control, Δ_2) taking into account seed germination energy (GE), root length (RL), and sprout height (SH). The value of PI is a generalized index calculated as the average value of the sum of GE, RL, and SH values expressed in fractions of a unit:

$$PI = \frac{(GE + RL + SH)}{3 \times 100},$$

Table 3. Integral intensities of spectral regions in the ^{13}C NMR spectra (%) and the structural parameters of coal and humic acid samples

Sample	Chemical shift, ppm							Structural parameter		
	220-187	187-165	165-145	145-108	108-90	90-48	48-5	f_a	$f_{h/h}$	$f_{ar/al}$
	C=O	COOH(*R*)	C_{Ar-OH}	C_{Ar}	$C_{O-Alk-O}$	C_{Alk-O}	C_{Alk}			
BUTS	4.4	4.7	4.2	19.1	3.5	7.5	55.6	23.3	0.3	0.3
HA HumK	4.4	6.1	5.0	15.1	4.2	8.0	55.2	20.1	0.4	0.3
HA HumNa	4.4	7.3	5.4	17.9	3.6	10.8	50.7	23.3	0.5	0.4
BUTSO	2.6	6.0	8.9	31.9	5.4	12.7	30.3	40.8	0.6	0.8
HA HumK	3.8	6.7	9.5	33.1	6.3	14.0	25.4	42.6	0.7	0.9
HA HumNa	3.5	7.4	8.2	31.7	6.3	14.8	26.8	39.9	0.7	0.8
BUT	4.2	5. 8	3.6	25.1	19.6		41.6	28.7	0.5	0.5
HA HumNa	4.3	7.9	6.8	22.5	4.9	16.3	36.5	29.3	0.7	0.5
BUM	4.3	4.1	4.5	28.3	6.1	12.5	40.2	32.8	0.5	0.6
HA HumNa	4.7	4.9	3.7	26.1	5.9	13.7	41.1	29.8	0.5	0.5
TK	2.7	8.2	4.8	11.4	55.7		17.2	16.2	2.5	0.2
HA HumNa	3.4	8.0	7.0	15.8	9.2	38.5	18.1	22.8	1.9	0.3

where GE, DK, and SH are the average values of the three trays measured on the fifth day after the start of the experiment.

The relative error in all of the experiments was 3–5% at the significance value $\alpha = 0.05$.

The high-resolution solid state ^{13}C NMR spectra were measured on a Bruker AVANCE III 300 WB instrument at 75 MHz using a standard cross-polarization and magic angle spinning (CP MAS) procedure.

RESULTS AND DISCUSSION

Based on an analysis of published data [10, 12, 23], we selected the following three parameters calculated from CP MAS ^{13}C NMR-spectroscopic data to detect a relationship of the structural-group composition of HAs with their biological activity:

(1) the degree of aromaticity

$$f_a = C_{Ar-OH} + C_{Ar};$$

(2) the hydrophilic–hydrophobic parameter

$$f_{h/h} = (C{=}O + COOH(R) + C_{Ar-OH} + C_{O-Alk-O} + C_{Alk-O})/(C_{Ar} + C_{alk});$$

(3) the aromaticity/aliphaticity

$$f_{ar/al} = (C_{Ar-OH} + C_{Ar})/(C_{O-Alk-O} + C_{Alk-O} + C_{alk}).$$

Table 3 summarizes the integral intensities of the spectral regions of coals and humic acids and the structural parameters of the test samples calculated from ^{13}C NMR spectra. The structural parameter f_a reflects the concentration of all aromatic structural groups, including phenolic and quinoid groups.

The destructive O-alkylation of solid fossil fuels (SFFs) with alcohols depolymerizes the organic matter of coal and, on the one hand, increases the yield of predominantly aliphatic bitumoids and , on the other hand, increases the aromaticity of a debituminized test sample [14–16, 24]. Correspondingly, the humic acids extracted from this material are more aromatic than those extracted from the starting SFFs. Thus, there are prerequisites that these HAs should have increased biological activity. Table 4 summarizes data on the structural-group composition of humic acid samples obtained from the initial coals and peat after destructive alkylation and debitumination (HAAs), with a significant variation in the values of f_a. Indeed, the data of Table 4 illustrate the increase in the degree of aromaticity of HAAs, as compared with those of the corresponding HAs for the entire test humic SFFs. Thus, f_a is 23.3 for the HAs extracted from brown coal from the Tisul'skoe deposit. The HAAs extracted from the same coal but previously alkylated with butanol and then debituminized have a f_a value of 31.9. At the same time, a minimal increase in the degree of aromaticity was observed for humic acids isolated from the Krapivinskoe peat: $f_a = 22.6$ for HAs and $f_a = 22.8$ for HAAs.

It was found that the biological activity of HAs, assessed by an increase in the crop, is directly proportional to the selected structural parameters. Figure 1 shows the dependences that indicate that an increase in the degree of aromaticity and in the hydrophilicity

Table 4. Integral intensities of the spectral regions of HA and HAA samples according to ^{13}C NMR-spectroscopic data, %

HA sample	Chemical shift, ppm							
	220–187 C=O	187–165 COOH(*R*)	165–145 $C_{Ar–O}$	145–108 C_{Ar}	108–90 $C_{O–Alk–O}$	90–48 $C_{Alk–O}$	48–5 C_{Alk}	f_a
Brown coal from the Tisul’skoe deposit								
HA	4.4	7.3	5.4	17.9	3.6	10.8	50.7	23.3
HAA	1.3	6.3	6.9	25.0	4.3	10.6	45.6	31.9
Brown coal from the Tisul’skoe deposit naturally oxidized in coalseam								
HA	3.5	7.4	8.2	32.7	6.3	14.8	26.8	40.9
HAA	1.6	5.3	10.2	32.9	5.1	11.0	33.8	43.1
Brown coal from the Tyul’ganskoe deposit								
HA	4.3	7.9	6.8	22.5	4.9	16.3	36.5	29.3
HAA	3.8	8.6	8.5	28.2	5.8	16.9	27.9	36.7
Brown coal from the Mayachnoe deposit								
HA	4.7	4.9	3.7	26.1	5.9	13.7	41.1	29.8
HAA	4.1	8.2	7.4	34.8	7.5	16.5	20.9	42.2
Peat from the Krapivinskoe deposit								
HA	3.4	7.9	6.7	15.9	8.6	35.4	22.2	22.6
HAA	3.4	8.0	7.0	15.8	9.2	38.5	18.1	22.8

of HAs leads to an increase in the crop of Novosibirskaya 89 wheat variety used as an example.

Figures 2 and 3 show the results of experiments with wheat and radish seeds, namely, the dependence of the excess length of the roots of wheat seeds over that in the control experiment Δ_1 and the phytoactivity index Δ_2 of radish seeds on the degree of aromaticity f_a of the humic acids used.

In Figs. 2 and 3, it can be seen that the biological activity of the HAs and HAAs of brown coals and peat, estimated using the parameters Δ_1 and Δ_2 in relation to the tested crops (wheat and radish) is also directly proportional to a structural parameter—the degree of aromaticity f_a. In terms of the degree of aromaticity, the humic acids isolated from prealkylated and debituminized coals are similar to the highly active natural humic substances of naturally oxidized brown coals (Table 4), and they exhibit enhanced biological activity, as compared with that of HAs isolated from the initial coals. At the same time, the sequential alkylation and debitumination of Krapivinskoe peat leads to

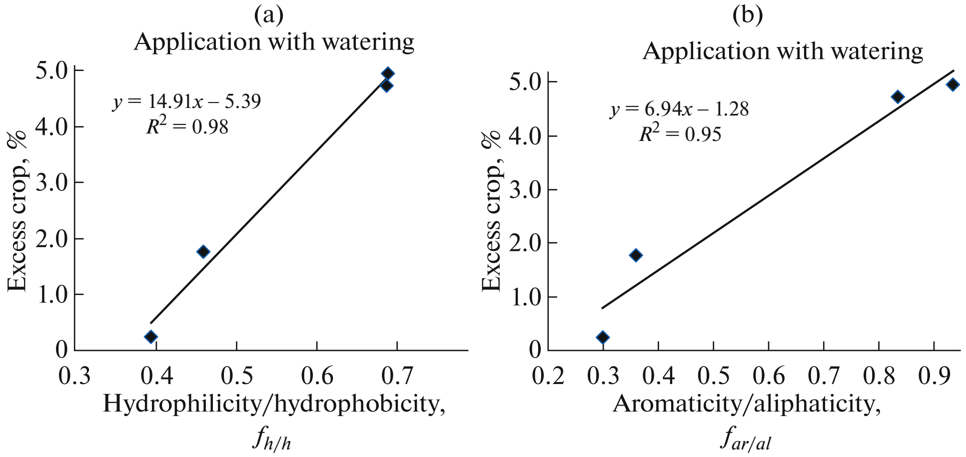

Fig. 1. Dependences of the crop of Novosibirskaya 89 wheat on (a) the hydrophilicity/hydrophobicity and (b) aromaticity/aliphaticity parameters of the HA samples.

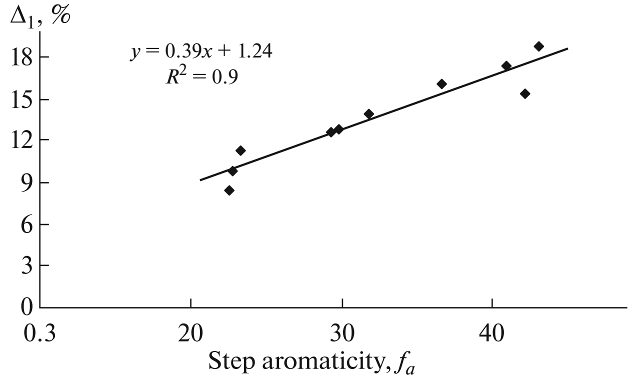

Fig. 2. Dependence of the length of wheat roots (excess above the control Δ_1,%) on the degree of aromaticity f_a of HA samples.

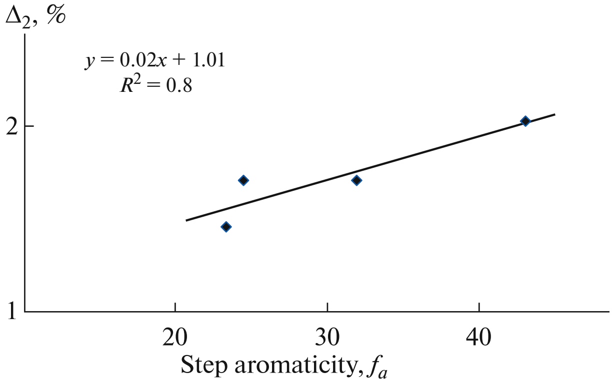

Fig. 3. Dependence of the phytoactivity index of radish seeds Δ_2 on the degree of aromaticity f_a of HA samples.

a minimal increase in the degree of aromaticity of HAs (Table 4), which exhibit the lowest biological activity.

CONCLUSIONS

The starting coals and the HAs obtained from them have different structural-group compositions. The naturally oxidized form of coal and the HAs obtained from it have a more aromatic character and a higher concentration of phenolic hydroxyls. It was established that the biological activity of HAs is directly proportional to the following structural parameters: the degree of aromaticity f_a, the hydrophilic–hydrophobic parameter f_{hh}, and the parameter $f_{ar/al}$, which reflects a ratio between the aromatic and aliphatic fragments of the organic matter of HAs (aromaticity/aliphaticity).

It was found that the sequential alkylation and debitumination of humus brown coals leads to an increase in the concentration of aromatic structures in the HAs obtained from the modified sources. These humic acids are similar in composition to the highly active natural humic substances of naturally oxidized brown coals, and they exhibit increased biological activity. The sequential alkylation and debitumination of the Krapivinskoe peat leads to a minimal increase in the degree of aromaticity f_a and biological activity.

The experimental results will be helpful for choosing a raw materials base of brown coals for the production of active HAs. For the conditions of Mongolia, humus brown coals from the Baganuur and Shivee-Ovoo deposits in Mongolia are promising coals, which are characterized by sufficiently high concentrations of phenolic and quinoid functional groups.

In addition, the target-oriented change in the functional-group composition of humic preparations with the use of the preliminary alkylation and debitumination of a primary source is promising in order to obtain substances with a specified structural-group composition and a high concentration of aromatic fragments. The results obtained can be used to predict the biological activity of HAs and to manufacture highly effective preparations based on them.

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