Bioactive properties of iron-nitrolignosulfonate complexes with a low content of ballast ions

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Yu G Khabarov[1], V A Veshnyakov[1], N Yu Kuzyakov[1] and N A Onokhina[2]

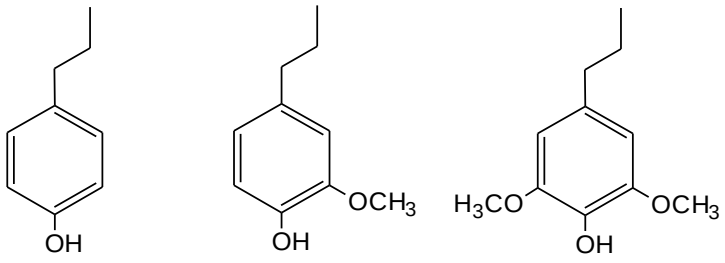
[1] Higher School of Natural Sciences and Technologies, Northern (Arctic) Federal University, Severnaya Dvina Emb. 17, Arkhangelsk, Russian Federation
[2] Department of General and Bioorganic Chemistry, Northern State Medical University, Troitskiy Ave., 51, Arkhangelsk, Russian Federation

E-mail: khabarov.yu@mail.ru

Abstract. The results of vegetation studies of the biological activity of iron-nitrolignosulfonate complexes with a low content of ballast ions are presented. It has been established that with root feeding of annual lupine growing on carbonate soil no appearances of chlorosis are observed and the plants reach the indicators of plants grown on normal soil. The iron-nitrolignosulfonate complex with a low content of ballast ions can be used in greenhouses including in the conditions of the Far North.

1. Introduction

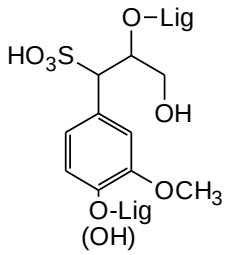
Native lignins are aromatic plant biopolymers, which are formed during a complex chain of biochemical and chemical reactions. Lignin macromolecules are constructed from *p*-hydroxyphenyl (a), guaiacyl (b), syringyl (c) phenylpropane structural units linked to each other by ether and/or carbon-carbon bonds.



a b c

Guaiacyl structures predominate in soft wood lignins. Lignins are characterized by a rather large set of functional groups: alcohol, phenolic, methoxy, carbonyl, carboxyl, C=C-bonds.

Lignosulfonic acids (LSA) and their salts (LS) are one of the types of technical lignins, which are formed during sulfite pulping, which is carried out at different pH of cooking acid. When lignin is sulfonated, sulfo groups appear in its structure in the propane chain:



The presence of sulfo groups leads to the appearance of properties that are not characteristic of other types of lignins. Lignosulfonic acids are strong acids soluble in aqueous solutions in a wide range of pH and capable of forming complexes with metal cations. Lignosulfonates are a versatile product with a wide range of consumer properties. Currently, a wide range of their direct use has been proposed in various industries. The main directions of use of lignosulfonates are given in table 1.

Table 1. Directions of use of lignosulfonates.

Branch	Purpose
Metal industry	casting binders for molding and core mixtures, non-stick pastes, paints, a binder additive that provides the necessary strength of refractory products, a means for pelletizing metallurgical raw materials, a binder for sintering metallurgical mixture [1], [2], [3], [4]
Cement industry	the thinner of the raw sludge to reduce its moisture and increase fluidity in the wet method of cement production [5], [6], [7]
Construction industry	preparation of concrete and reinforced concrete products in order to improve their plastic properties and improve water resistance and frost resistance, production of bricks, ceramic products [8], [9]
Geology, mining	reagents for drilling in the oil, gas industry and geology for the production of modified products, preparation of drilling fluids [10], [11], [12]
Light industry	production of synthetic tanning materials, production of artificial leather, porcelain products [13], [14], [15]
Chemical industry	production of chemical plant protection products and fertilizers [16], [17], [18]
Chemical and Forestry Industry	production of plywood, chipboard and fibreboard [19], [20], [21]
Forestry and Agriculture	production of micro- and macro-fertilizers, stimulators of biological processes [22], [23], [24], [25], [26]

The concept of biorefining involves the production of bioethanol, biodiesel, monomers for the production of polymers, plastics, films, carbon fibers in addition to cellulose and cardboard from plant biomass [27]. Modification of lignosulfonic acids is the main way of expanding the scope of their use [28]. One of the promising areas for the use of lignosulfonates is agriculture and forestry. Microfertilizers based on lignosulfonic acids are complexes with cations of biogenic metals [1]. The most important biogenic trace element is iron, since its ions are consumed by plants in much larger quantities than others. The production of iron derivatives of lignosulfonic acids can be carried out in various ways. The first work in this direction was the Bennett method [29], which was improved by us [30]. According to this method, an iron-lignosulfonate complex is obtained by mixing an alkaline solution of lignosulfonic acid with a salt of iron(III) in the presence of a sulfite anion that results in the formation of a water-soluble complex containing up to 28% of iron in a stable form in a wide pH

range. Nitrosation [31] allows to significantly increase the capacity of modified lignosulfonic acids to cations of biogenic metals. The preparation of a similar product can also be carried out by treating a solution of an lignosulfonic acids with nitric acid in the presence of a ferrous salt [32]. All these methods make it possible to obtain products, the use of which is economically preferable compared to the use of synthetic iron complexonates. However, the complexes obtained by the above methods necessarily contain ballast ions that are not absorbed by plants and in some cases have a negative effect when they are introduced into the soil. A product that does not contain ballast ions can be obtained by anodic dissolution of iron.

Attempts to obtain an iron-lignosulfonate complex by dissolving metallic iron in a solution of lignosulfonates or lignosulfonic acids did not succeed, because the rate of dissolution of iron is too low. The synthesis of the iron complex should be carried out in a mixture of lignosulfonic acids and nitric acid in order to increase the dissolution rate of metallic iron. The resulting product will contain only nitrate ions with nutritional properties for plants, since the addition of other anions (sulfates, chlorides, etc.) reduces the quality of the product.

Therefore, the aim of the work was to assess the biological activity of the iron-nitrolignosulfonate complex when growing plants on carbonate soils.

2. Materials and methods

2.1. Reagents and methods

In the experiments, a solution of technical lignosulfonates with a concentration of 48 g/L was used; nitric acid (analytical grade, 63%), gray iron shavings (fraction residue on a sieve of 0.5 mm), sulfuric acid (analytical grade, 94%), sulfosalicylic acid (analytical grade), ammonia solution (analytical grade, 23%).

2.2. Synthesis of iron-nitrolignosulfonate complex

The synthesis was carried out by adding to a 100 mL solution of lignosulfonates a predetermined volume of a solution of HNO_3 (0.5 g HNO_3/g LS) and 3 g of iron shavings. The reaction mixture was stirred for 24 h at room temperature, followed by filtration. In the filtrates, the iron content was determined by the photometric method [33].

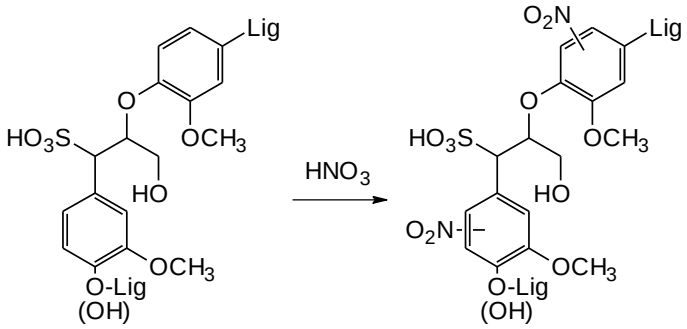
2.3. Determination of chlorophyll content

Green mass of plants was crushed with scissors. A portion of the green mass of 500 mg was ground in a mortar with a small amount of sand and $CaCO_3$ to a homogeneous mass. To extract chlorophyll, 3-4 mL of acetone was added and rubbing continued until the contents of the mortar were stained in an intense green color. The acetone extract was decanted onto a dry paper filter and filtered into a 25 ml volumetric flask. Extraction was carried out several times until the green color disappeared. The volume of the extract was adjusted to 25 mL with acetone. The absorbance of the solution obtained was measured on a photometer at 670 nm [34]. Humidity was determined by drying 4-5 g of green mass at 100°C.

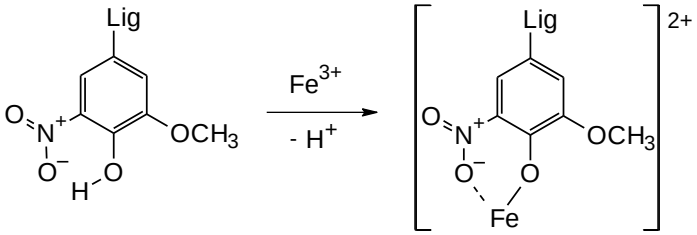
3. Results and discussions

The lack of iron during the growing season of plants is showed in the form of a disease such as iron chlorosis. It is due to the fact that iron is inaccessible to plants growing on carbonate soils. Chlorosis leads to large crop losses and therefore it can be attributed to world problems, since in the world more than 30% of agricultural land is carbonate [35]. Under natural conditions, the supply of plants with biogenic metals is determined by their availability. Soils often contain a sufficiently large amount of iron compounds in insoluble form, so they are not available for plants and this leads to chlorosis. The problem of chlorosis is characteristic not only of outdoor cultivation, chlorosis is also found in greenhouses [36]. This is due to the peculiarity of biochemical processes in the soil, which result in the release of ammonia that reduces the solubility and availability of iron cations by increasing the pH.

During the synthesis of the iron-nitrolignosulfonate complex, in addition to the dissolution of iron, the processes of nitration, oxidation and partial depolymerization of lignosulfonic acids, as well as complexation with iron cations, occur simultaneously. The quantitative ratio of these processes is determined by the conditions of synthesis (temperature, consumption of nitric acid and the concentration of lignosulfonic acids). In nitration by the electrophilic mechanism, the nitro group depending on the presence of a free or esterified phenolic OH group replaces hydrogen atom in the 5 or 6 position of the aromatic ring:



The most favourable conditions for complexation are realized when phenylpropane structural fragments have a free phenolic hydroxyl group. In this case, the formation of the complex due to chelation:



To study the biological activity of iron-nitrolignosulfonate complexes with a reduced content of ballast ions obtained by the nitric acid method, vegetation studies were carried out. The object of the study is annual lupine (*Lupinus luteus*). The chlorosis soil was produced artificially. To this end, healthy soil was mixed with 20% (by weight) calcium carbonate. After root treatments with an iron-containing preparation, the chlorophyll content, the height of the plants and their mass at the end of the experiment were determined.

The first treatment with an iron-containing drug was carried out 20 days after planting. As can be seen from Figure 1, the difference in chlorophyll content between healthy and chlorosis soils are 20% and reaches 32% over time. In this case, after the first treatment with an iron-containing preparation, this difference is reduced to 10% and 4% after the second treatment.

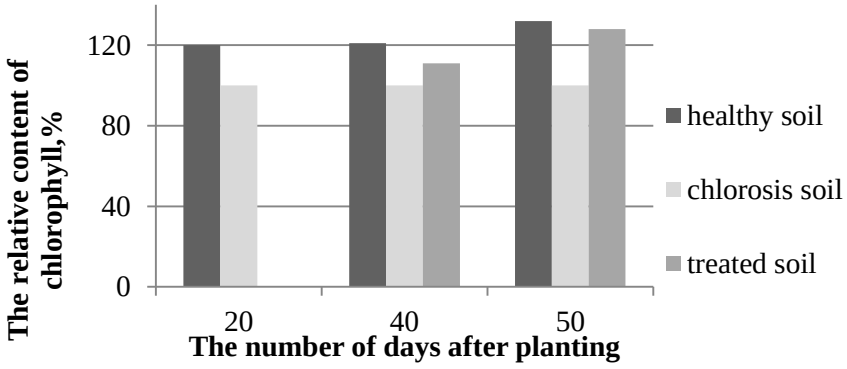


Figure 1. Changes in the relative content of chlorophyll.

Figure 2 shows the results of plant growth during the vegetative studies. As can be seen from the table, the difference in plant height is observed only at the last stage of the process. At the same time, 40 days after planting, the plants in growth are almost the same.

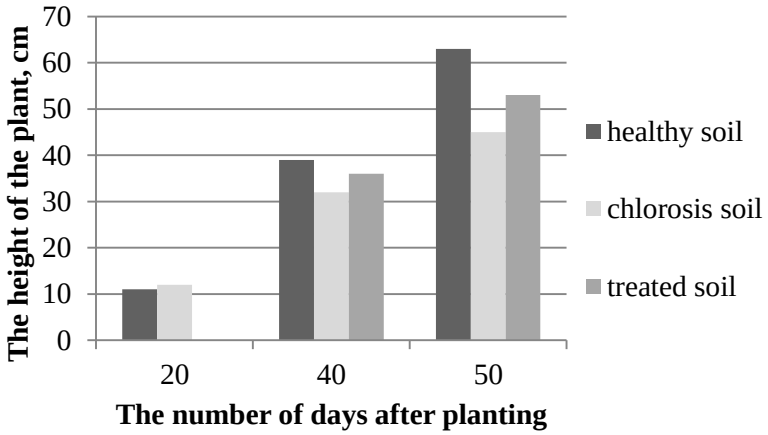


Figure 2. Height of ground part of lupine.

At the end of the growing season, the difference in height of plants planted on healthy soil and chlorosis soil is 39%, while after treatment, this difference was reduced to 17%. The green mass of plants after treatment with iron-containing preparations increased by 3 times compared with the control (chlorosis soil) and almost reached the mass of healthy plants (Table 2).

Table 2. Characteristics of lupine at the end of vegetation studies.

Soil type	Height of lupine		Weight of lupine	
	cm	%	g	%
chlorosis soil (control)	45	100	7.9	100
healthy soil (control)	63	139	24.9	315
Fe-NLS treated chlorosis soil	53	117	23.8	301

4. Conclusions

Thus, it has been established that with root feeding of annual lupine plants, which grow on carbonate soil, no manifestations of chlorosis are observed and the plants reach the values of plants grown on normal soil. Iron-nitrolignosulfonate complexes with a reduced content of ballast ions can be used in greenhouses, including in the conditions of the Far North.

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