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THE COMPOSITION OF BIOLOGICALLY ACTIVE COMPOUNDS IN PEAT FROM DIFFERENT CLIMATIC ZONES OF WESTERN SIBERIA

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Abstract. The paper studies the individual composition of n-alkanes, polycycloaromatic hydrocarbons, steroids, bi-, tri-, and pentacyclic terpenoids of two peat deposits of rich fen Kirek located in Western Siberia. Considering the individual n-alkanes concentrations, some indexes were calculated to estimate the humidity during peat formation. It was shown that the pH of peat medium primarily affects steroids, tri- and pentacyclic terpenoids transformations.

1 Introduction

Peat is an easily available natural material and a source of biologically active substances widely used, not only in agriculture but also in human and animal medicine. [1] The literature refers to a wide spectrum of beneficial effects of peat and various peat preparations on organisms: stimulating effects on digestion, growth, and the immune system of the animals [2].

One of the most important biologically active substances are steroids, terpenoids and tocopherols. Their composition in peat depends on the impact of different peat-forming plant groups to peat formation and gives information and on processes which take place during the peat decomposition.

Steroids are hormones that play a critical role in endocrine systems which control the regulation of metabolic processes. These hormones stimulate biological responses in a wide range of tissues to influence such processes as sexual differentiation, reproductive physiology, and maintenance of salt balance and sugar metabolism. They have also been implicated in responses to stress and behavior [3].

Terpenoids serve as secondary metabolites of mixed biosynthesis, like alkaloids, flavonoids, oligosaccharides etc. There is a growing interest in natural triterpenoids caused as much by the scientific aspects of structural analysis of these compounds, as by the fact of their wide spectrum of biological activities; they are bactericidal, fungicidal, antiviral, cytotoxic, analgetic, anticancer, cardiovascular, antiallergic and so on [4].

Tocopherols (vitamin E) is known for its antioxidant, immune-enhancing, anti-inflammatory, and antiplatelet aggregation effects. Vitamin E is used clinically to prevent cardiovascular disease, cancer, cataracts, complications of diabetes, and to improve immune function. [5]

Optimal choice of peat deposits for the production of biologically active preparations supposes the detailed comparative analysis of peat properties from different deposits.

2 Experimental

The raised bog Sredne-Vasuganskoye is located in the middle taiga subzone of Western Siberia. The peat deposit (4.0 m in depth) is a typical riam with low vegetation and is formed by sphagnum and cotton grass-sphagnum peat. The bog was formed as a result of paludification. Current average annual air temperature is -1.7°C.

The raised bog Temnoye is located in the southern taiga subzone of Western Siberia on the lake shore. The peat deposit (6.5 m in depth) is riam with growthy vegetation. The lower part of the deposit was formed by moss-bog-

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bean and typha-moss-equisetum peat, in higher layers they are replaced by peat, formed from scheuchzeria, then cotton grass and sphagnum; the top of the reservoir is formed by sphagnum peat. The bog was formed as a result of terrestrialization The average annual temperature of the raised bog Temnoye is +0.6°C.

Peat macrofossil composition was determined by microscopic method, decomposition degree – by centrifugation. All peat samples were dried and powdered before the analysis. Bitumens were concentrated by extraction with 7% methanol in chloroform at 60°C. Group and individual composition of tocopherols, steroids and terpenoids in peat samples were determined by gas chromatography-mass spectrometry (GC-MS). Thermo Scientific gas chromatograph with mass detector fused silica capillary column (30 m length, 0.25 mm bore, 0.25 µm film thickness) was used for biomarker molecule analysis. The operating conditions were: temperature was held at 80°C for 2 min, ramped to 300°C at 4°C/min, with He as carrier gas. The ionization energy of the mass spectrometer was set to 70 eV, with a scanning range from 50 to 550 amu. The compounds were identified by comparison of their mass spectra with those of reference compounds.

3 Results and discussion

Peat of the bog Sredne-Vasuganskoye is characterized by a higher content of studied lipid components in comparison to peat of the bog Temnoye. The average total lipid content in peat of the bog Sredne-Vasuganskoye is 179.3 mcg/g, in peat of the bog Temnoye – 38.6 mcg/g. This may be explained by the differences in ambient temperature during peat formation. Lower temperature along the bog Sredne-Vasuganskoye led to reduced microbiological activity and, as a consequence, inhibited the transformation of organic compounds presented in peat-forming plants.

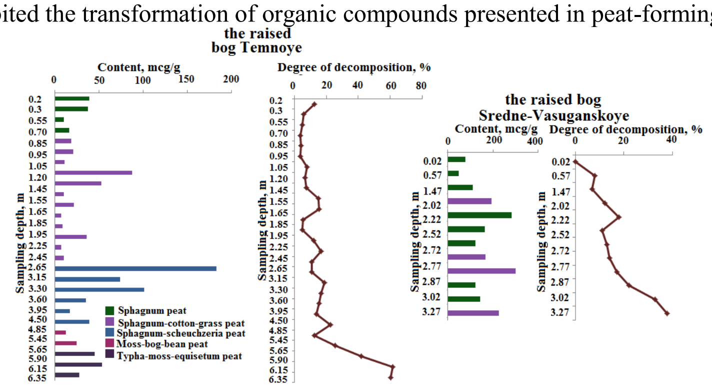

Figure 1. The total content of terpenoids, steroids and tocopherols in peat of bogs Temnoye and Sredne-Vasuganskoye.

The maximum total content of biologically-active compounds in the peat of bog Temnoye was recorded in fibric peat with increased content of herbaceous plants (Scheuchzeria, cotton grass and sedge) and reduced content of sphagnum moss or wood residues in the botanical composition (Figure 1). This may be due to the different total lipid content in peat-forming plants: sphagnum and sedge are characterized by low content of lipids (11.4 and 6.4 mcg/g, respectively), in cotton grass it is slightly higher (13.2 mcg/g). The total lipid content in Scheuchzeria is maximal among the herbaceous plants (41.4 mcg/g).

The highest total lipid concentrations in peat of the bog Sredne-Vasuganskoye was recorded in cotton grass-sphagnum peat and in sphagnum peat (2.22 m) with high proportion of cotton grass in the botanical composition.

The degree of decomposition of bog Sredne-Vasuganskoye peat grows from 0 to 38% alongside with depth increase. The same indicator for the bog Temnoye peat varies slightly with depth increase. The typha-moss-equisetum peat from the lowest part of the deposit is characterized by the maximum degree of decomposition.

The low values of peat decomposition degrees shows that peat was formed in moisture conditions. The raised humidity leads to increased proportion of grass in the bog plant community. It reduces the decomposition of organic matter, which helps to preserve high concentrations of lipids in peat.

The upper layer of sphagnum peat of the bog Temnoye is characterised by lower content of biologically-active substances in comparison to bottom layers and peat of the bog Sredne-Vasuganskoye. This is most likely due to the removal of peat decomposition products, diluvial water coming from the surrounding upland through the bog into a lake and bog water during the periods of climate aridity.

The main sources of geological sesquiterpenoids are terrestrial plants, these compounds were found in resins and essential oils [7]. The isomers of cadinene prevail among sesquiterpenoids in most peat samples of the bog Temnoye, as well as in the major peat-forming plants. The majority of peat samples of the bog Sredne-Vasuganskoye has the maximum content of calacorene isomers, which dominate in Sphagnum fuscum.

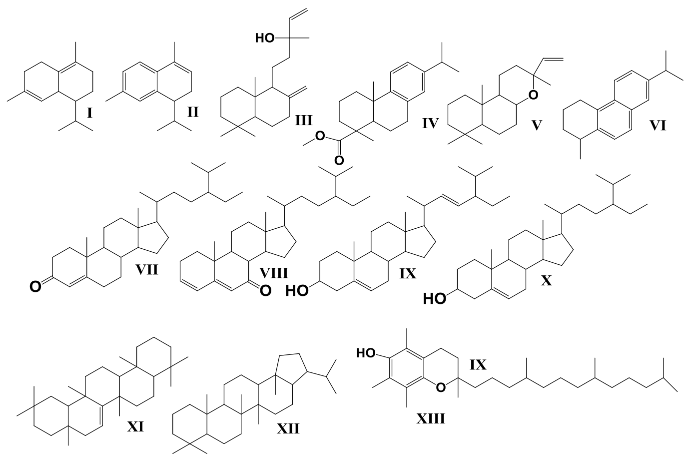

Figure 2. The structures of biologically-active compounds, dominating in peat: I- δ-cadinene, II-calacorene, III-labd-8,14-diene-13-ol, IV-methyldehydroabietate, V-manoyloxide, VI-10,18-bisnorabietapentaene, VII-stigmast-4-en-3-on, VIII- stigmast-3,5-dien-7-on, IX-stigmasterol, X-sitosterol, XI-D-friedoolean-14-ene, XII-homohopane C31, XIII-α-tocopherole.

The origin of diterpenoids may be associated with the transformation of abietic acid, which is widespread in higher plants resin [8]. Manoyloxide prevails among diterpenoids in herbaceous plants as well as in most peat samples of the bog Temnoye. In some sphagnum peat interlayers dominates methyldehydroabietate – the main representative of sphagnum moss diterpenoids. The high content of retene dominating in Scheuchzeria was found in one of the samples of sphagnum-scheuchzeria peat. Manool (labda-8(20),14-dien-3-ol) is present in herbaceous plants and prevails among diterpenoids in the upper part of the bog Sredne-Vasuganskoye deposit. At the depth exceeding 2 m 10,18-bisnorabieta-5,7,9(10),11,13-pentane begins to dominate (Fig. 2). This compound is absent in possible peat-forming plants. At the same time it is the possible product of retene partial hydrogenation.

The bog Temnoye peat differs from the bog Sredne-Vasuganskoye peat in significant prevalence of oxygen-containing compounds among diterpenoids. It can be explained by the intensive microflora development under more genial conditions of a southern taiga. In peat of the bog Sredne-Vasuganskoye such predominance was recorded only at the top of the deposit. At the depth below 2.20 m hydrocarbons begin to dominate. The proportion of diterpenoid hydrocarbons in all peat samples grows alongside with depth increase.

Geosteroids are commonly found in sediment organic matter. They take their origin from sterines, which are included in the structure of the eukaryotes cell walls [9]. Unsaturated stigmastane derivatives mainly with the keto-groups are typical for Sphagnum fuscum and cotton grass. Such structures prevail among steroids in the upper part of the bog Temnoye peat deposit in sphagnum and sphagnum-cotton grass peat (Fig. 2).

Saturated stigmastane derivatives with keto-group (stigmastane-3-one) dominate in the lower part of the bog Temnoye deposit in sphagnum-sheuchzeria peat and in peat with a predominance of green moss, typha, bog-bean and equisetum residues in botanical composition. Such structures can be the products of more deep diagenetic conversion of peat. Sitosterol prevails among steroids in Sredne-Vasuganskoye peat deposit. It can be formed as a result of partial hydrogenation of stigmasterol, which dominates in the near-surface peat layer.

A slight increase in the relative content of alcohol derivatives of steroids was found for sphagnum and sphagnum-cotton grass peat. It may indicate an active biodegradation processes.

The peculiarities in triterpenoid composition are connected, apparently, with the difference in plant associations of bogs located in middle and southern taiga. D-friedoolean-14-ene dominates among triterpenoids in most peat samples of the bog Sredne-Vasuganskoye, as well as in sphagnum and sphagnum-cotton grass peat of the bog Temnoye.

The lower part of the bog Temnoye peat deposit differs from the overlying layers and from peat of the bog Sredne-Vasuganskoye in prevalence of hopane derivatives among triterpenoids. This may indicate high degree of processing peat by aerobic bacterial. It is generally thought that the main source of hopane derivatives is a pentacyclic alcohol bakteriotetrol (C_{35}), which is the part of the lipid cell membrane of aerobic bacteria [10].

Among tocopherols in all peat samples predominates α-form, the content of γ-form is increased, α-tocopherol acetate was not detected. Maximum tocopherols concentrations in the bog Sredne-Vasuganskoye peat was detected in one of the cotton grass peat samples and in complex sphagnum peat, as well as sphagnum and sphagnum-cotton peat of the bog Temnoye.

4 Conclusion

The studied peat samples of the bog Temnoye are characterized by a predominance of cadinene isomers among sesquiterpenoids, manoyloxide and methyldehydroabietate among diterpenoids, stigmastane derivatives with keto-group – among steroids. Peat of the bog Sredne-Vasuganskoye differs in maximum content of calacorene among sesquiterpenoids, 10,18-bisnorabieta-5,7,9(10),11,13-pentane among diterpenoids and sitosterol among steroids. Both deposits are characterized by the dominance of D-friedoolean-14-ene among pentacyclic terpenoids and alpha-form among tocopherols.

The total content of biologically-active compounds is higher in peat, which was formed in the lower-temperature conditions by slowing down the decomposition processes. This peat is also subjected to less intense microbial oxidation. In addition, changes in the content of the studied compounds along the peat deposits are largely due to the diversity of peat botanical composition. The maximum total content of bioactive compounds was observed in peat with a high content of herbaceous plants such as cotton grass and Scheuchzeria and low content of sphagnum moss in the botanical composition. Thus, it is preferable to use for the production of biologically active peat formed in sufficiently cool conditions predominantly by herbaceous plants.

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