

One of the methods of ensuring the durability of dry wood during operation is its thermal modification, which inhibits the life processes of the fungus of the Ceratostomaceae family and leads to a change in its structure and properties. Therefore, the object of research was thermally modified dry pine wood affected by a fungus of the Ceratostomaceae family. Physicochemical studies of changes in the structure of thermally modified dry pine wood showed that the samples have absorption spectra that are characterized by fluctuations of the glucopyranose ring of cellulose and are an indicator of the beginning of destructive processes. At the same time, the data of thermogravimetric analysis show the processes of water loss and decomposition of hemicellulose, cellulose, and lignin, and burning of coke residue. Bending and compressive strength of thermally modified dry pine wood shows that as the wood dries, the strength limit decreases depending on the degree of fungus damage. Namely, with an area of biological damage within 10 %, the strength limit is reduced by more than 1.2 times when modified at 200 °C/3 hours, by more than 1.9 times at 200 °C/6 hours. With an increase in the degree of fungal damage to 30÷50 %, the strength limit decreases by more than 1.6 times when modified at 200 °C/3 hours, by more than 2.1 at 200 °C/6 hours. And when affected by a fungus in the range of 80÷100 %, the wood becomes softer, more plastic, while the bending strength is reduced by 1.7 times, and the compressive strength by 1.16 times. Thermal modification of dry pine wood at 200 °C for 3 hours reduces the level of water absorption by more than 1.5 times, and for 6 hours – by more than 1.7 times. The practical importance is that the results of determining changes in the structure and properties of thermally modified dry pine wood make it possible to establish the scope and conditions of its application

**Keywords:** dry pine wood, thermal modification, change in wood structure, strength limit

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# ESTABLISHMENT OF PATTERNS IN THE THERMAL MODIFICATION OF DRY PINE WOOD

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## 1. Introduction

Wood is one of the best building materials. The multifaceted use of wood is based on a combination of valuable

properties, in particular, wood appears as a strong and at the same time light material, which has high heat and sound insulation properties. At the same time, it dampens vibrations and oscillations very well, is easily processed with a cutting

tool, can be glued, and held fastening in its structure. However, today, under the influence of climatic changes, pathological processes in conifer plantations intensified, which led to their drying up. That led to an increase in the volume of “dry” wood, the main feature of which is damage by fungi.

But dry wood also has a number of advantages compared to freshly sawn wood, in particular, it does not cause settling and cracking since these processes have already taken place in it during drying. It limits the use of paint and varnish materials, which makes the product environmentally friendly and much lighter than freshly sawn wood, which saves less physical and material resources.

Considering the above, the issue arises regarding the use of such wood in construction and industry and, as a result, the need to stop the development of microorganisms in wood. For their disposal, it is desirable to use environmentally safe methods since the use of flame retardants reduces the environmental performance of the product, and the use of oil waxes is effective for surface action. One of the techniques of neutralizing microorganisms is thermal modification of wood, which reduces the development of bacteria and changes its structure and properties.

Therefore, research aimed at determining the properties of thermally modified dry wood and changes in its structure and properties, which are necessary to establish the scope of its use, are relevant.

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## 2. Literature review and problem statement

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Work [1] states that the wood that is exploited is prone to spoilage, when various fungi metabolize the wood, and carbon dioxide is released back into the atmosphere. The key prerequisite for the fungal destruction of wood is the presence of moisture. Conversely, keeping wood dry is the most effective way to protect wood from decay and long-term carbon sequestration. The structure of wood is porous and hygroscopic; it can absorb water in liquid and gaseous form, water is also released from wood by evaporation according to a given water vapor pressure gradient. The cited study reviews findings related to wood-water relationships and their role in fungal wood decay. Studies with chemically and thermally modified wood are included as examples of fungal wood substrates with altered moisture properties. The quantification and localization of water in capillaries and cell walls – especially in the superhygroscopic range – is considered key to determining the minimum moisture thresholds (MMThr) of wood-rotting fungi. Combinations of different methods and experimental setups to investigate wood-water relationships and their role in fungal decay are diverse. This combination could provide a new understanding of the balance between wood decay and wood-water interactions. However, it does not say what to do with dead wood.

Thermal treatment of wood, as stated in [2], appears as an ecological alternative in the field of wood processing. In general, thermal modification increases dimensional stability by reducing hygroscopicity and water absorption, but it makes bonding difficult in some cases. There are changes in the morphological, chemical, and physical properties of the wood cell wall as a result of compression and high temperatures that occur during welding and a decrease in some mechanical properties. Scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR) were used to

evaluate the properties of wood welding systems and their interaction. Mass spectrometry (MS) analysis was used to identify organic decomposition products released during thermosol welding. The experimental results show that the use of friction welding to bond thermal ash wood under dry conditions was feasible and we obtained good results. The best combination was with a welding time of 0.5 s and 3 s and a welding pressure of 2.5 and 4 MPa, respectively. The result can be compared with the result obtained with EPI adhesives. However, increasing the welding time by more than 3.5 seconds negatively affects the quality of the seam and gives low mechanical strength.

Research [3] focused on the characteristics of dry wood and the determination of features that are dominant and their potential functionality within the stand. The results showed that oak had the highest stand volume (379 m<sup>3</sup>/ha), dry volume (161.8 m<sup>3</sup>/ha), and carbon stock (31.43 t/ha). It was established that there was a greater amount of dry matter in deciduous forests than in pine forests. In addition, deciduous oak forest had a higher index of snag formation, fallen trees, and a higher index of past management compared to pine stands. Drywood volume increased with decay in deciduous oak forests, whereas this trend decreased in evergreen pine forests. The amount of felled forest was influenced by the type of plantation and the mode of forest management. Dynamic and past management of fallen tree indices indicates that their structure is still in the initial phase of establishment and decay in pine and oak forests. Comparison with other studies on similar types of forest showed that the range of variation of the main parameters of felled wood management fell within the variation of the studied parameters. However, the values of these parameters cover a wide range, but the populations of each forest type are extremely sensitive to different evolutionary periods of forest dynamics.

In [4], the authors incubated 196 logs of aspen (*Populus tremuloides*), birch (*Betula papyrifera*), and pine (*Pinus taeda*) of large diameters in the FACE Wood Decomposition Experiment, covering eight climatically different forest sites in the United States. Deadwood was sampled from these large-diameter logs, after 2–6 years of decay, and the type of decayed wood was determined as a continuous variable using the ratio of lignin loss/density loss (L/D). Wood-rotting fungal guilds were also evaluated using the ITS-2 marker High-Throughput Amplicon Sequencing System (HTAS). It was found that the L/D values correspond to the dominance of white rot in all three types of wood. Moreover, pine has lower L/D values than aspen and birch. According to HTAS data, white rot fungi were the most abundant and diverse guild of wood rotting fungi. And soft rot fungi were more abundant and diverse than brown rot fungi in logs with low L/D values. The results demonstrate that the type of decay is regulated by biotic and abiotic factors that differ depending on the tree species. However, there is no mention of methods of stopping the growth of fungi.

Study [5] analyzed the influence of wood surface area on decomposition through the interaction of basidiomycetes using laboratory incubation experiments with pine sapwood as a model. Two types of pine samples with the same volume but different surface area were prepared for colonization with one of the four species of white rot basidiomycetes. The infected samples were then placed on an agar medium already colonized by the same strain or one of the other

species, simulating a monoculture of fungi and interspecies interactions on the wood surface. The results showed that the rate of wood decay was higher in wood with a larger surface area, and wood decay was accelerated by the interaction of the two fungal species in wood with a larger surface area. In contrast, lignin decomposition was influenced by a competitor in wood with a smaller surface area. These results suggest that the observed promotion of decay by fungal interspecific interactions may not be due to resource partitioning between fungal species, but to accelerated carbon release. But this does not remove the question of suppressing the destruction of wood elements.

Study [6] monitored variations in the decay of drywood of Korean red pine and sawtooth oak in three ecologically different regions of the Republic of Korea. The variation in decomposition rate was significant only for dead pine trees. The most influential factor for the decomposition of dead pine trees was the exclusion of invertebrates (path coefficient 0.63). In contrast, decomposition of dead oak wood was strongly controlled by air temperature (path coefficient 0.88), with no significant effect of excluding invertebrates. These findings reflect differences in regional variation in the decomposition of fallen wood between pine and oak, which may result from different sensitivities to microclimate and pest exposure. However, it is not said how a dry year affects the rate of reproduction of pests.

Work [7] provides a deeper understanding of the variation in microbial abundance and community composition in relation to specific environmental parameters associated with the decay of fallen wood. The authors focused on the mesocosm experiment conducted with samples of dry black pine wood of different decay classes. The chemical properties and microbial communities of dead wood changed over time. The percentage of total nitrogen and the number of bacteria containing phylogenetic diversity of nitrogenase genes (*nifH*) increased significantly as decomposition progressed. This indicates enrichment of wood with nitrogen through microbial nitrogen immobilization and/or nitrogen fixation. The pH level decreased slightly during decomposition and was significantly correlated with the number of fungi. CO<sub>2</sub> formation was higher in the last 5 decay classes and was positively correlated with bacterial abundance. CH<sub>4</sub> formation was recorded in one sample of decay class 3, which correlates with the highest abundance of methanogenic archaea, which probably belonged to the genus *Methanobrevibacter*. N<sub>2</sub>O consumption increased with the progress of decomposition, indicating complete reduction of nitrate compounds to N<sub>2</sub> through denitrification, as confirmed by the highest *nosZ* gene copy number in decay class 5. However, the results highlighted the low participation of nitrifying groups in the decomposition of fallen wood.

Paper [8] characterized the diversity of fungi and bacteria in pieces of dead wood that had undergone 6.3–98.8% mass loss during decomposition in common garden “rotten patches” in a temperate oak-hickory forest in the Ozark Highlands, Missouri, USA. Communities were extracted from 21 tree species decaying over 1–5 years in spatially distinct habitats at the landscape scale (upper and lower reaches of watersheds) and within the trunk (upper and lower reaches). Co-occurring fungal and bacterial communities that constantly influenced each other regardless of their common environmental conditions. However, the relative influence of wood structure on spatial arrangement differs between fungi and bacteria, suggesting that the life history

characteristics of these nests structure spatial and temporal diversity during wood decomposition.

Article [9] assesses how ecosystem services can be incorporated into an economic planning model, using the provision of felled timber in commercial forests as an example. For a private forestry enterprise in Bavaria (Germany), different felled wood targets were combined with different classification options and included in the optimization approach as side conditions. By comparing different optimal solutions for different drought goals, it was possible to determine the costs of the optimal strategy. The results show that costs vary significantly not only by quantity but also by classification of felled wood types (whole tree, trunk, branches). As well as tree species (softwood, hardwood) and a given period of time to reach drywood. From a practical point of view, it is possible to combine environmental and economic goals in an optimal way. If dry wood is supplied from growing deciduous trees and not in a short time.

In work [10] it is indicated that the thermal degradation of wood is affected by a number of process parameters, which can also cause changes in resistance to decay fungi. Here, changes in chemical composition, water-related properties and decay resistance of pine sapwood that has been thermally modified (TM) in the dry state at temperatures ( $\geq 185$  °C) are compared. And also processed in hot water under pressure at mild temperatures ( $\leq 170$  °C). Thermal degradation of readily degradable hemicelluloses reduced the mass loss caused by *rhodonia placenta*. It has been suggested that cumulative mass loss is a better indicator of actual decay inhibition. Hot pressurized water extraction (HWE) did not improve rot resistance to the same extent as thermal modification, due to differences in wood–water interactions. Cross-linking reactions during thermal modification resulted in the inhibition of swelling and effective reduction of moisture content. This reduced the porosity of the water-swollen cell wall, which presumably impeded the transport of decomposition agents across the cell wall and/or reduced the availability of wood components to decomposition agents. But the effect was absent in wood extracted with hot water, and severe decay occurred even when most of the hemicelluloses had already been removed. Which shows decay of other structures.

Work [11] reports the results of the study of the influence of powdered fractions of wood biomass and biomass obtained from oil plants on the degradation of paint coatings and corrosion processes. During the study, the impact of port climate modeling, optical microscopy, scanning electron microscopy, and energy dispersive spectrometry techniques were used. It was established that the presence of a fraction containing protein compounds and amino acids (for example, rapeseed meal dust) stimulates the growth of microorganisms, the products of whose metabolism contribute to the destruction of protective coatings and the development of corrosion. Under the same conditions, the destruction of protective zinc coatings is observed. It was established that already 14 days of exposure to oily deposits of biomass leads to damage to the paint coating as a result of microbiological processes. 8-week exposure causes serious degradation of protective coatings and base material. However, woody biomass containing tannin-type compounds did not show such aggressive activity as biomass with protein compounds.

Bacteria found in wood are associated with wood decay and can indirectly affect the decay process [12]. The bacteria can affect the permeability of the wood, affect its structure, or work together with other bacteria and soft rot fungi to promote fungal damage. Bacteria that can colonize chemically

treated wood have been identified. The natural ability of some bacterial species to degrade creosote, mineralize pentachlorophenol, and tolerate chromic copper arsenate (CCA)-treated wood is discussed with respect to their role in the biodegradation of chemically preserved wood waste. But it is not indicated how these processes occur for dry wood.

Microbial biological degradation of wood and wood materials in buildings can cause expensive restoration procedures [13]. The study focuses on the fungus *Serpula lacrymans* (commonly known as dry rot), which causes the most damage to buildings in Europe. Although its morphology, lifestyle, and distribution have been intensively studied, studies of microorganisms that live in the same habitat and interact with the dry rot fungus are not as complete. Fungi have a high ability to manipulate the microbial community in their environment (e.g., by manipulating pH), and bacteria, in turn, can influence fungi. As by influencing the outcomes of (antagonistic) interactions or by preventing fungal feedback inhibition through the consumption of decay products. On the other hand, associated bacteria can play an important role for the fungus, as the bacteria can exert a significant influence on the physiology and behavior of the fungus. But in order to achieve prediction accuracy, a more acceptable and reasonable model of bacterial-fungal interaction should be created.

Study [14] was conducted to assess the effect of microwave (MW) radiation on the viability of wood-decomposing fungi. White rot (*Trametes versicolor*) and brown rot (*Rhodonía placenta*) fungi were grown on bamboo samples. Mycelial growth was observed in both controlled and microwave samples. The results showed that the viability of the fungi decreased according to the applied microwave exposure time. This study proved the ability of microwaves and MW3 exposure time (180 seconds) to kill fungal colonies and prevent the growth of fungal spores, i.e., the growth rate of fungal colonies is inversely proportional to the microwave exposure time.

Thus, it was established from literary sources that thermal modification of dry pine wood stops the vital activity of microorganisms, while both the structure and properties of the wood may change. All this gives grounds for conducting a study aimed at determining the parameters that ensure the use of such wood.

### 3. The aim and objectives of the study

The purpose of this work is to identify patterns of changes in the properties and structure of dry wood after thermal modification. This makes it possible to expand the scope of application of dry wood products.

To achieve the goal, it was necessary to solve the following tasks:

- to determine the structure of dry pine wood, thermally modified under different regimes;
- to conduct a study of absorption and technological properties of thermally modified dry pine wood.

## 4. The study materials and methods

### 4.1. The object and hypothesis of the study

The object of our research is dry pine wood. The subject of the study is the properties and structure of dry pine wood under the conditions of its thermal modification.

The hypothesis of the study assumes that through thermal modification it is possible to purposefully regulate the structure and technological properties of dry pine wood.

In the research process, the following assumptions and simplifications were adopted, which determine the impact of changes in external conditions on the object of research and the lack of interconnection between process implementations, namely:

- mass exchange processes in wood are the same, temperature, humidity, pressure during the study are not variable;
- a sample of thermally modified dry pine wood is homogeneous.

### 4.2. Investigated materials used in the experiment

For research, samples of dry pine wood were used with different degrees of damage by the fungus of the *Ceratostomaceae* family in the range of 0÷10 %, 30÷50 %, and 80÷100 %, and which were modified at a temperature of 200 °C for 3 and 6 hours. The size of the samples was 20×20×30 mm (Fig. 1).

Thermal modification caused some changes in wood depending on its damage by microorganisms (Table 1).

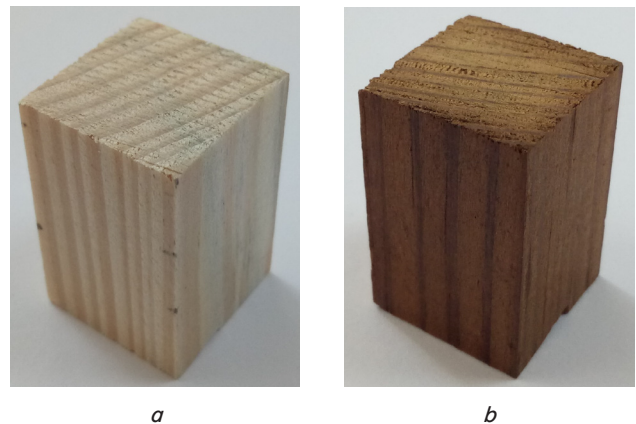


Fig. 1. Model samples: *a* – dead pine wood; *b* – thermally modified dry pine wood

Table 1

Change in the density of wood after thermal modification

Characteristics of the wood sample		Average sample weight, g			Density of wood, kg/m <sup>3</sup>		Density reduction level, %
Mode parameters of thermal modification T/τ	Damage level, %	Before	After	Weight loss, %	Before	After	
200 °C, 3 hours	0÷10	61.16	54.35	11.13	504.11	475.34	5.71
	30÷50	62.05	54.58	12.04	499.71	463.86	7.18
	80÷100	57.26	50.79	11.29	473.07	438.75	7.26
200 °C, 6 hours	0÷10	60.85	52.83	13.19	501.41	460.25	8.21
	30÷50	63.15	53.81	14.78	520.39	472.72	9.16
	80÷100	63.47	49.98	20.88	511.98	428.15	16.37

After aging the samples for 2 days, tests were carried out for moisture absorption, as well as for compression and bending.

#### 4. 3. Methods of research into the properties of wood and its structure

In order to identify patterns of changes in the properties and structure of dry wood during thermal modification, absorption and technological properties were determined, in particular, the ability to absorb moisture, as well as bending and compressive strength. Changes in the structure of dry wood during thermal modification were determined by Fourier transform infrared spectroscopy (FTIR) and identification by thermogravimetric analysis.

Determination of the amount of water absorption by wood samples was carried out according to the working procedure, the essence of which was the experimental determination of the amount of moisture absorbed by the sample during its exposure in a desiccator [15].

The bending and compressive strength of wood was determined according to ISO 13061-3:2014 [16].

Fourier transform infrared spectroscopy (FTIR) was performed taking into account [17]. Research method: 0.5 mg of the sample, crushed from 70 mg of potassium bromide (cleaved from a single crystal). From the resulting mixture, the tablet was compressed under a pressure of 10 MPa, achieving maximum optical transparency (to reduce scattering). The spectrum was recorded in the range of 4000–400  $\text{cm}^{-1}$ , with an optical slit width of 4  $\text{cm}^{-1}$ , the spectrum was averaged over 12 scans. The analysis was performed on a Spectrometer Spectrum One (Perkin Elmer) (USA).

Thermogravimetric analysis was performed according to [18]. In order to determine the range of temperatures at which the thermal destruction of wood occurs most intensively, a thermogravimetric study of destruction processes was conducted under dynamic mode. Thermogravimetric studies were carried out on a Linseis STA 1400 derivatograph (Germany). Samples weighing 10 mg were heated in an air atmosphere from 20 to 700  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}/\text{min}$ .

## 5. Results of research into the properties of dry pine wood after thermal modification

### 5. 1. Results of studying the structure of dry pine wood thermally modified under different regimes

Fig. 2, 3 show the IR spectra of the studied wood samples. The description of the IR spectra of samples of thermally modified dry pine wood is given taking into account the absorption bands of cellulose, lignin, and hemicellulose (4-O-methylglucuronoxylan) [19, 20]. Thermogravimetric analysis was performed to identify the individual characteristics of thermally modified dry pine wood. Graphic images of thermogravimetric analysis of wood samples are shown in Fig. 4–9.

The analysis of the acquired IR spectra for the thermally modified wood affected by the fungus of the *Ceratostomaceae* family did not reveal any significant differences when the wood was thermally modified for 3 hours with different degrees of damage and when the wood was modified for 6 hours, respectively.

Paper [21] provides a detailed description of the IR spectrum of non-thermomodified wood affected by the fungus of the *Ceratostomaceae* family. As a result of comparing the obtained IR spectra for thermally modified wood with different degrees of damage by the fungus of the *Ceratostomaceae* family with the IR spectrum of non-thermomodified wood affected by the same type of fungus, the following differences were revealed.

Presence of 1230  $\text{cm}^{-1}$  and 1335  $\text{cm}^{-1}$  absorption bands of lignin structural units in the spectra of thermomodified wood. The band at 1230  $\text{cm}^{-1}$  in guaiacyl compounds and the band at 1335  $\text{cm}^{-1}$  in syringyl derivatives are caused by valence vibrations of the ring and C–O bonds. In particular, a slight decrease in the band maximum at 1650  $\text{cm}^{-1}$  in the absorption region of 1650–1630  $\text{cm}^{-1}$  of cellulose. This absorption region is due to  $\delta\text{H–O–H}$  fluctuations of the water of crystallization. A decrease in the absorption maximum indicates water loss.

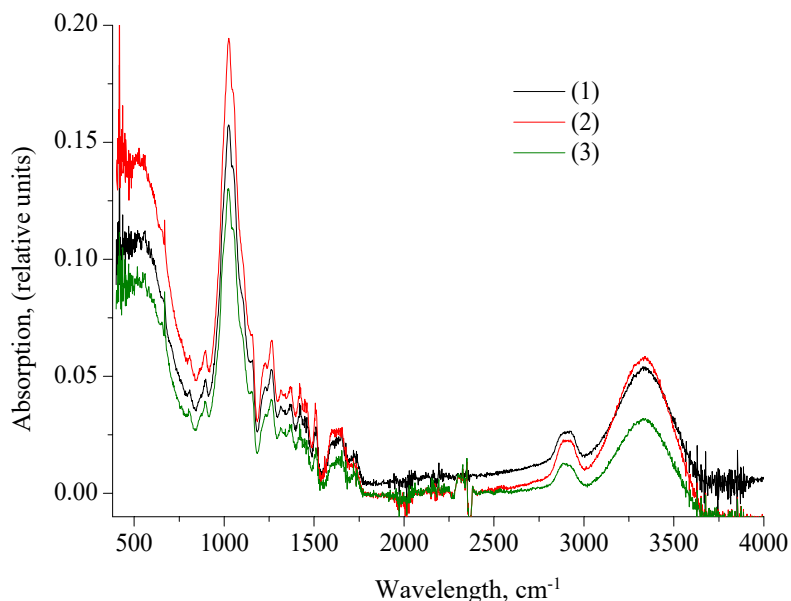


Fig. 2. Absorption spectra of samples of dry pine wood thermally modified with parameters of 220  $^{\circ}\text{C}/3$  hours for the level of damage by the fungus of the *Ceratostomaceae* family: 1 – 0÷10 %; 2 – 30÷50 %; 3 – 80÷100 %

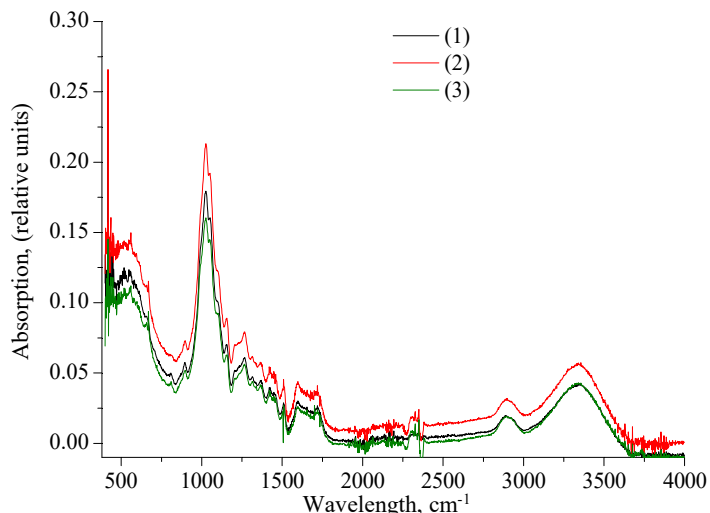


Fig. 3. Absorption spectra of dry pine wood samples thermally modified at 220 °C/6 hours for the level of damage by the fungus of the *Ceratostomaceae* family: 1 – 0÷10 %; 2 – 30÷50 %; 3 – 80÷100 %

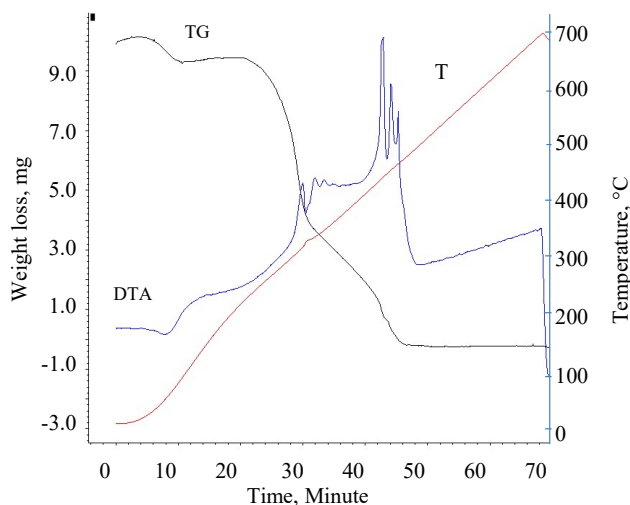


Fig. 4. Curves of thermogravimetric analysis for samples of thermally modified dry pine wood at 220 °C/3 hours for the level of damage by the fungus of the *Ceratostomaceae* family 1 – 0÷10 %: T – temperature curve; TG – mass loss curve depending on temperature increase; DTA – thermal effects curve

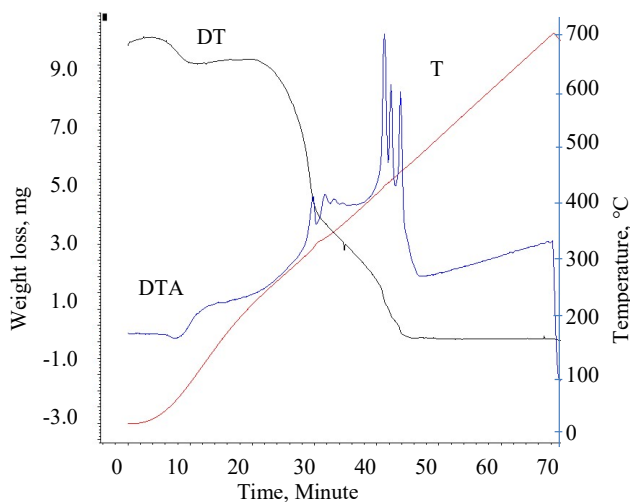


Fig. 5. Curves of thermogravimetric analysis for samples of thermally modified dry pine wood at 220 °C/3 hours for the level of damage by the fungus of the *Ceratostomaceae* family 1 – 30÷50 %: T – temperature curve; TG – mass loss curve depending on temperature increase; DTA – thermal effects curve

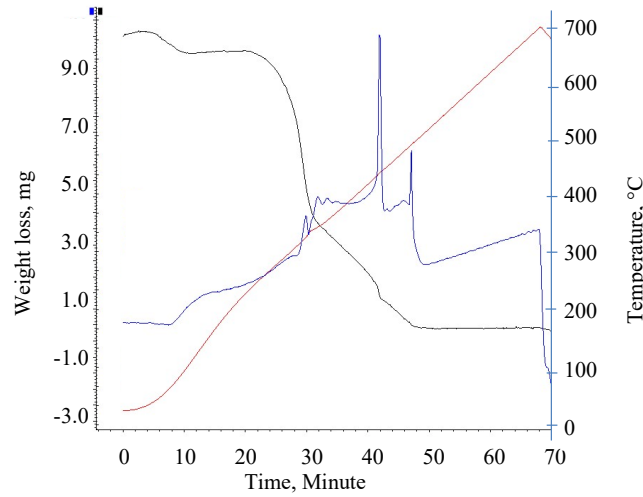


Fig. 6. Curves of thermogravimetric analysis for samples of thermally modified dry pine wood at 220 °C/3 hours for the level of damage by the fungus of the *Ceratostomaceae* family 1 – 80±100 %: T – temperature curve; TG – mass loss curve depending on temperature increase; DTA – thermal effects curve

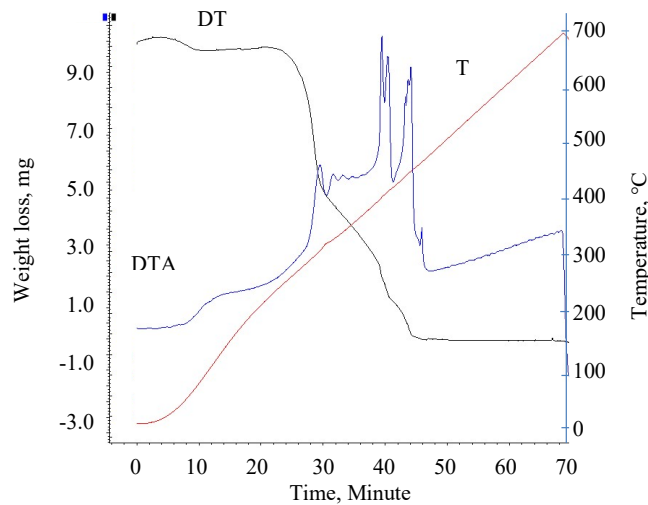


Fig. 7. Curves of thermogravimetric analysis for samples of thermally modified dry pine wood at 220 °C/6 hours for the level of damage by the fungus of the *Ceratostomaceae* family 1 – 0±10 %: T – temperature curve; TG – mass loss curve depending on temperature increase; DTA – thermal effects curve

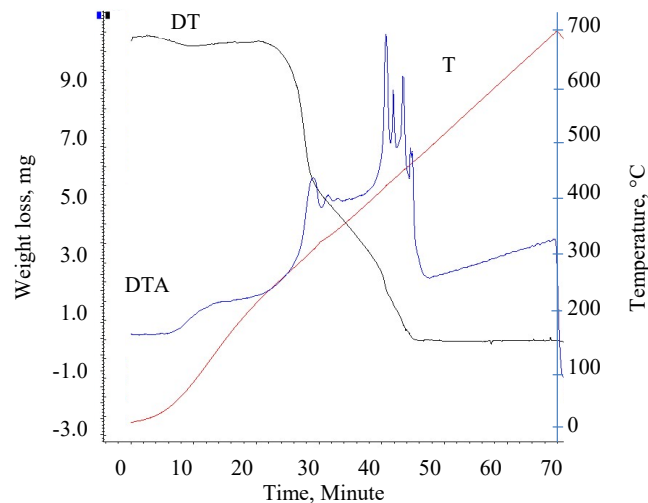


Fig. 8. Curves of thermogravimetric analysis for samples of thermally modified dry pine wood at 220 °C/6 hours for the level of damage by the fungus of the *Ceratostomaceae* family 1 – 30±50 %: T – temperature curve; TG – mass loss curve depending on temperature increase; DTA – thermal effects curve

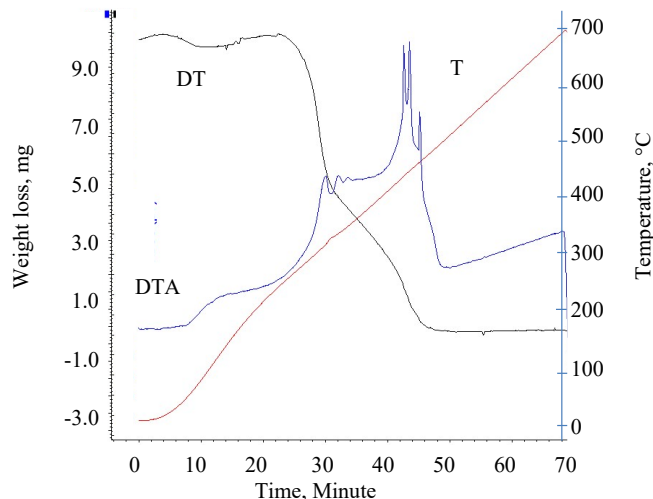


Fig. 9. Curves of thermogravimetric analysis for samples of thermally modified dry pine wood at 220 °C/6 hours for the level of damage by the fungus of the *Ceratostomaceae* family 1 – 80±100 %: T – temperature curve; TG – mass loss curve depending on temperature increase; DTA – thermal effects curve

The TG curves on the thermograms (Fig. 4–9) show the processes of water loss and decomposition of hemicellulose, cellulose, and lignin, and the burning of coke residue. When the temperature increases from 40 to 120–150 °C, the process of drying wood is completed, that is, the release of physical water.

Subsequent heating to a temperature of 150–180 °C causes the release of intracapillary and chemically bound water, the decomposition of the least thermally stable components of wood (luminic acids) mainly with the release of carbon dioxide and water. Thermal decomposition of hemicelluloses, cellulose, and lignin takes place in the ranges of 225–325, 305–375, and 250–500 °C, respectively.

At a temperature of 250 °C, pyrolysis of wood (mainly hemicellulose) takes place with the release of such gases as CO, CH<sub>4</sub>, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O. Such a gas mixture is already capable of ignition from an ignition source. At a temperature of 280–300 °C, intensive decomposition of wood begins, which is characteristic of thermal destruction with gas formation and burning of wood. The cessation of mass loss is recorded at approximately 500 °C. The DTA curves show a smooth rise from 40 °C to 140 °C and take the shape of a shoulder.

Further, the curve rises to 280–300 °C (thermal destruction of hemicelluloses, lignin). During the thermal action from 150 to 450 °C, two processes occur in parallel:

- dehydration, accompanied by the destruction of pyranose cycles and carbonization with the formation of a carbon residue and a complex mixture of volatile products;
- destruction of glycosidic bonds while preserving hydroxyl groups, which is accompanied by rearrangement into pyranose cycles with the predominant formation of levoglucosan.

On the DTA curves after a smooth rise, an endo effect with a maximum at 335 °C is observed, which is explained by the release of leucoglucosan. After the endothermic peak, the heat release increases to 350 °C – the final temperature of cellulose decomposition. After that, there is a sharp rise in the DTA curves with two or more exo-effects. The maxima at 446 °C and 456 °C are characteristic of the processes of thermal decomposition of lignin with the formation of a carbon residue, others – for the burning of this residue. After

burning the carbon residue, the DTA curves go down, indicating complete combustion to a non-combustible residue of an inorganic nature.

## 5.2. Results of studies of mechanical properties of thermally modified dry pine wood

The results of determining the static bending strength of thermally modified dry pine wood are shown in Fig. 10, 11.

As a result of the research (Fig. 11), it was established that when affected by the fungus, the pine wood becomes loose, therefore the bending strength limit decreases by more than 1.3 times, depending on the size of the spread of the fungus. Thermal modification, depending on the modification time, reduces the strength limit for the affected sample within 0±10 %: at 200 °C/3 hours by more than 1.3 times, at 200 °C/6 hours – by more than 1.9 times. With an increase in the area affected by the fungus in the range of 30±50 %, the strength limit decreases for the sample modified at 200 °C/3 hours by more than 1.6 times, at 200 °C/6 hours – by more than 2.1. For a sample affected by the fungus in the area of 80±100 %, dry wood becomes more plastic, while the strength limit decreases by 1.7 times.

Fig. 12 and Table 2 depict the results of studies of compressive resistance of pine wood.



Fig. 10. Determination of static bending strength of wood



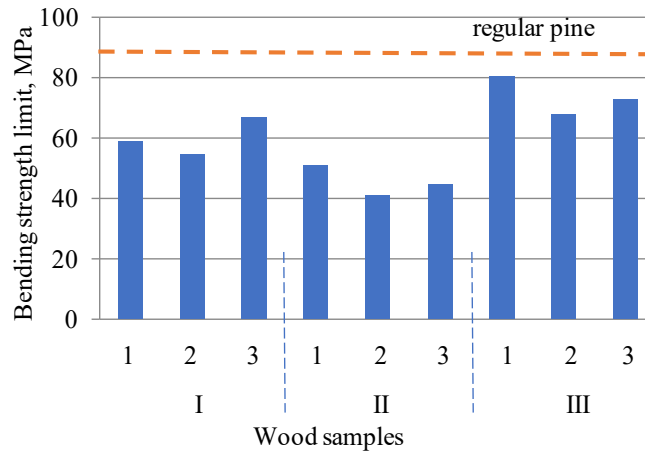


Fig. 11. The results of determining the static bending of pine wood: I – thermally modified dry pine wood at a mode parameter of 200 °C/3 hours, II – thermally modified dry pine wood at a mode parameter of 200 °C/6 hours, III – dry pine wood without thermal modification; affected by the fungus of the *Ceratostomaceae* family: 1 – within 80÷100 %, 2 – within 30÷50 %, 3 – within 0÷10 %



Fig. 12. Determination of the compressive strength of wood

A compression study showed that dry pine wood is more fragile when affected by the fungus up to 0÷10 %, so the strength limit decreases by more than 1.2 times. With an increase in the level of fungus damage in the range of 30÷50 %, the strength limit decreases by less than 1.19 times, and when the area is affected by the fungus in the range of 80÷100 %, the strength limit increases. Thermal modification of dry pine wood at 200 °C/3 hours turns it into a more plastic material and reduces the strength limit by 1.06 times.

Increasing the time of thermal modification to 6 hours reduces the strength limit by 1.16 times.

It is possible to reduce the level of water absorption by wood by applying thermal modification [21], which changes the structure of wood, and the use of an antiseptic polymer film enhances this process [22].

Fig. 13 shows the results of moisture absorption of a sample of dry pine wood from the level of thermal modification after exposure to water for 20 days.

Table 2

Compressive strength limit of wood samples

Characteristics of the wood sample		Results of studies of compressive strength of wood			
Mode parameters of thermal modification (TM) of wood T(°C)/τ(hours)	Damage level, %	Along fibers, MPa	Deformation, %	Across the fibers, MPa	Deformation, %
Pine without TM	0	50.26	6.37	8.26	6.84
Dry pine wood without TM	0÷10	40.60	6.10	6.77	6.00
	30÷50	42.10	5.86	8.28	6.41
	80÷100	51.09	7.01	6.44	9.52
Dead pine wood TM 200 °C/3 hours	0÷10	47.12	5.33	4.32	2.63
	30÷50	49.15	5.93	4.61	2.91
	80÷100	48.60	6.19	3.30	2.93
Dead pine wood TM 200 °C/6 hours	0÷10	43.26	4.61	4.80	3.06
	30÷50	48.72	4.90	3.43	3.13
	80÷100	44.20	5.21	3.45	3.14

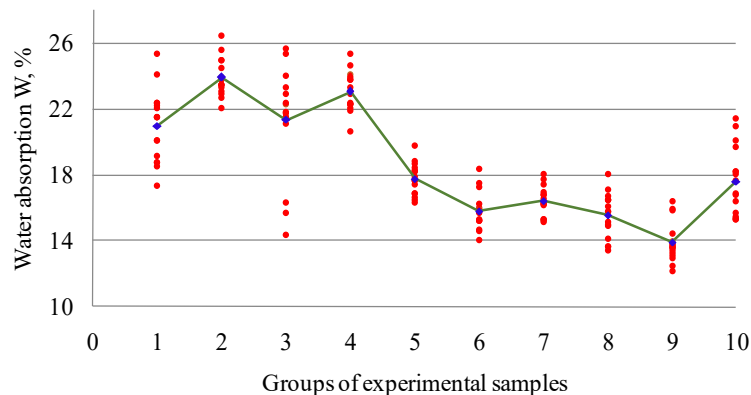


Fig. 13. Results of studying the influence of thermal modification (TM) on the resistance of wood to moisture absorption: 1 – pine; dry pine affected by a fungus of the *Ceratostomaceae* family: 2 – 80÷100 %, 3 – 30÷50 %, 4 – 0÷10 %; dry pine TM at 200 °C/3 hours affected by a fungus of the *Ceratostomaceae* family: 5 – 80÷100 %, 6 – 30÷50 %, 7 – 0÷10 %; dry pine TM at 200 °C/6 hours affected by a fungus of the *Ceratostomaceae* family: 8 – 80÷100 %, 9 – 30÷50 %, 10 – 0÷10 %

The analysis of the results of experiments on moisture absorption of wood shows that the maximum increase in mass during the action of water on samples of dry pine wood amounted to more than 24 %, depending on the area affected by the fungus of the *Ceratostomaceae* family. This value is more than 1.14 times higher compared to pine wood. Thermal modification of dry pine wood at 200 °C for 3 hours reduces the level of moisture absorption by more than 1.5 times, and at 200 °C for 6 hours – by more than 1.7 times.

## 6. Discussion of results of studying the properties of dry wood

In spectroscopic studies of samples of thermally modified dry pine wood, as follows from the obtained results (Fig. 2, 3), the process of changing the structure depending on the level of damage by the fungus of the *Ceratostomaceae* family of dry wood is natural. This is due to a change in the structure of wood during drying, which shows absorption spectra characterized by fluctuations of the glucopyranose ring of cellulose and a slight decrease in the absorption of individual absorption bands. The weak intensity of the absorption region shows a decrease in the vibration intensity during thermal modification and is an indicator of the beginning of destructive processes in cellulose. A decrease in the intensity of the absorption band during thermal modification indicates the dehydration process that takes place during thermal modification.

Thus, the data obtained by the method of IR-spectroscopy with Fourier transform indicate minor structural changes primarily in cellulose and lignin, which are associated with intramolecular rearrangement of wood components and changes in intermolecular bonds between them.

It should be noted that the indicator of wood decay is a decrease in the density associated with a change in the structure of dry wood, which decreased depending on the level of damage by the fungus. Obviously, this mechanism of wood decomposition is the factor regulating the process due to which the thermal decomposition of dry wood increases. In this sense, there is an interpretation of the

results of thermogravimetric analysis, namely the loss of mass of samples after thermal decomposition. Upon reaching 700 °C, samples of dry pine wood of the *Ceratostomaceae* family affected by the fungus completely lose mass. This indicates that the chemical composition of thermally modified dry pine wood is the same, namely polyaromatic hydrocarbons.

This means that taking this fact into account opens the possibility for effective use of wood directly under the conditions of industrial application.

A comparison of experimental studies on changes in the structure of wood during thermal modification and studies on determining the characteristics of the destruction of wood samples indicates a decrease in the compressive and bending strength of wood (Table 2, Fig. 11). This does not differ from the practical data, well known from works [3, 7], the authors of which, by the way, also associate the decrease in the strength limit of thermally modified dry wood with a change in structural composition. But, in contrast to the results of research reported in [6, 8], the obtained data on the effect of drying on the properties of wood, in particular, on bending, allow us to state the following:

- the main regulator of reducing the bending and compressive strength of thermally modified dry pine wood is a change in the structure of wood components;
- thermal treatment technologies have a significant impact on the elimination of biological processes (infection by microorganisms, apoptosis, etc.) of wood.

Therefore, the decrease in wood density is associated with the formation of bacteria in the structure, which is confirmed in [23]. At the same time, it is possible to carry out thermal modification of such wood, which reduces the moisture absorption of the product [24, 25] and at the same time stops the development of the fungus of the *Ceratostomaceae* family. All this increases the environmental friendliness of wood products and expands the scope of application of such wood. Such conclusions can be considered expedient from a practical point of view because they allow a reasoned approach to reducing the level of moisture absorption of wood [26, 27]. This allows us to assert the determination of the mechanism of wood disinfection, which are certain advantages of this study. From a theoretical point of view, they allow us to define

the mechanism of the processes of both the reduction of mechanical properties and changes in the structure of wood during thermal modification, which are certain advantages of this study.

However, it is impossible not to note that the results of the determination (Fig. 13) indicate an ambiguous effect of changing the structure of wood on moisture absorption. This is manifested, first of all, in the increase in the mass of the sample during tests of wood from stands weakened by drying and the decrease during thermal modification. Such uncertainty imposes certain restrictions on the use of our results, which can be interpreted as the shortcomings of this study. Because the disadvantage for dry pine wood is the interrelationship of structure and resistance to moisture absorption and strength. The impossibility of removing the mentioned limitations within the framework of this study creates a potentially interesting direction for further research. In particular, it can focus on detecting the moment of time when the intense decrease in wood strength begins. Such detection will make it possible to investigate the structural transformations of wood that begin to take place at this time, and to determine the input variables of the process that significantly affect the beginning of such a transformation.

However, it is impossible not to note that the results of determining the adhesion of the wood polymer shell (Table 1) indicate an ambiguous effect of the change in the wood structure on thermal decomposition. This is manifested, first of all, in the nature of the destruction of the polymer shell with a certain adhesion in tests of thermally modified wood. Such uncertainty imposes certain restrictions on the use of our results, which cannot be interpreted as shortcomings of this study. Since the disadvantage of thermal polymerization of powder paint on ordinary wood is the high temperature, which must be reduced much below 100 °C. The impossibility of removing the mentioned limitations within the framework of this study creates a potentially interesting direction for further research. In particular, the tests can focus on detecting the moment of time when the intensive decrease in the adhesion of the polymer coating to wood begins. Such detection will make it possible to investigate the structural transformations of wood that begin to take place at this time, and to determine the input variables of the process that significantly affect the beginning of such a transformation.

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## 7. Conclusions

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1. Samples of thermally modified dry pine wood have absorption spectra characterized by fluctuations of the glucopyranose ring of cellulose and a slight decrease in the absorption of individual absorption bands. The weak intensity of the absorption region shows a decrease in the vibration intensity during thermal modification and is an indicator of the beginning of destructive processes in cellulose. A decrease in the intensity of the absorption band during thermal modification indicates the dehydration process that takes place during thermal modification.

Thermogravimetric analysis data show the processes of water loss and decomposition of hemicellulose, cellulose, and lignin, and burning of coke residue. Heating in

the range from 40 to 150 °C contributes to the drying of wood, at temperatures from 150 to 450 °C, two processes take place in parallel. One of them is dehydration, which is accompanied by the destruction of pyranose cycles and carbonization with the formation of a carbon residue and a complex mixture of volatile products. The second is the destruction of glycosidic bonds while preserving hydroxyl groups, which is accompanied by rearrangement into pyranose cycles with the predominant formation of levoglucosan.

2. Bending and compressive strength of thermally modified dry pine wood shows that as the wood dries, the strength limit decreases depending on the degree of fungus damage. Namely, with the area of biological damage in the range of 0÷10 %, the strength limit decreases at the modification level of 200 °C/3 hours by more than 1.2 times, at 200 °C/6 hours – by more than 1.9 times. With an increase in the area affected by the fungus in the range of 30÷50 %, the strength limit for the sample modified at 200 °C/3 hours decreases by more than 1.6 times, at 200 °C/6 hours – by more than 2.1. When the fungus affects an area between 80 and 100 %, the wood becomes softer and more plastic, while the bending strength decreases by 1.7 times, and the compressive strength by 1.16 times.

The analysis of the results of experiments on moisture absorption of wood reveals that the maximum increase in mass during the action of water on samples of dry pine wood amounted to more than 24 %, depending on the area affected by the fungus. Thermal modification of dry pine wood at 200 °C for 3 hours reduces the level of moisture absorption by more than 1.5 times, and for 6 hours – by more than 1.7 times.

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## Conflicts of interest

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The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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## Data availability

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All data are available in the main text of the manuscript.

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