RADIATION DEGRADATION OF LIGNIN

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An analysis is given of literature information on the radiation degradation of lignin. The following questions are discussed: 1) the formation of radicals in the radiolysis of lignin and compounds modeling it; 2) the chemical properties of irradiated lignin; 3) the low-molecular-mass products of the radiolysis of lignin; and 4) the radioprotector properties of lignin.

Recently, there has been a considerable rise of interest in the radiation transformation of the polysaccharides of plant biomass into a state accessible for enzymatic and microbiological processing [1-4]. This is due in the first place to the intensive development of nuclear energy and to the creation on its basis of a powerful radiation technology [5], and also to the considerable resources of self-renewing plant raw material. Wood biomass is the most common source of organic raw material and its world reserves are estimated at $17 \cdot 10^{11}$ tons with an annual increase of $7.4 \cdot 10^{10}$ tons (approximately 4.4% of the world reserves) and, of this volume, industry processes only about 19% [6]. In view of the fact that lignin occupies the second place after polysaccharides in terms of occurrence in nature and it is present in the majority of forms of plant raw material, the study of its degradation by high-energy radiations is of both theoretical and practical interest. There is no systematic discussion of this question in the literature. The aim of the present paper, therefore, consisted in an analysis and generalization of the not very numerous facts on the radiation-chemical transformation of lignin.

PRIMARY EFFECTS CAUSED BY THE ACTION OF RADIATION

Of the whole combination of so-called intermediate products of the radiolysis of polymers (positive and negative ions, excited molecules, free radicals, etc.), for lignin there is literature information only on the radicals. The unpaired electron that is the bearer of radical properties may be present in the form of a cloud of probability density which extends over a distance of 10 Å for aliphatic polymeric systems and to 100-500 Å for aromatic systems [7, p. 72]. In conjugated polymeric systems, in contrast to isolated spin systems, the densities of individual radicals may overlap, which leads to a strong interaction (exchange interaction of radicals). The available information [8] indicates that condensed lignin preparations can be regarded as conjugated systems. The properties of a conjugated system are also, apparently, to a certain degree characteristic of natural lignin (more accurately, of the regions of its macromolecules with a high density of the network structure). The existence of exchange interaction between radicals in irradiated lignin is shown by an analysis of the lines in its ESR spectra. In the γ-irradiation of milled wood lignin (MWL) at 77 K in the range of doses from 10 to 300 kGy, the ESR spectrum consists of an isotropic singlet with a width measured at the point of maximum slope of approximately 1 mT [9]. An analogous spectrum with a width from 0.8 to 1.2 mT has been obtained in the photolysis of lignin [10]. The ESR spectrum of γ-irradiated (with a dose of 10 kGy) MWL at room temperature in vacuum has been represented as a single line [11]. In [9, 12] it was shown that up to the absorption of a dose of 50 kGy the intense singlet of the "lignin" radicals in the ESR spectrum of γ-irradiated wood the developed hyperfine structure (HFS) of the ESR signals of the "carbohydrate" radicals is smoothed out. With an increase in the dose to more than 50 kGy the relative contribution of the singlet decreases and the HFS appears quite clearly. The absence of HFS [7, p. 73] in the ESR spectra of irradiated lignin apparently indicates a delocalization of the unpaired electrons and, correspondingly, an exchange interaction between radicals.

The kinetics of the accumulation of radicals at 77 K in lignin, cellulose, and wood have been studied [9, 13, 14]. The dependence of the concentration of radicals on the dose of γ-radiation is well described by an equation taking into account the formation of radicals and their monomolecular disappearance:

$$[\mathrm{R}] = [\mathrm{R}]_{\mathrm{lim}} (1 - e^{-k_d D}),$$

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where R_{lim} is the limiting (stationary) concentration of radicals; D is the absorbed dose; and k_d is the constant of the monomolecular destruction of the radicals under the action of γ-radiation.

The kinetics of the disappearance of radicals in γ-irradiated samples of MWL on their heating in the temperature interval of 77-300 K has been investigated [15, 16]. During such heating the number of radicals in the samples decreased by approximately 90%. In [17], the kinetics of the destruction of radicals in γ-irradiated samples of dioxane lignin was studied as a function of their relative moisture content. With a rise in the relative moisture content of the samples to 4-6%, the number of radicals in them decreased by approximately 50%. The graphical dependence of the number of radicals on the temperature and moisture content of the sample has an exponential nature [15-17]. A different graphical dependence of the destruction of radicals in γ-irradiated MWL during its heating was shown in [18], and an extremely unexpected experimental fact was the rapid disappearance of the radicals in dried, as compared with air-dry samples.

The number of radicals present in irradiated lignin is limited not only by its temperature and moisture content but also by the time of storage of the samples. According to [11], the concentration of radicals in γ-irradiated lignin-modeling compounds stored at room temperature in vacuum for approximately 280 days decreased by factors of 1.08-9.33. Experimental investigations that we have performed have shown that the most intensive disappearance of radicals in absolutely dry samples of lignin, wood, and cellulose γ-irradiated at 77 K takes place in the first 5 min of heating to room temperature, and then the process of disappearance of the radicals slows down and after storage of 70 h the concentration of radicals in the samples has scarcely changed. Samples of cotton cellulose contained about 30% of their initial number of radicals, samples of lignin and wood about 10%.

In the literature, stable radicals have acquired the appellation of long-lived. At room temperature they possess a high stability and can be recorded over a long time (for example, for γ-irradiated cotton cellulose, for 4-7 years [13, 19]). In the opinion of the majority of workers [7, 11, 20], the stability of radicals is determined not so much by the nature of the radicals themselves as by the rigidity of the structure of the polymeric matrix. For example, the number of long-lived radicals depends on the degree of crystallinity of the polymer. Thus, in γ-irradiated cotton cellulose (cellulose I), of the initial number about 30% consists of long-lived radicals [21], in sulfite cellulose about 15-20% [22], in cellulose II about 10% [21], and for amorphous (regenerated) cellulose the ESR signal practically disappears [23]. Regions of the lignin macromolecule with a high density of cross-linkages may also be stabilizers of radical centers. The existence of long-lived radicals in γ-irradiated lignin preparations has been confirmed experimentally [11]. By using model compounds, the authors convincingly showed that the radiation-induced lignin radicals are not chemically stable but become so when fixed in the rigid structure of the lignin molecule.

An increase in the plasticity (mobility) of the structure of the macromolecules leads to the disappearance of the radicals. Thus, the phenomenon of chemiluminescence arising as the result of the intensive destruction of radicals takes place on the ultraviolet irradiation of solutions of dioxane lignin but not on the irradiation of solid samples [24]. Under the action on lignin of high-energy and low-energy radiations (radiolysis and photolysis, respectively), different chromophoric structures arise in which unsaturated bonds are conjugated with aromatic nuclei of the type of sterol and stilbene structures [25, 26]. α-Carbonyl and quinone groups are formed. Lignin preparations isolated from unirradiated wood in the absence of light and oxygen contain practically no unpaired electrons. In the light in the presence of oxygen the concentration of radicals ranges between 10^{16} and 10^{18} spins/g of sample [23]. During radiolysis or photolysis this magnitude may increase by several orders.

There is great similarity between the chemical changes in irradiated polymers and in their low-molecular-mass analogs [7, p. 9]. On this basis, Meshitsuka and Nakano [28], who investigated the γ-radiolysis of lignin-modeling compounds, put forward the hypothesis that the degradation of lignin may begin in three main positions: 1) the formation of phenoxyl radicals in the terminal structural unit or in condensed unit with free phenolic OH groups; 2) the elimination of a hydrogen atom at the β-C atom of a phenylpropane unit (PPU) adjacent to an α-CO group [3], and 3) cleavage at double bonds. On analyzing the spectra of the initial state obtained in the flash photolysis of solutions of preparations of lignin and of compounds modeling it, Neumann et al. [26, 27] came to the conclusion that systems of phenoxyl and ketyl radicals were formed in the excitation process.

TABLE 1. Amount of Soluble Lignin in γ-Irradiated Eucalyptus Wood (% on the initial wood) [29]

Dose, kGy	Soluble lignin*
0	1,2 (5,7)
50	1,5 (7,1)
100	1,4 (6,6)
178	3,7 (17.5)
316	6.7 (31.7)
560	10,5 (49,8)
1000	14,8 (70,1)
1780	16,8 (79,6)
3160	16,6 (78,7)

*In parentheses — in % on the Klason lignin.

TABLE 2. Lignin Preparations Isolated from Unirradiated and γ-Irradiated (with a dose of 1000 kGy) Pine Wood [30, 31]

Type of lignin	Yield, % on abs. dry wood*	
	unirradiation	irradiated
Brauns lignin	0,5 (1.6)	1.2 (3,9)
Dioxane lignin	0,2 (0.6)	0,8 (2,4)
Dimethyl sulfoxide lignin (DMSO-lignin)	9.0 (29.0)	20,2 (65,2)
Thioglycolic acid lignin (TGA-lignin)	25.3 (81.6)	30,9 (99,6)

*In parentheses — % on the Klason lignin.

CHEMICAL PROPERTIES OF LIGNIN

At absorbed doses ≥100 kGy the amount of the soluble sol fraction of lignin in plant raw material rises. The amount of soluble lignin depends not only on the amount of radiation absorbed but also on the nature of the solvent [29-35]. Table 1 [29, 30] gives information on the amount of soluble lignin obtained after the successive extraction of irradiated eucalyptus wood with 95% ethanol and with 0.12 N aqueous NaOH as a function of the absorbed dose of γ-irradiation.

When ethanol, 0.5% aqueous NaOH, anhydrous acetone, and 50% aqueous acetone were used as extractants for γ-irradiated wood (at a dose of 3160 kGy), 8.2, 10.8, 1.1, and 6.9% (on the absolutely dry wood) of soluble lignin were obtained, respectively. The elementary composition of this lignin depended on the type of solvent used and varied within the limits 47.2-62.1% C, 6.0-6.5% H, 6.6-23.1% OCH_3, and 0-1.4% ash [29]. Tables 2 and 3 give information on the yield of lignin on its isolation by various methods from γ-irradiated pine wood (dose 1000 kGy) and on the chemical properties of the lignin isolated. Thus, in lignin irradiated up to a dose of 10^4 kGy the changes in elementary composition did not exceed the limits of experimental error, while the composition of wood and cellulose changed at doses as low as 10^2 kGy [36].

The increase with the dose of the depth of solubility of lignin from irradiated wood in alkaline media, and also in the sulfonation process [31], is of applied value and can be used for increasing the efficiency of the delignification of plant raw material [37, 38]. The kraft pulp obtained from irradiated wood chips has papermaking properties considerably superior to those of pulp obtained from unirradiated wood.

Tables 4 and 5 present data on the chemical composition of irradiated Brauns [31] and dioxane [40] lignins. From them, it follows that the elemental composition of isolated lignin is not significantly changed by the process of radiolysis. With an increase in absorbed dose, the solubility of lignin in water and ethanol increases.

The following empirical formulas of a structural unit were obtained for the MWL of unirradiated beech wood: $C_9H_{8.63}O_{2.93}(OCH_3)_{1.41}$ according to [15, 16] and $C_9H_{8.50}O_{3.80}(OCH_3)_{1.30}$ according to [41]. Lignin from irradiated beech wood (doses of 53-100 kGy) had, respectively, the formulas $C_9H_{8.37}O_{3.19}(OCH_3)_{1.36}$ and $C_9H_{8.95}O_{3.45}(OCH_3)_{1.16}$. On the basis of these formulas, some authors [15, 16] consider that during the radiolysis of wood an accumulation of chemically bound oxygen and a decrease in the amount of bound hydrogen take place in lignin, while others [41] adhere to the opposite point of view. However, they have the opinion in common that during the radiolysis of wood the demethoxylation of the lignin takes place. A decrease (approximately 18%) in the number of methoxy groups in pine and beech lignins with an increase in their γ-radiation dose (0-1700 kGy) has also been shown in [42].

In the γ-irradiation of preparations of lignin [15, 16, 41] and of compounds modeling it [28, 43] the amounts of carbonyl and carboxy groups increase with the formation of structural units of phenolcarboxylic acids. As compared with lignin-modeling compounds, lignin preparations have a more developed system of polyconjugated bonds and, apparently because of this, possess an increased radiation resistance. Under identical conditions of irradiation, therefore, oxidative degradation was more pronounced for the lignin-modeling compounds. The depth of breakdown of such compounds is determined to a considerable degree by their initial structure. The maximum changes are undergone by a structure with free phenolic hydroxyls, and the minimum changes by compounds with blocked phenol groups [28, 43]. Double bonds in the side chain of the lignin PPU are unstable to the action of radiation [15, 16, 41]. The destruction of aromatic nuclei is unlikely and takes place only in solutions (suspensions) of lignin preparations when the system is aerated [41].

TABLE 3. Composition of Lignin Preparations Isolated from Unirradiated and γ-Irradiated (to a dose of 1000 kGy) Pine Wood [31]

Type of lignin	Elementary composition, rel. %*				Ratio of the number of phenolic OH groups to the number of OCH_3 groups
	C	H	OCH_3	S	
Brauns lignin	62,0	6,1	15,0	—	0,30
	(60,7)	(6,4)	(14,3)	—	(0,29)
Dioxane lignin	60,1	6,7	14,6	—	0,22
	(60,3)	(5,9)	(14,4)	—	(0,20)
DMSO lignin	59,2	5,8	12,6	—	. . .
	(59,9)	(6,0)	(12,2)	—	. . .
TGA lignin	53,5	5,9	13,9	8,7	0,23
	(52,6)	(5,7)	(13,8)	(8,4)	(0,26)

*The indices for the lignin isolated from the irradiated wood are given in parentheses.

TABLE 4. Composition of γ-Irradiated Brauns Lignin [31]

Sample	Elementary composition, rel. %			Ratio of number of phenolic (1) and aliphatic (2) OH groups to the number of OCH_3 groups	
	C	H	OCH_3	1	2
Unirradiated	62,7	6,2	14,5	0.45	1,59
Irradiated (dose 700 kGy)	61,3	6,2	14,5	0.43	1,58
Dissolved in dioxane (dose 500 kGy)	61,2	6,3	14.4	0,41	1.50

TABLE 5. Action of γ-Irradiation on Dioxane Lignin [40]

Index, %	Irradiation dose, kGy			
	0	500	1000	3000
Amount of Klason lignin	93	90	94	97
methoxy groups	12,7	11,8	12,0	11,6
carboxy groups	0.47	0.32	0,38	1.03
Solubility in water	0,0	4,0	4,9	6,8
in ethanol	4,2	14,8	16,5	17,8
in 2.5% aqueous NaOH	98,5	98,7	99,1	100,0

Table 6 gives information [15, 16, 44] on the number of functional groups and the number of dimeric structures per 100 PPU of MWL isolated from unirradiated and irradiated beech wood. The lignin obtained from the irradiated wood contained a smaller amount of aliphatic hydroxyls and double bonds in the PPU side chains and, at the same time, the number of biphenyl structures had increased considerably.

Hon and Chang [45], who investigated the photolysis of pine wood and MWL preparations by hard ultraviolet radiation, detected among the water-soluble degradation products the presence of aromatic compounds containing free phenolic hydroxyls conjugated with carbonyl groups. The total amount of phenolic hydroxyls in the MWL preparations decreased with the radiation dose. The maximum oxidation (11.4 carbonyl groups per 100 PPU) was undergone by the lowest-molecular-mass (water-soluble) fraction of the MWL. In the photolysis of soluble dioxane lignin, its molecular mass fell by a factor of almost 2 with a simultaneous increase (approximately 3 times) in the number of quinone and carboxy groups conjugated with an aromatic nucleus [24, 26].

The quantitative determination of the lignin content (by acid methods) directly in irradiated wood gives practically unchanged results up to absorbed doses of 1000-1800 kGy [31, 33, 34, 42, 46]. The unchanged content and, at the same time, the increased solubility of the lignin in aqueous and organic media [29-31, 35] can apparently be explained by the assumption that during its radiolysis oligomers are formed which are capable of dissolving partially in these media and of condensing to

TABLE 6. Functional Groups and Dimeric Structure of MWL [15, 44]

Names of the groups and structures	Number of groups and structures per 100 PPU of wood ligni	
	unirradiated	irradiated
Phenolic hydroxyls	21	22
Aliphatic hydroxyls	87	79
Sum of the hydroxyls	108	101
α-β-Unsaturation	4,7	3,3
Conjugated carbonyls	17	16
Biphenyl	3,5	6
Phenylcoumarane	5,7	5,2
β-Ether structure	49,8	48,4

form insoluble residues in concentrated solutions of acids [33, 34, 40]. According to [37], the lignin of γ-irradiated wood becomes more soluble in concentrated (43.6%) hydrochloric acid than the lignin of unirradiated wood. However, the maximum increase is slight, amounting to only 4.6% on the initial lignin content. In view of the fact that in the wood of deciduous species the amount of acid-soluble lignin changes within wide limits [48, p. 103], it is hardly possible to draw an unambiguous conclusion from the results obtained. The facts presented show indirectly that the degradation of lignin in wood obviously takes place by the laws of chance — without the formation of appreciable amounts of low-molecular-mass acid-soluble products.

On the basis of the change in their molecular masses, polymers can be divided into two groups: in one the molecular mass rises on irradiation, and in the other it falls. The first are called cross-linked and the second degradational polymers. During the radiolysis of lignin not only cleavages (as indicated by the investigations described above) but also linkages of polymeric chains take place. Reports have been published that dioxane lignin [49, 24] and the lignocarbohydrate complex isolated from spruce wood [50] behave as cross-linked polymers under the actions of laser, UV, and γ-radiations. As a result of condensation processes caused by the action of radiation, the solubility of these lignin preparations decreases. A cross-linking process in the radiolysis of lignin is shown by an accumulation of biphenyl structures in MWL (Table 6). Inaba et al. [43] have shown that on the γ-irradiation of guaiacylethane the formation of a dimeric product (5,5′-dehydroguaiacylethane) is possible.

On the basis of the facts given, lignin must apparently be regarded as a polymer on the irradiation of which the molecules not only break down but also undergo cross-linkage. It is interesting to note that, at equal doses, the lignin of irradiated wood possesses a higher solubility in alkaline media than, for example, irradiated MWL [45]. The MWL preparations obtained from irradiated wood possessed more uniform molecular-mass distributions than the MWL from unirradiated wood [15, 16]. On the whole, on irradiation natural lignin behaves as a predominantly degradational polymer (as is shown by the majority of published investigations) and forms soluble oligomeric products.

LOW-MOLECULAR-MASS PRODUCTS OF THE RADIOLYSIS OF LIGNIN

In the radiolysis of lignin, together with the main products (lignin oligomers) a small amount of so-called minor (low-molecular-mass) radiolysis products is formed. Table 7 gives information on the yield of steam-volatile phenols (phenol, cresols, xylenols, guaiacol) that were obtained on the "mild" hydrolysis of γ-irradiated wood raw material by a solution of orthophosphoric acid [33, 34, 51]. For the wood and the bark the relative yields of simple phenols, calculated to phenol, in the range of absorbed doses of 0-900 kGy rose by a factor of 1.5-2.0, and for birch bark by a factor of 3. The yield of phenols from birch wood does not depend appreciably on the absorbed dose of γ-radiation. The absolute amount of volatile phenols obtained in the hydrolysis of irradiated wood is low ($0.5 \cdot 10^{-4}$-$1.2 \cdot 10^{-3}$% on the absolutely dry wood or $2.5 \cdot 10^{-4}$-$6.0 \cdot 10^{-3}$% on the Klason lignin). On the hydrolysis of irradiated samples in water, the amount of phenols decreased by an order of magnitude. Formation of the simplest phenols directly in the irradiated lignin is apparently unlikely. The bulk of them obviously arises during the hydrolysis of the lignin oligomers [34, 51].

When γ-irradiated lignin preparations were dissolved in alkali, a very small amount of aromatic aldehydes (such as vanillin [52, 53]) was formed. Vanillin has also been obtained in very small amounts on the γ-irradiation of alkaline and dioxane solutions of lignin [52, 53]. By oxidizing with copper oxide in an alkaline medium cedar wood lignin that had been γ-irradiated to a dose of 700 kGy, Chawla and Puri [54] obtained the maximum yield — 3.67% on the absolutely dry wood (~12%

TABLE 7. Amount of Steam-Volatile Phenols [33, 34, 51] (μg of phenol/g of absolutely dry sample)

Dose, kGy	Pine			Birch		
	wood of the trunk	wood of the branches	bark	wood of the trunk	wood of the branches	bark
0	2.1	4,8	23,5	1.1	0,8	1,2
50	...	...	29,0	...	...	1,1
100	2.0	5,8	33,0	1,2	0,8	1.3
500	2,5	6,3	37,1	1.5	0,6	2,2
900	4,2	8,7	36,0	1,5	0,5	3,9
1800	6,5	12,1	...	1,1	0,9	...

TABLE 8. Efficiency of the Protective Action of Lignin on Wood Cellulose during γ-Irradiation, % [63]

Dose, kG	Pine	Spruce
12,5	122	107
25,0	93	75
50,0	69	59
100.0	4,5	3,4

on the Klason lignin) of aromatic aldehydes, of the total amount of which vanillin made up approximately 87%. An absorbed dose of 700 kGy was the optimum. A decrease or increase in this value led to a fall in the yield of aldehydes.

In the process of nitrobenzene oxidation, hydrochloric-acid lignin γ-irradiated to a dose of 0-225 kGy yielded practically unchanged amounts of vanillin and syringaldehyde [47]. These results agree well with those of Chawla and Puri [54], who observed a significant increase in the yield of aromatic aldehydes only at absorbed doses greater than 500 kGy. The formation of aromatic aldehydes directly in irradiated lignin is unlikely [52].

The formation of aromatic acids from lignin is minimal even at "high" (more than 1000 kGy) absorbed radiation doses. The amount of these acids in aqueous extracts of wood is therefore very small. Thus, at an absorbed dose of ~1700 kGy only traces of protocatechuic, vanillic, and ferulic acids were detected in extracts of beech wood [42].

The gaseous products formed in the process of irradiation (carbon monoxide and dioxide and hydrogen) must also be assigned to the low-molecular-mass products of the radiolysis of lignin, but their amounts have scarcely been studied at the present time. The available experimental results [42, 55] on the decrease in the mass of plant matter during its radiolysis shows that this magnitude rises in the sequence lignin—wood—cellulose. Lignin apparently gives a smaller amount of gaseous products than cellulose and wood. The presence of lignin in plant tissue lowers the radiation-chemical yields of gases [56, 58]. The authors connect this behavior of lignin with its high radiation stability and protective effect in relation to polysaccharides.

It follows from the facts presented that in the radiation degradation of lignin the formation of simple phenols and aromatic aldehydes and acids has a low efficiency. This conclusion is also confirmed by the results of the enzymatic hydrolysis of the polysaccharides of γ-irradiated wood. The low-molecular-mass products of the radiolysis of lignin, which possess a pronounced inhibiting action, had no appreciable effect on the depth of hydrolysis of wood polysaccharides [59].

THE PROTECTIVE PROPERTIES OF LIGNIN

As compared with other components, the breakdown of the structural units of lignin during the radiolysis of plant tissue is minimal. The increased radiation stability is apparently connected with the process of dissipation of the radiation energy absorbed by the lignin macromolecules [50, 57, 58]. The π-electronic systems of the aromatic groups of its molecules, forming a kind of screen, are obviously capable of disseminating the energy of the radiation in the form of heat or light [60, pp. 27, 61] in a similar manner to the protective effect of benzene [62, p. 279]. The possibility of the dissipation of the energy by the aromatic component of wood is also confirmed by the protector properties of lignin in relation to polysaccharides [57, 58, 63].

Ershov and Klimentov and their colleagues [9, 64] have shown that the lignin present in wood exerts a protective action on polysaccharides. The yield of carbohydrate radicals in wood was 3-5 times smaller than the yield expected as the result of the independent radiolysis of the cellulose [9]. On comparing the action of γ-irradiation on the initial wood, holocellulose, and wood without lignin (calculated figures), it was shown in [58] that lignin protects the carbohydrate fraction. An influence of lignin on the radiation degradation of holocellulose has been shown in [65]. The results obtained indicate that the radiation degradation of cellulose and hemicelluloses in wood takes place less intensively in the presence of lignin.

Useful information for a discussion of the protective action of lignin in relation to polysaccharides can apparently be obtained in an analysis of studies on the radiolysis of cellulose modified by aromatic groups [61, 66]. The introduction of aromatic substituents exerts a substantial influence on the localization of the absorbed energy in the cellulose macromolecules [67, 68]. Because of the intramolecular transfer of energy or its selective absorption, the resistance of cellulose to the action of radiation rises [60, 69, 70]. A decrease in the efficiency of the π-electronic cloud through the modification and destruction of aromatic groups unambiguously leads to a decrease in the radioprotector effect. The relative strength of cellulose fibers modified by a given substituent is a function of the degree of substitution of the hydroxy groups of the cellulose. The protective functions of aromatic substituents are determined in the first place not so much by their nature as by the strength of their bonds with the cellulose molecule. When this bond is weak, the bulk of the substituents (for example, benzyl groups C_6H_5—CH_2) are split out even at low doses. The cleavage of the bonds leads to the destruction of the "bridge" by which the transfer of energy takes place. The result of this is a local rise in the absorption of the energy of the radiation in the cellulose molecule and an intensification of its breakdown. Modified irradiated cellulose gives the same ESR signal as the initial cellulose [60, 68, 71]. The invariability of this signal probably indicates that in the modified cellulose (as in the native cellulose) there is a single type of free radicals, the appearance of which is due to the localization of energy on the C_1 and C_4 atoms of the glucopyranose units of the macromolecule. The concentration of radicals in irradiated cellulose that has been modified with aromatic substituents falls with an increase in the degree of substitution of its hydroxy groups, and this by an exponential relationship [68].

The authors of the papers mentioned above, using only monocyclic aromatic substituents based on the benzene ring, observed no appreciable influence of the nature of the substituent, at the same degree of substitution, on its protector properties. This conclusion is quite normal if it is borne in mind that the main protective function is borne by the π-electronic systems of the benzene nucleus. With an increase in the dimensions of the π-electronic system (for example, on the use of polycyclic or condensed aromatics) the efficiency of the radioprotector rises. To evaluate the efficiency of the protective action of various aromatic compounds, Wündrich [72] made use of the molar protection coefficient (P_m):

$$P_m = \frac{1}{C}\left(\frac{G}{G_p} - 1\right),$$

where G and G_p are the radiation-chemical yields of the breakdown of the polymer without the protector and with the protector, respectively; and C is the molar concentration of the protector.

The efficiency of the protective action of a protector decreased in the sequence: benz[a]anthracene, pyrene, anthracene, phenanthrene, biphenyl, naphthalene, and benzene, in a ratio of 12:11:8:6:5:5:1, respectively.

Skvortsov and Klimentov [63] have discussed the influence of the size of the absorbed dose on the efficiency of the protective activity of lignin in relation to cellulose on the γ-irradiation of wood. It can be seen from Table 8 that the efficiency of the protective action of lignin in the interval of absorbed doses of 0-100 kGy falls rapidly from 122 and 107% to 4.5 and 3.4% in pine and spruce woods, respectively. At absorbed doses greater then 200 kGy [63], there is practically no protective effect although the chemical changes in the lignin for such doses are minimal [31, 32]. A fall in the protective action of lignin on the polysaccharides of the lignocarbohydrate complex isolated from wood has been observed at absorbed doses greater than 500 kGy [50].

It follows from the investigation mentioned that although the fact of a protective action of lignin in relation to polysaccharides in the radiation of plant tissue was established experimentally long ago, the mechanism of protection has obviously been studied inadequately. The existence of three mechanisms of protection is possible theoretically [62, p. 390]: 1) "sacrificial" protection — the protective agent, itself, decomposes under the action of radiation; 2) protection in which the protective agent is incorporated in the polymer chain and repairs breaks; and 3) protection in which excess energy is removed from the polymer by the transport of energy over a distance.

It is obvious that for lignin the realization of the first mechanism is unlikely because of its fairly high radiation stability [29-31, 40]. Apparently, the realization of the second mechanism is possible, in part, in the range of "small" doses (≤ 100 Gy). In favor of this is the increase in the mechanical strength of wood through an increase in the number of radiation-induced cross-linkages in the wood matrix [40, 42, 73]. However, at doses ≥ 1000 Gy the mechanical characteristics of wood deteriorate and it begins to behave as predominantly a degradational polymer. At the present time, no polysaccharides with lignin molecules or fragments radiation-grafted onto them have been isolated from irradiated wood.

Because of its aromatic nature, the levels of excitation of lignin molecules are located above the levels of excitation of polysaccharide molecules. The lignin molecule may apparently, therefore, trap migrating energy (the third mechanism of protection) and consume it by various mechanisms of the dissipation of excitation energy [62, p. 134]. Interference with the transmission of energy between polysaccharide and lignin must lead to a fall in the protector effect. A decrease in the protective effect of lignin with a rise in the absorbed dose of γ-radiation has been shown experimentally [50, 63]. Apparently, on radiolysis the polysaccharides are "insulated" from the lignin through the cleavage of radiationally unstable lignocarbohydrate bonds [31], as a result of which the transfer of energy between the components is interrupted and the efficiency of the protective action of the lignin on the polysaccharides falls.

In conclusion, it must be mentioned that at the present time there are no generally accepted mechanisms for the radiolysis of polymers of plant origin. Consequently, much is still unclear in questions relating to the action of high-energy radiations on the components of plant tissue and, especially, on lignin.

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