Kinetics of oxidation of an arabinogalactan from larch (*Larix sibirica* L.) in an aqueous medium in the presence of hydrogen peroxide

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The oxidation of an arabinogalactan in an aqueous medium under the action of hydrogen peroxide and dioxygen is accompanied by accumulation of carbonyl and carboxy groups in the oxidized polysaccharide macromolecules and derived oligomers. The addition of iron sulfate accelerates the radical oxidation of the biopolymer, while the addition of phenol inhibits the oxidation. The influence of the temperature and the initial H_2O_2 and arabinogalactan concentrations on the kinetics of the initial oxidation stage of the natural polysaccharide was studied.

Key words: polysaccharides, arabinogalactan, hydrogen peroxide, oxidation process, kinetics, radical mechanism, functionalization.

Currently, polysaccharide-derived oligomers with different chain lengths are used in the pharmaceutical, cosmetic, and food industry.[1—3] The natural water-soluble polysaccharide arabinogalactan (AG) isolated from the Siberian larch exhibits immunomodulating activity. Its practical use requires further study of the structure and composition of the polysaccharide and development of methods for the synthesis of AG-derived oligomers with a specified chain length and their chemical characterization.

Polysaccharides used in medicine and in food and cosmetic industries are often subjected to preliminary destruction to give water-soluble oligomers[4—6] by treatment with acids,[5] alkalis,[6] ozone,[7] or hydrogen peroxide.[8,9] Cleavage of biopolymers with an acid or an alkali brings about the problem of purification of the target product from the remainder of the reagent, which increases the cost of the process. The peroxide method is free from these drawbacks and allows one to prepare oligomers suitable for the subsequent use without additional purification.

This study deals with the kinetics of the initial stage of AG oxidation in aqueous solutions with the hydrogen peroxide—dioxygen oxidation system. The goal is to obtain quantitative data for selecting the conditions of oxidative destruction and functionalization of the polysaccharide.

Experimental

The experiments were carried out using AG with a molecular mass of 40 000 isolated by aqueous extraction from larch wood.[10] The AG was isolated and purified to remove water-soluble phenolic compounds including dihydroquercetin on a polyamide sorbent.[10] This gave an aqueous solution of the polysaccharide containing traces of flavonoids. The galactose to arabinose ratio was 5.6 : 1.[11] The decrease in the molecular mass of AG upon oxidative destruction was estimated by viscometry. The characteristic viscosity (η_{char}) for aqueous solutions of AG and of its oxidation products was measured at 30±1 °C using a suspended level Ubbehlode viscometer.[12] The oxidation of solutions of AG in H_2O_2 with dioxygen was carried out in a glass bubble-type reactor maintained at a constant temperature; during the reaction, samples were withdrawn. The volume of the reaction mixture was 10 mL and the rate of air flow was 3 L h^{-1} (except for specified cases). Simultaneously, a series of experiments without passing air was carried out. In this case, AG was oxidized by oxygen formed upon the thermal decomposition of H_2O_2. After completion of the reaction, the polymeric fraction of the oxidized AG was separated from the oligomeric fraction by precipitation with four volumes of acetone. The oligomeric fraction was isolated from the supernatant liquid by evaporating the solvent. The functional groups in the polymeric and oligomeric fractions were analyzed by alkalimetry (KOH), IR spectroscopy (mineral oil, UR-20 spectrophotometer), and ^{13}C NMR spectroscopy. ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (75.47 MHz) with broad-band proton decoupling and in the JMODXH mode; 3—5% solutions of AG

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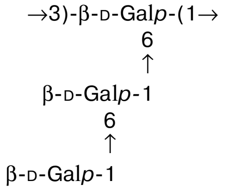
in D_2O were used and sodium 3-(trimethylsilyl)propane-1-sulfonate (DSS) was used as the internal standard. The spectra were measured at 35 °C with a 15 s delay between the pulses. The total concentration of peroxides (H_2O_2 + AG oxidation products) was determined by iodometry by addition of KI followed by titration of the liberated I_2 with $Na_2S_2O_3$. The content of galactose was determined using the reaction with the anthrone reagent for hexoses.[13] This color reaction is selective for hexoses, while pentoses, hexosamines, *N*-acetylhexosamines, uronic acids, or aromatic amino acids and proteins do not give products with an absorption maximum at 620 nm following reaction with the anthrone reagent. The protein admixtures were quantified according to Lowry,[14] bovine serum albumin being used for calibration. The content of uronic acids was found by the Dische method.[15] The reaction is selective for uronic acids, because neither galactose nor pentoses give products with an absorption maximum at 535 nm. Specific rotation was measured on a Perkin—Elmer 141 polarimeter.

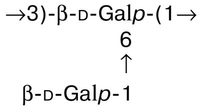
Results and Discussion

The AG macromolecules from *Larix sibirica* L. have a complex highly branched structure. The main structural fragments of arabinogalactan are presented below.[2,16]



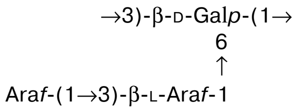
$$\begin{array}{c} \rightarrow 3)\text{-}\beta\text{-D-Gal}p\text{-}(1\rightarrow \\ 6 \\ \uparrow \\ \beta\text{-D-Gal}p\text{-}1 \\ 6 \\ \uparrow \\ \beta\text{-D-Gal}p\text{-}1 \end{array}$$

a



$$\begin{array}{c} \rightarrow 3)\text{-}\beta\text{-D-Gal}p\text{-}(1\rightarrow \\ 6 \\ \uparrow \\ \beta\text{-D-Gal}p\text{-}1 \end{array}$$

b



$$\begin{array}{c} \rightarrow 3)\text{-}\beta\text{-D-Gal}p\text{-}(1\rightarrow \\ 6 \\ \uparrow \\ \text{Ara}f\text{-}(1\rightarrow 3)\text{-}\beta\text{-L-Ara}f\text{-}1 \end{array}$$

c

The averaged structure can be represented as follows:

$$\rightarrow[a\rightarrow a\rightarrow a\rightarrow b\rightarrow c\rightarrow a\rightarrow a\rightarrow b]\rightarrow.$$

No thermal destruction or oxidation of the AG occurs on heating of its aqueous solutions at 50—95 °C. In this temperature range, AG is not oxidized even when air is passed through the solution. Under the same conditions but in the presence of H_2O_2 added to aqueous solutions of AG, oxidative destruction of the biopolymer takes place together with functionalization of macromolecules and oligomers, resulting in a change in the elemental composition of the reaction products (Table 1).

As can be seen from Table 1, the oxidized sample has a lower content of hexoses and a higher content of uronic acids. The change in the polysaccharide composition is also indicated by a substantial decrease in the specific rotation. The IR spectrum of natural AG shows vibrations at 3200—3600 cm^{-1} (HO groups) as a strong broad band, 1050—1100 cm^{-1} (pyranose and furanose rings), 890—910 cm^{-1} (C(1)—H deformation vibrations), and 1690 cm^{-1} (uronic acids) as a weak band. In the spectrum of the oxidized AG, the intensity of the band at 1690 cm^{-1} increases, indicating accumulation of uronic acids. The IR spectra of the polymeric and oligomeric fractions exhibit also medium and strong bands (1765—1750 cm^{-1}), which are typical of stretching vibrations of the carbonyl group; their content is higher for oligomeric than for polymeric fractions.[17]

Table 1. Characteristics of arabinogalactan (AG) and of its oxidation products*

Characteristics	Sample		
	unoxidized AG	Fractions of oxidized AG	
		polymeric	oligomeric
C_{exp} (%)	40.18	38.75	37.64
H_{exp} (%)	7.49	7.24	6.21
Uronic acids (%)	7.80	10.85	12.05
Hexoses (%)	71.8	46.3	20.0
Protein (%)	1.2	—	—
$[\eta]_{char}$**/dL g^{-1}	0.033	0.028	0.017
$[\alpha]_D^{20}$	+11.9	+8.4	+5.3

* 90 °C, $[H_2O_2]_0$ = 1 mol L^{-1}, $[AG]_0$ = 10% (w/w), 6 h; no ash.
** Characteristic viscosity.

The data from Table 1 suggest that oxidation of AG is accompanied by destruction of the polysaccharide macromolecule, as follows from a decrease in the characteristic viscosity of solutions of the oxidized fractions.

The structural composition of the initial polysaccharide is identical to the composition of AG from *Larix sibirica* L. reported previously.[10,18] Examination of the ^{13}C NMR spectrum of the high-molecular-weight fraction isolated after oxidation shows the presence of structural fragments built of the monosaccharide units that have not been oxidized and a substantial amount of fragments containing carboxy groups (Table 2). The presence of uronic acids in several structural fragments of the partial oxidation product of AG is confirmed by the presence of singlets at δ 177—180, which correspond to the carboxyl C atom. The pronounced decrease in the signal intensities for the terminal galactopyranose groups, compared to those in the spectrum of the starting AG, and the appearance of intense characteristic signals for the C(5) (δ 75.2) and C(6) (δ 178.9) atoms indicate that oxidation involves the C(6) atoms of the terminal β-Gal*p*-(1→ groups. The decrease in the intensity of the signals corresponding to the trisubstituted →3,6)-β-Gal*p*-(1→ unit

Table 2. ^{13}C NMR data for the oxidation products of arabinogalactan (AG) (D_2O, DSS, +30 °C)

Fragment	δ					
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
	High-molecular-weight fraction of oxidized AG					
β-Gal*p*A-(1→	105.9	71.9	73.7	72.2	75.2	178.9
β-Gal*p*-(1→	105.3	72.6	74.1	71.3	71.3	63.7
→3,6)-β-Gal*p*-(1→	106.4	71.6	84.5	69.1	74.9	68.5
→6)-β-Gal*p*-(1→	105.8	72.3	73.4	71.0	74.6	70.5
→3)-β-Gal*p*A-(1→	106.0	72.5	83.7	73.0	75.1	178.6
-L-β-Ara*p*-(1→	99.1	71.3	71.0	71.8	64.7	—
	Oligomeric fraction of oxidized AG					
β-Gal*p*A-(1→	105.9	71.8	73.8	72.1	75.2	179.5
β-Gal*p*-(1→	105.3	72.7	74.6	71.8	71.1	63.7
→3,6)-β-Gal*p*-(1→	106.5	71.8	84.4	69.0	74.8	68.6
→6)-β-Gal*p*-(1→	105.7	72.6	73.4	71.1	74.6	70.4
-β-Ara*p*-(1→	99.4	71.6	70.8	73.4	64.7	—
→3)-Ara	95.2	70.1	74.6	70.8	65.9	—

(broad doublets at δ 106.4 (C(1)) and δ 84.2 (C(3)) and a triplet at δ 68.5 for C(6)) and the appearance of narrow doublets at δ 106.0, 83.7, and 75.1 and a singlet at δ 178.6 imply that the AG oxidation is accompanied by a destruction of the polysaccharide backbone with splitting off the side chains giving rise to galacturonic acid units, →3)-β-Gal*p*A-(1→.

The ^{13}C NMR spectrum of the oligomeric fraction of the AG oxidation products contains a more diverse set of structural units. The spectrum shows lower intensities of the signals of monosaccharide residues, compared to those found for the high-molecular-weight fraction, and a higher intensity of the signal of uronic acids. In addition, a doublet corresponding to formic acid (δ 168.3, $^1J_{C,H}$ = 213.7 Hz) is observed in the spectra of the oligomeric oxidation products. The presence of formic acid in the oxidation products means that destruction is also accompanied by fragmentation of the monosaccharide units with elimination of formic acid. In order to elucidate the mechanism of the oxidative destruction of AG, the model oxidation of D-galactopyranose, which is the main structural unit of AG, was carried out using the same oxidation system. At an early oxidation stage, the ^{13}C NMR spectrum of D-galactose displays signals corresponding to the α- and β-anomers of galactopyranose (in special experiments, the spectral parameters for these anomers in D_2O were determined to be as follows: β-anomer: 99.2 (s), 74.6 (d), 75.5 (d), 71.1 (d), 77.8 (d), 63.7 (t); α-anomer: 95.0 (d), 72.0 (d), 71.1 (d), 71.9 (d), 73.2 (d), 63.9 (t)) and six additional signals (178.5 (s), 82.6 (d), 76.3 (d), 74.9 (d), 71.6 (d), 63.8 (t)). The positions of these signals, the multiplicity of the signals for the carboxyl C(1) and methylene C(6) atoms, and the lack of signal for the anomeric atom attest to the formation of galactonic acid. Further oxidation of this mixture gives rise to formic acid (^{13}C NMR data). The intensity of the signal for formic acid increases in the course of destruction. In addition, signals, apparently due to a set of C_2—C_5 aldonic acids appear in the spectrum.

Signals corresponding to the same products are also present in the spectrum of the oligomeric fraction of AG obtained at high H_2O_2 concentrations (2.5 mol L^{-1}), in addition to the signals due to the fragments of nonoxidized AG. This suggests that the oxidative destruction of AG proceeds similarly to the oxidation of D-galactopyranose, which includes cleavage of glycosidic bonds, elimination of monosaccharide units, ring opening, oxidation of the anomeric C atom to a carboxy group, and further stepwise liberation of formic acid, as in the ozonolysis and peroxide-induced cleavage of carbohydrates.[19,20]

To elucidate the mechanism of oxidative destruction and functionalization of AG under the action of H_2O_2, the kinetics of this process has been studied. When an AG + H_2O + H_2O_2 + O_2 reaction mixture is kept at 85—95 °C, the kinetics of changes in the concentration of peroxides is described by a first-order equation (Fig. 1, *a*)

$$\ln[\mathrm{O{-}O}]_t = \ln[\mathrm{O{-}O}]_0 - k_{\mathrm{eff}}t, \qquad (1)$$

where k_{eff} is the effective rate constant of peroxy compound consumption, $[\mathrm{O{-}O}]_0$ and $[\mathrm{O{-}O}]_t$ are the initial and current concentrations of peroxy compounds.

The effective rate constant of peroxy compound consumption was found by transforming the kinetic curves in the coordinates of Eq. (1). The rate of accumulation of carboxy groups (V_{COOH}) varies with time, an induction period being followed by the highest V_{COOH} value, and then the accumulation rate decreases (Fig. 1, *b*). To determine the V_{COOH} maximum, the kinetic curves for accumulation of the COOH groups were subjected to polynomial analysis.

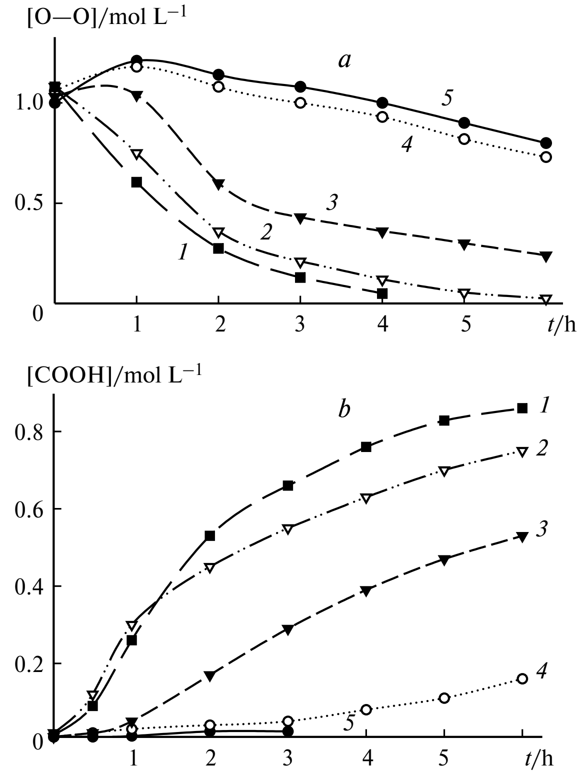


Fig. 1. Kinetic curves for the consumption of peroxy compounds (*a*) and accumulation of carboxy groups (*b*) at 95 (*1*), 90 (*2*), 80 (*3*), 70 (*4*), 60 °C (*5*) ($[AG]_0 = 10\%$ (w/w), $[H_2O_2]_0 = 1$ mol L^{-1}).

The presence of an induction period in the kinetic curves for the accumulation of carboxy groups (see Fig. 1, *b*) is apparently due to trace amounts of phenolic impurities present in the AG, which inhibit the oxidation of the biopolymer macromolecules.[1,11]

When phenol is added to an AG + H_2O + H_2O_2 + O_2 reaction mixture (PhOH was chosen as the inhibitor owing to its good solubility in water), the effective rate constant of peroxy compound consumption and the maximum rate of COOH accumulation decrease (Fig. 2, *a*). These data may indicate that the consumption of peroxy compounds and the accumulation of carboxy groups during the AG oxidation follow a radical mechanism and phenol (radical inhibitor) inhibits this process.

Transition metal ions (M^{n+}) catalyze the radical decomposition of hydrogen peroxide.[21]

$$H_2O_2 + M^{n+} \longrightarrow HO^- + HO^{\bullet} + M^{(n+1)+} \qquad (2)$$

Therefore, the addition of salts of such metals is expected to accelerate the AG oxidation induced by H_2O_2, as in the case of cellulose oxidation.[22] Indeed, the addition of $FeSO_4$ to the AG + H_2O + H_2O_2 + O_2 system entails an increase in V_{COOH} and k_{eff} (Fig. 2, *b*). The natural AG contains traces of transition metal compounds as impurities;[11] therefore, in the AG + H_2O + H_2O_2 + O_2 system, slight initiation of the oxidation according to reaction (2) takes place even without $FeSO_4$ additives.

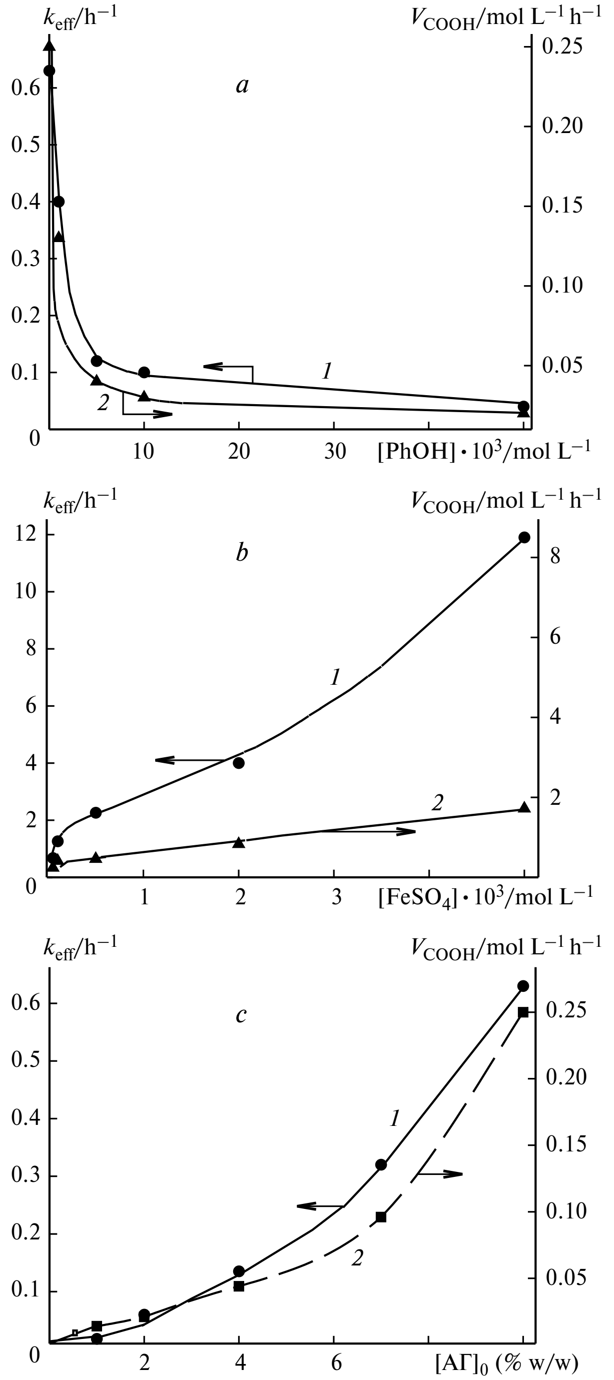


Fig. 2. Effective rate constants of peroxy compound consumption (k_{eff}) (*1*) and the maximum rate of carboxy group accumulation (V_{COOH}) (*2*) *vs.* content of phenol (*a*), $FeSO_4$ (*b*) (90 °C, $[AG]_0 = 10\%$ (w/w), $[H_2O_2]_0 = 1.1$ mol L^{-1}) and initial concentration of AG (*c*) (90 °C, $[H_2O_2]_0 = 1$ mol L^{-1}).

Hydroxyl radicals are active in the abstraction of hydrogen from C—H bonds. For example, the rate constants[23] for hydrogen abstraction in the $HO^{\bullet}$ + dioxane and $HO^{\bullet}$ + glycerol reactions in water at 298 K are $2.8 \cdot 10^9$ and $1.9 \cdot 10^9$ L mol^{-1} s^{-1}, respectively. It should be noted that the $HO^{\bullet}$ radicals would also be highly reactive with respect to all C—H bonds of arabinogalactan. Most likely, the primary site of hydrogen elimination in the AG macromolecules existing in solution as coils or globules would be determined by the accessibility of these bonds to the attack by the $HO^{\bullet}$ radicals rather than by the strength of these bonds. Therefore, the carbon-centered macroradicals resulting from homolysis of the C—H bonds in the reaction with $HO^{\bullet}$ may have the free valence both in the backbone and in the side chains of arabinogalactan (PH)

$$HO^{\cdot} + PH \longrightarrow H_2O + P^{\cdot}, \qquad (3)$$

where $P^{\bullet}$ is the set of various carbon-centered macroradicals formed from AG.

It is known that carbon-centered radicals rapidly add oxygen, being converted into peroxyl radicals.[24]

$$P^{\cdot} + O_2 \longrightarrow PO_2^{\cdot} \qquad (4)$$

Therefore, above a particular concentration of dissolved oxygen, the reaction rate no longer depends on this concentration, the radical oxidation being limited by reactions of peroxyl macroradicals.

This type of dependence on the oxygen concentration, which was varied by purging the reaction mixture with either argon or air, is observed in the AG oxidation (Table 3).

The data from Table 3 suggest that the rate of AG oxidation is limited by the subsequent reactions of peroxyl macroradicals rather than by their formation. It has been shown[24] that in the oxidation of polyolefins, the peroxyl macroradicals isomerize due to an intramolecular attack on their own C—H bonds. The AG peroxy radicals may izomerize in a similar way, for example, with participation of the →3,6)-β-D-Gal*p*-(1→ fragment. Apparently, the overall process involves also the $PO_2^{\bullet}$ radicals in the side chains of the AG macromolecules, for example, -β-D-Gal*p*-(1→. The isomerization reactions of peroxyl macroradicals end, apparently, in the formation of carboxy groups.

Table 3. Dependence of the effective rate constant of peroxy compound consumption (k_{eff}) and the maximum rate of the carboxy group accumulation (V_{COOH}) on the rate of gas bubbling (υ)*

Gas	υ/L h^{-1}	k_{eff}/h^{-1}	V_{COOH}/mol L^{-1} h^{-1}
Argon	3	0.16±0.03	0.10
Air	0	0.63±0.04	0.25
Air	1	0.63±0.04	0.21
Air	3	0.66±0.04	0.21
Air	5	0.58±0.06	0.23

* 90 °C, $[H_2O_2]_0$ = 1.1 mol L^{-1}, $[AG]_0$ = 10% (w/w).

The effective rate constant of peroxy compound consumption and the maximum rate of COOH group accumulation increase with an increase in the AG concentration when the $[O_2]$ and $[H_2O_2]_0$ values in the AG + H_2O + + H_2O_2 + O_2 system remain constant (Fig. 2, *c*).

These dependences are linearized in the logarithmic $\ln k_{\text{eff}}$—$\ln[AG]_0$ and $\ln V_{\text{COOH}}$—$\ln[AG]_0$ coordinates; this was used to calculate the reaction orders for the peroxy compound consumption ($n_{\text{O—O}}$ = 1.50±0.19 (without air bubbling) and 1.50±0.25 (with air bubbling)) and for the carboxy group accumulation (n_{COOH} = 1.19±0.08 (without air bubbling) and 1.16±0.05 (with air bubbling)).

It is worth mentioning that the degree of consumption of H_2O_2 (combined with the peroxides of the oxidized AG) depends on the initial AG concentration (for $[H_2O_2]_0$ = const), *i.e.*, it increases with an increase in $[AG]_0$. Thus when $[AG]_0$ = 10% (w/w), H_2O_2 is consumed almost entirely, whereas for $[AG]_0$ = 1% (w/w), it is consumed only by 11% and after that, the H_2O_2 concentration virtually does not vary with time.

$[AG]_0$ (% w/w)	1	2	4	7	10
Degree of H_2O_2 consumption (%)	11	37	72	85	97

These data, together with the data from Fig. 2, *c*, show that the products of AG oxidation induce the decomposition of H_2O_2. It was shown[24] that carbon-centered macroradicals derived from polyolefins cause decomposition of the hydroperoxy groups. Apparently, in the AG + H_2O + H_2O_2 + O_2 system, the carbon-centered radicals $P^{\bullet}$ formed upon AG oxidation also induce the decomposition of H_2O_2.

$$P^{\cdot} + H_2O_2 \longrightarrow POH + HO^{\cdot} \qquad (5)$$

The highest rate of COOH group accumulation increases also with an increase in the initial concentration of H_2O_2 for a constant $[AG]_0$ value in experiments both with and without air bubbling (Fig. 3, *a*).

To calculate the order of the reaction with respect to H_2O_2, the data from Fig. 3, *a* were processed in the $\ln V_{\text{COOH}}$—$\ln[H_2O_2]_0$ coordinates. The order of carboxy group accumulation with respect to H_2O_2 equals 0.48±0.08.

In the AG + H_2O + H_2O_2 + O_2 system, the carboxy groups are accumulated only provided that H_2O_2 is consumed. The process stoichiometry calculated as the ratio of the concentration of the accumulated carboxy groups to the concentration of the consumed peroxy compounds ([COOH]/Δ[O—O]) at the same moment remains constant to within the experimental error throughout the whole reaction, being equal, for example, to 0.6±0.1 at 90 °C.

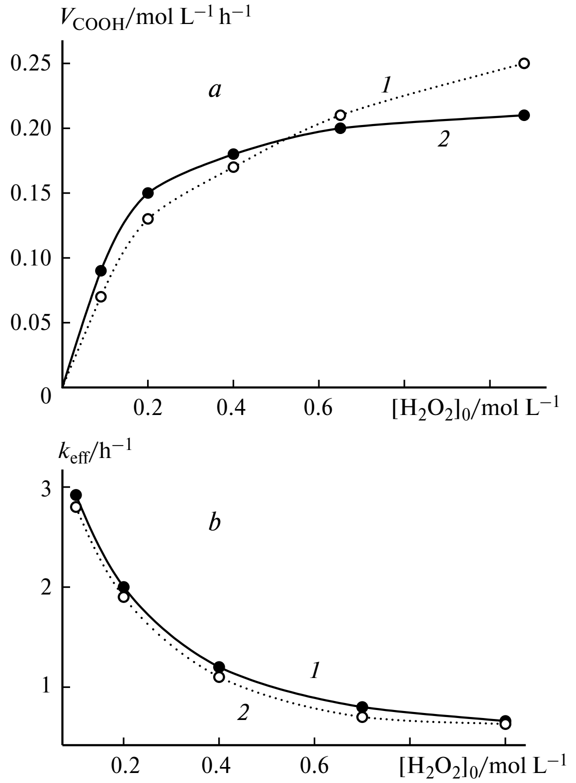


Fig. 3. Maximum rate of carboxy group accumulation (V_{COOH}) (*a*) and rate constants of peroxy compound consumption (k_{eff}) (*b*) *vs.* initial concentration of hydrogen peroxide without (*1*) and with air bubbling (*2*) (90 °C, $[AG]_0 = 10\%$ (w/w)).

The effective rate constant of peroxy compound consumption, unlike V_{COOH}, decreases with an increase in $[H_2O_2]_0$ at a constant $[AG]_0 = 10\%$ (w/w) (Fig. 3, *b*). The formal processing of the data from Fig. 3, *b* in the $\ln k_{eff}$—$\ln[H_2O_2]_0$ coordinates gives a negative value for the reaction order ($n = -0.66\pm0.15$). The negative order of the reaction with respect to H_2O_2 suggests that not only H_2O_2 consumption but also accumulation of the peroxide products of AG oxidation and further consumption of hydroperoxides take place in the AG + H_2O + H_2O_2 + O_2 system. Apparently, for high $[H_2O_2]_0$ values, the consumption of peroxides is compensated by accumulation of hydroperoxides to a larger extent than in the case of low $[H_2O_2]_0$. Since the iodometric method gives the total amount of peroxy compounds, a decrease in the specific rate of peroxy compound consumption (*i.e.*, k_{eff}) with an increase in $[H_2O_2]_0$ is observed in experiments.

In terms of this hypothesis, one can also explain the unusual behavior of the kinetic curves for the consumption of peroxy compounds (see Fig. 1, *a*) depending on the experimental temperature. These kinetic curves also reflect the simultaneous occurrence of, at least, three processes, namely, (1) consumption of hydrogen peroxide; (2) accumulation of the peroxy products of AG oxidation, and (3) the consumption of these products. At elevated temperatures (85—95 °C), reactions of peroxide decomposition predominate and, hence, the kinetic curves for the consumption of peroxy compounds for these temperatures are linearized in the coordinates of Eq. (1).

At lower experimental temperatures, the rate of destruction of peroxy compounds decreases, and the formation of peroxide products of AG oxidation becomes more significant; therefore, accumulation of the peroxy products predominates in early reaction stages, and subsequently, their consumption is the prevailing process. These regularities show themselves both with purging the reaction mixture with air at a flow rate of 3 L h^{-1} and without air bubbling.

The effective rate constants of peroxy compound consumption calculated using the data from Fig. 1, *a* and Eq. (1) depend linearly on the temperature in the Arrhenius coordinates

$$\ln k_{eff} = (39\pm5) - (118\pm15)\cdot10^3/RT \qquad (6)$$

(without air bubbling; correlation coefficient 0.998; R = 8.31 J mol^{-1} K^{-1}),

$$\ln k_{eff} = (44\pm18) - (134\pm53)\cdot10^3/RT \qquad (7)$$

(with air bubbling; correlation coefficient 0.978).

It can be seen from Fig. 1, *b*, the induction period for the accumulation of carboxy groups increases with a decrease in the experimental temperature. The maximum V_{COOH} values found from Fig. 1, *b* depend linearly on the temperature in the Arrhenius coordinates

$$\ln V_{COOH} = (32\pm6) - (90\pm17)\cdot10^{-3}/RT, \qquad (8)$$

the correlation coefficient is 0.990.

It has been shown**[17]** that H_2O_2 induces not only oxidation of AG but also its destruction. Hence, the alkalimetric analysis of the COOH groups in the AG + H_2O + + H_2O_2 + O_2 system determines the overall content of the carboxy groups in AG macromolecules and oligomers.

Relying on the data from Table 3, one can suggest that the peroxy macroradicals are involved not only in the rate-limiting step of AG oxidation but also in the termination step of the radical process

$$PO_2^{\cdot} + PO_2^{\cdot} \longrightarrow \text{Molecular products.} \qquad (9)$$

Phenols are known**[25]** to react with the peroxyl radicals and thus to inhibit oxidation. Evidently, the data presented in Fig. 2, *a* and the presence of an induction period on the curves for accumulation of the carboxy groups (see Fig. 2, *c*) can also be interpreted as being due to the reaction of phenol with $PO_2^{\bullet}$.

Thus, arabinogalactan is oxidized by dioxygen in an aqueous solution of hydrogen peroxide according to a radical mechanism. The oxidation of AG is accelerated by the addition of initiating systems (radical sources) and decelerated by the addition of an inhibitor (phenol). The oxidation of the polysaccharide is accompanied by functionalization, and, therefore, one can expected that the appearance of additional functional groups in the products of arabinogalactan oxidation would give rise to new chemical properties.

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