THE MECHANISM OF THE FORMATION OF QUINONIC ACIDS IN THE OXIDATION OF THE BARK OF THE SIBERIAN LARCH. I

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The oxidative degradation of bark in nitric acid is of practical and scientific interest, since it enables a waste-free processing of the raw material to be achieved. The absence of information on the chemistry and mechanism of the process is holding back progress in this field. The laws of the oxidation of hydrolysis lignin by nitric acid have been studied previously [1, 2]. Important information was obtained on the process which, however, cannot explain the chemistry of the oxidation of the bark. In actual fact, the chemical properties of bark, in spite of their similarity to the properties of wood, are nevertheless fairly specific. Thus, the lignin of the bark cannot be brought into solution completely by the same methods by which wood is delignified. The phenolic complexes of the bark include phenolic acids, in addition to true lignin. The bark of the Siberian larch contains more than 7% of suberin, the chemical nature of which has been studied far from completely. All this shows the desirability of studying the oxidative interaction of the bark of the Siberian larch with nitric acid.

As can be seen from Table 1, the bulk of the bark is decomposed into water-soluble products after reaction for six hours. The solid oxidation residue is practically completely free from hemicelluloses. The degradation has little effect on the cellulose over the whole period of oxidation. This agrees well with what is known from the nitric acid digestion of wood.

It is interesting to follow the changes in the phenolic complex of the bark during oxidation. The phenolic acids are particularly labile in relation to the oxidizing agent. Information on their chemical nature is inadequate, and therefore it is impossible at the present time to give an unambiguous explanation of the ease of their oxidation. However, it can be stated that aromatic hydrocarbons having oxygen-containing functional groups in the nucleus are readily oxidized. The phenolic acids differ from the lignin by a lower molecular weight and a considerable content of carboxy groups and phenolic hydroxyls [14]. In addition, the amount of methoxy groups, which stabilize an aromatic nucleus in relation to oxidizing agents, is 2.56% in the phenolic acids and 12.20% in the Koenig lignin.

TABLE 1. Influence of the Time of Oxidation on the Yield of Reaction Products

Time of oxidation, hours	Components of the solid residue, % on the absolutely dry bark						Components of the oxidate, % on the absolutely dry bark			
	readily hydrolyzable poly-saccharides	difficultly hydrolyzable poly-saccharides	alkali lignin	Koenig lignins	suberin	phenolic acids	oxalic acids	nitro-phenols	quinonic acids	hydroxy acids and their lactones
1	3,90	22,60	10,30	9,50	6,60	3,00	2,90	0,10	0,30	3,40
2	3,02	21,80	15,70	5,60	5,60	1,90	4,20	0,15	1,80	4,40
3	2,09	21,60	21,30	2,90	5,00	1,40	5,10	0,32	3,40	4,80
4	1,12	21,20	14,10	1,90	4,50	3,20	6,00	0,45	9,60	5,10
5	0,60	20,09	5,10	1,20	3,60	0,90	6,80	0,55	10,20	6,20
6	0,13	19,80	3,70	0,70	2,50	0,70	7,70	0,73	10,60	7,10
Initial bark	7,00	23,10		20,90	7,20	12,70				

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TABLE 2. Characteristics of the "Alkali Lignin" of Oxidized Bark

Time of oxidation, hours	Yield of alkali lignin, % on the Koenig lignin of the initial bark	Amt. of functional groups, % on the Koenig lignin of the initial bark			
		OCH_3	phenolic OH	COOH	quinone CO
1	49,44	7,47	1,13	2,30	4,06
2	75,16	5,60	1,59	7,90	5,57
3	100,67	3,27	2,02	14,37	7,48
4	67,69	1,09	1,41	7,84	5,39
5	24,59	0,17	0,75	4,61	4,48
6	17,71	0,09	0,55	5,44	2,93
Dioxane lignin of Siberian larch bark		17,02	2,46	—	—

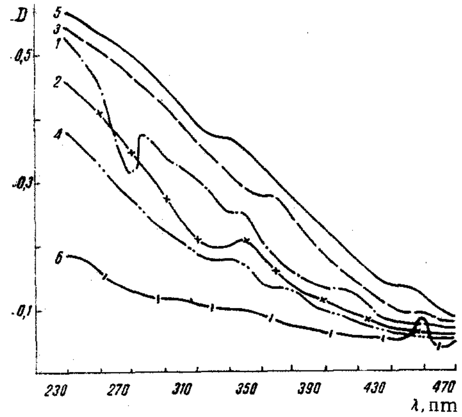


Fig. 1

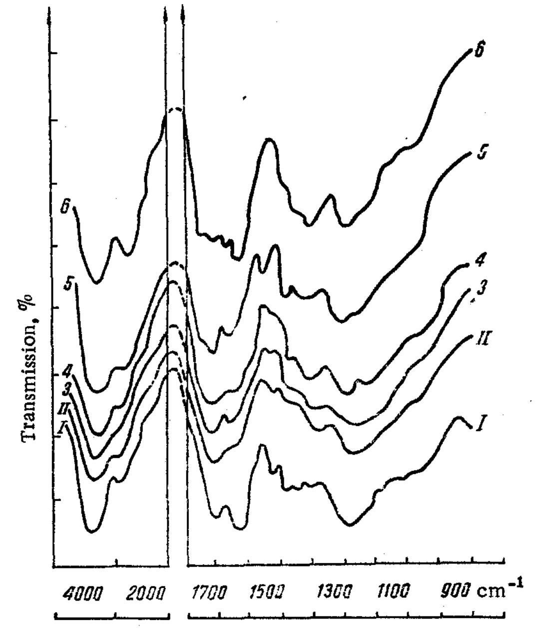


Fig. 2

Fig. 1. UV spectra of alkali lignins of bark obtained with oxidation times of from 1 t 6 h.

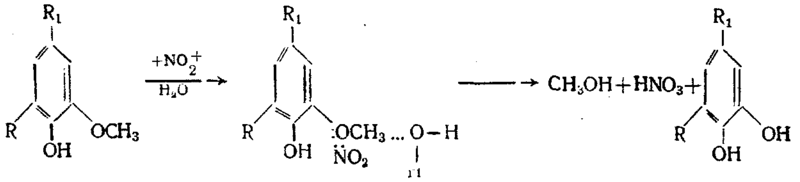
Fig. 2. IR spectra of alkali lignins of bark obtained on prolonged oxidation for from 1 to 6 h.

In view of this it must be expected that the phenolic acids will be oxidized more readily, and in this process the destruction of their aromatic structure is possible.

To check this hypothesis, the phenolic acids isolated from Siberian larch bark were oxidized under the conditions for the oxidation of the bark [2]. It was found that they were oxidized almost completely in an hour with the formation of a considerable amount (about 12%) of oxalic acid, which shows the decomposition of the aromatic structure of the phenolic acids. On the basis of the results obtained, it may be concluded that, although they have the same nature as simple phenolic acids, the substances that are determined in the solid oxidation residue after reaction for 2-6 h as phenolic acids are in fact degradation products of the lignin (fraction 2). Special experiments have confirmed this.

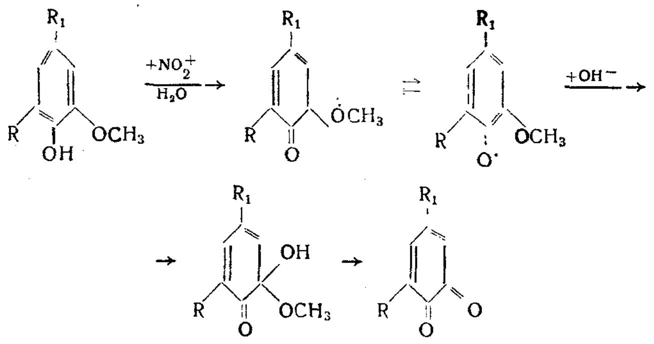
The results of a chemical analysis of fraction 1 of the oxidized lignin (Table 2) show that in the first period of the reaction (1-3 h), in spite of the increase in the amount of carboxylic, phenolic, hydroxylic, and quinone carbonyl groups the lignin is basically insoluble in an acid medium. It is apparently just this which may explain the existence of an induction period in the formation of quinonic acids (see Table 1) when their yield increases only slightly in spite of the occurrence of oxidation reactions of the lignin.

The rise in the amount of phenolic hydroxy groups shows a destruction of the lignin taking place with the cleavage of the β-aryl ether bonds. According to Ingold's theory [15], the demethylation of O-methylated phenols on reaction with nitric acid can take place hydrolytically. In this case, the NO_2^+ cation plays a role analogous to that of a proton in acid-catalyzed hydrolysis.



As a result of the hydrolysis of the alkyl-aryl bond, the guaiacyl structures of the lignin change into pyrocatechol structures, which are then readily oxidized to ortho-quinone structures [16].

Adler [17] has proposed a scheme for the oxidative demethylation of O-methylated phenols according to which the aromatic structure of the latter is converted into an ortho-quinolide and then into an ortho-quinoid structure:



The results of a chemical analysis of the oxidized lignin agree well with the proposed schemes: the amount of methoxy groups in the samples falls monotonically during oxidation, and the phenolic hydroxyls and quinone carbonyl groups reach a maximum by the end of the third hour.

The increase in the number of phenolic hydroxyls can also be explained by the cleavage of lignin–carbohydrate bonds. This is shown by the appreciable fall in the amount of readily hydrolyzable polysaccharides in the oxidized bark (see Table 1).

The formation of quinoid structures in the reactions of lignin is confirmed by the results of spectroscopic investigations. In the UV region (Fig. 1) the absorption band of an aromatic ring rapidly disappears during oxidation. The maxima on the curves shift in the long-range direction where many methylenequinones absorb [18], but the nature of the spectra remains more complex. The magnitude of the bathochromic shift, which is a criterion of the formation of quinoid structures, differs appreciably from the shift arising in the formation of ordinary phenoxide ions. The spectrum has a broad absorption band in the long-wave region which is characteristic for a charge-transfer system. All this is apparently explained by a considerable contribution of a quinoid structure to the basic state of the ionized form.

In the infrared spectra of samples of oxidized lignin (Fig. 2) there is likewise disappearance of the band at 1510-1515 cm^{-1} which unambiguously relates to the skeletal vibrations of the aromatic ring of lignin. Here an absorption band appears that is characteristic for a conjugated carbonyl group in quinoid compounds and which usually appears in the form of an averaged band at 1618 cm^{-1} or is split into a doublet in the 1610-1630 cm^{-1} region [18]. These results also show that the oxidation of bark lignin in nitric acid is accompanied by the conversion of the aromatic system of bonds into a cyclohexadienone system.

The decrease in absorption in the 1510-1515 cm^{-1} region may also be the result of a condensation of benzoid derivatives in the structural units of the lignin. Braun [19] has found that the 1515 cm^{-1} band disappears at an early stage of coalification. This band appears extremely feebly or is completely absent in the spectra of condensed aromatic hydrocarbons containing more than three benzene rings. In our case, the appearance of secondary aromatic structures is shown indirectly by the low yield of oxalic acid (see Table 1), in spite of the fact that the lignin macromolecule is intensively oxidized (see Table 2).

The strong absorption in the 1400-1000 cm^{-1} shows the saturation of the lignin by oxygen-containing functional groups [20], which is connected with oxidative processes and is confirmed by the results of chemical analysis (see Table 2).

A broad band at 3300 cm^{-1} characterizes the symmetrical vibrations of OH groups involved in hydrogen bonds [20]. Absorption in the 1140 cm^{-1} characterizes the symmetrical vibrations of OH groups involved in hydrogen bonds [20]. Absorption in the 1140 cm^{-1} region shows that a considerable number of these groups has a phenolic nature [20]. This is also shown by the chemical analysis of the alkali lignin.

The possibility of the formation of stable structures with a quinoid system of bonds on the oxidation of lignin is mentioned in a paper by V. V. Ershov et al. [21]. They have established that methylenequinones containing as substituents strongly electronegative functional groups, such as carboxy groups, are practically stable in an acid medium. Apparently, in this case conjugation between the electronegative substituent and the π-electrons of the methylene bond is so great that the existence of the quinoid system of bonds becomes preferred to that of a phenolic system. In this case, no quinone-phenol rearrangement of bonds takes place under the action of an acid medium.

EXPERIMENTAL

Depending on the conditions, in nitric acid both oxidation and nitration reactions of the main components of the bark may take place. We have previously found the optimum conditions for oxidative degration: temperature 92-95°C, ratio of liquid to solid 6, ratio of acid to raw material 2.25 parts by weight, rate of flow of air in oxidation 1.7-2.0 m^3/h per kg of bark, time 5 h 30 min [3]. Nitric acid with a density of 1.32-1.36 was added to the system gradually at a constant rate. In this way, in the first place, the O_2/NO_2 ratio was kept at a constant level and, in the second place, the decomposition of the quinonic acids formed was reduced. After the separation of the insoluble residue from the acid solution, the oxalic acid was precipitated in the form of calcium oxalate [4]. Then the nitrophenols were eliminated by successive extraction with benzene and chloroform, and the quinonic acids with methyl ethyl ketone [5]. After all the extractions, the hydroxy acids were precipitated in the form of the barium salts in acetone [6]. The solid oxidation residues were washed free from traces of nitric acid and were analyzed by a scheme generally adopted in bark chemistry [7] with the difference that the isolation of the suberin and phenolic acids was performed in a current of nitrogen at pH 11-12 in order to prevent condensation transformations of the lignin [8].

The presence of a considerable amount of functional groups in the lignin is responsible for its active role in the oxidative degradation of the bark. In a study of the macrokinetics of the process, we found that the oxidation of bark lignin in nitric acid takes place in two stages. The intermediate oxidation product, unlike the initial lignin of the bark, is readily soluble in 1% NaOH. By making use of this property, the unchanged lignin was separated from the oxidized product. By acidification of the alkaline extract, the latter was precipitated in the form of characteristic flocs (fraction 1). Part of the lignin remained in the acidified solution and on extraction with ether it was determined in the form of phenolic acids (fraction 2).

To elucidate the chemistry and mechanism of the oxidation of the lignin, these fractions were studied in more detail. In all the samples of oxidized lignin obtained at different reaction times, the following functional groups were determined by generally adopted methods [9-13]: methoxy, carboxy, phenolic and total hydroxylic, and carbonyl groups.

The changes taking place in the lignin macromolecule under the action of nitric acid and atmospheric oxygen were also studied spectrophotometrically. The UV spectra of the samples of oxidized lignin (fraction 1) were taken in 1% NaOH on a SF-16 spectrophotometer, and the IR spectra on a UR-20 instrument. The specimens were prepared in the form of tablets with KBr (3 mg of specimen to 600 mg of KBr).

SUMMARY

1. It has been established that in the reaction of Siberian larch bark with atmospheric oxygen in nitric acid, the hemicelluloses and the phenolic complex are oxidized most readily.

2. The phenolic acids are decomposed almost completely. The considerable yield of oxalic acid shows a degradation of their aromatic nucleus during oxidation.

3. In the oxidation of the bark lignin the cleavage of the lignin macromolecule to the final products does not take place directly. During oxidation an intermediate product with a quinoid system of bonds is formed in considerable amounts, and this then undergoes fragmentation as the result of the oxidative-hydrolytic action of the medium.

LITERATURE CITED

1. V. M. Nikitin, "The mechanism of the reaction of lignin with nitric acid," Trudy LTA, vyp. 75, 67-78 (1956).
2. N. N. Shorygina, L. L. Sergeeva, and A. A. Chuksanova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 250 (1956).
3. L. N. Davydova and É. D. Levin, Khimiya Drevesiny, No. 2, 117 (1974).
4. A. P. Kreshkov, Principles of Analytical Chemistry [in Russian], Part II (1956), p. 196.
5. M. I. Chudakov et al., Khimicheskaya Pererabotka Drevesiny, No. 2, 6 (1965).
6. N. A. Ivanov and V. N. Piyalkin, Izv. Vysshykh Uchebn. Zavedenii, Lesnoi Zhurnal, No. 6, 101 (1970).
7. V. I. Sharkov, N. I. Kuibina, and N. P. Solov'eva, The Quantitative Analysis of Plant Material [in Russian], Moscow (1968), p. 65.
8. US Patent No. 3,817,862 (1971).
9. A. V. Obolenskaya et al., Practical Work in Wood and Cellulose Chemistry [in Russian], Moscow (1965), p. 412.
10. V. N. Sergeeva et al., Khimiya Drevesiny, No. 2, 89 (1968).
11. V. A. Klimova and K. S. Zabrodina, Zh. Analit. Khim., 726 (1969).
12. B. D. Bogomolov, S. V. Pal'mova, and E. D. Gel'fand, Izv. Vysshykh Uchebn. Zavedenii, Lesnoi Zhurnal, No. 2, 139 (1968).
13. G. M. Vasil'eva, G. P. Grigor'ev, and K. P. Mishchenko, Zh. Prikl. Khim., 38, 27 (1965).
14. N. D. Barabash and É. D. Levin, Khim. Prirodn. Soedin., 385 (1970).
15. C. K. Ingold, Structure and Mechanism in Organic Chemistry, 2nd ed., Cornell University Press, Ithaca, New York (1969).
16. B. I. Zubkov and T. I. Temnikova, Izv. Akad. Nauk SSSR, Ser. Khim., 2615 (1961).
17. F. E. Brauns and D. A. Brauns, The Chemistry of Lignin, Academic Press, New York (1960).
18. V. V. Ershov et al., Sterically Hindered Phenols [in Russian], Moscow (1972), p. 350.
19. M. I. Chudakov et al., Some Lignin Condensation Processes in the Hydrolysis of Wood [in Russian], Moscow (1965), pp. 238-252.
20. K. Nakanishi, Infrared Absorption Spectroscopy. Practical, Holden-Day, San Francisco (1962).
21. V. V. Ershov et al., Izv. Akad. Nauk SSSR, Ser. Khim., 647 (1969).

THE MECHANISM OF THE FORMATION OF QUINONIC ACIDS IN THE OXIDATION OF THE BARK OF THE SIBERIAN LARCH. II

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The results of a chemical and spectroscopic study of the oxidative degradation of the bark of the Siberian larch have shown that the oxidation of the lignin of the bark to quinonic acids takes place through an intermediate complex with a quinoid system of bonds. This paper presents ideas on the mechanism of the formation of the latter.

The results of a study of the molecular-weight distribution of the samples (Table 1) shows an increase in molecular weight and a fall in the degree of polydispersity of lignin fraction 1 by the end of the third hour of oxidation. This is explained both by a fractionation of the lignin, since its low-molecular-weight fraction (fraction 2) does not precipitate when an alkaline extract is acidified, and also by a polycondensation of the radicals formed. The molecular weights of samples of fraction 1 have been calculated by means of Eq. (1) taking into account the maximum possible increase in them through the effect of fractional dissolution [6]:

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