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ON THE SECONDARY AROMATIC POLYNUCLEAR STRUCTURE OF LIGNIN

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The nature of the diverse condensation products of phenylpropane monomers formed during the biosynthesis of lignin is still not entirely clear. It may be considered proven, however, that a polynuclear aromatic structure, though to a very small extent, also exists in the natural lignin of plant tissue ([1],[2]). Alkaline oxidation of wood meal with permanganate ([3]) leads to the formation of 0.14% (of lignin) benzene-polycarboxylic acids. Although the yield of these acids is small, the possibility of obtaining them (chiefly benzenepentacarboxylic acid) is an argument in favor of the existence in natural lignin of a small amount of condensed nuclei. Lignin isolated by acid or alkaline methods, which has thereby undergone condensation effects, gives, upon oxidation with alkaline permanganate, a higher yield of benzene-polycarboxylic acids. For example, from periodate lignin heated to 160° at pH 2.2, oxidation yielded 5.15% benzenepentacarboxylic acid and 0.57% tetracarboxylic acid ([3]). Hydrolysis lignin treated for 1.5 hours with alkali at 270° gives, upon oxidation with alkaline permanganate, an even higher yield of benzene-polycarboxylic acids, isolated in the form of barium salts ([4]).

Mellitic acid has not been isolated in the oxidation of natural lignin. The possibility of obtaining it ([3], [5]-[7]) from technical lignins in low yield (0.2–0.4%), although it is not strict proof of the presence of carbon hexagonal lattices in the structure ([8]), nevertheless unquestionably indicates the existence of hexasubstituted benzene in the macromolecule of the initial product.

Obtaining benzene-polycarboxylic acids from technical lignins, as well as establishing the relationship between the yield of these products and the conditions of hydrolysis, is important for understanding and evaluating those changes in its structure that occur during the technochemical processing of wood. This is also significant for the search for new routes for the chemical utilization of lignin, since benzene-polycarboxylic acids are starting materials for the synthesis of valuable polyesters, adhesives, and plastics.

Spruce sawdust extracted with acetone and passed through sieve No. 3 was taken for the study. The acetone was removed by prolonged boiling with water. Wood samples containing 30.5% lignin were subjected to 6-hour treatment with sulfuric acid (0.5 and 1%) in an autoclave at 160, 180, and 200°. The liquid-to-solid ratio was 15. The lignin samples obtained under different hydrolysis conditions were washed free of acid, sugars, and humic products, dried, analyzed, and subjected to oxidation with alkaline permanganate at 80° for 22 hours ([4]). The acids formed were isolated as barium salts. To destroy oxalic acid, the salts were boiled for 12 hours with concentrated nitric acid (specific gravity 1.52). The latter was removed in vacuo, and the residue was extracted—

was treated with chloroform to extract nitrophenols, and then with ether. From the ether extract a white, solid, partially crystallizing mass was obtained—a mixture of benzenepolycarboxylic acids. The acids are readily soluble in water, alcohol, ether, and acetone, and insoluble in benzene and chloroform. Acid equivalent 60.2. By fractional crystallization from nitric-acid and then from hydrochloric-acid solutions, it was possible to isolate mellitic and benzenepentacarboxylic acids. The former was isolated as ammonium mellitate, then purified through the copper salt ([13]). Treatment with hydrogen sulfide gave the free acid, which was recrystallized from water. Despite repeated recrystallization, a completely pure preparation still could not be obtained. For mellitic acid:

Found, %: C 42.3; H 2.40
Calculated, %: C 42.1; H 1.75

For benzenepentacarboxylic acid:

Found, %: C 44.24; H 2.13
Calculated, %: C 44.29; H 2.01

Benzenepentacarboxylic acid melted in a sealed capillary at 241–242° with decomposition. According to the literature data ([2]), the melting point of this acid is 239–244°.

Table 1

Characteristics of lignins and yield of benzenepolycarboxylic acids upon oxidation with alkaline permanganate

No.	Hydrolysis conditions: H_2SO_4, %	Hydrolysis conditions: temperature, °C	Lignin characteristics: OCH_3, %	Lignin characteristics: lignin, %	Yield of benzenepolycarboxylic acids from lignin, %
1	0.5	160	7.05	50.98	1.41
2	0.5	180	9.72	85.13	3.20
3	0.5	200	10.02	96.05	10.20
4	1.0	160	8.69	60.18	4.60
5	1.0	180	10.26	92.50	7.90
6	1.0	200	10.08	94.35	12.20

No.	Hydrolysis conditions: H_2SO_4, %	Hydrolysis conditions: temperature, °C	Lignin characteristics: OCH_3, %	Lignin characteristics: lignin, %	Yield of benzenepolycarboxylic acids from lignin, %

Table 1 presents data on the oxidation of lignin. The actual yield of acids is considerably higher, since large losses occur during precipitation and washing of the barium salts; in addition, ether does not exhaustively extract the benzenepolycarboxylic acids.

It was of interest to check to what extent already isolated technical hydrolysis lignin is capable of undergoing additional condensation effects. For this purpose, lignin from pine wood from the glucose shop of the Kansk Hydrolysis Plant was taken. The product was washed free of acid and deresinated by prolonged extraction with acetone, followed by removal of the solvent by boiling with water. The lignin was subjected to additional condensation treatment in an autoclave with 5% H_2SO_4 for 6 h at 195–198°. The initial product contained: lignin 92.53%; OCH_3 9.68%; ash 0.84%. After condensation, respectively: 98.40%; 11.78%; 0.52%. The lignin samples were ground for 15 min in an M-10 vibratory mill.

100 g of lignin was poured over with a tenfold amount of nitric acid (specific gravity 1.35), and the mixture was kept for 4 days at 20°. Then the entire mass was boiled for 2.5 h on a water bath with a reflux condenser. The solution was filtered off and kept at 0° for repeated crystallization and removal of oxalic acid. After purification, the latter melted at 189°. Nitric acid was removed from the filtrate in vacuo; the residue was extracted for 4 h with chloroform to extract nitrophenols and, finally (to destroy the residue of oxalic acid and isolate the benzenepolycarboxylic acids), was subjected to 12-hour boiling with a tenfold

with concentrated HNO_3 (sp. gr. 1.52). At this stage an insoluble, slightly cream-colored precipitate separated very rapidly from the condensed-lignin samples, with a yield of up to 2.3% of the lignin. The precipitate dissolved in a small amount of hot water and, when poured into a concentrated aqueous solution of ammonia (sp. gr. 0.89) at 0°, yielded white, well-formed crystals of ammonium mellitate. From it the silver salt was obtained, on the basis of which, by reaction with methyl iodide, the hexamethyl ester of mellitic acid was synthesized. After recrystallization from benzene, the ester melted at 182.5°. According to the literature, the m.p. of the ester is 183° (^{7}) and 187° (^{2}). For the hexamethyl ester of mellitic acid:

Found %:	C 52.2;	H 4.52
Calculated %:	C 50.7;	H 4.22

We suppose that, together with ammonium mellitate, the ammonium salt of benzenepentacarboxylic acid also partially precipitates, because such a case has already once been described in the literature ([14]).

After separation of the mellitic-acid precipitate, the nitric acid was distilled off in vacuo, and, to remove the final traces of nitric acid, the residue was treated with several milliliters of formic acid. The resulting sticky, thick, orange-red mass was subjected to prolonged drying in a vacuum desiccator at 50°. As a result, a reddish-yellow powder remained, very hygroscopic, soluble in water, ether, alcohol, acetone, and methyl ethyl ketone, and insoluble in benzene and chloroform. The average equivalent of the acids obtained was 84. The character of the conductometric-titration curves showed the presence of a mixture of 3–4 acids differing in strength. Apparently, the products obtained represent a mixture of individual monocyclic benzenepolycarboxylic acids and high-molecular acids having a more complex polynuclear structure. In addition, the mixture probably contains nitrogen-containing substances and resinous impurities, which impart a dark color to the product ([9]). This complex mixture was subjected to additional oxidation with alkaline permanganate and then again with nitric acid (sp. gr. 1.52). In this way, from the reddish-brown powder, nearly white crystallizing acids were obtained. Chromatographically it was possible to show that they consist predominantly of hexa-, penta-, and tetracarboxylic acids ([10]). It may be assumed that, during the oxidation of condensed lignin with nitric acid, benzenepolycarboxylic acids are formed. Among the nitrophenols obtained in a yield of 3.9%, picric acid with m.p. 121.5° was isolated.

Found %: C 31.97; H 1.44; N 18.45
Calculated %: C 31.44; H 1.31; N 18.34

The yield of picric acid from condensed lignin (1.8%) was determined by the method of selective precipitation of Nitron picrate from aqueous acidic media ([15]). Table 2 gives the average results of several parallel experiments on the oxidation of lignin with nitric acid.

Table 2

Substance	Oxalic acid	Mellitic acid	Mixture of benzenepoly-carboxylic acids	Nitrophenols
Initial industrial pine lignin	16–18	Not detected	15–17	Not determined
Condensed lignin	24–25	2.0–2.3	30–32	3.92

The data we have obtained on the oxidation of lignin preparations with alkaline permanganate and nitric acid show that, in its macromolecule, under the action of condensing agents, a secondary polynuclear aromatic structure arises, by which the formation of a considerable amount of benzenepolycarboxylic acids can be explained. As a result of condensation, as is seen from the analysis of the initial products, lignin does not lose its principal methoxylated aromatic nucleus, but acquires secondary aromatic structures, apparently at the expense of the side propane chains.

Kratzl (^{1}) showed that various lignin preparations isolated by acids (for example, Willstätter or Scholler lignin) give, upon ethanolysis, Hibbert ketones (although in a considerably smaller yield than natural lignin). He thereby experimentally confirmed the comparative stability of the side chain of lignin.

As is known, the structure of guaiacylglycerol-β-aryl ether (^{11}), most frequently occurring in natural lignin, forms, as a result of acid hydrolysis, a derivative of oxiconiferyl alcohol (a). It is possible to propose, as a working hypothesis, the following scheme for the condensation of this reactive product:

$$2\,(\mathrm{a}) \longrightarrow (\mathrm{A}) + 2H_2O$$

On the basis of this or an analogous type of condensation, beginning, probably (during the isolation of lignin from plant tissue by acids), with the formation of α—β- or α—α_1-carbon bonds between the propane side chains (^{12}) and further leading to the appearance of products of the phenylnaphthalene type (A), a secondary aromatic polynuclear structure may accumulate in lignin to a greater or lesser degree. Its relative content in the macromolecule depends, as has been shown, on the conditions of condensation of lignin.

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Note: Figure translations are in progress. See original paper for figures.