HYDROGENOLYSIS OF WILLSTÄTTER LIGNIN

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In preceding papers [1-5] we have shown that the hydrogenolysis of hydrolysis lignins in an aqueous alkaline medium in the presence of an inhibitor (especially a phenol) gives high yields of low-molecular-weight products consisting of phenols, acids, and neutral substances.

Since acid-hydrolysis lignin differs from natural lignin (during the hydrolysis of the plant raw material it undergoes considerable changes as a result of the condensation processes that take place in an acid medium [6]), it was of interest to investigate the hydrogenolysis of lignin obtained by a mild method, i.e., similar to native lignin. We have studied the hydrogenolysis of spruce lignin isolated by Willstätter's method under the conditions that are the optimum for the hydrogenolysis of acid lignins [1] (Table 1).

The results obtained almost coincide with those for the hydrogenolysis products of the hydrolysis lignin of spruce [7]. A feature of hydrogenolysis in an aqueous alkaline medium is the presence of acids in the reaction products, which is not observed when this process is performed by the methods used by Japanese workers (absence of moisture and alkali and presence of a number of substances including phenols, oils, etc.). This confirms once more our previous conclusions [5] that hydrogenolysis in an aqueous alkaline medium in the presence of hydrogen and a catalyst is a process of oxidative degradation.

The hydrogenolysis products were studied by IR spectroscopy, thin-layer chromatography (TLC), and gas-liquid chromatography (GLC). The functional groups present in the initial lignin, the combined hydrogenolysis products, and their individual fractions were judged from their IR spectra. The absorption bands in the IR spectrum of the Willstätter spruce lignin were identified from information in the literature [8-10] (Fig. 1, curve 1). The absorption at 3550 and 3450 cm^{-1} corresponds to the stretching vibrations of hydroxy groups, that at 1230 and also at 1080 and 1150 cm^{-1} to the deformation vibrations of phenolic and secondary and tertiary alcoholic hydroxy groups of a propane chain, respectively. The strong absorption at 1040 and 1275 cm^{-1} shows the presence of a considerable number of methoxy groups. Maxima at 1520 and 1600 cm^{-1} correspond to the C=C stretching vibrations of a benzene nucleus and absorption at 1580 cm^{-1} to conjugated aromatic nuclei. The absorption at 1710-1730 cm^{-1} is connected with the vibra-

TABLE 1. Yields and Elementary Compositions of the Hydrolysis Products of Lignin

Initial lignin and hydrolysis products	Yield or content, %	Elementary comp., %		
		C	H	O
Willstätter lignin	24,0	62,31	5,70	31,99
Hydrogenolysis products:				
ether-soluble	80,0	78,47	8,68	12,85
acetone-soluble	2,2	—	—	—
dry residue	10,0	72,00	5,81	22,20
losses	7,8	—	—	—
Group composition of the ether-soluble products:				
phenols	43,7	73,73	8,70	17,57
acids	12,6	63,51	8,90	27,59
neutral	43,7	81,80	9,31	8,89

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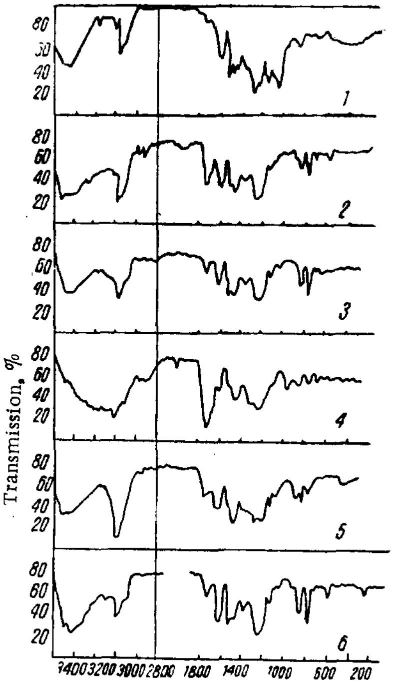

Fig. 1. IR spectra of Willstätter spruce lignin (1), of the combined hydrogenolysis products of spruce lignin (2), of the combined products without the acids (3), of the acids from the hydrogenolysis products (4), of the neutral products (5), and of the phenols (6).

tions of a β-carbonyl group in a propane chain or of carboxy or aldehyde groups. The nature of the functional groups and the intensities of the absorption bands have changed in the hydrogenolysis products (Fig. 1, curve 2). Thus, the absorption in the 1040 cm^{-1} region has disappeared almost completely; i.e., during hydrogenolysis demethoxylation takes place.

Absorption in the 1050, 1080, and 1120 cm^{-1} regions has become very slight, which shows a low content of functional groups of the type of alcohol groups (primary, secondary, and tertiary) in the hydrogenolysis products. In addition, the intensity of the bands at 1710 has markedly increased. This shows an increase in the number of carbonyl groups, and the appearance of inflections in the 1630 and 1650, 1670 cm^{-1} regions shows the presence of quinoid structures. Absorption at 3400, 3500, 1600, and 1500 cm^{-1} and at 1520, 1450, 1470, 1375, 1200, and 1230 cm^{-1} has assignments similar to those in the spectra of the original lignin.

To refine the assignment of the absorption at 1710 cm^{-1}, which is characteristic for carboxy or carbonyl compounds, the total ether-soluble products were separated into acids and mixture of neutral compounds and phenols. In the IR spectrum of the latter (Fig. 1, curve 3), the intensity of the $C=O$ absorption had fallen sharply because of the removal of the carboxy compounds and it had shifted to 1720 cm^{-1}. This absorption also remains after the saponification of the mixture of products mentioned, which enables ester groupings to be excluded from the combined products. In the IR spectrum of the acids, absorption remains intense in this region. Consequently the products mentioned contain both carboxy groups and carbonyl groups but no compounds with ester groups.

It can be seen from the spectrum of the acids (Fig. 1, curve 4) that the mixture contains both aliphatic and aromatic acids (absorption at 1500, 1520, and 1605 cm^{-1}); the presence of hydroxy aromatic structures is confirmed by absorption in the 1230 cm^{-1} region (deformation vibration of a phenolic hydroxyl).

In the IR spectrum of the phenolic fraction (Fig. 1, curve 6) the absorption bands can be interpreted in the following way: 3450 and 1230 cm^{-1} – stretching and deformation vibrations of a phenolic hydroxyl, 1520 and 1600 cm^{-1} – stretching vibrations of $C=C$ in an aromatic nucleus. An inflection at 1640 cm^{-1} shows the possible presence of quinoid structures, a band at 1710 cm^{-1} the presence of compounds with a carbonyl group in the β position with respect to the aromatic nucleus, and an inflection at 1580 cm^{-1} the possible presence of conjugated aromatic compounds in the mixture.

As the IR spectra (Fig. 1, curve 5) show, the neutral products contain the following functional groups: hydroxyl (stretching vibrations of hydroxyl at 3450-3530 cm^{-1}; deformation vibrations of alcoholic hydroxyls at 1050 and 1100 cm^{-1}), carbonyl (absorption in the 1710, 1730, and 1740 cm^{-1} regions), and quinoid compounds or compounds of the type of quinol ethers (1660, 1620, 1640 cm^{-1}). The aromatic nature of the products obtained is confirmed by absorption in the 1600, 1500, and 1520 cm^{-1} regions. For their complete characterization, the phenol, acid, and neutral fractions were studied by TLC and GLC (Tables 2 and 3).

The phenolic fractions of the hydrogenolysates of the hydrolysis lignin and the Willstätter lignin were identified by the TLC method. We have given the conditions of chromatography, the colors, the spots and the R_f values of the individual components previously [4]. The phenolic fractions contained phenol, p- and o-cresols, p- and o-ethylphenols, p-propylphenol, and 3,4- and 2,6-xylenols.

As in the hydrogenolysis of hydrolysis spruce lignins (see Table 3), the phenolic fraction contained a small percentage of phenol itself and a high percentage of cresols. In the hydrogenolysis of the hydrolysis spruce lignin the cresols amounted to 47.5% and in that of the Willstätter lignin 47.0% of the total mixture of phenols. In the hydrogenolysis of the Willstätter lignin the mixture of phenols also included phenols of higher molecular weight which we have not yet identified because of the absence of suitable models. In

TABLE 2. Results of the GLC of the Phenolic Fractions of Hydrogenolizates of Willstätter Spruce Lignin and Hydrolysis Spruce Lignin

Rel. reten-time	Amt. of component in mixt., %	Substance determined	Rel. retention time	Rel. retention time	Substance determined
Willstätter lignin*			Hydrolysis lignin†		
1,0	1,8	Phenol‡	1	3,8	Phenol‡
1,5	14,5	o-Cresol	1,17	12,5	o-Cresol
1,7	32,5	m- and p-Cresols	1,46	35	m- and p-Cresols
2,2	3,1	2,6-Xylenol	1,46	10	o-Ethylphenol
2,7	21,4	p-Ethylphenol; 2,5-xylenol	1,68	10,6	Not determined
3,2	3,7	3,4-Xylenol	2,00	14,9	p-Ethylphenol
6,9	12,5	Not determined	2,36	5,2	Not determined
10,2	10,5		2,7	5,2	p-Ethyl-3-methylphenol
			2,9	1,6	4-Ethyl-3-methylphenol
			3,9	1,2	Not determined

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*Chromatography of the phenols: Apiezon L, 15% on INZ-600; column 2 m long and 4 mm in diameter; rate of feed of the carrier gas, hydrogen, 100 ml/min; t 180°C; I 220 mA.

†Chromatography of the methyl ethers of the phenols: PEGC, 15% under the same conditions apart from the rate of flow of hydrogen, t 140°C and I 250 mA.

‡The amounts of phenol in the mixture are given with the deduction of the phenol added as inhibitor.

this connection, the amount of unidentified products in the phenols obtained on the hydrogenolysis of hydrolysis spruce lignin was considerably less than that from the Willstätter lignin. The yields of phenols were similar in the two cases (43.7% for the Willstätter lignin and 47.0% for the hydrolysis spruce lignin). On the basis of the Willstätter lignin, isolated by mild hydrolysis, we can see that the hydrogenolysis method enables a high yield of phenolic products (35% of the initial lignin) to be obtained.

We have provisionally called the products not passing into the alkaline solution when an ethereal solution of the hydrogenolysate was treated with a 10% solution of caustic soda the "neutral" substances [12]. They may include the following groups of substances: truly neutral products, i.e., substances containing no groups capable of reaction with alkalis (alcohols, ketones, hydrocarbons); spatially-hindered phenols; and complexes of phenols in which the phenolic hydroxyl does not react with 10% caustic soda solution.

By the method that we adopted previously [7], these products were treated with Claisen alkali and were separated into fractions soluble and insoluble in this reagent (75 and 25%, respectively). The fraction passing into the Claisen alkali was studied by IR spectroscopy. The IR spectrum showed bands at 1200-1210 cm^{-1} (deformation vibrations of phenolic hydroxyls) which were absent in the spectrum of the initial neutral products. The composition of this fraction of the products could not be identified by the TLC method because of the presence of products of higher molecular weight in the mixture. Consequently analysis by the TLC and GLC methods (see Table 3) was performed after the distillation of the neutral fraction, the distillate amounting to 83% of the neutral products.

The neutral products passing into the Claisen alkali were found by TLC to contain hydroquinone, phenol, o- and p-cresols, and p- and o-ethylphenols.

The results of TLC and GLC confirm that the part of the neutral products passing into the Claisen alkali consists of phenols. This agrees well with the facts given previously [7] for hydrolysis spruce lignin. The part of the products not passing into the Claisen alkali was not investigated.

The yield of acids obtained in the hydrogenolysis of the Willstätter spruce lignin (12.6%) was lower than that (27%) from the hydrolysis spruce lignin. Of the total amount of acids, 5.7% was volatile acids, including 0.3% of formic, 3.1% of acetic, and 2.3% of propionic acids. The fatty, cyclic, aromatic, and hydroxyaromatic acids amounted to 6.9%. Consequently, the yield of volatile low-molecular-weight acids (formic, acetic, and propionic) from the hydrogenolysis of the Willstätter lignin was considerably higher (45.2% of the total amount of acids) than the yield of these acids from the hydrogenolysis of the hydrolysis spruce lignin (22%). This is logical and follows from our results on the hydrogenolysis of models, from which it was established that the less condensed systems give the higher yields of low-molecular-weight volatile acids on hydrogenolysis.

TABLE 3. Results of the GLC of That Part of the Neutral Products Which Passes into Claisen Alkali from the Hydrogenolysates of Willstätter Lignin and Hydrolysis Spruce Lignin

Rel. retention time	Amt. of component in mixt., %	Substance deter.	Rel. retention time	Amt. of component in mixt., %	Substance deter.
Willstätter lignin*			Hydrolysis lignin†		
0,6	3	Not determined	0,9	1,3	Not determined
0,8	2,4	" "	1,00	2,9	Phenol
1,0	3,6	Phenol	1,44	2,0	o-Cresol
1,4	2,7	o-Cresol	1,53	2,9	m- and p-Cresols
			1,76	3,5	
1,7	3,6	m- and p-Cresols	1,92	11,3	o-Ethylphenol
2,0	1,6	o-Ethylphenol	2,31	12,1	2,5-Xylenol
2,7	30,0	p-Ethylphenol	2,78	13,0	p-Ethylphenol
3,6	8,0	Not determined	3,20	11,9	p-Propylphenol
4,0	12,0	Hydroquinone	3,68	8,2	3,4-Xylenol
4,4	10,0	Not determined	4,20	5,2	4-Ethyl-3-methylphenol
5,8	3,0	" "	5,68	2,7	Not determined
6,0	4,1	" "	6,6	2,2	Hydroquinone
7,0	1,6	" "	7,7	3,3	Methylguaiacol
			10,3	5,6	Not determined
			13,3	5,8	p-Propylphenol
			15,7	3,5	Not determined

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*For the conditions of separation, see Table 2.

†Chromatography of the methylethers: PEG-6000, conditions of separation the same as in Table 2, apart from t 160°C, I 260 mA.

To prove the presence of hydroxyaromatic acids in the mixture of acids from the Willstätter lignin, the acid fraction was distilled at atmospheric pressure. During distillation, the o- and p-hydroxyaromatic carboxylic acids decarboxylated and gave the corresponding phenols, which were analyzed by TLC and GLC.

The products of the distillation of the acids were found by TLC to contain hydroquinone, phenol, p-cresol, p- and o-ethylphenols, and 3,4-xylenol.

To analyze the phenols by GLC, the acids after distillation were treated in ethereal solution with a 10% solution of sodium bicarbonate in order to eliminate the undecomposed acids. As a result of the separation performed, the mixture was shown by GLC to contain the following substances (%): phenol (17.5), m- and p-cresols (27.4), o-ethylphenol (17.0), p-ethylphenol and 2,5-xylenol (15.2), 3,4-xylenol (12.0), hydroquinone (3.4); unidentified (7.5).

Gas-liquid chromatography showed that the mixture of acids obtained in the hydrogenolysis of the Willstätter lignin contained hydroxyaromatic acids, the composition of which before decarboxylation was fairly broad since a number of acids corresponds to each phenol. The composition of the acids was not studied in detail. However, the presence in the decarboxylation products of such a phenol as hydroquinone, which is not characteristic of the macromolecule of lignin, shows that the process of hydrogenolysis in an aqueous alkaline medium in the presence of a catalyst and hydrogen leads to oxidative processes giving rise to hydroxylated aromatic structures [5].

It follows from the experimental results that on the whole the process takes place similarly to that for the hydrolysis lignins, the yields of phenols being similar but the yields of acids being lower for the Willstätter lignin than for the hydrolysis lignin and the yield of neutral products being higher. It appears to us that the conditions of hydrogenolysis adopted for the hydrolysis lignins were too severe in this case and that under the more severe conditions decarboxylation and the subsequent recombination of the radicals took place to a greater extent.

The work that we have performed on the hydrogenolysis of model substances has shown that, depending on their structure, the models give different yields of phenols, acids, and neutral products on hydrogenolysis in an aqueous alkaline medium. In the case of the model 1-(4-hydroxyphenyl)propan-1-one, the yield of acids was 16.3%, including 13.9% of acetic and propionic acids, that of phenols was 83.7%, and there were no neutral products; for 1-(4-hydroxy-3-methoxyphenyl)propan-1-one the yield of acids was 55.5%, including 39.1% of volatile acids and 26.4% of hydroxyaromatic acids, that of phenols was 7.3%, and that of neutral products 36.6%. In the hydrogenolysis of biphenyl structures (dehydrodivanillin), the yield of acids was 22.3%, including 11.1% of volatile acids, that of phenols was 50.1%, and that of neutral products 27.6%.

On this basis, it may be assumed that the Willstätter spruce lignin does not contain a significant amount of free p-hydroxyphenyl and guaicylpropane fragments while, apparently, it does contain a considerable amount of them in the form of biphenyl structures. The method of hydrogenolysis in an aqueous alkaline medium probably provides the possibility of judging the degree of condensation of the lignin from the composition of the low-molecular-weight products.

EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument (KBr). The products were separated by TLC (on nonfixed Al_2O_3, activity grade II) and GLC (Tswett-1-64 chromatograph). In the case of TLC the mobile phase was methanol–chloroform–tridecane (1 : 15 : 3). The revealing agent was a 5% solution of formalin in conc. sulfuric acid. The substances investigated were identified by comparing the colors of the spots and their R_f values with markers. The neutral substances were distilled at atmospheric pressure.

Preparation of the Willstätter Lignin [13]. Wood flour (230 g) previously extracted with water and then with 80% (80 parts of acetone and 20 parts of water) and 100% acetone was suspended in 2.1 liters of supersaturated hydrochloric acid (d_4^{20} 1.220). The mixture was shaken at room temperature for 2.5 h. Then 1 liter of ice water was added to it and it was left overnight. After this, the lignin was filtered off, washed with water, pressed out (to eliminate as much moisture as possible) suspended in a 5% solution of sulfuric acid (6 liters) and heated under reflux for 5 h, filtered again, carefully washed with water, and dried at room temperature. The product was Willstätter lignin. Yield 24%. Moisture content 5%, ash content 0.5%, hydroxy groups by Verley's method 9.95%, methoxy groups 14.3%.

Hydrogenolysis of the Lignin. The process was performed in a rotating half-liter autoclave of the NF-1 (Hungary) type with an electric heater. The Willstätter lignin (50 g of organic substance) was mixed with 5% caustic soda solution (1 : 3), and the catalyst (CoS, 2%) and the phenol used as inhibitor (10 g) were added. The mixture was heated in the autoclave at an initial pressure of hydrogen of 100 atm and a temperature of 340-360°C for 2 h. After the end of the process, the contents of the autoclave were transferred to a beaker, and the autoclave was rinsed twice with water, the rinsing water being added to the main hydrogenolysate. (The yield of ether-soluble substances is given as a percentage of the organic matter of the lignin after deduction of the added phenol.)

Separation of the Ether-Soluble Products. The alkaline hydrogenolysate was acidified to pH 1 with 10% hydrochloric acid and extracted with ether. After drying with sodium sulfate, the filtered ethereal extract was distilled, and the total ether-soluble products were weighed. In separation into fractions, the ethereal extract was repeatedly and successively washed with 10% sodium bicarbonate solution to extract the acids and with 10% caustic soda solution to extract the phenols. The neutral products remained in the ethereal solution. The sodium carbonate and caustic soda solutions formed were acidified and exhaustively extracted with diethyl ether. After drying, filtration, and the evaporation of the ether, the acid and phenolic fractions were obtained.

SUMMARY

1. The hydrogenolysis of Willstätter spruce lignin has been performed under the optimum conditions. It has been shown that on hydrogenolysis in an aqueous alkaline medium in the presence of an inhibitor (phenol) the lignin macromolecules can be converted into low-molecular-weight ether-soluble products with a yield of about 80%.

2. A comparative study of the ether-soluble fractions of Willstätter spruce lignin and hydrolysis spruce lignin has shown that hydrogenolysis takes place similarly in the two cases: the yields of phenols and the proportion of cresols in them are similar. In the Willstätter spruce lignin, the yield of acids is higher and that of neutral products lower than in the hydrolysis spruce lignin.

3. Investigations of the group compositions of the hydrogenolysis products and of model substances have permitted the hypothesis that the Willstätter lignin contains a considerable amount of biphenyl structures.

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