REDUCTIVE CLEAVAGE BY METALLIC SODIUM IN LIQUID AMMONIA OF COTTON LIGNIN

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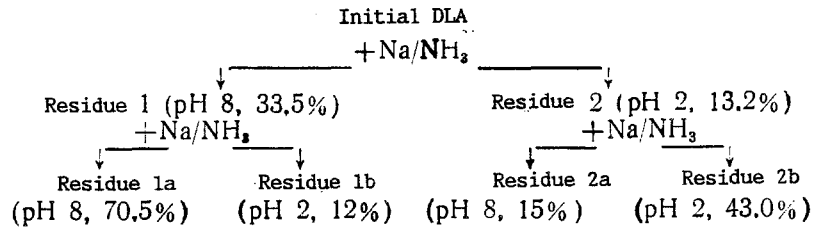
Twofold cleavage with sodium in liquid ammonia of the dioxane lignin and fourfold cleavage of the native lignin from cotton stems have shown that the uncleaved parts of lignin have molecular masses 2-4 times lower than the initial lignins and consist of 15-17 phenylpropane structural units.

The cleavage of the aryl-alkyl bonds of lignin with metallic sodium in liquid ammonia has been the subject of many publications [1]. We have previously used this reaction to study the composition of the structural units in lignins, to detect the presence of α- and γ-hydroxy groups in the phenylpropane chain, and to estimate the degree of condensation of the lignins. The dioxane lignins (DLAs) and native lignins of the cotton plant [2], of Althaea [3], and of kenaf [4] have been subjected to cleavage. Particular attention has been devoted to the monomeric phenols obtained by such degradation.

In the present work, together with the characteristics of the monomeric degradation products, great attention has been devoted to the products of the incomplete cleavage of the DLA and the natural lignin of cotton stems.

The dioxane lignin was obtained from the cotton stems by the procedure of Veksler et al. [5]. After its purification and drying over P_2O_5 it was cleaved with sodium in liquid ammonia at −33°C. A scheme of the cleavage and the yields of residues are given below:



After the first cleavage, 46.7% of uncleaved lignin (residue 1 + residue 2) remained and only 12.2% of total monomeric phenols was isolated. After the cleavage of residue 1, 82.5% of uncleaved lignin remained, and after the cleavage of residue 2, 58%. Consequently, both after the first and after the second cleavage the bulk of the DLA was not broken down into low-molecular-mass products. Previously, after the first cleavage with sodium in liquid ammonia of cuprammonium aspen lignin A. F. Semechkina and N. N. Shorygina [6] isolated 45.2% of uncleaved lignin, and after the second cleavage, 65%. Spruce lignin was cleaved less well, since after the first cleavage 79.5% of the initial lignin remained [6]. Only after nine successive treatments with sodium and liquid ammonia of spruce cuprammonium lignin was 89% of the lignin taken for the reaction cleaved into low-molecular-mass products [7].

Judging from the yields of uncleaved products, cotton DLA is cleaved better than spruce lignin.

For all the residues isolated, UV spectra were recorded (λ_{min} 260, λ_{max} 275-280 nm, ethanol), elementary analysis and analysis for methoxy groups were made, and molecular masses and degrees of polydispersity were determined. The results are given below.

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Substance	Empirical formula	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
Initial DLA [8]	$C_9H_{9.29}O_{2.87}(OCH_3)_{1.23}$	4500	12000	21000	2.69
Residue 1	$C_9H_{9.18}O_{3.0}(OCH_3)_{1.02}$	1900	4400	10700	2.30
2	$C_9H_{9.4}O_{3.35}(OCH_3)_{0.87}$	2000	3800	8400	1.90
1a	$C_9H_{10.34}O_{3.34}(OCH_3)_{0.95}$	1500	3100	5300	2.07
1b	$C_9H_{10.14}O_{3.62}(OCH_3)_{0.94}$	1700	3000	4900	1.76
2a	$C_9H_{10.06}O_{3.05}(OCH_3)_{0.82}$	1800	3250	5650	1.81
2b	$C_9H_{10.48}O_{3.29}(OCH_3)_{0.80}$	1600	3000	5650	1.88

In the uncleaved lignins, the OCH_3/C_9 ratio was also lower than in the initial lignin. The same situation was found for the cuprammonium aspen lignin [6].

The total yield of monomeric phenols from the cleavage of residue 1 (3.3%) was also four times lower than that of the same products from the initial DLA (12.2%). The GLC analysis of these total materials showed (Table 1) that in the products of the cleavage of residue 1 the amount of methoxylated substances was lower than in the same products from the cleavage of the initial DLA.

Thus, from the example of the cleavage of the initial DLA and the part of it uncleaved after the first treatment it can be seen that the products of the cleavage of DLA were richer in syringyl structures as compared with those from residue 1.

Although it has been confirmed on lignin models that no demethylation takes place during cleavage [9], there have been cases in which during this reaction methoxy groups were split out from bimolecular benzylisoquinoline and aporphine alkaloids [10]. The decrease in the number of OCH_3 groups of the uncleaved lignin and in the monomeric cleavage phenols can therefore be explained as the result of a hydrogenolysis reaction and also by the fact that the parts more condensed and more enriched with methoxyls are split out from the lignin molecule first.

Analysis of the IR spectra of the initial DLA and the product of its incomplete cleavage showed that, even after the second cleavage, the IR spectra of the cleavage products retained the bands of carbonyl groups (1670, 1720 cm^{-1}). Apparently, not all the C=O groups in lignins are reduced in this reaction.

A calculation of the protons in the PMR spectra of the initial DLA and the products of incomplete cleavage obtained from it showed that the latter were more condensed than the initial DLA (numbers of aromatic protons). In the cleavage products, the number of primary and secondary aliphatic hydroxyls had fallen because of side reduction reactions and the number of phenolic OH groups had increased through the cleavage of aryl-alkyl ether bonds.

The determination of molecular masses by gel filtration on a column of Sephadex G-75 in dimethyl sulfoxide as eluent and solvent showed (see above) that, after the treatment of the initial DLA, oligomeric fragments remained with molecular masses three times lower than that of the initial DLA. On the repeated cleavage of these residues, the molecular masses decreased only slightly and did not fall below 3000, i.e., they consisted of 15-16 phenylpropane structural units (PPSUs). The initial DLA contained 60 PPSUs. The degree of polydispersity of the residues obtained decreased; they became more homogeneous.

The native lignin of cotton stems was cleaved three times in a similar manner to the DLA. The plant residue after the first cleavage was washed repeatedly with water and was dried over P_2O_5, and was subjected to the second cleavage with sodium and liquid ammonia, and then the residue was treated a third time. After the separation of the uncleaved plant material and acidification, a residue deposited which was studied separately.

It had been established previously that the total ether-extracted material (pH 8) consisted mainly of monomeric phenols [2]. As cleavage proceeded, the yields of these extracts fell sharply: 1.68% (first cleavage); 0.75% (second cleavage); 0.30% (third cleavage). Consequently, a five times smaller amount of monomers was isolated from the products of the third cleavage than from the products of the first cleavage.

By the GLC of these combined extracts [2] it was found that the qualitative compositions of the products differed only slightly but their quantitative differences were great. As can be seen from Table 1, the monomeric products of the first cleavage were enriched with syringyl components and were impoverished in the p-coumaryl components. In the

TABLE 1. Monomeric Cleavage Products (in percentages of the DLA, of residue 1 and of the weight of the plant)

Substance	DLA	Residue 1	Cotton stems after the given cleavage		
			first	second	third
1. p-Hydroxyphenylethane	0,12	0,27	—	—	—
2. p-Hydroxyphenylpropane	0,18	0,20	0,04	0,06	—
3. p-Hydroxyphenylpropan-3-ol	1,95	1,75	—	—	0,06
4. Guaiacol	—	0,04	—	0,04	—
5. Guaiacylethane	0,15	—	0,01	—	0,02
6. Guaiacylethanol	0,99	0,84	—	—	—
7. Guaiacylpropane	2,58	1,83	0,66	0,67	0,09
8. Guaiacylpropan-1-ol	1,95	0,38	0,23	0,15	0,02
9. Guaiacylpropan-3-ol	0,14	0,18	0,07	0,04	—
10. Syringylpropane	0,81	0,19	0,50	0,08	0,01
Ratio of structural units:					
p-coumaryl	0,33	0,68	0,05	0,06	0,46
guaiacyl	1	1	1	1	1
syringyl	0,12	0,06	0,50	0,09	0,06

products of the third cleavage, the pattern was the opposite. This can be explained in the same way as in the case of the cleavage of the DLA.

After the first and second cleavages of the native lignin, lignin-like residues deposited (1.36 and 0.25%, respectively) which were purified in the same way as the uncleaved part of the lignin and were analyzed. After the third cleavage no lignin residue deposited.

The residue after the first cleavage: $C_9H_{12.5}O_{3.9}(OCH_3)_{1.11}$; $\bar{M}_n$ = 2700, $\bar{M}_w$ = 7800, $\bar{M}_z$ = 13600, $\bar{M}_w/\bar{M}_n$ = 2.9.

The residue after the second cleavage: $C_9H_{12.73}O_{3.94}(OCH_3)_{0.84}$; $\bar{M}_n$ = 1800, $\bar{M}_w$ = 3400, $\bar{M}_z$ = 6400, $\bar{M}_w/\bar{M}_n$ = 1.89.

As can be seen, the cleavage of the native lignin took place by the same laws as the cleavage of the DLA: in the uncleaved lignins the number of OCH_3 groups had fallen. The molecular mass of the lignin uncleaved after the second treatment was only half that of the lignin remaining after the first cleavage. The residue after the first cleavage consisted of 33-36 PPSUs, and after the second cleavage of 16-17 PPSUs.

EXPERIMENTAL

Cleavage with Sodium in Liquid Ammonia. Metallic sodium (11 g) was added in portions with periodic shaking to 13.82 g of cotton-stem DLA that had been dried over P_2O_5 and placed in an ampul with 400 ml of liquid ammonia. Each successive portion of sodium was added after the disappearance of the blue coloration of the reaction mixture. After the end of the evaporation and the evaporation of the liquid ammonia, moist ether was added to the reaction mixture and then water. The resulting mixture was acidified with hydrochloric acid to pH 8. The precipitate that deposited was separated off by centrifugation, washed with water, dried, dissolved in aqueous dioxane (1:9), and precipitated in acidified ice water. The purified residue 1 was dried in a vacuum desiccator over P_2O_5 and was recleaved with sodium and liquid ammonia. After the separation of residue 1, the supernatant liquid was extracted with ether. The ethereal extract was dried over sodium sulfate, concentrated to small volume, and analyzed by GLC [2]. Then the solution was acidified by hydrochloric acid to pH 2. The newly deposited residue 2 separated and was treated in the same way as residue 1. The acidic aqueous solution was extracted with ethyl acetate. Both residues (1 and 2) were cleaved again with sodium in liquid ammonia and the products were worked up as in the case of the DLA. In this way, residue 1 yielded substances 1a and 1b and residue 2 substances 2a and 2b, respectively.

In the case of the native lignin, the reaction was performed similarly with a ratio of plant to sodium of 1:1 by weight.

UV spectra were taken on a SF-26 spectrophotometer in ethanol. Methoxy groups were determined by the method of Vieböch and Schwappach [11]. The results of the analyses (in percentages) are as follows:

residue 1 — C 61.77; H 5.25; OCH_3 16.21;

residue 2 — C 60.36; H 5.24; OCH_3 13.8;

residue 1a — C 59.87; H 5.68; OCH_3 14.85;

residue 1b — C 58.64; H 5.46; OCH_3 14.35;

residue 2a — C 61.68; H 5.71; OCH_3 13.92;

residue 2b — C 60.54; H 5.82; OCH_3 12.76;

residue after the first cleavage of the plant — C 55.84; H 6.28; OCH_3 15.86;

residue after the second cleavage of the plant — C 56.74; H 6.53; OCH_3 12.55.

IR spectra were taken on a UR-20 spectrophotometer (in KBr tablets).

PMR spectra of samples acetylated as described in [12] were taken on a JNM-4 H-100 MHz spectrometer. T 22-24°C; C = 10-12%; 10 — HMDS; τ scale; solvent deuterochloroform. The interpretation of the spectra and calculation of the protons were performed as in [13].

The gel chromatography of the residues was carried out on an analytical column of Sephadex G-75 with dimethyl sulfoxide as solvent and eluent. The molecular masses were calculated by the method of [14], using the coefficients found in [15].

SUMMARY

It has been shown by two cleavages with sodium and liquid ammonia of the DLA and by three cleavages of the native lignin of cotton stems that the uncleaved parts of the lignin are impoverished in methoxyls, have molecular masses 2-4 times lower than those of the initial lignins, and consist of 15-17 phenylpropane structural units.

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