A STUDY OF THE STRUCTURE OF THE HYDROCHLORIC ACID LIGNIN OF COTTON-PLANT STEMS BY REDUCTIVE DEGRADATION WITH METALLIC SODIUM IN LIQUID AMMONIA

A. A. Geronikaki and Kh. A. Abduazimov

UDC 547.458.84+549.927.2

We have previously isolated the hydrochloric acid lignin of the stems of the cotton plant Gossypium hirsutum of variety 108-F in the late vegetation period, have determined its semiempirical formula, and have studied the products of its nitrobenzene oxidation [1].

In the present paper we give the results obtained in an investigation of the cleavage of the hydrochloric acid lignin by metallic sodium in liquid ammonia. The cleavage products [2-8] were identified on a Khrom-4 gas–liquid chromatograph.

To identify the peaks on the chromatogram we obtained individual phenols and checked their purity from their chromatograms. The mixtures of phenols in the acid and alkaline fractions were analyzed separately. In the alkaline fraction of the degradation products it was possible to identify and thereby to establish the presence in it of three monomeric phenols of the guaiacyl type, two monomeric phenols of the syringyl type, and vanillin and vanillyl alcohol. The details of the analysis are given below.

Phenolic Substance	Relative Retention Time, min	Relative Content of the Phenols on the Chromatogram	Content of Phenols, % of the Lignin
Unidentified	8.00	0.65	0.025
Vanillyl alcohol (V)	9.4	2.28	0.088
(4-Hydroxy-3-methoxyphenyl)ethane (III)	9.8	3.77	0.145
(4-Hydroxy-3-methoxyphenyl)propane (I)	14.7	35.72	1.373
Vanillin (IV)	18.6	15.81	0.608
(4-Hydroxy-3-methoxyphenyl)propan-1-ol (II)	23.6	7.79	0.299
(4-Hydroxy-3,5-dimethoxyphenyl)propane (VI)	27.8	3.38	0.130
1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanol (VII)	36.0	30.61	1.179
Total	–	100.01	3.84

In addition to phenolic alcohols, the phenolic fraction contained vanillin and vanillyl alcohol (Fig. 1). Their formation from lignin has been shown previously [9, 10].

The comparatively high yield of (I) shows that during the reaction the elimination of the hydroxy group in the γ-position of the side chain must take place, which was confirmed by experiments with model compounds [11].

The phenols of the acidic ethereal fraction of the reaction products did not appear under these analytical conditions. They were sorbed completely in the column.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 646-648, September-October, 1976. Original article submitted January 28, 1976.

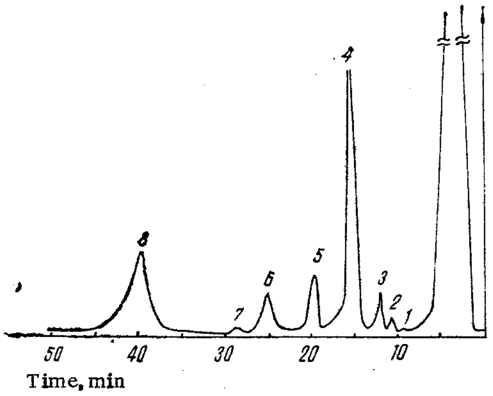


Fig. 1

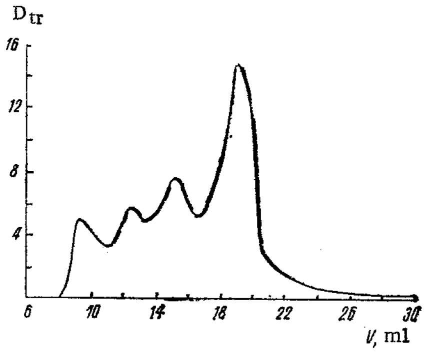
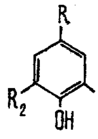


Fig. 2

Fig. 1. Chromatogram of the decomposition products of the lignin (alkaline fraction): 1) unidentified compound; 2) vanillyl alcohol; 3) (4-hydroxy-3-methoxyphenyl)ethane; 4) (4-hydroxy-3-methoxyphenyl)propane; 5) vanillin; 6) (4-hydroxy-3-methoxyphenyl)propan-1-ol; 7) (4-hydroxy-3,5-dimethoxyphenyl)propane; 8) 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanol.

Fig. 2. Gel chromatogram of the decomposition products from the acid fraction.



I. $R=CH_2-CH_2-CH_3$; $R_1=OCH_3$; $R_2=H$
II. $R=CHOH-CH_2-CH_3$; $R_1=OCH_3$; $R_2=H$
III. $R=CH_2-CH_3$; $R_1=OCH_3$; $R_2=H$
IV. $R=CHO$; $R_1=OCH_3$; $R_2=H$
V. $R=CH_2OH$; $R_1=OCH_3$; $R_2=H$
VI. $R=CH_2CH_2-CH_3$; $R_1=R_2=OCH_3$
VII. $R=CHOH-CH_3$; $R_1=R_2=OCH_3$

For a more complete characterization of this fraction, we used gel filtration on LH-20 gel. The eluent was DMFA. A gel chromatogram of this fraction (Fig. 2) was similar to that obtained by Nimz [12] in an investigation of the products of the reductive degradation of lignin previously treated with thioacetic acid. On the gel chromatogram there are four peaks corresponding to oligomers (13.82%), tetramers (11.14%), trimers (20.97%), and dimers (54.06%), the last-mentioned predominating. No monomeric fraction was detected.

Thus, the study of the cleavage products of hydrochloric acid lignin once more confirms the conclusion drawn previously [1] that it is a modified lignin and therefore many fragments obtained from the plant itself are not formed in this case.

EXPERIMENTAL

Decomposition of the Hydrochloric Acid Lignin by Metallic Sodium in Liquid Ammonia. The absolutely dry lignin (5 g) was treated with a solution of metallic sodium (4.25 g) in liquid ammonia (400 ml) at −33°C for five days. After this time, the solution had become completely decolorized. Then the ammonia was evaporated off in a current of dry nitrogen, and the residue was treated with moist ether. The mixture was diluted with water (500 ml), the alkaline solution was neutralized with CO_2 to pH 8, the hemicellulose that had precipitated was separated off and washed with water, and the wash-waters were added to the filtrate, which was then extracted with ether. The solution was acidified with H_2SO_4 (5%) to pH 2 and was again extracted with ether and then with chloroform. The yields of products obtained from the individual fractions (alkaline and acid), after the elimination of the solvents, were as follows:

Fraction	Yield, % on the Lignin
Ether, pH 8	3.84
Ether, pH 2	6.50
Chloroform, pH 2	5.33
Total amount of extracted substances	15.67

GLC Conditions. A Khrom-4 chromatograph was used with a flame-ionization detector. Separation was carried out on a stainless-steel column, 370 × 0.3 cm, containing 15% of Apiezon L on Chromaton NAW at 205°C with a rate of flow of the carrier gas (helium) of 40 ml/min. Quantitative evaluation was performed by the area-normalization method [13].

SUMMARY

The decomposition of the hydrochloric acid lignin of the stems of the cotton plant Gossypium hirsutum of variety 108-F by metallic sodium in liquid ammonia gives 3.8% of a mixture of phenols, among which the following were identified by GLC: dihydroeugenol, 4-hydroxy-3-methoxyphenylpropan-1-ol, (4-hydroxy-3-methoxyphenyl)ethane, (4-hydroxy-3,5-dimethoxyphenyl)propane, and 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanol, and also vanillin and vanillyl alcohol.

LITERATURE CITED

1. A. A. Beronikaki and Kh. A. Abduazimov, Khim. Prirodn. Soedin., 5 (1975).
2. N. N. Shorygina, T. Ya. Kefeli, and A. F. Semechkina, Dokl. Akad. Nauk SSSR, 5, 689 (1949); Zh. Org. Khim., 29, 1558 (1949).
3. N. N. Shorygina and A. F. Semechkina, Zh. Org. Khim., 28, 3265 (1958); Trudy ILPiKhD Akad. Nauk LatvSSR, 19 (1960).
4. A. F. Semechkina and N. N. Shorygina, in: The Chemistry of Wood [in Russian], Vol. 1, Riga (1968), p. 57; Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 884 (1964); Zh. Org. Khim., 23, 1593 (1953).
5. A. F. Semechkina, Author's Abstract of Candidate's Dissertation, Moscow (1963), p. 50.
6. W. Schweers, Holzforschung, 23, 120 (1968).
7. T. Higuchi and J. Kawamura, Holzforschung, 20, 16 (1966).
8. N. P. Mikhailov, N. N. Shorygina, and N. K. Vorob'eva, in: The Chemistry and Use of Lignin [in Russian], Riga (1974), p. 321.
9. V. M. Reznikov and V. F. Novitskii, Khim. Prirodn. Soedin., 81 (1975).
10. A. Yamaguchi, Mokuzai Gakkaishi, 19, No. 1, 29 (1973).
11. A. Yamaguchi, Mokuzai Gakkaishi, 19, No. 3, 141 (1973).
12. H. Nimz, Chem. Ber., 102, 799 (1969).
13. H. McNair and E. Bonelli, Basic Gas Chromatography, Varian Aerograph, Walnut Creek, California, 4th ed. (1968).