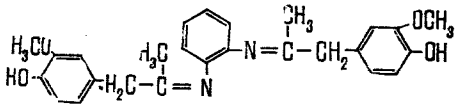
The hydrolysis lignins and their derivatives were dark brown substances sparingly soluble in water and organic solvents but fairly readily soluble in dilute solutions of alkalis.

The semiempirical formulas of the HLs and their derivatives were calculated on the basis of the elementary and functional analyses shown on the previous page.

As can be seen from the semiempirical formulas of the HLs and of substances (III and VI), they were formed by the reaction of the C=O groups of the lignin with the amino groups of the phenylenediamines. In the production of (III-V), under the action of a high temperature demethylation apparently took place, leading to a fall in the number of OCH_3 groups in them and to a rise in the number of hydroxy groups. The IR spectra of (III-VI) contain absorption bands at (cm^{-1}) 3300-3400 (OH and NH), 1710 (C=O), 1640, 1660 (C=N, NH), and 1510 (aromatic ring). To confirm that the reaction takes place at the expense of the C=O groups of the HLs [3], we studied the reaction of a model lignin compound 1-(4-hydroxy-3-naphthoxyphenyl)propan-2-one (a β-ketone) with o- and p-phenylenediamines.

By a method given elsewhere [4], with o-phenylenediamine we obtained a new compound (VII) with mp 151-152°C, composition $C_{26}H_{28}O_4N$. Its mass spectrum showed the peaks of ions with m/e 432 (M^+), 254, 240, and 137.



With p-phenylenediamine a substance (VIII) was formed, $C_{16}H_{18}O_2N_2$, mp 189-190°C, in which the β-ketone had reacted with an equimolecular amount of p-phenylenediamine.

LITERATURE CITED

1. N. A. Veksler, L. S. Smirnova, and Kh. A. Abduazimov, Khim. Prirodn. Soedin., 645 (1974).
2. A. D. Alekseev, L. T. Matusevich, and V. M. Reznikov, Khimiya Drevesiny, No. 9, 57 (1971).
3. V. M. Reznikov, in: General and Applied Chemistry [in Russian], No. 3 (1970), p. 164.
4. Z. K. Saipov and Kh. A. Abduazimov, Khimia Drevesiny, No. 2, 78 (1976).

DETERMINATION OF CATECHOL GROUPS IN COTTON-PLANT LIGNINS

B. Kh. Pulatov and Kh. A. Abduazimov

UDC 547.992.3

In the semiempirical formulas of the dioxane lignins (DLAs) and ultrasonic lignins (USLs) of the cotton plant, there is more than one phenolic hydroxy group to one phenylpropane structural unit [1]. This led us to the idea of the possibility that cotton-plant lignins contain catechol groups. Such groups have been found in certain lignin preparations [2-4].

We applied to the natural lignin the well-known method of determining catechol in phenol-containing tars which is based on the color reaction of catechol in an alkaline medium [5]. The results of the determination of catechol groups in model compounds of lignin and in natural lignins are shown below:

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent.

Translated from Khimiya Prirodnykh Soedinenii, No. 6, p. 835, November-December, 1976. Original article submitted June 23, 1976.

Substance	Amount of catechol groups, %	
	Calculated	Found
Catechol	30.87	30.1
Protocatechuic aldehyde	24.64	24.00
Protocatechuic acid	22.05	21.46
5-Hydroxy vanillin	20.22	19.65
DLA from an early vegetation period	-	6.9
DLA from the flowering period	-	5.08
DLA of the bolls	-	1.55
DLA of green stems	-	1.43
USL of green stems	-	6.36

The relative error for the model compounds does not exceed 2.5-3%. With the growth of the cotton plant, the amount of catechol groups in the lignins falls, probably because of their methylation in the lignins [1]. In the USL, the large amount of catechol groups is connected with the cleavage of alkyl—aryl bonds under the action of ultrasound [6].

The samples of lignins were obtained from the cotton plant of variety 108-F, as described elsewhere [1, 6]. About 0.050 g (accurately weighed) of lignin was dissolved in 5 ml of aqueous dioxane (9:1). To a test tube were added 1 ml of the lignin solution, 3.5 ml of water, and 0.5 ml of 10% aluminum sulfate solution and the mixture was stirred. Into each of two calorimetric test-tubes was transferred 1 ml of the solution obtained, and then 0.1 ml of a 10% solution of sodium nitrite and, after stirring for 2-3 min, 0.5 ml of a 50% solution of caustic soda were added. If catechol groups were present, a cherry-red coloration appeared the intensity of which depended on their amount. The solutions were diluted with 3.5 and 3 ml of water. To the sample with the smaller volume a 0.4% solution of potassium ferricyanide was added in drops until the red color changed to orange. The orange solution was treated with a standard solution of dye prepared by the method described by Maslennikov and Poryvaeva [5] until the color was the same as that in the parallel tube. At the end of titration, if the volumes of the solutions in the tubes were different, they were made equal by the addition of water.

The concentration of catechol was calculated from the formula given by Maslennikov and Poryaeva [5] and the percentage of catechol groups in the other models and the natural lignins by means of the formula

$$\text{catechol groups, \%} = \frac{V \cdot 0.0002 \cdot 5 \cdot 5 \cdot 30.87}{P},$$

where V is the volume of the standard solution of dye consumed in titration ml; P is the weight of the sample, g; 0.0002 is the amount of catechol in the standard azo dye; and 30.87 is the percentage of catechol groups in catechol.

LITERATURE CITED

1. N. A. Veksler, L. S. Smirnova, and Kh. A. Abduazimov, Khim. Prirodn. Soedin., 80 (1976).
2. G. F. Prokshin, Izv. Vyssh. Uchebn. Zaved. Lesn. Zh., No. 5, 141 (1967).
3. G. F. Prokshin, and L. F. Tushina, Izv. Vyssh. Uchebn. Zaved., Lesn. Zh., No. 6, 113 (1969).
4. B. D. Bogomolov and S. B. Pal'mova, Scientific Papers of the Archangel Institute of Wood Technology [in Russian], No. 38 (1973), p. 51.
5. A. S. Maslennikov and G. N. Poryvaeva, Zh. Prikl. Khim., 38, No. 6, 1327 (1965).
6. S. A. Saidalimov, L. S. Smirnova, and Kh. A. Abduazimov, Khim. Drev., 2, 75 (1976).