

are probably isoenzyme spectra of the aminopeptidase. The aminopeptidase preparation isolated from the materials mentioned were found to be homogeneous and each showed one protein band in the gel. Intense coloration was observed in zones with relative electrophoretic mobilities of 0.86 and 0.90 for the aminopeptidases of *Asp. oryzae* and *Asp. flavus*, respectively (see Fig. 1, a and b, columns 3 and 4). The molecular weight of the aminopeptidase from *Asp. oryzae* was determined in PAAG by the method of Weber and Osborn [4] in the modification of Fairbanks et al. [5] in the presence of the anionic detergent sodium dodecyl sulfate. The following proteins were used as markers: ribonuclease (13,500), egg protein lysozyme (17,500), chymotrypsinogen (25,700), pepsin (35,000), egg albumin (43,000), and bovine serum albumin (68,000). The determinations were performed in 10% gel in 0.01 M tris acetate buffer, pH 7.2. The mobilities (calculated by a standard formula [3] were plotted on a graph against known molecular weights expressed on a semilogarithmic scale. The molecular weight of the aminopeptidase was 60,000. It has been shown previously that the molecular weight of the enzyme from *Asp. flavus* determined by gel filtration on Sephadex G-2000 was 59,000 [6]. Thus, the molecular weights of the two aminopeptidases are practically identical.

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THE INTERACTION OF HYDROLYSIS LIGNIN WITH PHENYLENEDIAMINES

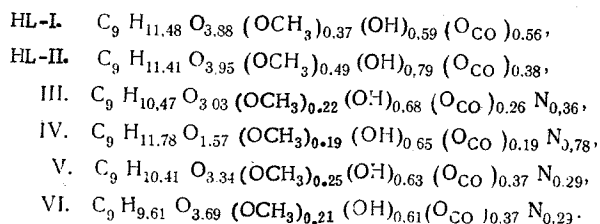
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UDC 634.813.11.0.813.1

Hydrolysis lignins of the pods of the seeds of the cotton plant (HL-I) and from the sawdust of coniferous trees (HL-II) are waste materials from hydrolysis factories. As compared with dioxane lignins [1, 2], obtained by a milder method, they contain smaller amounts of methoxy and hydroxy groups and larger amounts of oxygen, hydrogen, and carbonyl groups. This shows that the HLs are highly condensed.

To expand the range of practical utilization of lignin, we have obtained a number of nitrogen-containing derivatives (III-VI) from HL.

Products (III) and (IV) were formed by heating HL-I with o-phenylenediamine in a ratio of 2:1 (by weight) in dimethylformamide (DMF) at 145-148°C for 4-6 h. Substance (IV), unlike (III), was readily soluble in DMF. Under similar conditions the reaction of lignin with p-phenylenediamine gave a product (V). Ammoniated lignin (VI) was obtained by moistening HL with a 5% solution of ammonia at room temperature.



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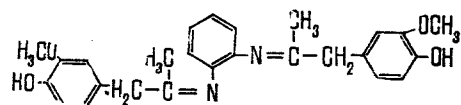
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The hydrolysis lignins and their derivatives were dark brown substances sparingly soluble in water and organic solvents but fairly readily soluble in dilute solutions of alkalis.

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 OCH₃ 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-naphthoxy-phenyl)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 C₂₆H₂₈O₄N. 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, C₁₆H₁₈O₂N₂, mp 189-190°C, in which the β-ketone had reacted with an equimolecular amount of p-phenylenediamine.

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DETERMINATION OF CATECHOL GROUPS IN COTTON-PLANT LIGNINS

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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:

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