# A COMPARATIVE STUDY OF THE DIOXANE LIGNINS OF *Althea*

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Continuing a study of the dioxane lignin of plants of the family Malvaceae [1], and supplementing our earlier study of the species *Althaea rhyticarpa*, we have investigated two other representatives of this family. *A. nudiflora*, which is one of the most widespread species [2], was collected in the territory of Chimgan in September (lignified stem) and *A. rosea* (hollyhock), which is a cultivated plant, was collected on the territory of the trial production section of the Kibri sovkhoz, Tashkent oblast, in November, 1974. The dioxane lignin (DLA) was isolated from the Althea stems by Petter's method [3]. The yields of DLA (in percentages both of the weight of the plant and of the Komarov lignin) from the different raw materials, on working under the conditions that we selected, proved to be different:

| Product | Yield, % on the weight of the plant | Yield, % on the Komarov lignin |
|---|---|---|
| DLA from the stems of | | |
| A. rhyticarpa (DLA-1) | 5.0 | 33.18 |
| A. nudiflora (DLA-2) | 6.4 | 53.79 |
| A. rosea (DLA-3) | 6.2 | 46.61 |
| Cotton plant [4] | 2.2 | 8.30 |

In contrast to the cotton plant, in all cases the altheas yielded a fairly large lignin fraction.

The preparations obtained consisted of light brown amorphous powders readily soluble in aqueous solutions of alkalis, moist dioxane, and dimethyl sulfoxide (DMSO), and 90% acetic acid, and sparingly in n-butanol and water.

After purification by Björkman's method [5], the resulting preparations contained 2.4, 5, and 5.4% of bound carbohydrates, respectively, the amount of which was determined by a known method [6], and this was taken into account in drawing up the semiempirical formulas. The semiempirical formulas of the phenylpropane structural units were calculated on the basis of the results of elementary and functional analyses.

DLA of *A. rhyticarpa*: molecular weight of the structural unit 206.1.

$$C_9H_{7.6}O_{1.00}(OCH_3)_{1.07}(OH_{phen})_{0.43}(OH_{alip})_{0.93}(O_{ar\text{-}alk})_{0.57}O_{co})_{0.52}$$

DLA of *A. nudiflora*: molecular weight of the structural unit 201.

$$C_9H_{6.84}O_{1.21}(OCH_3)_{1.20}(OH_{phen})_{0.38}(OH_{alip})_{0.77}(O_{ar\text{-}alk})_{0.62}$$
$$(O_{co})_{0.41}(OOH_{COOH})_{0.08}$$

DLA of *A. rosea*: molecular weight of the structural unit 205.8.

$$C_9H_{6.35}O_{0.82}(OCH_3)_{1.25}(OH_{phen})_{0.20}(OH_{alip})_{0.97}(O_{ar\text{-}alk})_{0.80}$$
$$(O_{co})_{0.30}(OOH_{COOH})_{0.056}$$

DLA of ripe stems of the cotton plant [4]:

$$C_9H_{6.89}O_{1.01}(OCH_3)_{1.0}(OH_{phen_{0.30}}/(OH)_{2/0.1}(OH_{alip})_{0.87}(O_{ar\text{-}alk})_{0,6}$$
$$(O_{co})_{0.21}(OOH_{COOH})_{0.045}$$

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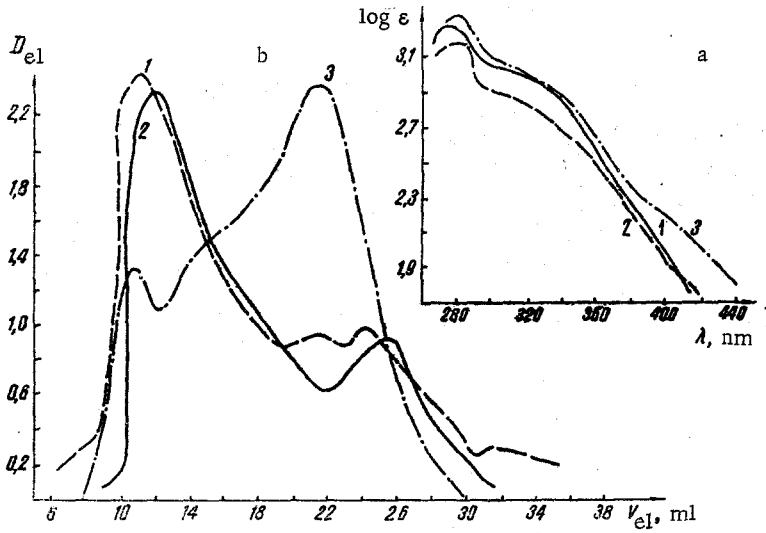


Fig. 1. UV spectra (a) and gel chromatograms of the DLA of *Althea rhyticarpa* (1), *nudiflora* (2), and *rosea* (3).

It follows from the figures given that the DLAs of the altheas differ in composition both from one another and from that of ripe cotton-plant stems. Differences are observed mainly in the amounts of hydrogen, oxygen, and carbonyl and methoxy groups. It can be seen from the formulas that the althea lignins are more highly methoxylated than in the cotton-plant DLA. The amounts of CO groups in them are higher, and so are the amounts of unassigned oxygen, except for DLA-3 where it is less than cotton-plant DLA. This oxygen all probably belongs to other ether bonds, the amount of which in these types of lignin must therefore be higher than in the lignin of the cotton plant and of other woody plants.

In the UV spectra of the althea and cotton plant [4] DLAs (Fig. 1a) there are two bands, at $\lambda_{max}$ 275-280 nm at 300-360 nm in the form of a shoulder; the 280 nm maximum characterizes the absorption of an aromatic ring and the 300-360 nm band is connected with the absorption of a benzene ring having substituents with conjugated double bonds and C=O:

| Preparation | $\lambda_{max}$ | $\varepsilon_{280}$ | $OCH_3/C_9$ | $OH_{ph}/C_9$ |
|---|---|---|---|---|
| DLA-1 | 275 | 1760 | 1.07 | 0.43 |
| DLA-2 | 277 | 2000 | 1.20 | 0.38 |
| DLA-3 | 280 | 2400 | 1.25 | 0.20 |

The molar extinctions of the althea DLAs are between 1760 and 2400. They are composed of the extinctions of each phenylpropane structural unit by the additivity rule. Taking into account the molar extinctions for the guaiacylpropane ($\varepsilon_{280}$ = 2800), the p-hydroxyphenylpropane ($\varepsilon_{280}$ = 1620), and the syringylpropane ($\varepsilon_{280}$ = 1150) series [7], it is possible to analyze the results obtained and to deduce the types and amounts of the chromophores in the DLA.

In the case of the althea DLAs, as can be seen from the semiempirical formulas, in each phenylpropane unit there are more $CH_3$ groups than in the cotton-plant DLA (because of the syringyl structures), as is shown by the products of alkaline nitrobenzene oxidation [1]. The fairly high extinction may be due to the predominance of guaiacyl units over syringyl units in the lignin molecule in some cases.

The IR spectra of all the lignins show bands characteristic of a benzene ring with substituents (1615, 1520, 1450 $cm^{-1}$) and of hydroxy (3400 $cm^{-1}$), carbonyl (1720 $cm^{-1}$), and ether (1280, 1230, 1040 $cm^{-1}$) groups. Appreciable differences are observed only in the region of the absorption of C=O groups conjugated with a benzene ring. The band at 1660 $cm^{-1}$ of α-CO (responsible for the 300-360 nm shoulder in the UV spectrum) that is present in the IR spectrum of all the althea DLAs is absent from the cotton-plant DLA.

The polydispersity of all the lignins was studied by gel chromatography on Sephadex G-75. DMSO was used as eluent. The gel chromatograms of the lignins (1b) showed that the althea DLAs, like the DLA from ripe cotton-plant stems, are polydisperse. The molecular weights of these fractions were calculated by means of the coefficients found previously [8]:

| Preparation | Molecular Weight × $10^3$ High mol. wt. fraction | Low mol. wt. fraction | $\overline{M}_w$ | $\overline{M}_n$ | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|
| DLA-1 | 17—20 (56.5%) | 2—4 (22.7%) | 12035 | 5880 | 2,05 |
| DLA-2 | 15—23 (45%) | 1.6—2.4 (18,5) | 10990 | 4230 | 2,60 |
| DLA-3 | 13—26 (20,1%) | 1.4—3.2 (52,8) | 7440 | 4000 | 1,86 |
| DLA of ripe cotton stems | 18—24 | 3—6 | | | |

It can be seen from Fig. 1b and the figures given above that in the case of the DLAs of wild-growing species of *Althea* — *A. rhyticarpa* and *A. nudiflora* — the high-molecular-weight fraction is predominant, while in the case of DLA-3 it is the low-molecular-weight fraction. The nature of the molecular weight distribution in DLA-3 resembles that of the lignin of mechanically ground spruce [9] (the maximum of the molecular-weight distribution of spruce lignin corresponds to 3000-4000, and of althea lignin to 3000), although, unlike the latter there are two maxima on the curve of the molecular-weight distribution of DLA-3 (the second maximum being less distinct than the first). The multimodal nature is the result of the coexistence of several polymerization mechanisms [10]. The first peak corresponds to approximately 44 phenylpropane structural units and the second to 15. Similarly, in DLA-1 the first maximum corresponds to approximately 92 structural units and the second to 13. For DLA-2, these figures are 96 and 8 phenylpropane structural units, respectively.

For the study of the althea DLAs we used the method of alkaline nitrobenzene oxidation [11] and decomposition with metallic sodium in liquid ammonia [12-15]. The products of nitrobenzene oxidation were separated and the DLAs were investigated by the GLC method [16], the results being given below (%)

| Substance | A. rhyticarpa | A. nudiflora | A. rosea | Cotton-plant | DLA-1 | DLA-2 | DLA-3 | Cotton-plant DLA |
|---|---|---|---|---|---|---|---|---|
| p-Hydroxybenz-aldehyde | 0.50 | — | — | — | 0.72 | — | 2.02 | 0.58 |
| p-Hydroxybenzoic acid | 0.35 | 0.25 | — | 0.26 | 1.17 | 2.64 | 3.51 | 0.34 |
| Vanillin | 2.36 | 0.59 | 1.25 | 8.33 | 12.85 | 5.77 | 5.89 | 18.0 |
| Acetovanillone | 0.93 | 0.04 | 0.03 | — | — | 0.39 | 3.48 | 0.73 |
| Ferulic acid | 0.89 | 0.06 | 0.23 | 0.13 | 0.79 | 0.60 | 1.93 | 0.31 |
| Vanillic acid | — | — | — | — | 1.01 | — | — | — |
| Spring-aldehyde | 3.08 | 1.55 | 0.68 | 7.78 | 32.13 | 15.31 | 6.92 | 10.30 |
| Sinapic acid | — | 0.03 | 0.13 | — | — | 0.17 | 3.36 | — |
| Syringic acid | — | — | — | — | 1.67 | — | — | — |

Althea lignin, like cotton-plant lignin, contains all three types of structural units: p-coumaryl, from which p-hydroxybenzaldehyde and p-hydroxybenzoic acid are formed; guaiacyl, from which vanillin, acetovanillone, and ferulic and vanillic acids are formed; and syringyl, which is responsible for the formation of syringaldehyde and sinapic and syringic acids. The amount of syringyl derivatives in the althea lignins is somewhat higher than in the cotton-plant lignins, except for *Althea rosea* in which the amount of these structures is approximately the same as in the cotton plant.

By decomposing the natural lignins of althea stems and the DLA with metallic sodium in liquid ammonia, as the result of which the alkyl-aryl ether bonds present in them are cleaved, it was found that the yield of monomers was 1.27% on the weight of the dry plant for *Althea rhyticarpa*, 1.42% for *A. nudifora*, and 2.38% for *A. rosea*, or 8.42, 10.74, and 16.8% of the Komarov lignin, respectively, which is in complete agreement with the number of alkyl-aryl ether bonds calculated from the formula.

Among the identified products of the decomposition by metallic sodium in liquid ammonia of the natural lignins of althea stems and the DLAs substances were detected by the GLC method corresponding to the p-coumaryl, guaiacyl, and syringyl structural units (Fig. 2). The decomposition and oxidation products are identified from their retention times and by the addition of markers.

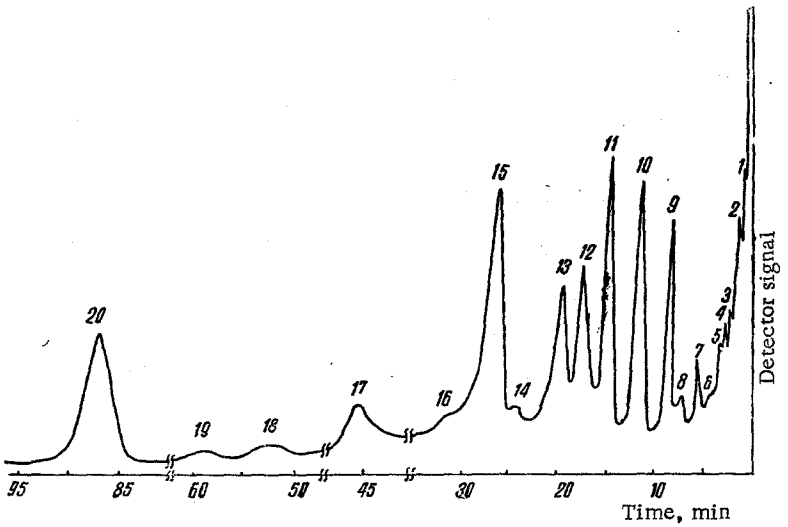


Fig. 2. GLC of the products of the decomposition of the natural lignin of *Althea rosea* (alkaline fraction): 1) unidentified; 2) unidentified; 3) phenol (I); 4) guaiacol (VI); 5) unidentified; 6) p-hydroxyphenylethane (III); 7) vanillyl alcohol (VIII); 8) 1-(4-hydroxyphenyl)propane (IV); 9) (4-hydroxy-3-methoxyphenyl-ethane (IX); 10) 1-(4-hydroxy-3-methoxyphenyl)propane (XI); 11) vanillin (VII); 12) 1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (XII); 13) unidentified; 14) unidentified; 15) 1-(4-hydroxy-3,5-dimethoxyphenyl)propane (XV); 16) 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol (XIII); 17) 1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol (XVI); 18) unidentified; 19) 3-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol (XVII); 20) unidentified.

The amounts of phenolic substances in the decomposition products were as follows:

| Substance | Althea myticarpa | A. nudiflora | A. rosea | DLA-1 | DLA-2 | DLA-3 |
|---|---|---|---|---|---|---|
| Phenol (I) | — | 0,040 | 0,030 | — | 0,010 | 0,025 |
| p-Hydroxybenzoic acid (II) | 0,060 | — | — | — | — | — |
| (4-hydroxyphenyl)ethane (III) | — | 0,025 | 0,007 | — | 0,018 | 0,035 |
| (4-Hydroxyphenyl)propane (IV) | — | 0,130 | 0,100 | — | — | 0,103 |
| 3-(4-hydroxyphenyl)propan-1-ol (V) | — | — | — | — | 0,067 | 0,201 |
| Guaiacol (VI) | — | 0,038 | 0,050 | 0,016 | 0,011 | 0,050 |
| Vanillin (VII) | 1,160 | 1,450 | 1,840 | 0,076 | 1,403 | 2,367 |
| Vanillyl alcohol (VIII) | 0,033 | 0,030 | 0,007 | 0,055 | 0,012 | 0,095 |
| (4-Hydroxy-3-methoxyphenyl)ethane (IX) | 0,035 | — | 0,800 | 0,073 | 0,069 | — |
| 1-(4-hydroxy-3-methoxyphenyl)ethan-1-ol (X) | — | 0,020 | — | — | — | — |
| (4-hydroxy-3-methoxyphenyl)propane (XI) | 1,370 | 2,990 | 1,340 | 0,631 | 1,577 | 4,903 |
| 1-(4-hydroxy-3-methoxyphenyl)propan-1-ol (XII) | 0,310 | 0,650 | 1,300 | 0,140 | 0,059 | 0,168 |
| 3-(4-hydroxy-3-methoxyphenyl)propan-1-ol (XIII) | 0,220 | 0,400 | 0,057 | — | 0,165 | 0,455 |
| 1-(4-hydroxy-3,5-methoxyphenyl)ethan-1-ol (XIV) | 0,087 | — | — | — | — | — |
| (4-hydroxy-3,5-dimethoxyphenyl)propane (XV) | 4,590 | 1,450 | 2,900 | 2,849 | 4,152 | 3,129 |
| 1-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol (XVI) | — | 0,620 | 0,780 | 0,320 | 0,296 | 0,282 |
| 3-(4-hydroxy-3,5-dimethoxyphenyl)propan-1-ol (XVII) | — | 0,466 | 0,260 | — | 0,405 | — |

As can be seen from the figures given, here also a difference is observed between the althea lignins, both qualitatively and quantitatively, which shows some differences in the structures of the lignins of different species of *Althea*. Thus, in the decomposition products of the natural lignins of *A. rhyticarpa* nine substances were identified that were based on guaiacyl- and syringylpropane derivatives. p-Coumaryl structural units were almost completely absent from the products of its degradation. Conversely, in the products of the re-

action of two other samples 13 substances were identified and here p-coumaryl structural elements are represented fairly completely.

Together with the phenolic alcohols, the alkaline phenolic fraction contained vanillin and vanillyl alcohol, the presence of which has been found previously [18, 19]. The comparatively high yield of (XI) shows that during the reaction a hydroxy group in the γ position of the side chain must be eliminated, as has been confirmed [20] by experiments with model compounds. The formation of α-guaiacylpropanol and α-syringylpropanol from lignin is a direct proof of the presence of free benzyl alcohol groups in the lignin.

Taking into account the specific nature of the action of the reagent used and the formation of the phenols mentioned, it is possible to deduce the structures of the lignins. Thus, the phenols (XII, XIII, and XVI, XVII) detected in the reaction products show the presence of guaiacyl- and syringylpropane units with free OH groups in the side chains in the α and γ positions in the aromatic nucleus in the initial lignin, which is in harmony with Efendieva's results [21]. On the other hand, the detection of α-CO bands in the IR spectra of the althea DLAs permits the assumption that some of the OH groups are products of the reduction of CO groups. Similarly, the detection of the phenol (V) in the reduction product shows the presence of p-hydroxyphenylpropane units with free OH groups in the side chain in the γ position to the aromatic nucleus in the initial lignin.

The detection of phenols derived from p-hydroxyphenylpropane (II-V) from guaiacylpropane (XI-XIII), and from syringylpropane (XV-XVII) indicates the presence of "uncondensed," — i.e., unconnected by —C—C— bonds — structural units of the lignin [21].

The combined water-soluble raw material obtained from the acid (pH 2) ethereal solutions of the decomposition products of the natural lignin of the stems of *A. rhyticarpa, nudiflora,* and *rosea* were obtained in yields of 3.76, 1.56, and 1.28%, respectively, and were products of incomplete cleavage. For the fuller characterization of these fractions we used gel chromatography on Sephadex LH-20 with DMFA as the eluent and solvent. It is interesting to note that the gel chromatograms of these fractions are fairly close to the chromatograms obtained by Nimz [22] in an investigation of the products of the reductive degradation of lignin previously treated with thioacetic acid. It follows from the gel chromatograms that the combined ether-soluble materials from the *Althea rhyticarpa* stems consists of tetramers (57.09%), trimers (20.84%) and dimers (22.09%), that from the stems of *A. nudiflora* of oligomers (20.84%), tetramers (17.46%), trimers (18.20%), and dimers (43.5%), and that from the stems of *A. rosea* of tetramers (67.3%), dimers (26.0%), and monomers (6.96%). Thus, in this case, as well, structural differences are observed between the lignins of different species of *Althea.*

## EXPERIMENTAL

The dioxane lignin was isolated by a procedure which we have described previously [1].

Methoxy groups were determined by the method of Vieböck and Schwappach [23], and total hydroxy groups by a method described in a handbook [24]. Phenolic hydroxy groups were found by comparing the amounts of methoxy groups in the lignin before and after methylation with diazomethane. The aliphatic hydroxy groups were calculated by difference between the total hydroxy groups and the phenolic. Carbonyl groups were determined by the method of Gierer and Soderberg [25], and readily hydrolyzable hydrocarbons by Bertrand's method [5].

The IR spectra were taken on a UR-20 instrument in tablets of KBr, and the UV spectra on an SF-4 spectrophotometer using a mixture of dioxane and water (9:1) as solvent. Gel chromatography was performed by a method which we have described previously [1]. The nitrobenzene oxidation of natural althea lignin was performed by Leopold's method [11] and that of the DLA by our own method [1]. The products of nitrobenzene oxidation were investigated by the GLC method [1]. The peaks were evaluated quantitatively by the area normalization method [26].

Action of Metallic Sodium in Liquid Ammonia on the Lignin of the Stems of *Althea rhyticarpa*. A 10-g sample of a flour of the althea stems previously extracted with a mixture of ethanol and benzene (1:1) to eliminate extractive substances and dried in a vacuum desiccator over $P_2O_5$ was treated with 500 ml of liquid ammonia, and 10 g of metallic sodium was added gradually. The reaction was continued for 8 days. After evaporation of the ammonia, the pulverulent matter remaining in the vessel was treated with water-saturated ether and

then with 350-400 ml of water. The alkaline solution was neutralized with gaseous carbon dioxide to pH 8 and filtered, and the insoluble powder was washed to neutrality. The filtrate and the wash-waters were combined and extracted exhaustively with ether. The ethereal extracts were dried over calcined magnesium sulfate and evaporated, and the residue was weighed and subjected to GLC analysis.

The aqueous solution was acidified with 5% sulfuric acid (with cooling and stirring) to pH 2 and was again exhaustively extracted with ether and then with chloroform. The ethereal and chloroform extracts were dried separately over calcined magnesium sulfate and evaporated. The yields of products obtained from the individual fractions (alkaline and acid), after the elimination of the solvents, were as follows (% on the weight of the plant): from the ethereal fraction extracted at pH 8 — 1.27, at pH 2 — 3.76; from the chloroform fraction extracted at pH 2 — 0.41. The total amount of substances extracted was 5.44%. The decomposition and analysis of the natural lignin of the stems and the DLA of the samples of *A. nudiflora* and *A. rosea* were performed similarly.

## SUMMARY

1. The dioxane lignins have been extracted from three species of *Althea* for the first time. On the basis of elementary and functional analyses, the semiempirical formulas of the phenylpropane structural units have been calculated.

2. The molecular weight distributions have shown that the DLAs of these species of *Althea* are polydisperse, and in the case of the DLAs of the wild-growing species — *A. rhyticarpa* and *A. nudiflora* — the high-molecular weight fraction is predominant, while for the DLA of *A. rosea* the low-molecular-weight fraction is predominant.

3. In a study of the products of nitrobenzene oxidation it has been established that the DLA of all three species of *Althea* includes p-coumaryl, guaiacyl, and syringyl structural units.

4. In the products of decomposition with metallic sodium in liquid ammonia 18 phenols have been identified the structures of which show the presence in the initial lignins of guaiacyl- and syringylpropane units with free OH groups in the side chains in the α- and γ-positions to the aromatic nucleus.

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# CHANGE IN THE STRUCTURAL ELEMENTS OF COTTON-PLANT LIGNINS IN THE VARIOUS VEGETATION PERIODS

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In studying the lignin of the cotton plant and its changes during the growth of the plant, we isolated and investigated [1, 2] the dioxane lignin (DLA) from the stems of the cotton plant of variety 108-F in its various vegetation periods.

For the dioxane lignins of the earlier vegetation period (DLA-I and DLA-II) Björkman's method of purification [3] is the best, since it gives a lignin practically free from carbohydrates and having a larger proportion of methoxy groups than that purified by other methods [2]. Having adopted this method of purification and having generalized results obtained previously, we calculated the semiempirical formulas of the lignins per single phenylpropane unit:

Dioxane lignin of the early vegetation period (DLA-I)

$$C_9H_{7,47}O_{1,38}(OCH_3)_{0,47}(OH_{phen})_{1,05}(OH_{alip})_{0,93}(O_{CO})_{0,35}(OOH_{COOH})_{0,17};$$

Dioxane lignin of the flowering period (DLA-II)

$$C_9H_{7,81}O_{1,39}(OCH_3)_{0,73}(OH_{phen})_{0,92}(OH_{alip})_{1,04}(O_{CO})_{0,31}(OOH_{COOH})_{0,065};$$

Dioxane lignin of the ripe stems of the cotton plant (DLA-III)

$$C_9H_{6,85}O_{1,56}(OCH_3)_{1,0}(OH_{phen})_{0,4}(OH_{alip})_{0,87}(O_{CO})_{0,21}(OOH_{COOH})_{0,045}$$

We found catechol groups in all the lignins.

Various methods of determining catechol groups in lignins have been described in the literature, and these groups have been found not only in technical [4, 5] and demethylated [6] lignins but also in natural lignins [7]. To confirm the presence of catechol groups in the dioxane lignins of the cotton plant, we studied the kinetics of the absorption of oxygen by these lignins, and also by some model substances (Fig. 1). For clarity, the amount of oxygen absorbed has been calculated in moles per mole of oxidized substance. In the case of lignins, the calculation was referred to the molecular weight of a phenylpropane structural unit (ppsu).

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