

On the chromatograms, the products of nitrobenzene oxidation were identified by their retention times and by the addition of markers. Quantitative evaluation was performed by the area-normalization method.

SUMMARY

1. The developed semiempirical formula for the dioxane lignin from the stems of *Althaea rhyticarpa* has been found from the results of elementary and functional analyses.
2. It has been shown that the lignin consists of high- and low-molecular-weight fractions.
3. It has been shown by the nitrobenzene oxidation method that p-coumaryl, guaiacyl, and syringyl structural units are present in the lignin.

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STUDY OF THE LOW-MOLECULAR-WEIGHT ULTRASONIC LIGNIN FROM

Pinus sylvestris

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An ultrasonic lignin (USL) has previously been obtained from *Pinus sylvestris* (Scotch pine) with the aid of ultrasound; its properties are very close to those of the Björkman lignin but differ from it by its low molecular weight [1]. We have isolated the USL from the plant mentioned by the method described [2]. The preparation obtained, after purification according to Björkman [3], proved to be identical with that characterized previously [1]. The results of an investigation of its molecular-weight distribution (MWD) on a column of Sephadex G-75 showed that the lignin is bimodal. The high-molecular-weight fraction (weight-average molecular weight 10,000) makes up 27% and the main, low-molecular-weight fraction 65% (weight-average molecular weight 1600). To fractionate the USL we used dialysis through a semipermeable membrane (Cellophane) against distilled water. After dialysis, the MWD of the lignin had changed insignificantly.

It may be considered that the USL that we had isolated consisted mainly of low-molecular-weight molecules.

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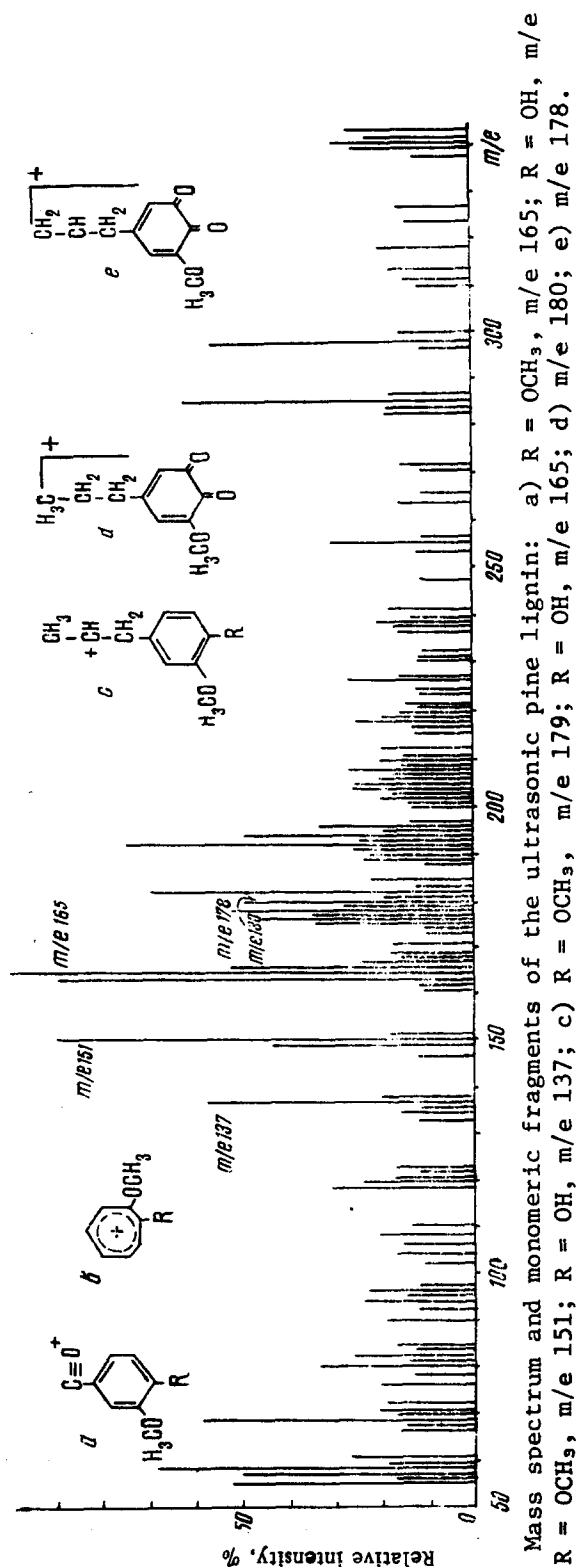


Fig. 1. Mass spectrum and monomeric fragments of the ultrasonic pine lignin: a) R = OCH₃, m/e 165; R = OH, m/e 151; b) R = OCH₃, m/e 151; R = OH, m/e 137; c) R = OCH₃, m/e 178; d) R = OH, m/e 180; e) m/e 178.

To study the behavior of the USL under conditions of mass-spectrometric fragmentation, we recorded the mass spectra of a sample of USL previously methylated with diazomethane in instruments fitted with means for the direct introduction of the sample into the ionization chamber (Varian MAT-311 and MKh-1303) at temperatures of 280 and 200°C. No peaks corresponding to the molecular ion and to the ions of lignin oligomers with high masses were observed in either spectra.

The main intense ions of the monomeric fragments of the lignin were similar in the two spectra. With a rise in the temperature to 280°C, the intensity of the peaks corresponding to the dimeric degradation products (240-350 amu) fell considerably and the intensity of the fragmentary ions with low masses (50-100 amu) increased as a result of the thermal decomposition of the lignin [4].

The strongest ions are those corresponding to the monomeric fragments of the lignin, the possible structures of which are shown in Fig.1.

The absence from the spectrum of the strong ion with m/e 195 — the syringyl analog of the ions shown in Fig. 1 — is evidence for the absence of syringyl structures from the USL.

In cases of natural lignins [5-7] and dimeric model compounds of lignin [8], it has been shown that, as a rule, the functional groups are not split out from the aromatic nucleus during mass spectrometry. In the case of the USL, a series of ions differing by 14 amu (CH₂) is probably formed by the β- and γ-cleavages of C-C bonds in the phenylpropane chain (m/e 165, 151, 137).

The structure of the dimeric ions can be represented by a combination of monomeric ions. Their low intensity is evidence that they are formed mainly through thermal degradation.

Thus, analysis of the mass spectra of pine USL has shown a complex pattern due to the process of ionization and thermal degradation. The strongest ions confirm the gualacyl structure [2] of the pine USL.

EXPERIMENTAL METHOD

Isolation of the USL. The "sonication" of the ground (0.25 mm) pine sawdust which had previously been extracted with ethanol-benzene (1:1) and with hot water was performed in thin-glass beakers on an apparatus consisting of a trough with a magnetostriction transducer of type PMS-6a fed from a UZG-10M ultrasonic generator. The intensity of the ultrasonic vibrations in the trough was kept constant in the range between 2.5 and 3.0 W/cm² at a frequency of the ultrasonic vibrations of 20.5 kHz. The

temperature of the water in the bath did not rise above 35°C. As the solvent we used 15% aqueous acetone with a ratio of material to solvent of 1:22, and a sonication time of 10 min.

The sawdust was separated from the solution and was washed three times with aqueous acetone, and the acetone solutions were evaporated to dryness under vacuum. The dry residue was dissolved in aqueous dioxane (9:1) and precipitated in absolute ether. The lignin that deposited was separated from the ether, washed twice with absolute ether, and dried in a desiccator over P₂O₅.

Characteristics of the USL. The USL formed a sand-colored powder readily soluble in aqueous dioxane, acetic acid, DMSO, DMF, and alkalis. Its composition was as follows (%): C 62; H 5.93; OCH₃ 14.78. IR spectrum, cm⁻¹: 3450, 2950, 2895, 2865, 1720, 1660, 1610, 1520, 1430, 1370, 1275, 1229, 1150, 1090, 1042.

Gel chromatography was performed by the method described previously [9] in a column of Sephadex G-75 with DMSO as the eluent and the solvent, using the factors for calculating the molecular weights given by Babikova et al. [10].

The mass spectra were taken on spectrometers fitted with means for the direct introduction of the sample into the ionization chamber — Varian MAT-311 (70 eV, 280°C) and MKh-1303 (40 eV, 200°C) instruments.

SUMMARY

1. The ultrasonic lignin from *Pinus sylvestris* is bimodal with its main fraction being of low molecular weight (mol. wt. 1600).
2. On mass spectrometry, far-reaching decomposition of the complex lignin molecule takes place under the action of electron impact and thermal decomposition.
3. The structure of the monomeric ions confirms the guaiacyl nature of the USL.

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