

A STUDY OF RICE LIGNIN

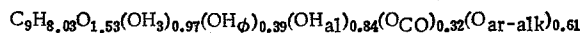
Z. K. Saipov, E. V. Borodina,
and Kh. A. Abduazimov

UDC 547.992.002.61

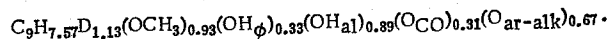
For a comparison study of the dioxane lignins of rice husks and of ripe rice stems, the DLA of ripe rice stems has been isolated by a modification of Pepper's method with a yield of 5.25% on the plant and 25% on the Komarov lignin. The amounts of the main functional groups in the two lignins are similar. The semiempirical formulas have been calculated on the basis of elementary and functional analysis. IR, UV, and PMR spectra of the DLA have been taken. It has been established by gel chromatography on Sephadex G-75 that the DLA of ripe rice stems is polydisperse and the molecular weight has a number-average value of 3900, a weight-average value of 5300, and a mean value of 9800.

The lignin of the rice plant has been studied less than that of the cotton plant [1, 2]. We have studied the dioxane lignins (DLAs) from rice husks and ripe stems, which are similar in nature. The DLA was isolated from ripe stems of the rice plant (variety UzROS-59) that had been comminuted, extracted with ethanol-benzene (1:2), and washed with hot water. The preparation was purified by two reprecipitations from aqueous dioxane (1:2) solution into absolute ether.

The DLA from rice husks has been isolated and characterized previously [3]. The lignin obtained from the ripe rice stems consisted of a light brown amorphous powder readily soluble in the usual solvents for lignins. Its semiempirical formula was calculated on the basis of elementary and functional analyses, no account being taken of the carbohydrate content (1.97). $MM\ 1\ PPSU^* = 197.4$.



For the rice husk DLA [3], $MM\ 1\ PPSU = 198.9$



As can be seen from the formulas, these lignins are similar with respect to their amounts of functional groups.

The molecular mass distribution of the DLAs isolated was studied with the aid of gel chromatography on Sephadex G-75. DMSO was used as eluent and solvent. The eluogram and the integral and differential curves of the molecular mass distribution of the DLAs of rice husks [3] and of ripe rice stems were very similar and, consequently, we do not give them.

The number-average (\bar{M}_n), the mass-average (\bar{M}_w) and the mean (\bar{M}_z) molecular masses were calculated with the aid of the coefficients found previously [4] by a standard method [5]. $\bar{M}_n = 3900$; $\bar{M}_w = 5300$; $\bar{M}_z = 9800$. Both lignins were polydisperse with a wide interval of molecular masses. For the rice husks DLA, the ratio $\bar{M}_n/\bar{M}_w = 1.72$, and for the ripe rice stems $\bar{M}_n/\bar{M}_w = 1.36$.

The UV spectrum of the rice husk DLA had a maximum at 280 nm and a shoulder at 320 nm, and that of the ripe rice stem DLA a maximum at 290 nm and a shoulder at 330 nm.

The relative optical densities (RODs) of the absorption bands in the IR spectra of the rice husk and ripe rice stems DLAs relative to the aromatic band (1520 cm^{-1}), calculated by the method of Karklin' and Érin'sh [6] are given in Table 1. The IR spectra of the DLAs have all the absorption bands that are characteristic of lignins, but with different values of the RODs.

*Molecular mass of 1 phenylpropane structural unit.

TABLE 1. Relative Optical Densities of the Absorption Bands in the IR Spectra of Rice Dioxane Lignin

Rice husk DLA		Ripe rice stem DLA		Assignment
frequency, cm ⁻¹	ROD	frequency, cm ⁻¹	ROD	
3430	0,61	3420	0,59	Stretching vibrations of OH groups and hydrogen bonds
2940	0,33	2940	0,53	Stretching vibrations of C-H bonds
2850	0,21	2860	0,38	Stretching vibrations of C-H bonds in CH ₃ and OCH ₃ groups
1710	0,41	1713	0,55	Stretching vibrations of C=O and COOH groups
1665	0,33	1660	0,53	Stretching vibrations of C=O or quinoid groups
1610	0,76	1610	1,00	Skeletal vibrations of a double bond
1520	1,00	1520	1,00	Vibrations of an aromatic ring
1470	0,57	1470	1,00	Scissoring deformation vibrations of C-H bonds in methylene groups and in aryl alkyl ethers
1430	0,50	1430	0,66	C-H deformation vibrations in OCH ₃ groups
1330	0,45	1335	0,53	Symmetric vibrations of OCH ₃ groups
1270	1,23	1270	1,12	Stretching vibrations of C-O bonds
1230	0,88	1175	1,04	
1130	0,84	1133	1,07	
1035	0,66	1040	0,58	Stretching vibrations of alcoholic OH groups

TABLE 2. Distribution of Protons and Phenyl Propane Units of Rice Husk and Ripe Rice Stem Dioxane Lignins

Zone of chemical shifts	Limits of the zone, ppm	No. of protons per C ₉ DLA of		Type of protons
		rice husks	ripe rice stems	
I	2,2-3,7	2,88	2,92	Aromatic proton
II	3,7-4,3	0,45	0,47	β-Vinyl and benzyl ether protons of side chains
III	4,3-4,8	0,28	0,29	Protons of coumarane structures
IV	4,8-7,5	5,83	6,09	
IVa	6,0-6,65	2,79*	2,91*	Methoxyl protons
Remainder				
V	7,5-7,95	3,05	3,18	Protons of the side chain
VI	7,95-8,5	2,40	2,58	Protons of aromatic acetoxy groups
VII	8,5-9,5	0,20	0,22	Protons of aliphatic acetoxy groups
				Highly screened protons of CH ₃ and CH ₂ groups
Total		13,23	13,82	

* Found from the semiempirical formulas.

The PMR spectra of the acetylated rice husk and ripe rice stem dioxane lignins were recorded. They were interpreted quantitatively as described previously [7]. The spectra were divided into seven regions corresponding to definite types of protons. The total integral intensity of the signals of all the protons was taken as 100%. Then the percentage intensities due to methoxyl protons (VIa) and to each region corresponding to protons of a given type were determined. Knowing, from the empirical formulas, the number of methoxy groups in the DLAs and the percentage intensities of the OCH₃ groups in the PMR spectra, the value of one proton was calculated. For the rice husk DLA and the ripe rice stem DLA it amounted to 7.56% and 7.30%, respectively.

The results of the calculation are given in Table 2.

According to the PMR spectra, the total number of protons in the rice husk DLA was 10.85, and in the ripe rice stem DLA 11.29. The amounts of hydrogen in the semiempirical formulas for the rice husk and ripe rice stem DLAs were 11.58 and 12.17, respectively.

EXPERIMENTAL

The dioxane lignins were isolated from ripe rice-plant stems by a modification of Pepper's method [8]. The yield amounted to 5.25% of the weight of the plants or 25% of the Komarov lignin. It had the following elementary and functional composition (%): C - 60.3, H - 5.78, O - 33.92, OCH₃ - 15.22, OH_{tot} - 10.36, OH_{phen} - 3.3, C=O - 4.67.

The determination of the functional groups and the calculation of the semiempirical formula were done by standard methods [9]. Gel chromatography was carried out by the method of Alekseev et al., and the results were calculated by a standard method [5]. UV spectra were recorded in aqueous dioxane (1:9) on a SF-26 spectrophotometer at a concentration of lignin of $(3.5 \cdot 10^{-4} \text{ M})$. IR spectra of the lignin molded into tablets with KBr were recorded on a UR-20 instrument. The PMR of the acetylated DLA was taken on a JNM-4H-100/100 MHz spectrophotometer at room temperature with 10-12% by weight of DLA; 10 - HMDS; τ scale; solvent deuteriochloroform.

SUMMARY

1. The dioxane lignins of ripe rice stems has been isolated and its semiempirical formula has been determined. The amounts of the main functional groups of the DLAs of rice husks and of ripe rice stems are similar.
2. It has been deduced from the results of gel chromatography that the DLAs of ripe rice stems, like the DLAs of rice husks, are polydisperse, their bulk being of low molecular mass (MM 3000-4000).
3. It follows from the PMR spectra that rice-plant DLAs are less condensed than cotton-plant DLAs.

LITERATURE CITED

1. T. Sadykov, E. Seitmuratov, L. S. Smirnova, B. Khodzhamuratova, A. Zhumamuratova, and Kh. A. Abduazimov, Vestn. Karakalpaksk. Fil., Akad. Nauk Uzb. SSR, 3, 12 (1976).
2. G. P. Lomova, Resp. Mezhved. Nauchn. Tekh. Sb., "Vopr. Khim. Khim. Tekhnol.," Khar'kov, 51, 76 (1978).
3. Z. K. Saipov, L. S. Smirnova, and Kh. A. Abduazimov, Khim. Drev., 2, 40 (1977).
4. A. D. Alekseev, V. M. Reznikov, B. D. Bogomolov, and O. M. Sokolova, Khim. Drev., 4, 49 (1969).
5. S. R. Rafikov, S. A. Pavlova, and I. I. Tverdokhlebova, Methods of Determining Molecular Weights and Polydispersities of High-Molecular-Weight Compounds [in Russian], Moscow (1963), p. 7.
6. B. B. Karklin's and P. P. Erin'sh, Khim. Drev., 7, 83 (1971).
7. N. A. Veksler, K. L. Seitanidi, L. S. Smirnova, and Kh. A. Abudazimov, Khim. Prir. Soedin., 388 (1979).
8. J. M. Pepper and M. Sidiguellan, Can. J. Chem., 39, 1454 (1961).
9. G. F. Zakis, L. N. Mozheiko, and G. M. Telysheva, Methods of Determining the Functional Groups of Lignin [in Russian], Riga (1975).