

LIGNINS FROM *Oryza sativa*

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Lignins, p-coumaryl, guaiacyl, and syringyl structural units, which are characteristic of annual grassy and perennial bushy plants, were found chromatographic analysis in the nitrobenzene oxidation products of natural and dioxanelignin rice husk and straw.

Key words: *Oryza sativa*, rice straw, rice husk, natural lignin, dioxanelignin, nitrobenzene oxidation.

Lignin structures and their industrial use have recently attracted much interest. Although the structures of plant lignins have been studied several times and the complicated nature of the polymerization processes occurring during lignin formation have been noted, rice lignins are relatively unstudied.

We have previously investigated dioxanelignin (DL) from rice stems (Nukus-2 variety) [1]. Herein we report an investigation of rice husk and straw (Zhaikhun variety). The contents of Komarov lignin, hydrochloric lignin, ash, and DL in the investigated samples were determined (Table 1). The Komarov lignin content in plants of the family Gramineae was less than 16.8-22.1% [2]. However, the observed high content of Komarov lignin in Zhaikhun rice husk indicated that the investigated sample was highly lignified. A peculiarity of the rice husk and straw was the anomalously high (16.4-25.0%) ash content [2]. Ash is practically pure SiO₂, which enables the investigated samples to be considered sources of inexpensive and pure Si-containing raw material.

The isolated DL was light brown in color and very soluble in typical solvents for lignins.

Based on the elemental and functional group analysis for DL, the semi-empirical formulas per single phenylpropanoic structural unit (PPSU) were calculated:

Rice husk DL: C₉H_{7.51}O_{1.72}(OCH₃)_{0.81}(OH_{al})_{0.84}(OCO)_{0.30}(OH_{Ph})_{0.32}; OCH₃/C₉, 0.55;

Rice straw DL: C₉H_{7.72}O_{1.82}(OCH₃)_{1.04}(OH_{Ph})_{0.52}(OH_{al})_{0.56}(OCO)_{0.33}(OOH_{COOH})_{0.05}; OCH₃/C₉, 1.04.

Because lignin is a phenolic substance, it can be oxidized by homolytic and heterolytic mechanisms depending on the type of oxidant and the conditions. Oxidation of lignin by nitrobenzene in alkaline medium is one of the most well-known and commonly used methods for analyzing and comparing various lignin preparations [2]. The principal product from nitrobenzene oxidation (NBO) of Gymnospermae plants is vanillin. Dicotyledonous Angiospermae give a mixture of vanillin, syrenic aldehyde, and *p*-hydroxybenzaldehyde; monocotyledonous, a mixture of vanillin, syrenic aldehyde, and *p*-hydroxybenzaldehyde. It has been reported that the structural units in natural and isolated lignins from rice husk and straw can be found by NBO in alkaline medium at T = 160°C for 3 h using an improved GC method for determining the products of NBO [3].

The structures of natural and isolated rice husk and straw lignins were studied using alkaline NBO. The yields and compositions of NBO products from the studied samples are given below:

Studied sample	Yield, %
Rice husk	16.7
Rice straw	11.4
Rice husk DL	43.1
Rice straw DL	48.6.

*Deceased.

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TABLE 1. Properties of Zhaikhun Rice Husks and Straw, % of Absolute Dry Mass

Sample	Dioxanelignin		Hydrochloric lignin		Komarov lignin	Ash in raw material
	yield	OCH ₃	yield	ash		
Rice husk	6.8	13.0	28.5	23.4	27.2	25.0
Rice straw	6.61	11.5	18.1	24.4	21.1	16.4

TABLE 2. Content of Aromatic Aldehydes, Ketones, and Acids in NBO Products of Natural and Isolated Lignins of Rice Husk and Straw

Substance	Rice husk, wt. %	Rice straw, wt. %	DL husk, wt. %	DL straw, wt. %
Vanillin	3.2	1.24	13.5	5.7
Acetovanillone	0.2	0.1	0.9	0.3
<i>p</i> -Hydroxybenzaldehyde	1.1	0.4	4.0	2.6
Syrenic aldehyde	0.8	0.6	1.2	5.0
Vanillic acid	Tr.	0.1	Tr.	0.4
<i>p</i> -Hydroxybenzoic acid	0.6	Tr.	2.9	Tr.
Syrenic acid	0.2	0.5	0.7	2.5
Total	6.3	2.9	23.2	16.5
Ratio				
syringyl:guaiacyl: <i>p</i> -coumaryl	0.3:1:0.5	0.8:1:0.07	0.13:1:0.26	1.17:1:0.05

Judging from the data, the yield of NBO products from natural lignins was much less than that for total substances from NBO of isolated lignins.

The NBO analytical results for the studied lignins showed that guaiacyl structures dominated in the oxidation products of natural lignins and rice husk DL. Syringyl structures dominated in the oxidation products of rice straw DL. It is well known that guaiacyl units dominate in lignins from Gramineae plants [2]. The dominance of syrenic structures in the oxidation products of rice straw DL indicated that this lignin was loosely condensed.

Isolated rice husk and straw DL was also studied spectroscopically.

The UV spectrum of rice husk DL contained an absorption maximum at 320 nm (λ_{\max} , nm): 280 (log ϵ 3.20). Such spectra are characteristic of lignins from monocotyledonous grassy plants. The long-wavelength maximum is typical of a CO group conjugated to aromatic rings of lignin.

IR spectrum (KBr, ν , cm⁻¹): 1600, 1510 (benzene ring), 3440, 3400 (OH), 1710, 1660 (C=O), 1470, 1250, 1230 (OCH₃), 1040 (–CH₃), 1070 (secondary OH), 1130 (tertiary OH), 1085 (C=O in secondary alcohols and aliphatic ethers), 835 (CH in aromatic rings).

EXPERIMENTAL

DL preparations were isolated by mild acidolysis under N₂ (modification of the Pepper method) [4]. UV spectra were recorded on an SF-26 spectrophotometer; IR spectra, on a Specord-76 instrument in KBr disks. The contents of Komarov lignin, hydrochloric lignin, and ash were determined as before [5]; of hydroxyls, carbonyls, carboxylates, and methoxyls, by the literature methods [6].

NBO in Alkaline Medium. A quartz ampul was charged with lignin (20–25 mg), NaOH solution (2 mL, 2 N), and nitrobenzene (0.15 mL). The ampuls were quickly placed into a heated cabinet and stabilized at 180°C after 5–6 min. The mixture was heated with constant stirring at 180°C for 2 h. The ampuls were quickly cooled. The contents of the ampuls were centrifuged and immediately used for qualitative and quantitative determination of the oxidation products.

Leningrad No. 2 grade C paper was used for descending paper chromatography using petroleum ether:dibutylether:water (6:1:1). A strip of paper was spotted once or twice in three places with the alkaline oxidized mixture

(5-7 μL). Without allowing the spots to dry out, the paper was passed several times through vapors of boiling acetic acid until the spots were fully developed. This converted fully phenolates into the mobile phenolaldehyde forms. Then the paper was dried in air for 2-3 min and placed into a chamber for 30 min. Solvent (descending method) was poured through an opening in the lid. The chromatograms were removed from the chamber after 14-15 h and dried in air for about 1 h [3].

The positions of the aldehyde spots were found from their fluorescence in UV light. The control strip used 2,4-dinitrophenylhydrazine.

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