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NATURAL LIGNIN FROM STEMS OF *Zea mais* AND *Sorghum saccharatum*

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Corn (*Zea mais*) and sorghum (*Sorghum saccharatum*) are annual herbaceous plants of the family Gramineae. The sugar content in sorghum stems reaches 12-18% [1]. Processing of these plants is complicated by the formation of multi-ton wastes of corn stems and cobs and sorghum stems. A comprehensive study of the compositions of these wastes is needed in order to find recycling pathways (Table 1). We used ground corn stems that were extracted with an alcohol:benzene mixture (1:2) [2] and the solid residue of sorghum stems after separation of sugars.

The observed high Komarov lignin and cellulose contents in corn stems indicated that this sample was more woody. The comparatively high difficultly hydrolyzed polysaccharide (DHPS) content compared with that of readily hydrolyzed polysaccharide (RHPS) suggested that the carbohydrate complexes of corn and sorghum stems were DHPS, i.e., cellulose and hemicellulose.

We performed basic hydrolysis of the studied plants by NaOH solution (8%) according to the literature [3]. A total of 19.2% of corn stems (suspended particles, 0.1 g; phenolic compounds, 0.43%) and 68.2% of sorghum stems (suspended particles, 1.6 g; phenolic compounds, 0.27%) underwent basic hydrolysis.

Acidification of the basic hydrolysate by dilute HCl until the pH was 7 precipitated a dark-brown amorphous powder of suspended particles that were insoluble in water. It was found previously that a finely dispersed powder that precipitated was a fragment of the plant ligno-carbohydrate complex (LCC) [4]. Acid hydrolysis by H_2SO_4 (2 N) of suspended particles and paper chromatography of the hydrolysates detected monosaccharides, mostly xylose and traces of arabinose and glucose. Furthermore, hydrolysates of suspended particles gave a positive reaction to phenol:H_2SO_4, thereby confirming that the sutdied samples contained lignin fragments. Therefore, the suspended particles were lignocarbohydrates, in other words, fragments of the LCC of the studied plants.

An analysis of the basic components in the solid (remaining plant) showed that the lignin content decreased during basic hydrolysis. This was consistent with degradation of the macromolecule (Table 2).

Extraction by $CHCl_3$ of the hydrolysates after removal of the LCC isolated fractions of phenolic compounds that were analyzed by HPLC (Table 3).

The hydrolysis products contained aromatic aldehydes (*p*-hydroxybenzaldehyde, vanillin, syringaldehyde) and acids (vanillic, syringic, cinnamic, caffeic, veratric). This was characteristic of Gramineae plants. The phenolcarboxylic acids identified after basic hydrolysis may have been formed by hydrolysis of ether bonds of the lignin macromolecule. The dominant species in hydrolysates of both plants were *p*-coumaric, in contrast with those of rice husks and straw. The high content of *p*-hydroxybenzoic acid in the products from basic hydrolysis of natural lignin was characteristic for lignins of Gramineae plants.

Basic hydrolysis of the studied plants showed that low-molecular-weight phenolic compounds could be produced.

HPLC was performed on an AT 1100 HPLC (Agilent Technology) with a diode-matrix detector, autosampler, and thermostatted column by the Poliphenol method using a Hypersil C8 column (5 μm, 150 × 4 mm) and gradient mobile phase (solution A, 80%, 0.1 M NaH_2PO_4 buffer, pH 3; solution B, 20%, MeOH) at flow rate 1.25 mL/min with a column thermostatted at 20°C and peak detection at 210 nm.

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TABLE 1. Chemical Composition of Corn and Sorghum Stems, %

Sample	Komarov lignin	Cellulose	RHPS	DHPS
Corn stems	27.4	52.5	0.9	8.1
Sorghum stems	15.6	24.8	2.2	11.7

RHPS, readily hydrolyzed polysaccharides, DHPS, difficultly hydrolyzed polysaccharides.

TABLE 2. Composition of Solid Precipitate After Basic Hydrolysis, %

Solid precipitate	Komarov lignin	Cellulose	RHPS	DHPS
Corn stems	12.7	55.9	0.44	7.2
Sorghum stems	6.8	78.3	0.44	11.7

TABLE 3. HPLC Analysis of Total Phenolic Compounds from Basic Hydrolysis of Corn and Sorghum Stems, % in Mixture

Compound	Corn stems	Sorghum stems	Compound	Corn stems	Sorghum stems
p-Hydroxybenzoic acid	37.54	40.19	Phenol	0.77	–
Vanillic acid	0.75	–	Caffeic acid	–	0.50
Syringaldehyde	6.23	2.94	Veratric acid	0.75	2.98
Syringic acid	0.48	–	Ratio of *p*-coumaric: guaianic:syringic	1.0:0.07:0.18	1.0:0.08:0.07
p-Hydroxybenzaldehyde	–	0.59			
Vanillin	1.18	1.96			

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