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CHEMICAL PROCESSING OF AGRICULTURE WASTES INTO VANILLIN, PULP AND GLUCOSE[*]

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Materials and methods

Study of lignoacids obtained in the oxidation process by NMR. Alkali-soluble products of catalytic oxidation were dissolved in DMSO-d6 (for ^{13}C and HSQC NMR) or in a Pyr/$CDCl_3$ mixture (for ^{31}P NMR). The dissolved lignin substances were separated from the insoluble white precipitate, hemicelluloses, by centrifugation. To carry out a quantitative analysis, the mass of the sample was corrected taking into account the mass of hemicelluloses insoluble fraction.

To determine the content of hydroxyl groups, the sample was phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) followed by registration ^{31}P NMR spectra. About 40 mg of the sample was dissolved in 400 µl of a freshly prepared mixture of non-deuterated pyridine and deuterated chloroform (1.6:1, v/v). A hundred µl of the internal standard N-hydroxy-5-norbornene-2,3-dicarboximide (0.12 M) and 50 µl of a relaxant (solution of chromium (III) tris-acetylacetonate, 11.4 mg/ml) were added to the sample. Solutions of both reagents were prepared using the mixture of solvents, which was mentioned above. Thus, the ratio of internal standard to sample was of 1:20. For the phosphitylation of hydroxyl groups, 100 µl of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) was added to the mixture in excess to obtain the calibration signal in the spectrum, corresponding to the product of the reaction of the TMDP with water. After completion of the phosphitylation reaction (~5 min), the contents of the tube were thoroughly mixed. Then 600 µl of the solution was transferred into an NMR sample tube of 5 mm diameter.

The calculation of hydroxyl group content was based on the data of the integral intensity of ^{31}P NMR signals, normalized by the intensity of the internal standard signal. The mass fraction of hydroxyl groups of various types was determined by the equation (1):

$$C_{OH(COOH)} = \frac{I_{OH(COOH)} \cdot m_{IS} \cdot 1000}{I_{IS} \cdot M_{IS} \cdot m_S}, \text{mmol/g} \quad (1)$$

where $I_{OH(COOH)}$ – integrated intensity of the corresponding OH- or COOH-group; I_{IS} – integral signal intensity of the internal standard; m_{IS} – mass of the internal standard, g; M_{IS} – molecular weight of internal standard, g/mol; m_s – sample weight, g.

Deuterated dimethyl sulfoxide was used as a solvent for the determination of methoxyl groups. About 100 mg of sample was dissolved in 600 µl of DMSO-d6 and mixed thoroughly. The solution was transferred into an ampule for NMR analysis. In 2D HSQC NMR experiments, a thoroughly mixed for analysis lignoacids sample (70-80 mg) was dissolved in 600 µl of DMSO-d6.

High-resolution NMR spectra were registered using the Bruker AVANCE III 600 NMR spectrometer (600 MHz for protons) at 298 K. The ^{31}P NMR spectra were registered with pulse duration of 12 µs, the acquisition time was 1.1 s, the delay was 5 s, and the number of scans was 128. The ^{31}P NMR spectra were calibrated by the signal of the product of the reaction between phosphitylating agent and water (132.2 ppm). ^{13}C NMR spectra were registered using a standard single-pulse sequence with pulse duration of 12 µs. The acquisition time was 1.4 s, the delay was 2 s, the number of scans was 20480. The spectrum was calibrated by the solvent signal (39.5 ppm).

In 2D HSQC NMR experiments, the acquisition time of 77.6 ms was set for the ^{1}H-dimension, and 36 scans per block were collected using the 1024 collected complex points. For the ^{13}C-dimension, the acquisition time was 3.94 ms, and 256 time increments were registered. The delay was equal to 2.0 s, and the total experiment time was 5 h 50 min. The 2D HSQC NMR data were processed with 1024 × 1024 data points applying the Qsine function for both the ^{1}H and ^{13}C dimensions. The DMSO peak at δC/δH 39.5/2.49 ppm was used for the spectra calibration [18, 19]. The baseline was corrected manually using the polynomial function. The experiments were carried out in two repetitions.

Catalytic oxidation of lignocellulosic feedstock

This residual alkali-soluble lignin (lignoacids) was studied by nuclear magnetic resonance spectroscopy (NMR). ^{31}P NMR spectroscopy was used for the analysis of free hydroxyl groups belonging to various structural units in lignin. A typical ^{31}P NMR spectrum of the products of flax shives oxidation is shown in Figure 1S. Along with the signals corresponding to aliphatic and phenolic OH groups, there is a strong signal corresponding to carboxyl OH groups (134–136 ppm).

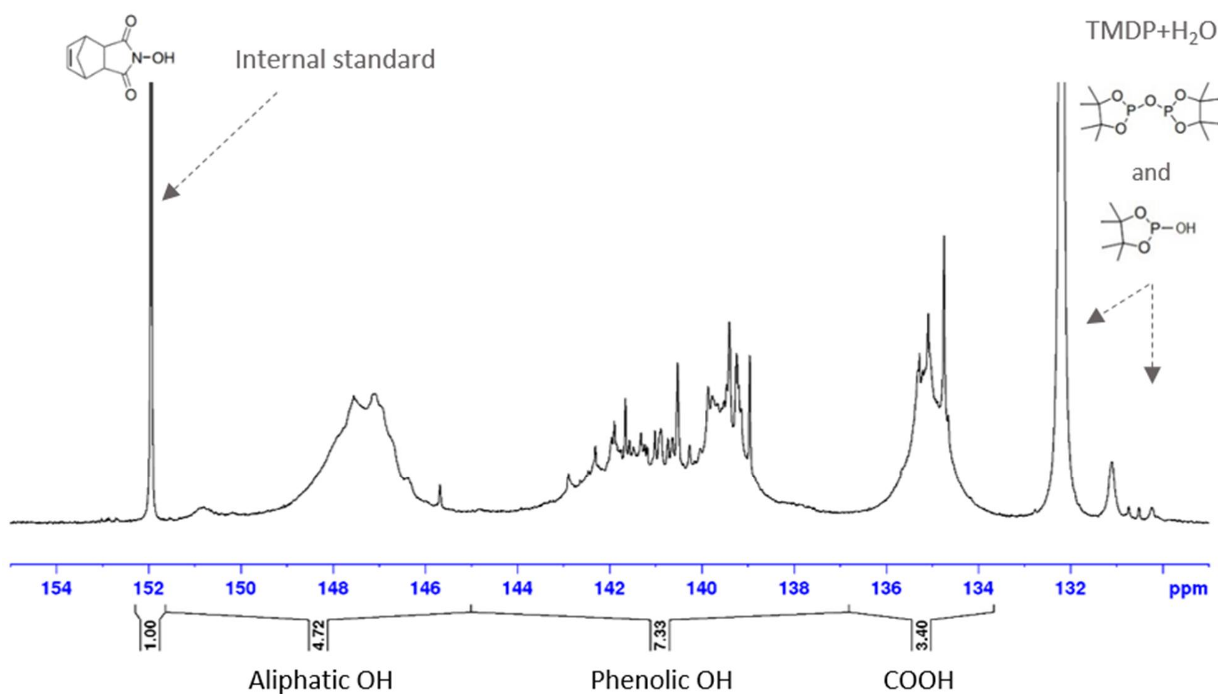

Figure 1S. ^{31}P NMR spectrum of lignoacids obtained by flax shives oxidation

Figure 3 shows the ^{13}C NMR spectrum of lignoacids obtained by flax shives oxidation. The determination of methoxyl groups is based on the data of the integrated intensity of the corresponding signal (~55.3 ppm). The part of methoxyl groups per 100 PPUs was determined by normalizing the aromatic region of the spectrum (160-100 ppm) to 600 (i.e. 6 carbon atoms per PPU).

In the region of phenolic OH groups in the ^{31}P NMR spectra (Figure 1S) a strong overlap of signals is observed, and this is due to the contribution of a large number of condensed structures (4-O-5' and 5-5'). Additionally, a semi-quantitative analysis was carried out by HSQC NMR spectroscopy. It has been established that the structures of β-aryl ethers are almost completely destroyed. The structures of resinol (β-β') and phenylcoumaran (β-5') are found in trace amounts (0.5-3.5 and 0.9-1.5 per 100 PPUs, respectively).

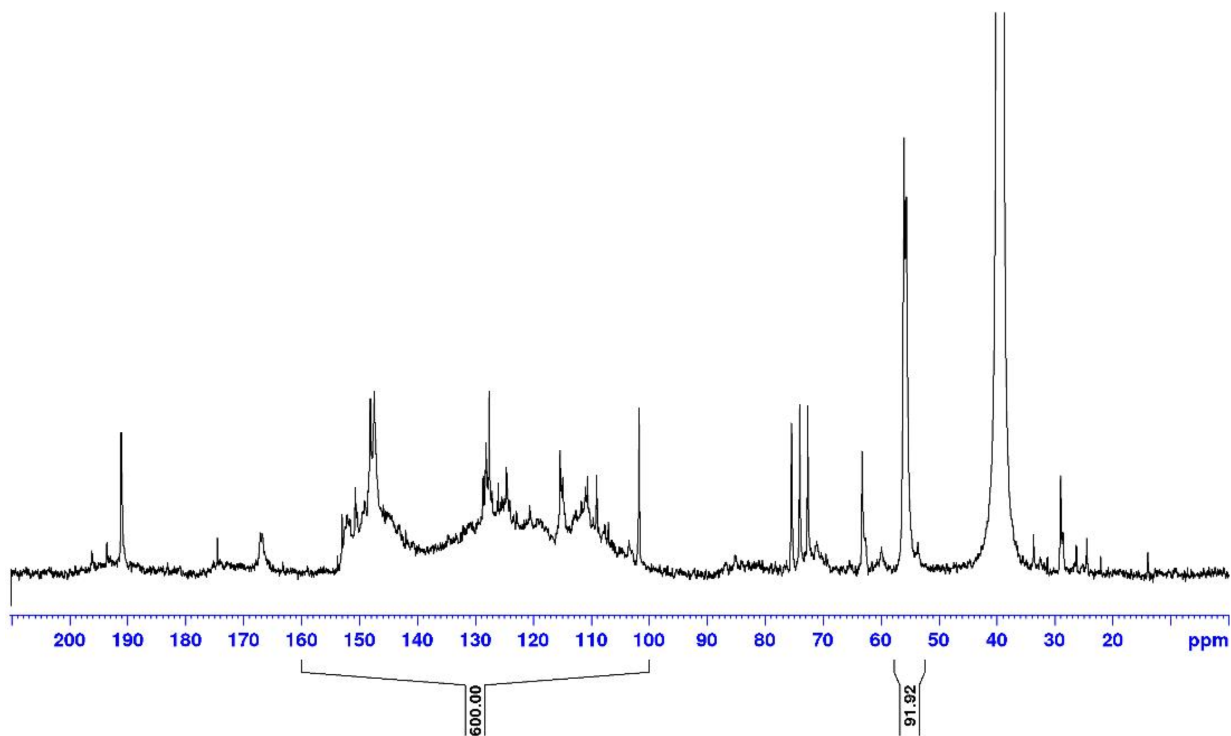

Figure 2S. ^{13}C NMR spectrum of lignoacids obtained by flax shives oxidation