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REACTION OF WHEAT-STRAW STRUCTURAL COMPONENTS WITH A NITRATING MIXTURE CONTAINING TRIFLUOROACETIC ACID

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*The reactions of wheat-straw (*Triticum aestivum*) cellulose, hemicellulose, and lignin with a mixture of nitric and trifluoroacetic acids and certain properties of the nitration products were studied for straw directly and for structural components isolated from it. The nitration products could be separated into nitrates of structural polysaccharides and nitrolignin by treatment with hot bases.*

Key words: wheat straw, cellulose nitrate, trifluoroacetic acid.

The low content (30-36%) of cellulose in wheat straw relative to the elevated content of hemicellulose (HC) is the main obstacle to the extensive use of straw to produce cellulose.

The production of chemical derivatives of cellulose directly from straw is of great interest because the global reserves of wood are gradually decreasing whereas straw is a waste that requires recycling.

The nitration of cellulose in trifluoroacetic acid (TFA) has been well studied [1]. If pretreatment of cellulose with TFA is excluded from the nitration procedure, cellulose trinitrate is formed. Pretreatment can regulate the degree of substitution in the product, up to production of cellulose 2,3-*O*-dinitrate.

A method for preparing cellulose nitrates in TFA by treating wood with a nitrating mixture has been published [2]. According to the results, nitrolignin and HC dissolve in the mother liquor as a result of treating sawdust with a nitrating mixture.

We investigated the potential of this method to produce cellulose nitrates from wheat straw and studied the conversion of straw structural components during the nitration using wheat straw with the following properties (calculated for absolutely dry material): cellulose (by Kuerschner) 47.2%, lignin (by Komarov) 19.6%, holocellulose 61.1%, α-cellulose 36.2%, HC 22.7% (all values uncorrected for protein and ash); compounds extracted by alcohol:toluene mixtures and hot water 11.8%; compounds soluble in boiling HCl (2%) 41.6%; easily hydrolyzed polysaccharides 25.8%; difficultly hydrolyzed polysaccharides 36.0%; ash 7.1%.

The polysaccharide component of the resin-free straw was freed of lignin by peracetic acid. The holocellulose obtained by base extraction was separated into α-cellulose and HC. Treatment of resin-free and pretreated wheat straw with HCl (42-44%) produced hydrochloric lignin.

The α-cellulose and HC were nitrated both with TFA pretreatment and without it. The results indicated that significant losses of HC did not occur in any of the nitration steps of the typical procedure. HC nitrates were formed in rather high yields of 120-130%. It is interesting that the HC preparation was completely soluble in TFA after 10-15 min and formed optically transparent yellowish solutions. However, adding HNO_3 caused it to precipitate. All products had a bright white color. α-Cellulose nitrates were distinctly fibrous (cottony). HC nitrates were amorphous powders. Table 1 shows the content of bound N in the products and the solubilites in acetone and alcohol:ether (1:2).

It can be seen that the amount of N incorporated into HC is much less than that incorporated into cellulose under otherwise equal conditions. The HC preparation is preliminarily represented as a xylan, which can theoretically contain up to 12.6% N (dinitrate). It is interesting that xylan does not contain primary hydroxyls. Nevertheless, HC showed a faster decrease in the amount of bound N as the duration of TFA pretreatment increased than did cellulose. It was expected that treatment of HC lignocarbohydrate materials with the nitrating mixture would first nitrate their hydroxyls, which are more accessible than cellulose hydroxyls, and provide a more thorough conversion of them.

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TABLE 1. Properties of Nitration Products of α-Cellulose (NC) and Hemicellulose (HC) from Wheat Straw by HNO_3/CF_3COOH Nitrating Mixture (40:60) for 60 min

Duration of TFA pretreatment, min	N, %		Solubility, %*		
	NC	HC	acetone	alcohol:ether mixture	
			HC	NC	HC
0	13.7	10.9	95	5	15
60	13.3	10.2	95	5	45
120	12.9	9.1	90	10	40
180	12.3	7.9	95	40	20

*Solubility of NC in acetone, 100%.

TABLE 2. Properties of Nitration Products of Wheat Straw by HNO_3/CF_3COOH (40:60)

Duration of TFA pretreatment, min	Duration of nitration, min	N, %	Solubility in acetone, %
0	15	10.2	90
0	30	10.8	92
0	60	11.5	97
60	60	10.2	86
120	60	10.7	90
180	60	10.5	87
0	120	11.4	98

We did not wash the nitrolignin product with an ammonia solution (stabilizing), in contrast with the nitration of α-cellulose and HC. The hydrochloric lignin changed color during nitration from brown to yellow or red (bright rust-colored). The color of nitrolignin changed color on treatment with hot water to light brown (resulting yield 105-115%). The resulting nitrolignin preparations were partially soluble in ethanol and acetone in addition to cold dilute base, including ammonia (1%). They were completely soluble in hot dilute bases, e.g., NaOH (1%). This is their most important property in this instance. It makes it necessary to wash the lignocarbohydrate material after nitration with hot water and ammonia (1%). Under these conditions, the resulting preparations were almost completely soluble. When the nitrolignin that was heated with hot water comes into contact with cold ammonia solution, local heating zones arise in which the nitrolignin almost completely dissolves. The HC nitrates are insoluble under these conditions.

Isolation of HC by the method used by us not only cleaves lignocarbohydrate bonds but also depolymerizes them. Obviously, this should significantly increase the tendency of HC to dissolve during nitration, as was previously postulated [2]. Thus, the lack of significant losses of HC during nitration of the isolated preparation rather convincingly indicates that nitration of the lignocarbohydrate material leads to little loss of it. Lignin is probably lost not during the nitration itself but during the stabilization of the product and its treatment with hot water and dilute ammonia solution. However, this is impossible to confirm unambiguously from the nitration of hydrochloric lignin, which is not completely soluble even on boiling with sulfite and sulfate.

IR spectroscopy was used to investigate the delignification process. The most suitable absorption band for determining the lignin content in broadleaf wood was 1595 cm^{-1}; in evergreen wood, 1600 cm^{-1}. This band appeared also in the IR spectrum of wheat straw (KBr) and the hydrochloric lignin preparation isolated from it. This band was absent in spectra of α-cellulose and HC. However, this band could not be found after nitration even in the spectrum of nitrolignin, which was due to the appearance of a very strong and broad band with a maximum at 1655 cm^{-1} for the symmetric stretching vibrations of the nitrate esters. Thus, the lack of a maximum at 1600 cm^{-1} cannot be taken as proof that lignin is absent in the nitration products of lignocarbohydrate materials.

TABLE 3. Properties of Nitration Products of Wheat Straw Pretreated with HCl (2%) by HNO_3/CF_3COOH (40:60)*

Duration of TFA pretreatment, min	Duration of nitration, min	N, %
0	15	12.5
60	15	11.9
120	15	12.5
180	15	12.3
0	30	13.4
0	60	13.4

*Solubility in acetone, 100%.

Furthermore, the reaction of lignin with the nitrating mixture led to not only the formation of nitrate esters but also the nitration of aromatic rings. Asymmetric stretching vibrations of the nitro groups appeared "free" from other peaks in the range 1500-1560 cm^{-1}. The spectrum of nitrolignin in particular contained a well resolved peak with a maximum at about 1550 cm^{-1} that was present in the spectrum of the straw nitration product, although weaker. Treatment of the preparation with ammonia (1%) caused a significant decrease in the strength of this peak. Heating in base reduced it to only a shoulder.

We nitrated wheat straw both with and without TFA pretreatment. The nitration products were yellow or orange, which changed to light brown on boiling in water (i.e., the color change was analogous to that for nitration of hydrochloric lignin). Final treatment of the product with hot water and ammonia imparted to it a lighter color. Treatment with NaOH solution (1%) produced a white or yellowish product.

Table 2 lists the properties of the nitration products from resin-free wheat straw treated with hot NaOH solution (100-105% yields). HC was removed by hydrolysis of the straw beforehand with HCl (2%). Table 3 gives the properties of the nitration products of prehydrolyzed straw (70-75% yields per starting resin-free straw).

The wheat-straw nitrogen content rose to 11.5% after 60 min of nitration. Increasing the nitration time to 120 min did not increase it further. Prehydrolyzed straw was nitrated more rapidly. The nitrogen content stabilized after 30 min of nitration at 13.4%. All products of nitrating prehydrolyzed straw were white. Those obtained from straw that was not prehydrolyzed were light gray or light yellow.

IR spectra of nitration products of prehydrolyzed straw (film), which contained 13.4% nitrogen, essentially lacked absorption in the range 3700-3100 cm^{-1}, typical of hydrogen bonds. This indicated that there was a high degree of substitution in the samples. However, the nitrogen content for cellulose trinitrate was noticeably higher at 14.1%. The difference could be explained by the incomplete removal of pentosans during prehydrolysis (according to the literature [3], difficultly hydrolyzed wheat-straw polysaccharides contain 36.2% glucose and 7.6% xylose of the starting straw) and the presence of proteins and ash-forming sustances.

The range of CH_2 stretches contained a double maximum at 2920 and 2970 cm^{-1} for the cellulose nitrates, well resolved peaks at 1650 cm^{-1} for $\nu_a(NO_2)$; 1420, (CH_2); 1370, $\delta(CH)$; 1320, $\gamma_W(CH_2)$, 1280, $\nu_s(NO_2)$; 1150, pyranose; 1110 and 1060, $\nu(C–O)$; 990, $\nu(N–O)$; 820, $\nu(NO)$; 740, $\gamma_W(NO_2)$; and 690, $\delta(NO_2)$.

Thus, nitration of lignocarbohydrate materials in TFA did not fully transfer HC and lignin into the mother liquor. Stabilization with ammonia (1%), which was necessary during nitration of cellulose to remove nitrogen oxides and components of the nitrating mixture, became mandatory during nitration of lignocarbohydrate materials to remove nitrolignin, which did not completely occur. Treatment of the products with hot NaOH solution (1%) were significantly more effective and produced products that were completely free of nitrolignin.

EXPERIMENTAL

Wheat straw (*T. aestivum*) collected in Zalesov Region of Altai Territory (Russia) was used. Straw was ground in a mill. The 0.5-mm fraction was collected. Resins were extracted as before [4, pp. 81-82]. Air-dried resin-free straw was used in all procedures.

Holocellulose was isolated as before [4, pp. 102-103]. HC and α-cellulose were separated by treating holocellulose sequentially with KOH solution (10%) and NaOH solution (17.5%) by methods analogous to those previously published [5]. Hydrochloric lignin was prepared as before [6] (Goss and Phillips). Cellulose was determined by the Kuerschner method [4, pp. 106-107]; lignin, by the Komarov method [4, pp. 162-164]; readily hydrolyzed and difficultly hydrolyzed polysaccharides, as before [4, pp. 134-138]; straw hydrolysis by HCl (2%), as for determination of readily hydrolyzed polysaccharides and ash content, according to the literature [4, pp. 74-75]; nitrate N in the products, by the ferro-sulfate method [7].

IR spectra were recorded on a Specord-75 instrument using KBr mixtures (1%) or films deposited from acetone solutions.

Nitration used TFA (99%) and nitric acid (97%). A portion of straw, α-cellulose, HC, or hydrochloric lignin (1 g) was treated with TFA (60 mL), stirred at 20-22°C for a given time, treated with nitric acid (40 mL), and heated at 30°C. The product was filtered off. HC and cellulose nitrates were washed successively with hot water and aqueous ammonia (1%) and boiled in water for 2 h. Nitrolignin was not treated with ammonia (1%). For straw nitration, the product was washed 2-3 times on the filter with hot (70-80°C) NaOH solution (1%) and boiled several times for 2-3 min in NaOH solution (0.04%) until the solution no longer became colored upon boiling. The product was washed with water until the washings were neutral and dried at 70°C to constant mass.

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