

REACTION OF XYLAN WITH AQUEOUS SOLUTIONS OF ALKALI

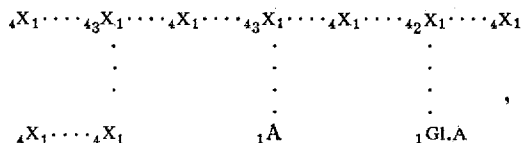
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Nonnutritive vegetable material contains a considerable amount of xylan [1], which consists mainly of hemicelluloses. The chemistry of the reaction of this polysaccharide with aqueous solutions of alkalis, which is used in various industrial processes, has been little studied.

It was necessary to elucidate the chemistry of the reaction of aqueous solutions of NaOH on the xylan of wheaten straw at low temperatures.

The xylan of wheat straw belongs to the araboglucuronoxylan type and, according to Aspinall and Meek [2], has the following structure:



where X is an anhydroxylose residue;

A is an anhydroarabofuranose residue; and

Gl.A is a glucuronic acid residue.

Experimental

The xylan was isolated from purified wheat straw with a 4% solution of alkali in the cold in an atmosphere of nitrogen with subsequent precipitation by methanol. The polysaccharide was purified through the copper complex, washed with alcohol, and dried with ether. The following composition of wheaten straw xylan OD-16 was found: mol. wt. 18 500, pentosans 96%; carbohydrate composition: xylose, 70%; arabinose, 12%; glucuronic acid, 15% -OCH₃, 2.50%; and -COOH, 2.64%.

The amount of pentosans and the carbohydrate composition were determined by complete hydrolysis with subsequent quantitative chromatographic analysis of the carbohydrates, the methoxyl groups were determined by a modified Zeisel method, and the carboxyl groups by the calcium acetate method.

To calculate the molecular weight we used Staudinger's equation:

$$\eta_{sp} = K_m \cdot P \cdot C.$$

The value of K_m was taken as 5×10^{-4} , following Huseman [3].

The xylan isolated was treated with alkali. A weighted sample of the polysaccharide was stirred with a definite amount of water for 20-30 min and then the calculated amount of concentrated aqueous caustic soda solution was added. The alkali-xylan formed was precipitated with ethanol. The precipitate was filtered off through a glass filter and the adsorbed alkali was washed out with a suitable alcohol until the reaction to phenolphthalein was negative.

The bound alkali was determined by two methods; gravimetrically and volumetrically. The number of moles of caustic soda per 100 moles of pentose residues (the γ value of the xylan) was calculated.

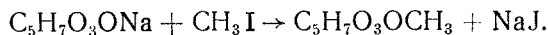
The change in the value of γ was studied as a function of the concentration of alkali, the nature of the alcohol used for washing out the alkali, and the temperature (table).

It can be seen from the table that the composition of the alkali-xylan depends on the concentration of alkali and the nature of the alcohol used for washing out the adsorbed alkali. The amount of bound alkali increases with an increase in the concentration of caustic soda. This can explain the low sensitivity of the compound obtained to water. The higher the concentration of alkali in solution, the less intensively does the process of hydrolysis take place and the higher is the γ value of the alkali-xylan obtained.

The same can be said about the influence of the alcohol used. The greater its molecular weight, the lower the hydrolyzing capacity of the alcohol and, therefore, the higher the γ value of the compound obtained.

On considering the influence of the temperature on the composition of the alkali-xylan, we observed that when the temperature was lowered to -5°C , i. e., when a solution of xylan in 8% NaOH was frozen, a product with $\gamma = 75$ was obtained. Consequently, at low temperatures, with a fall in the ratio of hydrolysis, the γ value of the xylan rises.

In a study of the nature of the reaction of the alkali solution with the xylan, we used its methylation with methyl iodide, which takes place according to the reaction



Weighed samples of alkali-xylan were dispersed in isoamyl alcohol (at a liquor ratio of 50) and 5 moles of methyl iodide was added per mole of pentose residue. The mixture was heated in the water bath under reflux for 1 hr. Then the xylan was filtered off, washed with ethanol until the reaction for halogen was negative, and dried with ether. The methylated product isolated was subjected to methanolysis with subsequent hydrolysis and determination of the amount of methylated sugars formed by the procedure described previously [4].

From the results of the chromatography of the hydrolysates in the presence of reference samples, it was found that the methylation process yields 2-O-methylxylan (methoxyl groups only in the xylose residues). On hydrolysis, this xylan gave 2-O-methyl-D-xylose. No other methylated sugars were found to be formed under these conditions.

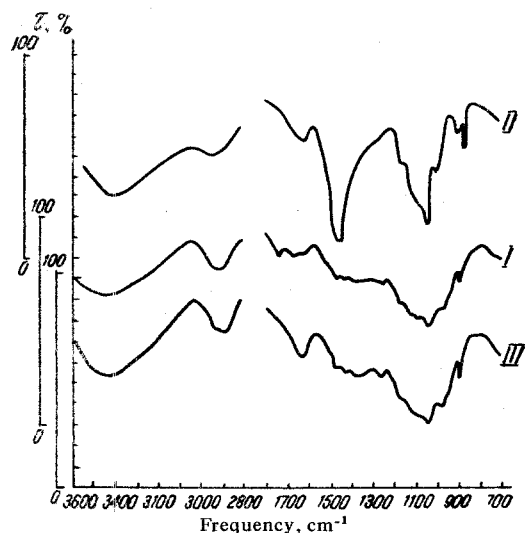


Fig. 1. IR spectra of the initial xylan (I), the alkali-xylan (II), and the regenerated xylan (III).

The amount of methylated sugar, and, hence, the amount of the alkoxide form of the compound increase with a rise in the concentration of the alkali used for treating the xylan. The remainder of the alkali is probably present in the form of a molecular compound.

The formation of 2-O-methyl-D-xylose on methylation of the alkali-xylan under fairly mild conditions shows the increased reactivity of the hydroxyl at C_2 of the xylose residues.

Consequently, under the conditions considered, the alkoxide form is not characteristic of all the monosaccharide residues forming the xylan. The xylose residue is the most reactive and the arabinose and glucuronic acid residues the least. Among the hydroxyls of the xylose residues that at C_2 is the most reactive. This is due, in the first place, to the fact that it is present in the α -position to the acetal bond which, as is well known [5], increases the acidic properties of hydroxyl groups in polysaccharides. It is also possible that the hydroxyl at C_2 , being in the equatorial position, is less shielded and is more accessible to the attacking reagent than the hydroxyl at C_3 .

We have studied the nature of the reaction of xylan with alkali by means of IR spectroscopy (the experiments were carried out in Prof. A. I. Skrigan's laboratory at the Institute of Physical Organic Chemistry of the Academy of Sciences of the Bulgarian SSR). The IR spectra of the initial xylan, the alkali form, and the acid-regenerated xylan were recorded (Fig. 1).

A comparison of the spectra of the xylans before and after their treatment with alkali showed that they were different. The alkali-xylans lacked an absorption line at 980 cm^{-1} . However, lines had appeared in the 880 and 885 cm^{-1} regions, confirming the chemical interaction of the xylan with the alkali. The alkali-xylans had no absorption line at 1330 cm^{-1} corresponding to the vibrations of hydroxyl groups. Intense absorption lines were observed at 1470 cm^{-1} and $1450\text{--}1460\text{ cm}^{-1}$, which are very sensitive to various chemical reactions [6]. The same conclusion can be drawn from the results of an X-ray structural analysis (Fig. 2).

Influence of the Concentration of Alkali and the Molecular Weight of the Alcohol on the γ Value of the Xylan

Concentration of NaOH, %	Value of γ after washing with the following alcohols		
	ethyl	butyl	isoamyl
8	9	37	56
16	22	46	135
32	26	46	134
40	32	56	137

Below we give information showing the amount of 2-O-methyl-D-xylose accumulating in the hydrolysates as a function of the concentration of alkali used to obtain the alkali-xylan.

Conc. of NaOH, %	Bound alkali, %	2-O-methyl-D-xylose, %
8	11.7	7.32
10	14.61	14.20
32	14.70	14.50
40	17.60	15.10

The amount of methylated sugar, and, hence, the amount of the alkoxide form of the compound increase with a rise in the concentration of the alkali used for treating the xylan. The remainder of the alkali is probably present in the form of a molecular compound.

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A characteristic feature of the xylans is a branched macromolecule with a considerable number of hydroxyl groups, which favors intermolecular interaction in the polysaccharide through hydrogen bonds. Because of this, xylans crystallize poorly. The X-ray patterns of such a xylan show a low degree of order of the chains of the molecule (see Fig. 2a).

The X-ray patterns were recorded in the physical laboratory of the Institute of Physical Organic Chemistry of the Academy of Sciences of the Bulgarian SSR directed by M. V. Zaretskii on a URS-60 X-ray apparatus using copper radiation from a BSV-4 tube by the Debye-Scherrer method in a VRS-8 camera with a cassette diameter of 143.25 mm. The radiation was unfiltered. A column 0.6 mm thick was prepared by filling a thin-walled celluloid capillary.

The production of the alkoxide form of xylan as a result of the reaction of caustic soda leads to the replacement of some of the hydrogen of the hydroxyl groups by the metal. Consequently, the number of intermolecular hydrogen bonds decreases which, in its turn, leads to an increase in the crystallinity of the polymer. This is confirmed by the X-ray diagram of the alkali-xylan (see Fig. 2b) with a well-defined structure.

The X-ray diagram of the acid-regenerated xylan (see Fig. 2c) shows that its structure approximated to the characteristics of the initial polysaccharide but has a diffusion nature showing that the polymer was in a more amorphous state.

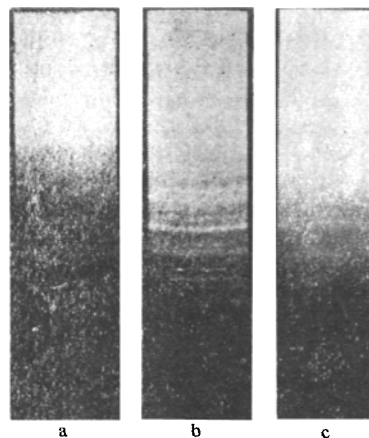


Fig. 2. X-ray patterns of the xylans: a) the initial xylan, b) the alkali-xylan, c) the regenerated xylan.

Conclusions

1. The action of an aqueous solution of caustic soda on xylan leads to the formation of both a molecular and an alkoxide form of this polysaccharide. The composition and amount of the alkoxide formed depend on the conditions of treating the xylan with alkali.
2. In the reaction of an aqueous solution of caustic soda with xylan, the hydrogen of the alcohol grouping on the second carbon atom exhibits the greatest reactivity.
3. The result of IR spectroscopy confirm the existence of a chemical interaction of the xylan with caustic soda.
4. According to X-ray analysis, the action of a solution of caustic soda on xylan leads to a decrease in intermolecular interaction, to a more ordered supermolecular structure, and to the appearance of crystallinity.

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