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Short communication

The glucomannan from ramie

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Abstract

The different fractions of ramie hemicellulose were sequentially extracted with alkali solution. The hemicellulose fraction, which is rich in D-glucose and D-mannose residues was extracted and fractionated by treatment with a solution of barium hydroxide. Four distinct polysaccharide fractions were obtained. Sugar analysis showed that two fraction were composed almost entirely (98 and 99%) of D-glucose and D-mannose residues. It was concluded that these polysaccharides could be regarded as glucomannans.

1. Introduction

It is usually considered that the ramie (*Boehmeria nivea*) non-cellulosic polysaccharides are hemicellulose and pectin. The polysaccharides extracted with ammonium oxalate solution were termed pectin and the non-cellulosic polysaccharides extracted with alkali solution from the ramie fiber after pectin separation were regarded as hemicellulose. Recent investigations have shown that the ramie hemicellulose included several distinct polysaccharides. Some of these were rich in D-glucose and D-mannose residues and were considered to belong to a glucomannan (Zhang, Yang & Zhang, 1991). In this paper, the results of a further investigation on the ramie glucomannan have been described.

2. Experimental

2.1. Ramie samples

Luzhuqing ramie from Hunan province in China was cut into small pieces and the portion passing through a 20 mesh was collected for experiment.

2.2. Extraction of waxy, water-soluble substances and pectin

The ramie sample (40 g) was first extracted with a mixed solvent of ethanol and benzene (1:2 V/V), followed by cold water (320 ml, 25°C) for 48 h and hot water (320 ml, 100°C) for 3 h successively. The ramie pectin was extracted from the residue twice with 0.5% ammonium oxalate solution (each 320 ml) first at 80°C, for 2 h and then at 100°C, for 3 h.

2.3. Sequential extraction of hemicellulose

The hemicellulose were extracted successively from the residue (25 g), after the pectin had been removed, with alkali solution of increasing concentration of 2, 5, 10, 17.5% KOH and twice with a solution of 17.5% NaOH containing 4% H_3BO_3 (each 400 ml) at 25°C, under a nitrogen atmosphere, for 48 h. The extracts were acidified with acetic acid to pH 5.5–6.0, then the hemicelluloses were precipitated with ethanol. The centrifuged hemicelluloses were washed in succession with 75, 95% aqueous ethanol and anhydrous ethanol for each sample and finally dried over P_2O_5 under a reduced pressure.

2.4. Purification of ramie glucomannan

The purification procedure of ramie glucomannan is

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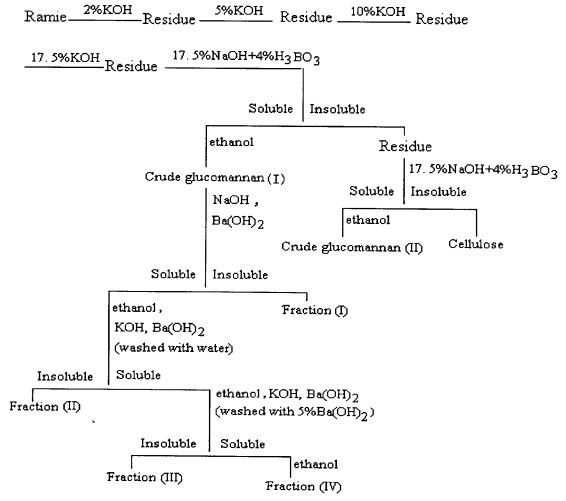
Table 1
The neutral sugar components in the hydrolysates of ramie hemicelluloses

Components	Relative contents of sugar components (%)					
	2% KOH	5% KOH	10% KOH	17.5% KOH	17.5% NaOH + 4% H_3BO_3(I)	17.5% NaOH + 4% H_3BO_3(II)
L-Rhamnose	34.5	25.0	23.7	41.6	4.2	8.6
L-Fucose	0.3	0.2	0.2	0.2	0.6	–
L-Lyxose	1.8	0.9	–	0.2	0.1	–
L-Arabinose	8.4	3.3	2.2	5.2	2.4	4.6
D-Xylose	2.2	8.0	11.6	3.9	1.3	3.5
D-Mannose	–	–	–	–	25.6	12.8
D-Glucose	15.1	14.8	29.0	13.9	58.4	59.3
D-Galactose	37.3	47.4	32.9	34.7	7.0	11.1
Yield of hemicellulose on raw ramie (%)	2.91	3.12	2.95	2.74	5.12	2.35

schematically shown as follows:



(a) The crude glucomannan (I) was dissolved in 10% aqueous sodium hydroxide, then 5% aqueous barium hydroxide solution was added drop by drop. The precipitate formed was recovered by centrifugation and washed twice with water. It was then shaken with ice-cold 50% aqueous acetic acid, and the mixture was poured into four times its volume of ethanol. The precipitate formed was centrifuged. The centrifuged polysaccharide fraction was retreated in the same way as described above, finally the polysaccharide was washed with 50, 75, 95% aqueous ethanol and anhydrous ethanol successively to give fraction I.

(b) The centrifugate and washings were combined and acidified with acetic acid, then concentrated under reduced pressure. The concentrated solution was poured into four times its volume of ethanol to precipitate the polysaccharides. The centrifuged polysaccharides was dissolved in 10% aqueous potassium hydroxide solution, then 5% aqueous barium hydroxide solution was added, and the precipitated polysaccharides were separated, washed as described in (a) above so that the polysaccharide fraction II was obtained.

(c) The polysaccharide fraction III was obtained from the mixture of centrifugate and washings from polysaccharide fraction II by the above method (b), but the polysaccharide fraction, which was precipitated with barium hydroxide, was washed with 5% aqueous barium hydroxide solution instead of water.

(d) The centrifugate and washings from polysaccharide fraction III were combined and acidified with acetic acid, then concentrated, precipitated, separated and washed in the same way as experiment (c) to obtain fraction IV.

2.5. Determination of the specific rotation of polysaccharide

The polysaccharides were dissolved in a 10% NaOH aqueous solution to a concentration of about 1%. Optical rotation was determined using a WZZ-1 instrument.

2.6. Acid hydrolysis of polysaccharides

Samples of polysaccharides were mixed with 72% H_2SO_4(1 ml) and allowed to stand as a paste at 15°C, then diluted to 0.5 M acid concentration with water, and refluxed at 100°C for 6 h. The hydrolysate was neutralized to pH 5.5 with a saturated solution of barium hydroxide. Barium sulfate precipitate was removed by filtration. The filtrate was concentrated into syrup and dried over P_2O_5 under a reduced pressure.

2.7. Chromatographic analysis of the sugars in the polysaccharide hydrolysate

The sugars in the hydrolysate were converted to acetylated aldononitriles, and analyzed using a GC column packed with XE-60 + DEGS.

3. Results and discussion

The ramie sample which was cut into small pieces, and

after passing through the 20 mesh was extracted according to the methods described in Sections 2.2 and 2.3. Yields were as follows: benzene and ethanol extract 0.92%, water extract 7.08%, pectin 4.77% and hemicellulose 19.18%. All yields of extract were based on raw ramie.

Previous investigation showed that most of the hemicelluloses from ramie were only composed of neutral sugar residues and a few of them were essentially composed of neutral residues with small amounts of acid sugar residues (Zhang et al., 1991). It could be considered that the neutral sugar residues were largely responsible for physical and chemical properties of ramie hemicellulose. In this paper, the attention was focused on the components of neutral sugar residues of ramie hemicellulose.

The neutral sugars in hydrolysates of different hemicellulose fractions, extracted gradually with alkali solution were analyzed by GC, the results are presented in Table 1 together with the extraction yields of hemicelluloses.

Inspection of data in Table 1 revealed that the hemicelluloses extracted with 2–17.5% KOH were found to have a similar sugar composition, but the relative contents of various neutral sugar residues, which form the main structural units of polysaccharides, varied with different fractious. The fraction of hemicelluloses extracted with a solution of 17.5% NaOH containing 4% H_3BO_3 were found to be mainly (more than 70%) composed of D-glucose and D-mannose residues. These fractions belonged to glucomannan and were not extracted easily from the ramie with KOH.

Table 2
Sugar composition of the four polysaccharide fractions

Components	Relative contents of sugar components (%)			
	I	II	III	IV
L-Rhamnose	2.1	43.7	6.2	0.1
L-Fucose	0.3	–	0.3	0.2
L-Lyxose	2.9	5.0	8.4	0.3
L-Arabinose	2.9	4.6	16.1	0.1
D-Xylose	38.4	11.9	20.1	35.5
D-Mannose	52.7	26.4	42.3	63.7
D-Glucose	0.6	8.3	6.5	–
D-Galactose	1.37	2.22	2.15	1.79

The ramie hemicelluloses were isolated in the total yield of 19.18% based on raw ramie, and the hemicellulose fractions extracted with 17.5% NaOH + 4% H_3BO_3 were obtained in the yield of 7.47%, corresponding approximately to 39% of the total extracted hemicelluloses. It appears from the above evidence that the ramie hemicellulose was rich in glucomannan, and obviously different from other grass hemicelluloses containing mainly xylan, which were isolated from bagass, reed and straw etc.

The hemicellulose fraction first extracted with a solution of 17.5% NaOH containing 4% H_3BO_3 was purified by treatment with 5% aqueous barium hydroxide, so four distinct polysaccharide fractions were obtained. The sugars in the hydrolysates from four polysaccharide

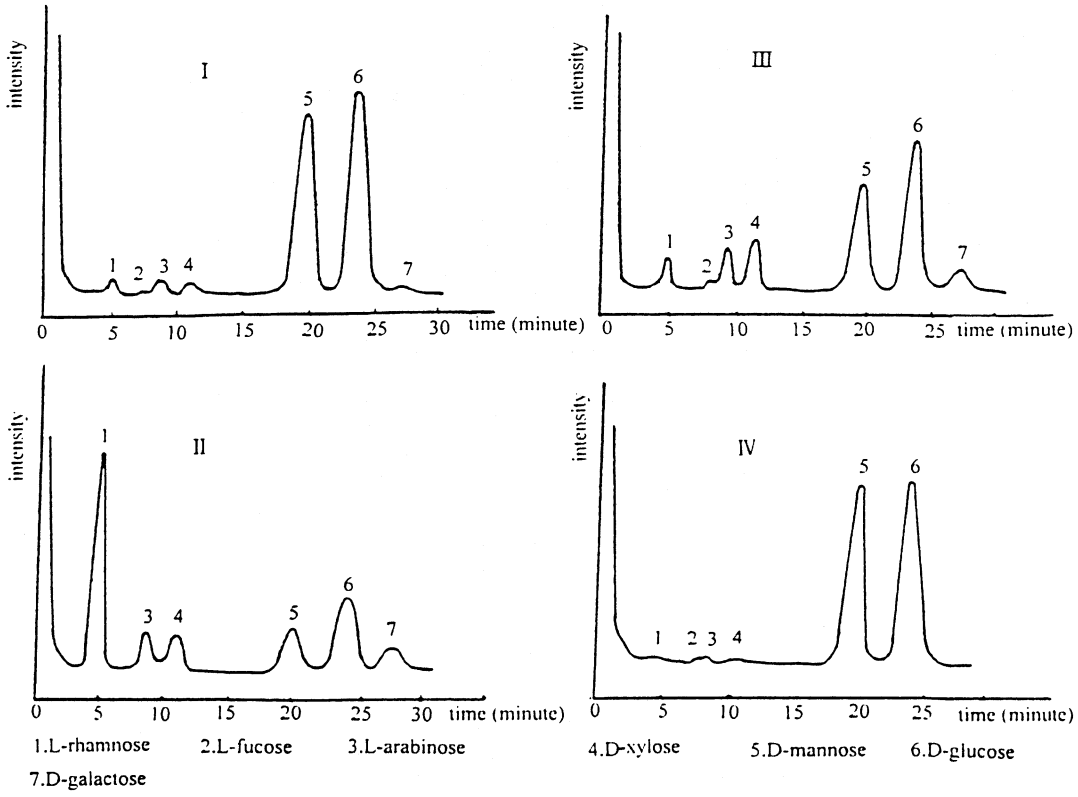


Fig. 1. Gas chromatograms of the hydrolysates of four polysaccharide fractions (I, II, III, IV).

fractions were converted to acetylated aldononitriles, and analyzed by GC. The experimental data are presented in Table 2 and the chromatograms are shown as depicted in Fig. 1.

The results given in Table 2 and the chromatograms indicated that the polysaccharide fractions I and IV were composed of D-glucose and D-mannose residues chiefly, amounting to more than 90–99% for fraction IV (Fig. 1). So it could be concluded that these polysaccharide were characterized as "glucomannan". Compared to the glucomannan of wood, the 1.37–1.79:1 of higher ratio of D-glucose and D-mannose units was also noticed. For the most investigated glucomannan of hardwood and softwood, the ratio of D-glucose and D-mannose units is about 1:1.5–2 and 1:3, respectively (Ebrigerora, Kramar & Domansky, 1972; Mian & Timell, 1960; Timell, 1960a,b, 1961, 1967).

The polysaccharide fraction II was rich in L-rhamnose, D-mannose and D-glucose residues. In terms of sugar composition, it exhibited features of both glucomannan and other ramie hemicellulose polysaccharides, which were extracted with aqueous potassium hydroxide.

The sugar composition of the polysaccharide fraction III was similar to the fractions I and IV, but the contents of D-xylose, L-arabinose and L-rhamnose residues were higher, the contents of D-glucose and D-mannose residues were lower than that of fractions I and IV.

The above considerations lead to the conclusion that the polysaccharide fractions (I–IV) apparently constitute a series of closely related hemicelluloses, differing mainly in the relative contents of various sugar residues. Some of them were composed of D-glucose and D-mannose residues, some were rich in L-rhamnose and D-galactose residues. However, the L-rhamnose, L-arabinose, D-xylose, D-mannose and D-glucose residues can be discovered in all the polysaccharide fractions, though their relative contents varied considerably between fractions. It may be that the ramie glucomannan was linked with L-rhamnose, D-xylose, L-arabinose residues to which some other polysaccharides may be attached. The polysaccharides of ramie hemicelluloses were complex, varied and interrelated they cannot be classified precisely.

Specific rotations of the polysaccharides were determined in 10% aqueous sodium hydroxide solution. The specific rotation of polysaccharide fractions I, II, III and IV were −22.5, −7.0, +23.1 and +26.0, respectively. The fractions I and IV, which were very similar in composition of sugar residue exhibited a very large difference in specific rotation. It could be considered that there were some differences in their structure.

4. Conclusions

The ramie hemicelluloses were found to be a closely related series of polysaccharides, differing mainly in relative contents of various sugar residues. Some of them were rich in L-rhamnose and D-galactose residues, some were composed of D-glucose and D-mannose residues and could be regarded as a glucomannan and others had structural features intermediate between the two species of polysaccharide described above. Most of the sugar residues which form the structural units of ramie hemicelluloses can be invariably discovered in all polysaccharide fractions, though their relative contents varied considerably between different fractions. It is difficult to classify them precisely.

The purified ramie glucomannan was found to contain 90–99% of D-glucose and D-mannose residues in a ratio of 1.37–1.79:1.

The different ramie glucomannan fractions, which were very similar in the composition of sugar residues exhibited different specific rotation, showing that there were some differences in their structure.

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