

## STRUCTURE OF THE ARABINOXYLAN OF RICE HULL\*

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(Received May 18th, 1983; accepted for publication, June 15th, 1983)

### ABSTRACT

Successive extraction of rice hull with hot water, 0.5% ammonium oxalate, 4% potassium hydroxide, and 24% potassium hydroxide, followed by neutralization of the alkaline extracts, yielded seven polysaccharide fractions. An electrophoretically homogeneous arabinoxylan was obtained as a precipitate (HC-1A) after neutralization of the 4% potassium hydroxide extract. The homogeneity of the rice-hull arabinoxylan was confirmed by ultracentrifugation, and by gel filtration through Sepharose CL-6B. It contained a small proportion of uronic acid (1.5%) and, on complete hydrolysis with acid, gave xylose and arabinose in the ratio of ~19:1. This value is in close agreement with those calculated from the results of methylation analysis, and fragmentation analysis with endo-(1→4)- $\beta$ -D-xylanase. The results from the methylation analysis, and from fragmentation analyses with acid and with endo-(1→4)- $\beta$ -D-xylanase, indicated that the repeating unit of this arabinoxylan consists of a linear chain of 19 (1→4)-linked,  $\beta$ -D-xylosyl residues and an arabinofuranosyl side-chain joined through a (1→3) linkage.

### INTRODUCTION

Rice hull is obtained in large quantities in Japan from the process of refining rice grain. This material is used, in part, as stuffing, but is mostly discarded as an agricultural waste. With a view to more effective utilization of this material, we have now examined the properties and structures of the polysaccharides of rice hull.

Rice hull is known to contain 37% of cellulose and ~20% of hemicellulose composed mainly of xylan<sup>1,2</sup>. In the present study, the structure of an arabinoxylan obtained by extraction of rice hull with 4% potassium hydroxide, followed by neutralization of the extract, was examined by complete hydrolysis with acid, methylation analysis, and fragmentation analyses with acid and an endo-(1→4)- $\beta$ -D-xylanase from a strain belonging to a *Streptomyces* species.

\*Cell-wall Polysaccharides of Rice Hull, Part I

## EXPERIMENTAL

*Plant material.* — Unhulled rice (2.14 kg; Toyonishiki, harvested in Miyagi Prefecture in 1979) was threshed, and the liberated rice hull (388 g) was ground with a ball mill. The powdered rice hull was extracted twice with 1:2 ethanol-benzene for 8 h at 80°. The defatted, powdered rice hulls (298 g) were used in this study.

*Enzyme.* — *Streptomyces* sp. endo-(1→4)- $\beta$ -D-xylanase was a generous gift of Professor T. Yasui, Tsukuba University.

*General methods.* — All evaporations were conducted under diminished pressure below 40°. Optical rotations were measured with a Nippon Bunko Model DIP-SL polarimeter. Paper chromatography was performed on Toyo No. 50 filter paper by the multiple ascending method with the following solvent systems: (A) 6:4:3 (v/v) 1-butanol-pyridine-water, and (B) 18:4:3:1 (v/v/v/v) ethyl acetate-water-acetic acid-formic acid. The silver nitrate dip method<sup>3</sup> was used for the detection of sugars. Gas-liquid chromatography (g.l.c.) was performed with a Yanagimoto Model G-80 gas-liquid chromatograph fitted with a flame-ionization detector. Total carbohydrate was determined by the phenol-sulfuric acid method<sup>4</sup>.

*Complete hydrolysis of the polysaccharide with acid.* — Complete hydrolysis of the polysaccharide was achieved by heating a sample (10 mg) with M hydrochloric acid (1 mL) for 4 h at 100°, and the hydrolyzate was cooled, made neutral with silver carbonate, treated with Amberlite IR-120 (H<sup>+</sup>) resin, and evaporated.

With fraction HC-1A or HC-1IA, a sample (10 mg) was heated with 90% formic acid (0.5 mL) for 30 min at 100°. After removal of formic acid by evaporation, 0.5M sulfuric acid (1 mL) was added to the residue. The mixture was heated for 4 h at 100°, and the hydrolyzate was cooled, made neutral with barium carbonate, treated with Amberlite IR-120 (H<sup>+</sup>) resin, and evaporated.

With fraction CL, a sample (10 mg) was treated with 72% sulfuric acid solution (0.3 mL), and the mixture was stirred for 5 h at 0–5°, and then diluted with de-ionized water (2.4 mL). The solution was heated for 3 h at 100°, and the hydrolyzate was made neutral as before.

*Complete hydrolysis of the oligosaccharides with acid.* — Complete hydrolysis of the oligosaccharides with acid was achieved by heating a sample (0.1–2 mg) with 2M trifluoroacetic acid (TFA; 0.1–0.5 mL) for 2 h at 100°. The hydrolyzates were examined by paper chromatography and g.l.c.

*Neutral-sugar analysis of the polysaccharide.* — After complete hydrolysis of the polysaccharide with acid, the monosaccharides in the hydrolyzates were converted into the corresponding alditol trifluoroacetates<sup>5</sup>, which were analyzed by g.l.c. with a glass column (0.4 × 200 cm) packed<sup>6</sup> with 1.5% of QF-1 on Chromosorb W. Analysis was performed at 135° at a nitrogen flow-rate of 15 mL/min.

*Partial hydrolysis of the polysaccharide with acid.* — Partial hydrolysis of the polysaccharide with acid was performed by heating a sample (1.0 mg) with 0.2M TFA (1.5 mL) for 1, 2, and 4–5 h at 100°.

Mild, partial hydrolysis with acid was conducted by heating a sample (1 mg) with 0.1M TFA (1.5 mL) for 1 h at 80°. The hydrolyzates were evaporated, and the residues examined by paper chromatography.

*Determination of uronic acid.* — Rice-hull arabinoxylan (20 mg) was hydrolyzed with 2M TFA (4 mL) for 6 h at 100°, and the TFA was evaporated under diminished pressure. The hydrolyzate was applied to a column (1 × 5 cm) of Dowex-1 X-8 (acetate form), and eluted with water (50 mL) and 3M acetic acid (50 mL). The eluate was evaporated to dryness, and the uronic acid in the fraction eluted with 3M acetic acid was determined by the carbazole-sulfuric acid method<sup>7</sup>. Uronic acid was calculated as glucuronic acid.

*Methylation analysis.* — The poly- and oligo-saccharides were methylated by the method of Hakomori<sup>8</sup>. The methylated poly- and oligo-saccharides were hydrolyzed, and the sugars converted into the corresponding alditol acetates by the method of Lindberg<sup>9</sup>. The partially methylated alditol acetates were analyzed by g.l.c. with a glass column packed with 3% of OV-210 on Supelcoport<sup>10</sup>, or by g.l.c.-m.s. The g.l.c. analysis was made at 180° at a nitrogen flow-rate of 20 mL/min. For g.l.c.-m.s., a combined gas-liquid chromatograph-mass spectrometer, JEOL-JMS-OISG-type 2 (25 eV), fitted with a glass column (0.3 × 100 cm) containing 3% of OV-210 was used.

## RESULTS

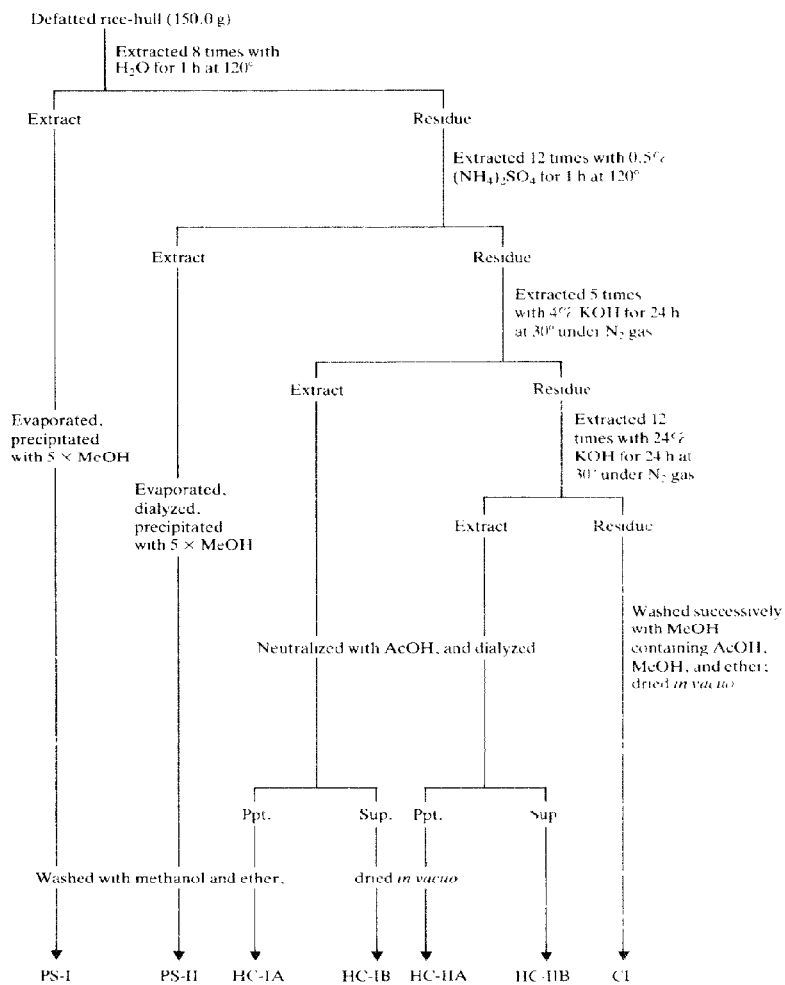
*Extraction, and fractionation, of the polysaccharides in rice hull.* — The polysaccharides in defatted rice-hull (150 g) were extracted, and fractionated, by the conventional method. The flowsheet of the fractionation of the polysaccharides in rice hull is shown in Scheme 1. The carbohydrate content of each fraction was determined by the phenol-sulfuric acid method.

Fraction HC-I was fractionated into subfraction HC-IA (precipitated by neutralization), and HC-IB (not precipitated by neutralization) by neutralization

TABLE I

YIELDS, TOTAL SUGAR CONTENT, AND NEUTRAL-SUGAR COMPOSITION (MOL %) OF THE FRACTIONS OBTAINED FROM RICE HULL

Fraction	Yield (%)	Total sugar content(%)	Un-identified	Rha	Fuc	Ara	Xyl	Man	Glc	Gal
PS-I	3.8	18	1.3	1.4	1.0	18.7	33.8	3.1	23.4	17.3
PS-II	0.8	29	2.5	0.8	0.5	15.4	57.9	1.0	7.3	14.6
HC-IA	1.7	60	—	—	—	11.6	88.4	—	—	—
HC-IB	28.4	13	1.1	—	0.9	15.4	74.5	—	2.1	6.0
HC-IIA	1.8	69	—	—	—	7.0	90.5	—	2.5	—
HC-IIB	5.7	57	1.0	—	0.5	9.9	80.1	—	6.8	1.7
CL	38.7	20	—	—	0.4	1.9	6.3	—	86.9	4.5



Scheme 1. Flow-chart for fractionation of the polysaccharides of rice hull

of the alkali solution. Similarly, fraction II was fractionated into subfraction HC-IIA and HC-IIB.

The neutral sugar compositions of the fractions from rice hull are shown in Table I. Major components were xylose, arabinose, glucose, and galactose.

*Purification of arabinoxylan.* — The fraction HC-IA (1.2 g) was dissolved in 0.5M potassium hydroxide, the base was neutralized with acetic acid, and the precipitate was collected by centrifugation. Three such preparations were made, and the combined precipitate was used as the purified arabinoxylan (yield 416 mg). On complete hydrolysis with acid, the purified arabinoxylan yielded xylose and arabinose in the ratio of 19.3:1.0. It had  $[\alpha]_D^{25} -75^\circ$  ( $c$  0.3, 0.5M sodium hydroxide). The uronic acid content of the rice-hull arabinoxylan was 1.5%, and glucuronic acid was detected in the acid hydrolyzate by paper chromatography (solvent B).

*Homogeneity of the purified arabinoxylan.* — The homogeneity of the purified arabinoxylan was examined by gel filtration, sedimentation analysis, and zone electrophoresis.

(a) *Gel filtration.* A solution of the purified arabinoxylan (2 mg) in M sodium hydroxide (0.5 mL) was applied to a column ( $1.3 \times 70$  cm) of Sepharose CL-6B. The column was eluted with 0.5M sodium hydroxide solution, and the carbohydrate content of each tube (1 mL) was determined by the phenol-sulfuric acid method. As shown in Fig. 1, only one peak was observed on the elution profile. The approximate molecular weight of rice-hull arabinoxylan was estimated to be 15,000.

(b) *Ultracentrifugation.* As shown in Fig. 2, the purified arabinoxylan revealed one peak on ultracentrifugation.

(c) *Zone electrophoresis.* Zone electrophoresis indicated that the purified arabinoxylan was homogeneous (see Fig. 3).

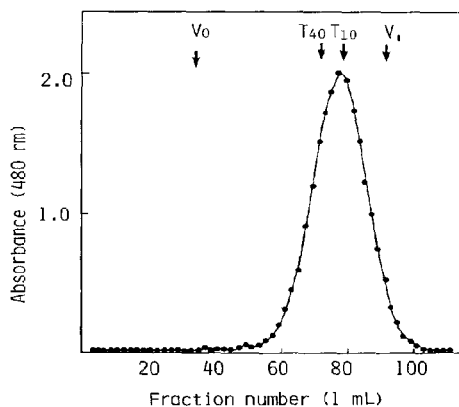


Fig. 1. Gel filtration of arabinoxylan on Sepharose CL-6B.

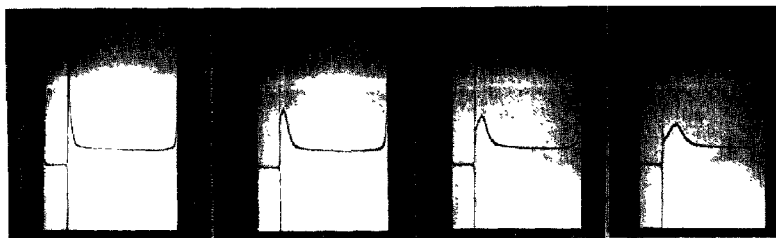


Fig. 2. Ultracentrifugal pattern of the purified arabinoxylan. [The pictures were taken at 9, 36, 60, and 120 min (from left to right) after full speed (60,000 rpm) was reached. Arabinoxylan concentration was 0.8% in 0.5M NaOH.]

*Structural analysis of arabinoxylan.* — (a) *Hydrolysis with acid.* On complete hydrolysis with acid, the rice-hull arabinoxylan gave xylose and arabinose in the ratio of  $\sim 19:1$ . On partial hydrolysis with acid, it yielded xylose, arabinose, xylobiose, xylotriose, and xylotetraose. On mild, partial hydrolysis with acid, arabinose was preferentially liberated, suggesting that the arabinose occurred in the furanose form.

A linear relationship was observed (see Fig. 4a) when  $\log \alpha'$ , namely,  $\log [R_F/(1 - R_F)]$ , of each component of the partial hydrolyzate of the arabinoxylan was plotted against the degree of polymerization (d.p.)<sup>11</sup>. This result indicated that the partial hydrolyzate of the arabinoxylan was a mixture of  $\beta$ -(1 $\rightarrow$ 4)-linked xylo-oligosaccharides.

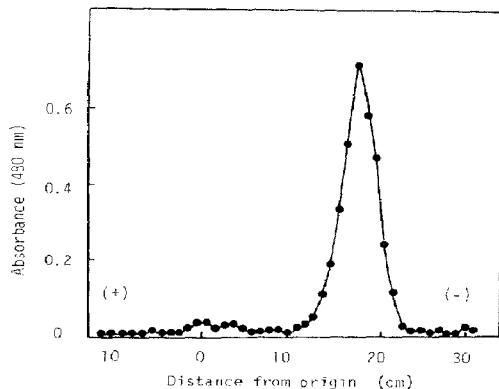


Fig. 3. Zone electrophoresis of arabinoxylan. [Electrophoresis was performed on Toyo GA-100 glass filter-paper at 1.350 kV for 70 min with 0.1M sodium tetraborate (pH 9.3). The filter paper was cut into strips which were then eluted with de-ionized water. The carbohydrates in the eluted solutions were determined by the phenol-sulfuric acid method.]

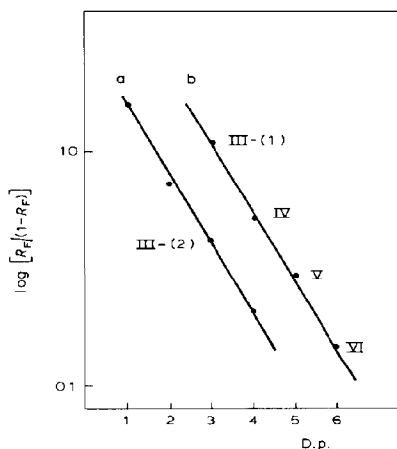


Fig. 4. (a) Paper-chromatographic mobilities of the partial hydrolyzate of rice-hull arabinoxylan and saccharide III-(2). (b) Paper-chromatographic mobilities of saccharides III-(1), IV, V, and VI. (Developed twice by the ascending method, with solvent system A.)

(b) *Methylation analysis.* The purified arabinoxylan (10 mg) was methylated three times by the method of Hakomori. The methylated arabinoxylan was hydrolyzed by the method of Garegg and Lindberg<sup>12</sup>. The hydrolyzate was converted into the corresponding alditol acetates<sup>9</sup>, and these were analyzed by g.l.c. and g.l.c.-m.s. The results are shown in Table II.

2,3- and 3,4-Di-*O*-methylxylose were not distinguished from each other by means of g.l.c. and g.l.c.-m.s. The di-*O*-methylxylose was, however, characterized as 2,3-di-*O*-methylxylose, because  $\beta$ -(1 $\rightarrow$ 4)-xylo-oligosaccharides were isolated from the acid hydrolyzate of the arabinoxylan.

TABLE II

METHYLATION ANALYSIS OF RICE-HULL ARABINOXYLAN

Methylated sugar <sup>a</sup>	T <sup>b</sup>	Molar ratio
2,3,5-Me <sub>3</sub> -Ara	0.50	1.6
2,3,4-Me <sub>3</sub> -Xyl	0.69	1.0
2,3-Me <sub>2</sub> -Xyl	1.48	32.7
2- and 3-Me-Xyl	2.76	2.9

<sup>a</sup>2,3,4-Me<sub>3</sub>-Ara = 2,3,4-tri-*O*-methyl-D-arabinose, and so on. <sup>b</sup>Retention times of the corresponding alditol acetates on an OV-210 column, relative to 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol as unity.

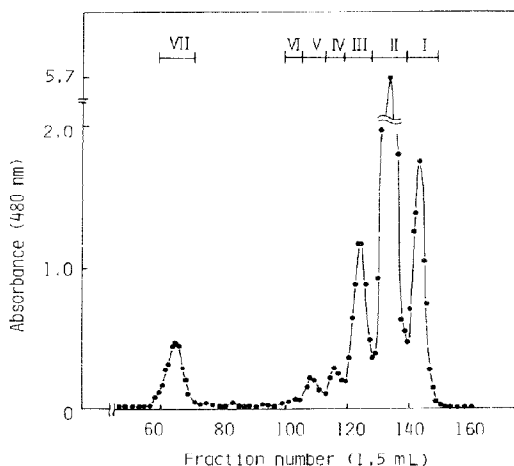


Fig. 5 Elution profile, on Bio-Gel P-2, of the *endo*- $\beta$ -(1 $\rightarrow$ 4)-xylanase digest of arabinoxylan

G.l.c. and g.l.c.-m.s. of the alditol acetates obtained from the hydrolyzate of the methylated arabinoxylan showed that 2,3,5-Me<sub>3</sub>-arabinose, 2,3,4-Me<sub>3</sub>-xylose, 2,3-Me<sub>2</sub>-xylose, and 2- and 3-Me-xylose were present in the ratios of 1.6:1.0:32.7:2.9.

(c) *Treatment of the arabinoxylan with endo*-(1 $\rightarrow$ 4)- $\beta$ -D-xylanase from *Streptomyces* sp. To a solution of the purified arabinoxylan (23.6 mg) in 0.02M sodium acetate buffer, pH 5.5 (3 mL) were added *endo*-(1 $\rightarrow$ 4)- $\beta$ -D-xylanase (30  $\mu$ L) from *Streptomyces* sp. and a few drops of toluene. After incubation for 48 h at 40°, the enzyme reaction was stopped by heating for 5 min in a boiling-water bath, the insoluble material was removed by centrifugation, and the supernatant liquor was treated with Amberlite IR-120 (H<sup>+</sup>) resin, and concentrated. The concentrate was centrifuged, and the supernatant liquor was applied to a column (1.5  $\times$  140 cm) of Bio-Gel P-2 (kept at 50°). As may be seen from the elution profile (see Fig. 5), the hydrolyzate of the arabinoxylan was separated into seven saccharide fractions (fractions I–VII).

*Molecular size of the endo*-(1 $\rightarrow$ 4)- $\beta$ -D-xylanase digest of the arabinoxylan. — The molecular size of the oligosaccharides produced by treatment of the arabinoxylan with *endo*-(1 $\rightarrow$ 4)- $\beta$ -D-xylanase was determined by gel filtration on a column (1.5  $\times$  140 cm) of Bio-Gel P-2. The column was calibrated with a nonasaccharide, a heptasaccharide, and a tetrasaccharide, obtained from the cellulase digest of the xyloglucan of soybean suspension-cultured cells<sup>13</sup>.



TABLE III

YIELDS AND PROPERTIES OF THE ENDO- $\beta$ -(1 $\rightarrow$ 4)-XYLANASE DIGEST OF ARABINOXYLAN

Saccharide	Yield (mg)	D.p. <sup>a</sup>	R <sub>F</sub> <sup>b</sup>	Sugar composition		Methylation analysis			
				Sugar	%	2,3,4-Me <sub>3</sub> -Xyl	2,3-Me <sub>2</sub> -Xyl	2,4- or 3,4-Me <sub>2</sub> -Xyl	2,3,5-Me <sub>3</sub> -Ara
I	4.12		0.67	Xylose					
II	14.40	2	0.45	Xylose		57.8	42.2		
III (1)	0.94	3	0.53	Xylose	67		38.1	32.9	29.0
				Arabinose	33				
III (2)	0.77	3	0.24	Xylose		36.5	63.5		
IV	0.46	4	0.35	Xylose	71				
				Arabinose	29				
V	0.30	5	0.22	Xylose	75				
				Arabinose	25				
VI	0.12	6	0.13	Xylose	80				
				Arabinose	20				

<sup>a</sup>D.p. was determined by gel filtration on a column of Bio-Gel P-2. <sup>b</sup>Developed twice by the ascending method with solvent A.

Oligosaccharides II, III, IV, V, and VI were eluted at the positions of d.p. 2, 3, 4, 5, and 6. Each fraction was evaporated, and the residue examined by paper chromatography. The degree of polymerization of each oligosaccharide fraction is summarized in Table III.

From the results of gel filtration and paper chromatography, fractions II, III, IV, V, and VI respectively had d.p. 2, 3, 4, 5, and 6.

*Characterization of the saccharide fractions.* — The characterization of the saccharide fractions was performed by examination of their complete hydrolyzates, determination of the molar ratios of the component monosaccharides, the relationship between log  $\alpha'$  and the d.p. of the saccharide fractions, methylation analysis, and determination of the degree of polymerization by gel filtration on a column of Bio-Gel P-2. The results are summarized in Tables III and IV.

(1) *Saccharide II* (disaccharide). On complete hydrolysis with acid, saccharide II ( $R_F$  0.45, solvent A) gave only xylose (by paper chromatography). Methylation analysis of saccharide II yielded 2,3,4-Me<sub>3</sub>-Xyl and 2,3-Me<sub>2</sub>-Xyl in the molar ratio of 57.8:42.2; d.p. = 2. From these results, saccharide II was characterized as 4-*O*- $\beta$ -xylopyranosylxylose.

(2) *Saccharide III-(1)* (trisaccharide). Saccharide III was divided into two spots on a paper chromatogram. The zones having  $R_F$  0.53 and 0.24 were excised, and eluted with water. The eluate was evaporated to dryness.

On complete hydrolysis with acid, saccharide III-(1) ( $R_F$  0.53, solvent A) gave xylose and arabinose in the ratio of 2:1. Methylation analysis of saccharide III-(1) yielded 2,3-Me<sub>2</sub>-Xyl, 2,4-Me<sub>2</sub>-Xyl, and 2,3,5-Me<sub>3</sub>-Ara in the molar ratios of

TABLE IV

STRUCTURE OF THE ENDO- $\beta$ -(1 $\rightarrow$ 4)-XYLANASE DIGEST OF RICE-HULL ARABINOXYLAN

Saccharide	Structure
I	Xyl
II	Xyl $\xrightarrow{\beta}$ <sub>1-4</sub> Xyl
III (1)	$\begin{array}{c} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \\ \text{1-4} \\ \uparrow 3 \\ \text{Ara} \end{array}$
III (2)	Xyl $\xrightarrow{\beta}$ <sub>1-4</sub> Xyl $\xrightarrow{\beta}$ <sub>1-4</sub> Xyl
IV	$\begin{array}{c} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \\ \text{1-4} \quad \text{1-4} \\ \uparrow 3 \\ \text{Ara} \end{array}$
V	$\begin{array}{c} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \\ \text{1-4} \quad \text{1-4} \quad \text{1-4} \\ \uparrow 3 \\ \text{Ara} \end{array}$
VI	$\begin{array}{c} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \xrightarrow{\beta} \text{Xyl} \\ \text{1-4} \quad \text{1-4} \quad \text{1-4} \\ \uparrow 3 \\ \text{Ara} \end{array}$

38.1:32.9:29.0; d.p. = 3. From these results, saccharide III-(1) was characterized as 3<sup>2</sup>- $\alpha$ -arabinofuranosylxylobiose.

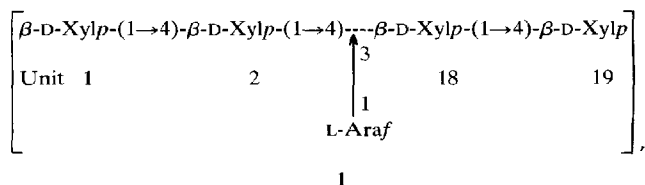
(3) *Saccharide III-(2)* (trisaccharide). The  $R_f$  values of saccharide III-(2) were identical with those of authentic  $\beta$ -(1 $\rightarrow$ 4)-linked xylotriose. On complete hydrolysis with acid, saccharide III-(2) ( $R_f$  0.24, solvent A) gave only xylose. Methylation analysis of saccharide III-(2) yielded 2,3,4-Me<sub>3</sub>-Xyl and 2,3-Me<sub>2</sub>-Xyl in the molar ratio of 36.5:63.5; d.p. = 3. A linear relationship was observed when log  $\alpha'$  of each component of the partial hydrolyzates of saccharide III-(2) was plotted against degree of polymerization. From these results, saccharide III-(2) was characterized as  $\beta$ -(1 $\rightarrow$ 4)-linked xylotriose.

(4) *Saccharide IV* (tetrasaccharide). On complete hydrolysis with acid, saccharide IV ( $R_F$  0.35, solvent A) gave xylose and arabinose in the ratio of 71:29, d.p. = 4. The plot of  $\log \alpha'$  against d.p. was linear for III-(1), IV, V, and VI (see Fig. 4b). From these results, saccharide IV was presumed to be 3-*O*- $\alpha$ -arabinofuranosylxylotriase.

(5) *Saccharide V* (pentasaccharide). On complete hydrolysis with acid, saccharide V ( $R_F$  0.22, solvent A) gave xylose and arabinose in the ratio of 3:1, d.p. = 5. From these results and the relationship between  $\log \alpha'$  and d.p., saccharide V was presumed to be 3-*O*- $\alpha$ -arabinofuranosylxylo-tetraose.

(6) *Saccharide VI* (hexasaccharide). On complete hydrolysis with acid, saccharide VI ( $R_F$  0.13, solvent A) gave xylose and arabinose in the ratio of 4:1, d.p. = 6. From these results and the relationship between  $\log \alpha'$  and d.p., saccharide VI was presumed to be 3-*O*- $\alpha$ -arabinofuranosylxylopentaose.

*Proposed structure for rice-hull arabinoxylan.* — The structural analysis of arabinoxylan in the hemicellulose I fraction of rice hull indicated that the repeating unit of this arabinoxylan consists of a linear chain of 19 (1 $\rightarrow$ 4)-linked,  $\beta$ -D-xylosyl residues and an arabinofuranosyl side-chain joined through a (1 $\rightarrow$ 3) linkage, as shown in 1.



Proposed structure for rice-hull arabinoxylan ( $n = 5-6$ )

The results of methylation analysis suggested the occurrence of a small proportion of terminal xylose in the rice-hull arabinoxylan. However, neither branched oligosaccharides containing xylose as a side chain nor a xylobiose having a linkage other than  $\beta$ -(1 $\rightarrow$ 4) were detected in the endo-xylanase digest of the arabinoxylan from rice hull. Therefore, most, if not all, of the xylosyl residues constitute the backbone of the arabinoxylan.

## DISCUSSION

Compared with other cereal hemicelluloses, the hemicellulose of rice has been less extensively investigated. The earliest study on rice hemicellulose was reported by Bevenue and Williams<sup>14</sup>, who isolated an arabinoxylan from rice grain. This arabinoxylan was composed of equal proportions of arabinose and xylose. Small proportions of galactose, mannose, and a uronic acid were detected as

minor, component sugars. Matsuo and Nanba<sup>15</sup> later isolated arabinoxylans from rice hull, rice bran, and rice endosperm. Among these three arabinoxylans, the one from rice hull showed the highest content of xylose. Unlike that of Bevenue and Williams<sup>14</sup>, these arabinoxylans did not contain mannose, although the arabinoxylan from rice hull or rice bran contained a small proportion of galactose, and that from rice endosperm contained glucose. The arabinoxylan from rice bran was also studied by Kurasawa *et al.*<sup>16</sup>, who reported that this arabinoxylan contained a small proportion of galactose, but neither mannose nor glucose.

Fukumoto *et al.*<sup>17</sup> isolated an arabinoxylan by extraction of chlorite-delignified rice-straw with 10% sodium hydroxide. The ratio of xylose to arabinose in this arabinoxylan was reported to be 3:1. Further structural study of this arabinoxylan by fragmentation analysis with a xylanase from *Aspergillus niger* was reported by Takenishi and Tsujisaka<sup>18</sup>, who isolated two fragment oligosaccharides from the enzymic hydrolyzate, and characterized them as 3'- $\alpha$ -L-arabinofuranosylxylobiose and 3'- $\alpha$ -L-arabinofuranosylxylotriose. These results indicated that the arabinoxylan consisted of a backbone of  $\beta$ -(1 $\rightarrow$ 4)-linked D-xylosyl residues and side chains of a single L-arabinofuranosyl group attached to some of the backbone residues through an  $\alpha$ -(1 $\rightarrow$ 3) linkage. A similar arabinoxylan was isolated from the cell walls of rice endosperm<sup>19</sup>; this was found to be a highly branched arabinoxylan in which 78% of the D-xylosyl residues are substituted with short side-chains of L-arabinose at O-3. The hemicellulose of rice hull was also studied by Sasaki and his co-workers<sup>20</sup>, who reported that rice hull contained a polysaccharide composed mainly of xylose and glucose. However, no detailed information on the structure of this polysaccharide has yet been made available.

Our present study has revealed the structural features of an arabinoxylan isolated from the 4% potassium hydroxide extract of rice hull. The main structure of this arabinoxylan was found to be similar to those reported for the ones isolated from rice straw or rice endosperm. The rice-hull arabinoxylan, however, seems to have a less-branched structure, as compared with those from rice straw or rice endosperm. This structural feature is rather similar to that of a wheat-straw arabinoxylan<sup>21</sup>, which is composed of eleven parts of xylose and one part of arabinose. The foregoing results suggest the occurrence of structural heterogeneity among the arabinoxylans from different parts of the same plant.

#### ACKNOWLEDGMENTS

We thank Prof. T. Yasui, Tsukuba University, for supplying endo-xylanase. We also thank Mr. T. Chiba, Agricultural Experimental Station, Miyagi Prefecture, for supplying unhulled rice (Toyonishiki).

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