Rye Water-Soluble Arabinoxylans Also Vary in Their 2-Monosubstituted Xylose Content

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Rye (*Secale cereale* L.) is rich in total and water-soluble arabinoxylans. Recently, a large variability in the structure of the water-soluble arabinoxylans from rye was described (Bengtsson and Åman 1990, Bengtsson et al 1992a, Vinkx et al 1993). In the article by Vinkx et al (1993), structural information was mainly gained by ^{1}H-nuclear magnetic resonance (NMR) and ^{13}C-NMR spectroscopy using peak assignments reported for wheat (Hoffmann et al 1992) and rye arabinoxylans (Bengtsson and Åman 1990). This article provides additional information obtained by methylation analysis.

MATERIALS AND METHODS

Arabinoxylan Fractions

Isolation of water-soluble arabinoxylan fractions from rye (cv. Danko harvested in 1991) was described previously (Vinkx et al 1993). The method involved extraction of rye whole meal with water, amylolysis, ammonium sulfate fractionation, clay adsorption of proteins, and dialysis.

Methylation Analysis

The fractions were methylated by a modification of the Hakomori method (Sanford and Conrad 1966), dialyzed, and dried in a stream of air. This procedure was repeated once to improve completeness of the reaction. Glycitol acetates were prepared (Englyst and Cummings 1984) after hydrolysis of the samples using 2.0*M* trifluoroacetic acid (1 hr, 121°C). Samples were analyzed with gas chromatography (GC) using flame ionization detection; identities were confirmed by GC-mass spectrometry as described by Gruppen et al (1992a). The 2- and 3-*O*-methylated xylitol acetates coeluted. Relative amounts were calculated from the relative abundance of the ions at m/z 117 and m/z 129 (ratios of molecular mass to charge).

RESULTS

The results of the methylation analysis are given in Tables I and II. In Table I, the molar proportions of the individual partially methylated compounds are given. In Table II, the relative proportions of the partially methylated xylose residues are presented.

The data confirm the large variation in the structure of water-soluble rye arabinoxylans as found by ^{1}H-NMR analysis (Vinkx et al 1993). For fraction AX50, 47% of the xylose residues were 2,4- or 3,4-linked (monosubstituted), and 3% were 2,3,4-linked (disubstituted); the remainder were unsubstituted. For fraction AX75, these figures were 22 and 41%, respectively; for AX100, these figures were 19 and 60%, respectively. When inspecting the individual amounts of 2- and 3-monosubstituted xylose, the amounts of 2-monosubstituted xylose increased from 1 to 14% of total xylose on going from AX50 to AX100, whereas the amount of 3-monosubstituted xylose decreased from 46 to 4%.

DISCUSSION

With increasing arabinose-xylose ratio (on going from AX50 to AX100) the relative abundance of 2-monosubstituted and disubstituted xylose increased, whereas the relative amount of unsubstituted and 3-monosubstituted xylose decreased. The structural variation as a function of arabinose-xylose ratio was larger than what was reported for wheat arabinoxylans (Gruppen et al 1992b). For barley arabinoxylans, the relative amount of 3-monosubstituted xylose was independent of the arabinose-xylose ratio of the arabinoxylan (Viëtor et al 1992).

Much as Aspinall and Sturgeon (1957), Bengtsson and Åman (1990) and Bengtsson et al (1992a,b), Vinkx et al (1993) reported that rye water-soluble arabinoxylans contain xylose residues that are unsubstituted, 3-monosubstituted or 2,3-disubstituted by

TABLE I
Methylation Analysis of Rye Arabinoxylan Fractions[a]

Methylated Compound	Linkage Mode	Molar Proportion (%)		
		AX50	AX75	AX100
2,3,5-Me_3-Ara	t-Ara*f*	37.6	53.2	60.3
3,5-Me_2-Ara	2-Ara*f*	0.1	0.2	0.6
2,5-Me_2-Ara	3-Ara*f*	0.1	...	0.2
2,3-Me_2-Ara	5-Ara*f*	0.3	0.3	0.7
2,3,4-Me_3-Xyl	t-Xyl*p*	0.3	0.5	0.8
2,3-Me_2-Xyl	4-Xyl*p*	30.5	16.4	7.7
2-Me-Xyl[b]	3,4-Xyl*p*	28.6	9.6	6.6
3-Me-Xyl[b]	2,4-Xyl*p*	(37.4)	(1.9)	(0.3)
Xyl	2,3,4-Xyl*p*	1.6	18.2	21.3
2,3,6-Me_3-Glc	4-Glc*p*	1.1	1.7	1.3

[a]Me = methyl, Ara = arabinitol, Xyl = xylitol, Glc = glucitol, t = terminal, Ara*f* = arabinofuranosyl, Xyl*p* = xylopyranosyl.
[b]2-Me-Xyl and 3-Me-Xyl coeluted, the sum as determined by gas chromatography-flame ionization detection. Figures in parentheses represent the ratio 2-Me-Xyl/3-Me-Xyl as determined by gas chromatography-mass spectroscopy.

TABLE II
Relative Proportion of the Partially Methylated Xylose Residues[a]

	AX50	AX75	AX100
%uxyl	50	37	22
%3mxyl	46	14	4
%2mxyl	1	7	14
%dxyl	3	41	60
A/X	0.55	1.09	1.42

[a]%uxyl = percent of total xylose residues that are unsubstituted with arabinose; 3mxyl = 3-monosubstituted xylose; 2mxyl = 2-monosubstituted xylose; dxyl = disubstituted xylose residue; A/X = arabinose-xylose ratio as determined by gas chromatography of alditol acetates (standard deviation = 0.02, Vinkx et al 1993).

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