Physico-Chemical and Functional Properties of Rye Nonstarch Polysaccharides. I. Colorimetric Analysis of Pentosans and Their Relative Monosaccharide Compositions in Fractionated (Milled) Rye Products

J. A. DELCOUR, S. VANHAMEL, and C. DE GEEST[1]

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ABSTRACT

The water-soluble, enzyme-extractable, and total pentosans (WSP, EEP, and TP, respectively) of rye kernels were estimated by a modification of the orcinol-hydrochloric acid method of Hashimoto et al (1987a). Modifications included absorbance readings both at 670 and 580 nm to minimize the small but significant interference by hexose sugars in the analytical figures and appropriate dilution of the pentosan extracts before analysis, as rye contains more pentosans than wheat. The relative monosaccharide ratios in the different milling extracts were estimated by gas chromatography of the alditol acetates of the monosaccharides released upon hydrolysis of the pentosan extracts. The highest proportion of TP was in the bran, whereas the shorts contained the highest proportion of both the WSP and the EEP. The proportion of WSP and EEP relative to the TP varied widely. D-(+)-Xylose and L-(+)-arabinose were the most abundant monosaccharides, along with significant amounts of D-(+)-glucose. D-(+)-Galactose, and D-(+)-mannose were present in trace amounts. The WSP in different milling fractions had smaller variations in the arabinose/xylose ratios (0.76–0.81) than was observed for the EEP (0.58–0.80) and TP (0.74–1.09). The EEP and TP were relatively richer in xylose for the bran and the short fractions as opposed to what was found for the fine flour fractions.

Many research efforts have been devoted to the nonstarch polysaccharides of cereal grains (D'Appolonia 1973), to their impact on the breadmaking value of wheat, and, to a lesser degree, rye flours (Meuser et al 1986; Meuser and Suckow 1986a,b). Both wheat and rye pentosans are complex groups of nonstarch polysaccharides that in some instances are covalently linked to proteins. A major part of these substances is not soluble in water, and every attempt to solubilize these compounds unfortunately necessitates a drastic change in their physico-chemical properties.

Much has been written about the properties of and the mechanisms by which wheat pentosans contribute to the breadmaking value of wheat flours (Ciacco and D'Appolonia 1982a,b; D'Appolonia et al 1970; D'Appolonia and McArthur 1975, 1976; Geissmann and Neukom 1971, 1973a,b; Hashimoto et al 1987a,b; Hoseney and Faubion 1981; Kim and D'Appolonia 1976, 1977a,b; Lineback et al 1977; McArthur and D'Appolonia 1977; Neukom and Markwalder 1978; Patil et al 1975a,b, 1976; Shogren et al 1987). Despite the published work, further research is clearly needed in order to reach an understanding of the impact of wheat pentosans on the breadmaking process.

The same holds true in the case of rye hemicelluloses, because relatively few reports are available on the physico-chemical and functional properties of this group of substances. In rye breadmaking the insoluble pentosans have been reported to be responsible for the characteristics typical of rye bread denoted as "dark grey, dull surface, and bitter taste." The soluble pentosans on the other hand are assumed to have a beneficial impact on product quality (Meuser et al 1986; Meuser and Suckow 1986 a,b).

Despite this qualitative data, we fully agree with Hoseney (1986) who states that "even with the relatively high concentration and the apparent importance of these [= rye] pentosans, relatively little has been reported on their chemical composition."

Although the research efforts published on rye pentosans (Ali and D'Appolonia 1979; Anger et al 1986; Aspinall and Sturgeon 1957; Casier et al 1973; Casier and Soenen 1967; Fengler and Marquardt 1988; Holas et al 1972; 1973a,b; Holas and Hampl 1973; Hromadkova and Ebringerova 1987; Jankiewicz and Michniewicz 1987; Meuser et al 1986; Meuser and Suckow 1986a,b; Schneider et al 1984a,b; Schneider and Pietsch 1985; Thomann and Piechaczek 1982; Weipert and Zwingelberg 1980) have all yielded much useful information, we nevertheless feel that in order to understand the mechanisms of the impact of rye pentosans in breadmaking, thorough insight in their physico-chemical nature is clearly desired. We therefore have started a systematic study of the structure of rye pentosans and their physico-chemical and functional properties.

As a preliminary step we felt it was important to study the distribution of these polysaccharides in different milled rye products and to apply the methods of Hashimoto et al (1987a). We preferred these recently published procedures over those developed by Cracknell and Moyce (1970), Douglas (1981), and Ford (1981) because they allow for a distinction between water-soluble, enzyme-extractable, and total rye pentosans.

We also determined the relative monosaccharide contents of the pentosan fractions by gas chromatography of the peracetates of the sodium borohydride reduction products prepared from the monosaccharides formed during the hydrolysis steps in the colorimetric assays of Hashimoto et al (1987a).

MATERIALS AND METHODS

Chemicals

D-(+)-Xylose, ferric chloride (hexahydrate), acetic anhydride, and pyridine were obtained from Merck, D-(+)-mannose and orcinol monohydrate from Aldrich, D-(+)-glucose and D-(+)-galactose from UCB, 2-deoxy-D-glucose and inositol from Janssen Chimica, L-(+)-arabinose and sodium borohydride from Fluka, and Veron HE from Rohm Tech.

Rye Sample and Rye Milling

The rye sample was of the Danko variety (1987 harvest) and grown in the Province Limburg, Belgium. It was milled at a moisture level of 14.5–15.0% with a roller mill (Bühler MLU-202 laboratory mill). The flow sheet of this mill is given in Figure 1. The moisture and ash contents of the rye sample itself and of the milling fractions were estimated according to AACC methods (1984). Kjeldahl nitrogen was determined as outlined in Analytica (1987).

Colorimetric Estimation of Water-Soluble, Enzyme-Extractable, and Total Pentosans in Milled Rye Products

The pentosans were estimated according to the colorimetric methods of Hashimoto et al (1987a). In these assays, pentosan-containing extracts are hydrolyzed, and the pentoses released are estimated by an orcinol-hydrochloric acid-ferric chloride procedure based on the original method by Albaum and Umbreit (1947). In view of our experimental results with regard to the interference of glucose in the assays (Results and Discussion), and in light of the findings by Fernell and King (1953) and Thomann

[1]Senior research assistant, research assistant, and graduate student respectively, Laboratorium voor Toegepaste Organische Scheikunde, Katholieke Universiteit Leuven, Kardinaal Mercierlaan 92, B-3030 Heverlee, Belgium.

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and Scheinemann (1982), we measured not only the A_{670} values of the resulting mixtures but also their A_{580} readings.

The water-soluble pentosans were extracted with water. The enzyme-extractable pentosans were extracted with a 0.1*M* sodium acetate buffer at pH 4.5–4.6 in the presence of a standardized quantity of a pentosanase (Veron HE). The total pentosans were determined after acid hydrolysis of the entire sample and subsequent fermentation (with bakers' yeast) of the hexose sugars formed.

Because rye contains more pentosans than wheat, we adjusted the three procedures in order to meet the requirement of estimation in the linear portion of the absorbance versus pentosan concentration curve. The methods applied in this work are therefore as follows.

Water-soluble pentosans. One hundred milligrams of sample and 10.0 ml water were shaken at 30° C for 120 min. After centrifugation, 1.0 ml of the clear supernatant was mixed with the same volume of 4*N* hydrochloric acid and heated at 100° C for 120 min in a sealed tube. After cooling, an equal volume of water was added to a portion of the hydrolyzed sample, and 1.0 ml of the resulting mixture was transferred to a test tube. The addition of the chromogen reagents and water and the further manipulations were performed as described in the original method (Hashimoto et al 1987a) with evaluation of both the A_{670} and the A_{580} readings. The percent pentosan is then given by the formula

$$(A_{670} - A_{580}) \times 4 \times 0.88 \times 0.01 \times m_1$$

or (as in the original method) by the formula

$$(A_{670}) \times 4 \times 0.88 \times 0.01 \times m_2$$

with m_1 and m_2 being the slopes of the respective calibration plots.

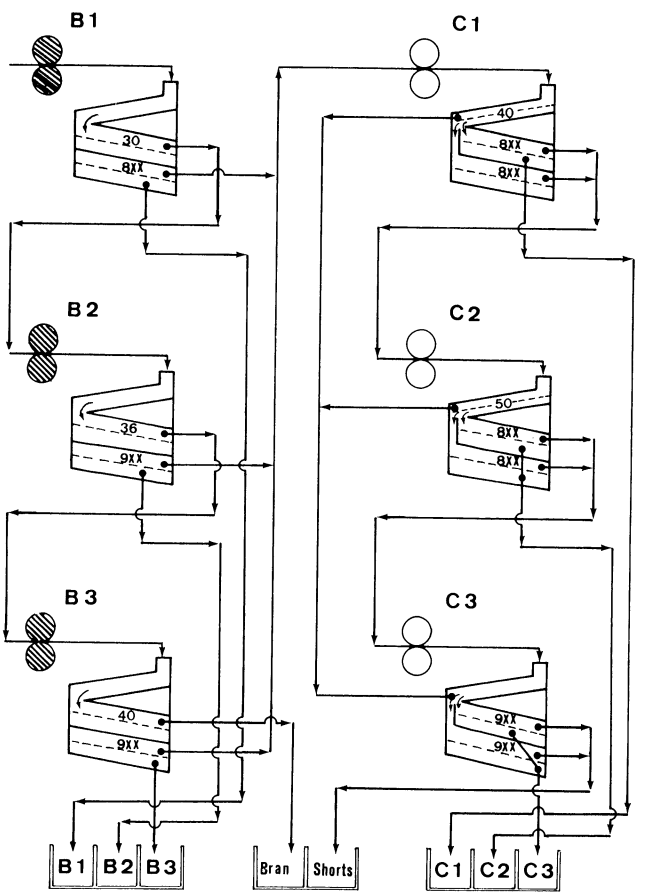

Fig. 1. Milling flow sheet for a Buhler MLU-202 laboratory mill. **B1**, **B2**, and **B3**: successive break rolls and corresponding milling fractions; **C1**, **C2**, and **C3**: successive reduction rolls and milling fractions.

Enzyme-extractable pentosans. One hundred milligrams of sample was mixed with 10 ml of a 0.1*M* sodium acetate buffer (pH 4.5–4.6) and 200 µl of 1.0% of Veron HE in the same buffer. After shaking for 20 hr at 30° C and subsequent centrifugation, 1.0 ml of the supernatant was mixed with 1.0 ml of 4*N* hydrochloric acid and hydrolyzed and further manipulated as above. In this case the percent pentosan was then given by the same formulas as those for the water-soluble pentosans.

Total pentosans. One hundred milligrams of sample was hydrolyzed by the addition of 20.0 ml of 2*N* hydrochloric acid and subsequent heating of the mixture at 100° C for 150 min. After cooling, 20.0 ml of 2*N* sodium carbonate solution and 20.0 ml of yeast suspension (25 mg/ml in 0.2*M* sodium phosphate buffer, pH 7.0) were added, and a 120 min fermentation at 30° C was then allowed to take place under continuous shaking. After centrifugation, 2.0 ml of the supernatant was diluted with 10.0 ml of water, and 2.0 ml of the resulting mixture was added to 1.0 ml of water and the chromogen reagents as described in the original procedure, again with evaluation of the $(A_{670} - A_{580})$ value as well as of the A_{670} value.

The percent total pentosan can then be calculated as

$$(A_{670} - A_{580}) \times 18 \times 0.88 \times 0.01 \times m_1$$

or by the formula

$$(A_{670}) \times 18 \times 0.88 \times 0.01 \times m_2$$

with m_1 and m_2 as explained above.

Gas Chromatography of the Alditol Peracetates of the Monosaccharides Released in the Hydrolysis Step

Preparation of derivatives. Samples (1.5 ml) of the monosaccharide solutions obtained in the hydrolysis steps of the methods of Hashimoto et al (1987a) for water-soluble and enzyme-extractable pentosans, and 4.5 ml of the corresponding solutions in the method for total pentosans were neutralized to a pH value between 6.0 and 8.0 first by the addition of 2*M* and then 0.1*M* sodium hydroxide.

To the neutralized solutions, 0.5 ml of a 0.01*M* solution of 2-deoxy-D-glucose was added as an internal standard. The reduction of the component sugars to their corresponding alditols was then performed with 50 mg of sodium borohydride. The mixture was allowed to stand for 60 min. After that time, a few drops of acetic acid were added and the solution was lyophilized. The borate was removed as methyl borate by treatment with 5× 3.0 ml of 1% hydrochloric acid in methanol and evaporation with a rotary evaporator (40° C). The residue was subsequently dissolved in a mixture of 5.0 ml of acetic anhydride and 0.12 ml of concentrated sulfuric acid. After heating at 100° C for 60 min in sealed tubes in a water bath, the solution was poured into a previously frozen mixture of 5.0 ml of pyridine and 10.0 ml of water. After complete thawing, the resulting mixture was extracted with 15 ml of chloroform. The chloroform phase was then successively washed with 15-ml portions of water, 1*N* sulfuric acid, 5% sodium bicarbonate, and finally water before being dried over sodium sulfate and evaporated as above. It was then dissolved in 1.0 ml of dry chloroform and submitted to gas chromatography. The method listed here is a procedure developed at this laboratory and based upon earlier work by Albersheim et al (1967), Knapp (1979), and Shaw and Moss (1967).

Gas chromatography. A Perkin Elmer Sigma 3 gas chromatograph with flame ionization detector was used for the separation of the alditol acetates. The analytical conditions were as follows: a glass column (1.80 m × 3 mm i.d.) was packed with 3% SP-2330 on Supelcoport 100/120 mesh. Temperatures were 225° C for the column and 250° C for the injection port and the detector. The flow rate of nitrogen (carrier gas) was 20 ml/min and the sample size 1.0 µl.

Peak retention times and areas were automatically recorded by an Intersmat ICR-1B electronic integrator. In those instances

where peak heights were out of range, the samples were diluted in a suitable manner and injected again.

RESULTS AND DISCUSSION

Rye Milling Fractions

The results of the laboratory rye milling and of the routine analyses of the fractions obtained are listed in Table I.

The data obtained are in line with those of Drews and Seibel (1976), who found that flours from the inner endosperm (break streams) are relatively rich in starch and poor in protein. Flours obtained by the reduction of the middlings were richer in protein, thus confirming earlier reports (Drews and Seibel 1976). The rather low rye flour yields were probably a result of using a pilot scale wheat flour mill in this work. Contrary to what has been reported in the literature (Holas and Hampl 1973, Drews and Seibel (1976), we did not find that higher protein contents systematically implied higher ash contents.

Colorimetric Estimation of Water-Soluble, Enzyme-Extractable, and Total Pentosans

Construction of the calibration plot. It was observed by Fernell and King (1953) and Thomann and Scheinemann (1982) that there is a small but significant interference from the presence of hexoses in orcinol-hydrochloric acid estimations of pentoses. In contrast to what is reported in the procedure of Hashimoto et al (1987a), we also observed such interference. We therefore used the ($A_{670} - A_{580}$) values in addition to the A_{670} values to construct the calibration plot with xylose and to estimate pentosan contents in the different samples, as was suggested by Thomann and Scheinemann (1982) to reduce the impact of the presence of hexoses in the samples.

It was found that fresh reagents needed to be prepared daily for both construction of the calibration plot and for the colorimetric analysis of pentosans. The calibration plot was constructed with different concentrations of xylose within an interval of 0–360 μg/3.0 ml.

The regression curves of reproducible calibration plots are

$$A_{670} - A_{580} = 3.62 \times 10^{-3} \times [\text{xylose}] - 0.005 \quad (r^2 = 0.995)$$

or alternatively

$$A_{670} = 6.56 \times 10^{-3} [\text{xylose}] + 0.014 \quad (r = 0.994)$$

with [xylose] in μg/3.0 ml.

The corresponding graphs are shown in Figure 2. From the above it follows that m_1 and m_2 in the formulas (Materials and Methods) equal 276.4 and 152.37, respectively. From this last figure it can easily be deduced that the calibration plot of A_{670} versus the xylose concentrations yields a slightly different slope from that that can be deduced from the plot shown by Hashimoto et al (1987a).

Estimation of water-soluble, enzyme-extractable, and total pentosans. In this part of the work, and in the case of the study of the relative monosaccharide compositions of pentosans, we limited our efforts to the quantitatively most abundant rye milling fractions, i.e., B_2, C_1, the bran and the shorts. Triplicate analyses were necessary to yield acceptable variation coefficients, i.e., 0.01, 0.18, and 1.86% for WSP, EEP, and TP, respectively.

The results of this work are listed in Table II. It is clear from this data that the use of ($A_{670} - A_{580}$) readings to evaluate the pentosan concentrations leads to lower pentosan content readings, and it is noteworthy that the evaluation of the total pentosans by this formula yielded results that agree better with what has been reported by Henry (1987) on the basis of a gas chromatographic analysis.

Of further interest is that the highest proportion of total pentosans was in the bran, whereas the shorts contained the highest proportion of both the water-soluble and enzyme-extractable pentosans. Similar data were obtained for wheat by Hashimoto et al (1987a). It is noteworthy that our quantitative data on water-soluble and total pentosans were in line with what has been reported by Drews and Seibel (1976) and Holas and Hampl (1973). Thus, the percentage of soluble pentosans in endosperm material is a lot higher than what was observed in the bran and shorts fractions.

Our findings were equally in line with the data recently reported by Fengler and Marquardt (1988), who showed that rye flour

TABLE I
Laboratory Milling of Rye Sample[a]

Fraction[b]	Yield (%)	Nitrogen Content (%)	Ash Content (%)
Whole kernel	100	1.56	1.71
B1	5.3	0.76	0.77
B2	13.1	0.82	0.73
B3	3.6	1.10	1.00
C1	29.2	1.12	0.83
C2	3.5	1.44	0.98
C3	1.2	1.46	0.99
Bran	22.5	2.43	4.49
Shorts	21.5	2.28	2.80

[a] All results are reported as percentages of the dry matter.
[b] Fractions termed according to the mill stream scheme (Fig. 1).

TABLE II
Water-Soluble, Enzyme-Extractable, and Total Pentosan Contents in Rye Milling Fractions[a]

	Water-Soluble Pentosans[c]		Enzyme-Extractable Pentosans		Total Pentosans	
Fraction[b]	C_{670}	C_{dif}	C_{670}	C_{dif}	C_{670}	C_{dif}
Whole kernel	2.40	1.94	5.44	5.09	11.20	9.44
B2	1.88	1.52	2.81	2.43	2.84	1.82
C1	2.40	1.94	3.52	3.11	4.28	3.52
Bran	1.96	1.44	6.21	5.88	19.92	19.92
Shorts	4.17	3.78	8.37	7.93	11.44	10.37

[a] All results are reported as percentages of the dry matter.
[b] Fractions termed according to the mill stream scheme (Fig. 1).
[c] C_{670}, Calculated with the A_{670} readings; C_{dif}, calculated with the $A_{670} - A_{580}$ readings.

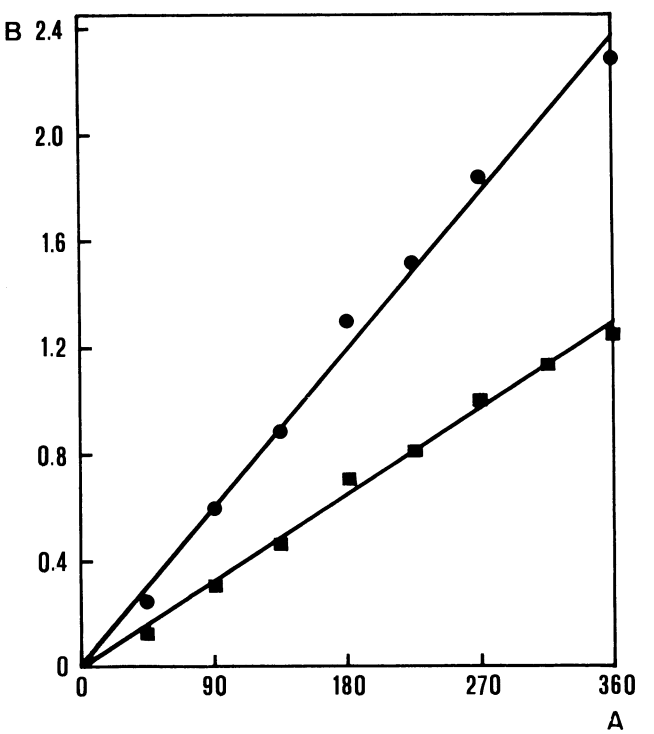

Fig. 2. Calibration plot for absorbance (**B**) versus xylose concentrations (**A**, μg/3 ml). A_{670} (•); $A_{670} - A_{580}$ (■).

contains the highest portion of water-soluble pentosans, in contrast to what is reported for bran.

Under the experimental conditions applied here, the proportion of the percentages of enzyme-extractable to total pentosans varies widely. Veron HE is a fungal hemicellulase-pentosanase preparation. Ter Haseborg and Himmelstein (1988) report that the product thoroughly hydrolyzes high-polymer insoluble pentosans and that it is free of protease activity. Unfortunately, no information is available with regard to the exact composition of the enzyme preparation such that we would be able to deduce what the structural requirements would be for the pentosans to be hydrolyzed by the enzyme.

Gas Chromatographic Separations of Alditol Acetates of Sugars

Typical retention times and response factors for alditol acetates of different hexose and pentose sugars under the gas chromatographic conditions given above are listed in Table III.

In the case of rye hemicelluloses, we found that for quantitative work 2-deoxyglucose could successfully be applied as an internal standard. Indeed, the rye hemicelluloses mainly consist of arabinose and xylose. Since inositol or a compound yielding the same retention time in gas chromatography was detected, this substance cannot serve as an internal standard in studies on the hemicelluloses of rye. We found the detector molar response factor of xylose to be identical to that of arabinose. From this and the respective gas chromatograms of the hydrolyzed and derivatized samples, the arabinose/xylose ratios can easily be calculated. It is believed that the ratio of the concentration of arabinose to that of xylose is indicative of the degree of branching of the biopolymers. A low ratio would imply a xylan chain with relatively few insertions of arabinose side chains. Such a polymer would then have less pronounced interaction possibilities than its counterpart characterized by a higher arabinose/xylose ratio.

Table IV summarizes the arabinose/xylose ratios and the ratios of other monosaccharides to xylose for water-soluble as well as enzyme-extractable and total pentosans for the quantitatively most abundant milling fractions.

The average of two separate determinations of arabinose/xylose ratios $[A/X]_{av}$ were evaluated as

$$[A/X]_{av} = [(A_1/R_1) + (A_2/R_2)] \times [(X_1/R_1) + (X_2/R_2)]^{-1}$$

with the A, X, and R values the areas found upon integration of the peaks for, respectively, the alditol acetates of arabinose, xylose, and the reference compound 2-deoxyglucose in the chromatograms indicated by the subscripts 1 and 2. The other ratios listed were calculated in a similar manner.

The water-soluble pentosans in different milling fractions had less variation in arabinose/xylose ratios than what was observed for the enzyme-extractable and the total pentosans (Table IV). Xylose and arabinose were clearly the most abundant monosaccharides in the three pentosan categories estimated, with galactose and mannose only occurring as minor constituents. The arabinose/xylose ratios of the water-soluble pentosans in different milling fractions were within a 0.76–0.81 range. Our data are therefore at variance with those of Fengler and Marquardt (1988), who found an arabinose/xylose ratio of 0.61 in a rye water-soluble pentosan fraction. As was to be expected, the water-soluble extracts upon hydrolysis also contained some glucose. Of further importance is that the pentosanase (Veron HE) released a significant proportion of glucose, and this must therefore be indicative of some α- or β-glucan hydrolyzing ability.

Whereas the water-soluble pentosans occurring in different milling fractions had similar arabinose/xylose ratios, it is clear that the enzyme-extractable pentosans are relatively richer in xylose for the bran and short fractions as opposed to what was observed in the fine flour fractions. The same holds for the total pentosans. Our results here confirm the experimental evidence of Henry (1987), who states that the pentosan from the whole grain contains relatively more xylose than that from the endosperm.

TABLE III
Retention Times of Inositol Acetate and of the Alditol Acetates of Different Monosaccharides Under the Gas Chromatographic Conditions Described in the Text

Compound	Retention Time (sec)	Response Factor
L-(+)-Arabinose	498	1
D-(+)-Xylose	651	1
2-Deoxy-D-(+)-glucose	723	1.04
D-(+)-Mannose	978	1.15
D-(+)-Galactose	1,100	1.15
D-(+)-Glucose	1,232	1.15
Inositol	1,508	1.32

TABLE IV
Ratios of the Relative Concentrations of Several Monosaccharides to that of Xylose in Extracts of Water-Soluble, Enzyme-Extractable, and Total Pentosans in Rye Milling Fractions

Pentosan Category/ Milling Fraction[a]	Arabinose/ Xylose	Mannose/ Xylose	Galactose/ Xylose	Glucose/ Xylose
Water-soluble				
B2	0.81	0.19	...[b]	2.00
C1	0.76	0.21	...	0.12
Bran	0.76	...	0.12	2.76
Shorts	0.76	0.14	0.08	1.94
Enzyme-extractable				
B2	0.80	0.17	...	6.56
C1	0.85	0.21	0.09	6.25
Bran	0.58	0.13	0.04	2.17
Shorts	0.61	0.14	0.04	2.41
Total				
B2	1.09	0.16	0.14	...
C1	1.06	0.10	0.12	0.09
Bran	0.74	0.03	0.12	0.04
Shorts	0.85	0.06	0.09	0.05

[a] Fractions termed according to the mill stream scheme (Fig. 1).
[b] Traces found.

CONCLUSIONS

Different milling fractions of rye contain pentosans with varying structures and compositions. Those pentosans accordingly have distinct physico-chemical properties such as enzyme extractability and water solubility. Rye milling can therefore be a good step in pentosan fractionation efforts.

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