POLYSACCHARIDES AND LIGNIN IN RAPESEED

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INTRODUCTION

Rapeseed (Brassica napus L.) grown in Sweden contains about 45 % oil, 25 % protein, 10 % carbohydrates, 5 % Klason lignin, 1-4 % glucosinolates and 2 % phytic acid (Table 1; Anjou et al., 1977) and the hulls form 15-20 % of the seeds. Great interest has been focused in recent years on producing non-toxic rapeseed protein concentrates (RPC) or isolates (RPI) from dehulled rapeseed meal (RM), which has a very well balanced amino acid composition. Since the carbohydrates and Klason lignin constitute a large part of the seeds, the composition and properties of these components are of great importance to people working with these projects. We have previously summarized our studies on the low-molecular carbohydrates and glucosinolates (Theander and Åman, 1975). The fractionation and characterization of polysaccharides and Klason lignin in dehulled RM and hulls will be discussed in this paper.

TABLE 1

COMPOSITION OF RAPESEED (% OF DM)

	Content
Oil	45
Protein	25
Carbohydrates	12
Klason lignin	5
Glucosinolates	1-4
Phytic acid	2

POLYSACCHARIDES IN DEHULLED SEEDS

The variation in polysaccharide content between different rapeseed and turnip rapeseed cultivars grown in Sweden in 1974 was rather small (Anjou et al., 1977). Arabinose and glucose were the predominant constituents; and xylose, galactose and galacturonic acid were the other major constituents in all the seeds investigated.

In order to obtain information about the polysaccharide composition, dehulled heat-treated and 80 % ethanol-extracted RM was successively extracted with water, 2 % EDTA and 10 % NaOH. All fractions were respectively precipitated with ethanol, deproteinized and separated by column chromatography, and the isolated polysaccharide materials were structurally investigated (Theander and Åman, 1977). The yields of carbohydrates, crude protein (N x 6.25) and Klason lignin (the insoluble residue obtained after acidic treatment) in each fraction given as % of RM are shown in Table 2. Most of the polysaccharides were found in the water-soluble, EDTA-soluble and hemicellulose B fractions and the "cellulose" residue, and most of the uronic acid residues in the EDTA-soluble fraction. Small amounts of Klason lignin were found in the "cellulose" residue, probably originating from traces of remaining seed hulls. The cell walls of dehulled RM do not seem to be lig-

nified to any significant extent.

TABLE 2

COMPOSITION OF RAPESEED FRACTIONS. THE RESULTS ARE GIVEN AS % OF THE DRY WEIGHT OF DEHULLED RM

Fraction	Neutral carbohydrates[a]	Uronic acids[a]	Crude protein	Klason lignin
Water-soluble polysaccharide	1.7	0.12	6.5	
EDTA-soluble polysaccharide	3.2	1.3	9.2	
Hemicellulose A	0.24	c	5.9	
Hemicellulose B	3.0	0.30	2.9	
Hemicellulose C	b	c	7.4	
"Cellulose"	2.8	c	1.2	0.60

Small amounts of highly branched arabinan (Fig. 1) containing $\alpha(1\rightarrow3)$ and $\alpha(1\rightarrow5)$ linkages were isolated from the water-soluble fraction (Larm et al., 1975). An oxalate-soluble arabinan of similar structure was isolated from turnip rapeseed by Siddiqui and Wood (1974). A highly branched neutral arabinogalactan (Fig. 2) was also isolated from the water-soluble fraction (Larm et al., 1976). The role of these polysaccharides in the seeds is not known today.

EDTA-soluble pectins and associated polysaccharides accounted for about 1 % of dehulled RM. They consisted mainly of galacturonic acid, arabinose, xylose, galactose, fucose and rhamnose residues. Pectin and associated polysaccharides of RM contained unusually high proportions of neutral sugars. Pectins of similar composition have been isolated and structurally investigated from turnip rapeseed (Siddiqui and Wood, 1976). Structural features of seed pectins are summarized in Fig. 3. Pectins are generally found in primary cell walls and intercellular layers in land plants.

Highly branched acidic arabinogalactans containing arabinose, galactose and terminal galacturonic acid units as main constituents accounted for about 4 % of dehulled RM. These polysaccharides have been isolated and investigated from the water-soluble, EDTA-soluble and alkali-soluble fractions. Siddiqui and Wood (1972) isolated and structurally investigated water-soluble acidic arabinogalactan of similar composition from turnip rapeseed. The main structural units of acidic arabinogalactans are shown in Fig. 4. These polysaccharides are obviously important components of the cell wall matrix.

Fucogalactoxyloglucans have been isolated from both water-soluble and alkali-soluble fractions (Theander and Åman, 1978) and they account for about 4 % of dehulled RM. Separation of an alkali-soluble fucogalactoxyloglucan fraction on a Sepharose 4B-CL column is shown in Fig. 5. The polysaccharide material was very polydisperse with a non-symmetrical high-molecular weight fraction (S 1) and a symmetrical low-molecular weight fraction (S 2). Sugar analysis, however, revealed that the fractions had very similar chemical composition. Structural investigations have shown that these polysaccharides consist as a main chain of $\beta(1\rightarrow4)$ linked glucose units with side chains of xylose, galactose and fucose units

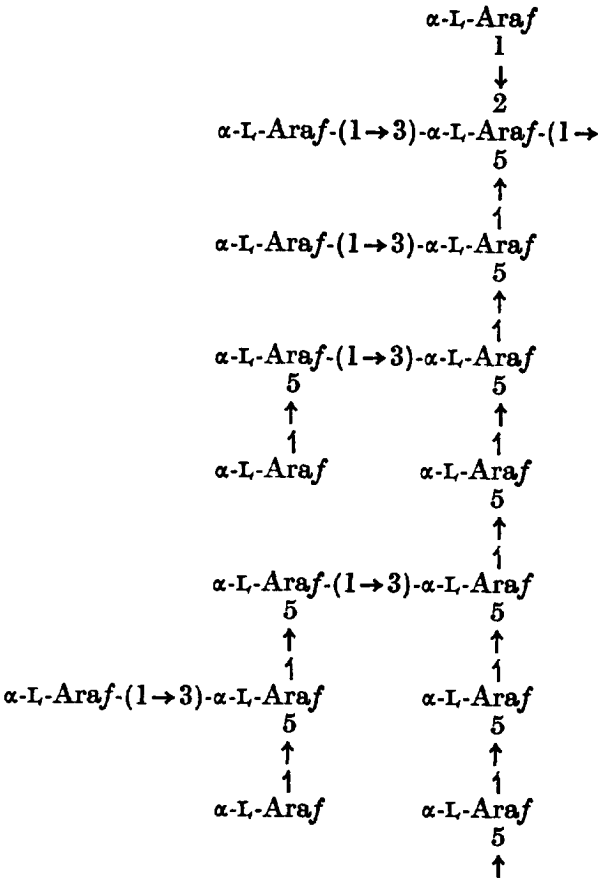


FIG. 1

STRUCTURAL FEATURES OF A WATER-SOLUBLE ARABINAN IN DEHULLED RM

(Fig. 6). Traces of arabinose may also be found in these polysaccharides. They can form hydrogen bonds with the cellulose and are important components of the cell wall matrix. Siddiqui and Wood (1971 and 1977 b) isolated and structurally investigated both a water-soluble and an alkali-soluble xyloglucan from turnip rapeseed.

Dehulled RM contained about 3 % of cellulose (Fig. 7), the common plant cell wall component consisting of $\beta(1\rightarrow 4)$ linked glucose units. The spatial arrangement of the cellulose molecules favours the formation of strong intermolecular and intramolecular hydrogen bonds and thereby the formation of fibrils making up the mechanically strong fibres in the cell wall.

Traces of low-molecular weight mannose-containing polysaccharides were detected in both the water-soluble and the alkali-soluble fractions and an acidic xylan was detected in small amounts in the alkali-soluble fraction. These polysaccharides may also be cell wall components. Small amounts

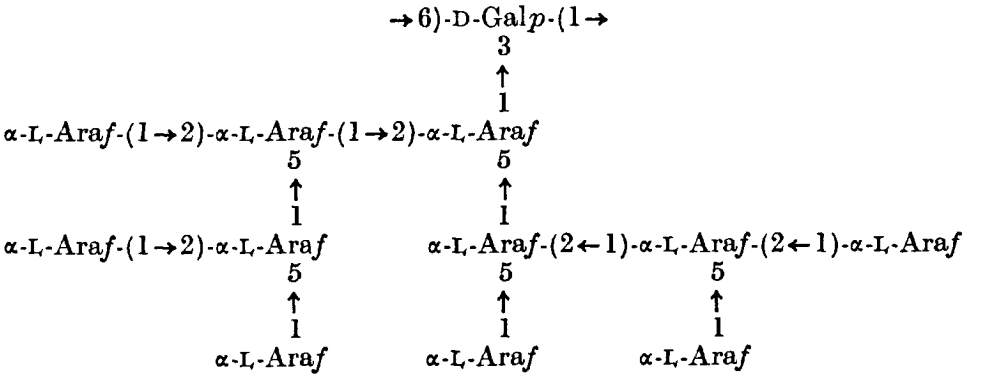


FIG. 2

STRUCTURAL FEATURES OF A WATER-SOLUBLE NEUTRAL ARABINOGALACTAN IN DEHULLED RM

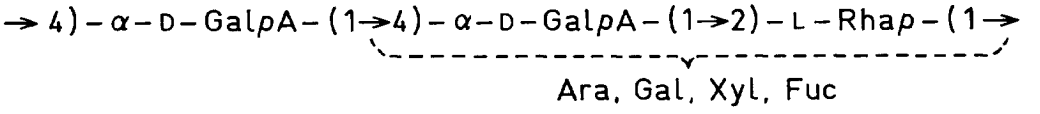


FIG. 3

STRUCTURAL FEATURES OF EDTA-SOLUBLE SEED PECTINS

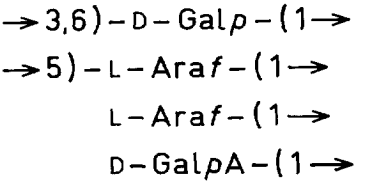
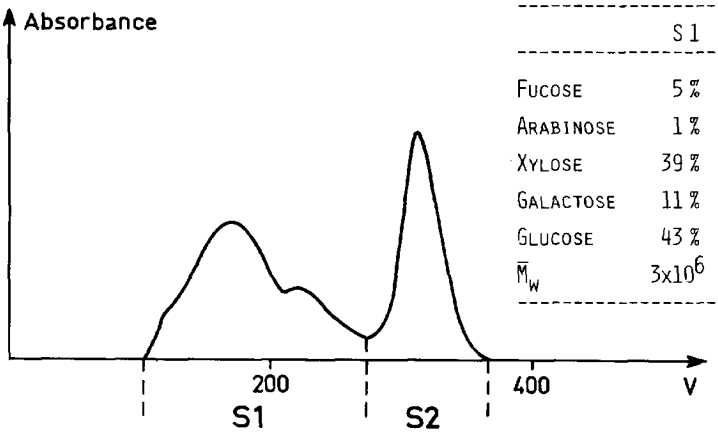


FIG. 4

STRUCTURAL UNITS OF ACIDIC ARABINOGALACTANS IN DEHULLED RM



	S1	S2
Fucose	5 %	6 %
Arabinose	1 %	2 %
Xylose	39 %	36 %
Galactose	11 %	11 %
Glucose	43 %	44 %
$\bar{M}_w$	$3x10^6$	$1x10^4$

FIG. 5

FRACTIONATION OF AN ALKALI-SOLUBLE FUCOGALACTOXYLOGLUCAN ON SEPHAROSE 4B-CL COLUMN. ABSORBANCE AT 485 NM IN PHENOL-SULPHURIC ACID. ELUTION VOLUME (V) IN ML.

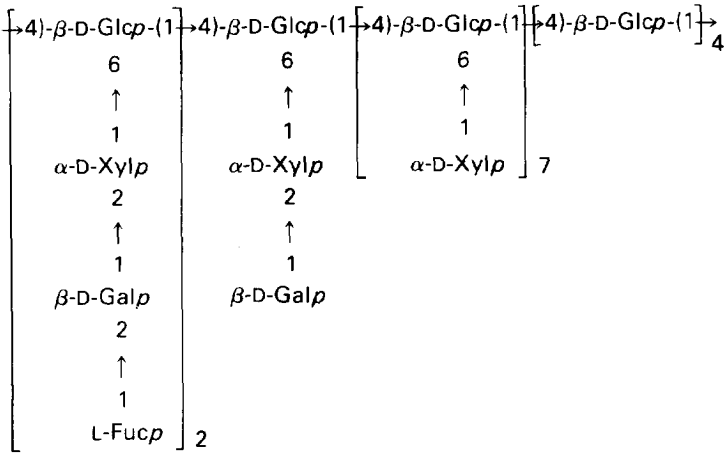


FIG. 6

STRUCTURAL FEATURES OF AN ALKALI-SOLUBLE FUCOGALACTOXYLOGLUCAN IN DEHULLED RM

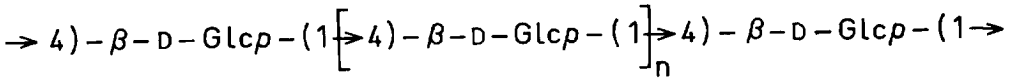


FIG. 7

CELLULOSE

of an alkali-soluble acidic xylan, containing xylose and 4-O-Me-glucuronic acid residues have been isolated from turnip rapeseed and structurally investigated (Siddiqui and Wood, 1977 a).

CARBOHYDRATES AND KLASON LIGNIN IN SEED HULLS

Carbohydrates and Klason lignin were the major components of rapeseed, turnip rapeseed and white mustard hulls (Theander et al., 1977; Anjou et al., 1978). Glucose, arabinose, galactose, xylose and galacturonic acid were the main constituents of the polysaccharides. Yellow hulls contained more polysaccharides than dark hulls (Table 3), but the relative composition of the sugars obtained after acid hydrolysis were rather similar for the three types of hulls. The amount of Klason lignin was higher in dark hulls than in yellow hulls. The Klason lignin, however, represent not only the lignin but also polyphenols and contains some proteins and products from the acid degradation of carbohydrates. It was shown by oxidative degradation of methylated lignin samples that dark hulls had a high content of condensed polyphenols and that yellow hulls had a low content; the lignin contents, however, were about the same.

TABLE 3

COMPOSITION OF SEED HULLS (% OF DM)

	Turnip rapeseed			White mustard
	Bele	Lute	Sv 72/60029	Sv 67/670
Colour	dark	60 % yellow	yellow	yellow
Neutral sugar constituents	26	33	38	38
Uronic acid constituents	+++	+++	+++	+++
Klason lignin	36	18	8	8
Condensed polyphenols	+++	++	+	+
Lignin	+	+	+	+

A pectin, accounting for at least 7 % by weight of the hulls and containing about 30 % galacturonic acid and small amounts of arabinose, galactose, xylose, rhamnose and fucose, was isolated and structurally investigated

in turnip rapeseed hulls by Aspinall and Jiang (1974). A fucogalactoxyloglucan has also been isolated as a major component in turnip rapeseed hulls (Aspinall et al., 1977).

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