ELSEVIER

Animal Feed Science Technology 67 (1997) 319–338

ANIMAL FEED SCIENCE AND TECHNOLOGY

Carbohydrate and lignin contents of plant materials used in animal feeding

Knud Erik Bach Knudsen [1]

Danish Institute of Agricultural Sciences, Department of Nutrition, Research Centre Foulum, PO Box 50, DK-8830 Tjele, Denmark

Accepted 21 November 1996

Abstract

A total of 115 samples representing 38 different feedstuffs was analysed for carbohydrates and lignin. The samples were analysed for low-molecular weight (LMW) sugars by high-performance liquid chromatography, starch, fructan and mixed linked β(1 → 3;1 → 4)-D-glucan by colorimetry, total, soluble and insoluble non-starch polysaccharides (NSP) by gas-liquid chromatography and lignin by gravimetry. For all but alfalfa meal, almost quantitative recovery of carbohydrates and lignin was obtained with a deviation between calculated and analysed values of less than 2 g kg^{-1} dry matter. The correlation between calculated and analysed values was 0.985 ($P < 0.0001$).

The concentration (g kg^{-1} dry matter) of LMW-sugars varied from 5 g kg^{-1} and up to 137 g kg^{-1} with the lowest values found in cereal substitutes, whole grain cereals and by-products while the protein concentrates in general had the highest content of LMW-sugars (57–137 g kg^{-1}). Starch was the main polysaccharide in whole grain cereals where it varied from 468 g kg^{-1} in oats to 690 g kg^{-1} in maize, in cereal by-products (93–902 g kg^{-1}) and in tapioca (768 g kg^{-1}). In contrast, the concentration of starch was low in all protein concentrates but peas and faba beans. The lowest levels of NSP and lignin were found in maize flour (NSP, 21 g kg^{-1}; lignin, 4 g kg^{-1}) and the highest levels in oat hull meal (NSP, 503 g kg^{-1}; lignin, 148 g kg^{-1}). There was also a significant variation in NSP and lignin in protein concentrates with the NSP value varying from 189 g kg^{-1} in faba beans to 451 g kg^{-1} in white lupins and with lignin varying from 12 g kg^{-1} in white lupins to 133 g kg^{-1} in sunflower cake. Grass meal, alfalfa meal and sugar beet fibre had in general high concentrations of NSP and lignin with values in grass and alfalfa meals of NSP: 329–426 g kg^{-1} and lignin: 128–169 g kg^{-1} and in sugar beet fibre 779 g kg^{-1} and 35 g kg^{-1}, respectively. © 1997 Elsevier Science B.V.

Keywords: Carbohydrates; Lignin; Low-molecular weight sugars; Polysaccharides; Plant materials; Feedstuffs

[1] Telephone: # +45 89991143; fax: # +45 89991378.

PII S0377-8401(97)00009-6

1. Introduction

The carbohydrates, which include the low molecular-weight (LMW) sugars, starch and various cell wall and storage non-starch polysaccharides (NSP) are the most important energy sources for non-ruminant and ruminant animals. The NSP and lignin are the principal components of cell walls and are commonly referred to as dietary fibre (DF) (Theander et al., 1993; Theander et al., 1994). Intracellular NSPs such as fructans and mannans may also be constituents of some plant materials, e.g. mannans in palm cake (Düsterhöft et al., 1991; Stephan, 1983). The polysaccharides, because of their large size and structure, encompass a wide range of chemical and physical properties. Starch is present within plant cells as discrete granules and with a size and form characteristic for the individual plant species. Within each granule, amylopectin forms a branched helical crystalline system in which amylose, of linear form, is dispersed (e.g. Gallant et al., 1992). The plant cell walls consist of a series of polysaccharides often associated and/or substituted with proteins and phenolic compounds, in some cells together with the phenolic polymer lignin (Selvendran, 1984; Theander et al., 1993). The building blocks of the cell wall polysaccharides are the pentoses arabinose and xylose, the hexoses glucose, galactose and mannose, the 6-deoxyhexoses rhamnose and fucose, and the uronic acids glucuronic and galacturonic acids. The main polysaccharides of plant cell walls are cellulose, arabinoxylans, mixed linked β(1 → 3; 1 → 4)-D-glucans (β-glucans), xyloglucans, xylans, rhamnogalacturonans, arabinogalactans to mention the major ones (Selvendran, 1984; Stephan, 1983; Theander et al., 1989). Lignins can be described as very branched networks build up by phenylpropane units. Lignins are partly linked to cell wall cellulose and non-cellulosic polysaccharides (Iiyama et al., 1994) and serves in principle two main functions. It cements and anchors the cellulose microfibrils and other matrix polysaccharides and in this way stiffen the walls thus preventing biochemical degradation and physical damage of the walls.

Although it was early recognised in nutrition that the various carbohydrate fractions neither were digested nor utilised to the same extent, chemical methods have not been used extensively to predict the feed value. The crude fibre method, invented in the middle of last century, and the neutral detergent fibre (NDF) method, based on the pioneering work of Van Soest, are still the methods most frequently used to determine the feed value for ruminant animals and pigs (Henneberg and Stohmann, 1859; Van Soest, 1963; Van Soest and Wine, 1967). Both methods, however, have their limitations. In the crude fibre method only a small and variable fraction of the total DF is measured, while the water-soluble NSP and water-insoluble pectic substances are lost in the NDF procedure (Bailey and Ulyatt, 1970; Carre and Brillouet, 1986; Reichert, 1981). Moreover, starch and protein may contaminate the NDF residue (Theander and Åman, 1980).

There has over the last two decades been a rapid growth in the development of robust and reproducible enzymatic-chemical methods for the determination of LMW-sugars, starch and cell wall and intracellular NSP (Bach Knudsen and Li, 1991; Englyst et al., 1994; Theander et al., 1994; Åman et al., 1985). These methods were in most cases developed for the analysis of foodstuffs but they can also be applied to feedstuffs. Over the last few years we have performed systematically characterisation of the carbohydrate composition and lignin content of a broad range of plant materials used in animal

production. These analyses include quantification of the LMW-sugars, fructan, starch, β-glucan and analysis of individual soluble and insoluble NSP constituents and lignin. This paper deals with the carbohydrate composition of the plant materials while a separate paper will correlate these findings to the energy values measured in pigs.

2. Materials and methods

2.1. Materials

A total of 115 samples covering 38 feedstuffs from cereal grains (barley, wheat, rye, oat and corn), cereal by-products (hull, bran, middling, feed meal and flour), cereal substitutes (tapioca), protein concentrates (meal and cake of soy bean, rape seed, cotton seed and sunflower and white and coloured flowered peas, faba beans and white lupin), grass meals, alfalfa meal and dried sugar beet fibre were used in the present study. The samples represent a broad range of feedstuffs present on the Danish and European feedstuff market.

Before the chemical analysis the samples were ground in a hammer sample mill to pass a 1.0 mm screen when determining Klason lignin and in a Tecator cyclone sample mill to pass a 0.5 mm screen for the analyses of the other chemical components.

2.2. Methods

All samples were analysed in duplicate. The dry matter (DM) content was determined by drying to constant weight at 105°C. Ash was analysed according to the Association of Official Analytical Chemists (1975), protein (N × 6.25) by the Kjeldahl method using a Kjell-Foss 16200 autoanalyser while fat (hydrochloric acid-fat) was extracted with diethyl ether after acid-hydrolysis and analysed as described by Stoldt (1952). The LMW-sugars method is a modification of that described by Bach Knudsen and Li (1991). Samples of approximately 500 mg were weighed into 50 ml centrifuge tubes with screw caps. Ten to fifteen millilitres (depending on the sugar concentration) of 50% (v/v) ethanol including an internal standard (arabinose, 1 mg ml^{-1}) were added and the samples sonicated and extracted in a water bath for 60 min at 65°C. During extraction the centrifuge tubes were mixed (vortex mixer) at least three times and finally centrifuged (2200 *g*, 20 min). An aliquot of 5 ml were removed from the supernatant and filtered through a Bond Elude C_{18} cartridge (Analytichem International, Harbor City, CA, USA) prewetted with 2 ml of methanol and 5 ml deionized water; the first 1.5 ml of eluate was collected and further filtered through a 0.22 μm PTFE filter (Minisart NMLPF, Sartorius AG, Göttingen, Germany), taken to dryness under vacuum at 50°C (Vortex-Evaporator, H. Haake Buchler Product, Saddle Brook, NJ, USA) and 20 μl used for HPLC determination. The HPLC system used consisted of a Model 510 solvent delivery pump, Model 410 refractive index detector, temperature control module (Waters Chromatography Division, Milford, MA, USA), Model 7126 injector valve (Rheodyne Inc. Catati, CA, USA), Model LCI-100 recording integrator with build-in printer/plotter (Perkin-Elmer Inc., Norwalk, CT, USA) and an Shodex Ionpak KS-901 (8 mm × 300

mm) resin-based column in the sodium form (Showa Denko K.K., Tokyo, Japan). Water was used as mobile phase, flow rate was 0.6 ml min^{-1} and column temperature was kept constant at 85°C. Fructan was extracted with acetate buffer (0.1 mol l^{-1}, 65°C, pH 5.0), hydrolysed to monosaccharides with sulphuric acid (0.037 mol l^{-1}, 80°C, 70 min) and quantified by specific enzymes (Larsson and Bengtsson, 1983). Fructan was calculated as total fructose in hydrolysate corrected for free fructose and fructose from sucrose and converted to oligosaccharides by the factor 0.92. Starch was analysed enzymatically using a modification of the method of Bach Knudsen et al. (1987). The samples (150 mg) were weighed into 50 ml centrifuge tubes with screw caps. Acetate-buffer (0.1 M, pH 5.0, 30 ml) and thermostable α-amylase (EC 3.2.1.1, Termamyl® 120L, Novo Nordisk A/S, Copenhagen, Denmark, 120 KNU g^{-1}, 100 μl) were added and the samples incubated for 1 h at 100°C. During the incubation, the centrifuge tubes were mixed (vortex mixer) at least three times. Further degradation of the released oligosaccharides to glucose monomers was achived by incubation with amyloglucosidase from *Aspergillus niger* (EC 3.2.1.3, Boehringer Mannheim, GmbH, Mannheim, Germany, Cat No. 737 160, 140 U ml^{-1}, 200 μl) for a further 2 h at 60°C. The tubes were centrifuged (2200 *g*, 10 min) and the glucose monomers released in the supernatant after dilution (1000 μl, 50 ml) quantified with a glucose oxidase reagent (EC 1.1.3.4, Boehringer Mannheim GmbH, Cat No. 124001 or Megazyme Ltd., Altona Place, Australia, Cat No. K-Gluc). Total mixed linked β-glucan in the feed sample was hydrolysed to β-gluco-oligosaccharides with lichenase (EC 3.2.1.73, MegaZyme Ltd., Altona Place, Australia, Cat No. E-Lichn) and to glucose by β-glucosidase (EC 3.2.1.21, MegaZyme Ltd., Cat No. E-BGluc) and the released glucose monomers finally quantified by the glucose oxidase reagent (Boehringer Mannheim GmbH or MegaZyme Ltd.) (McCleary and Glennie-Holmes, 1985).

Total, soluble and insoluble NSP and their constituent sugars were determined as alditol acetates by gas-liquid chromatography (GLC) for neutral sugars, and by a colorimetric method for uronic acids using a modification of the Uppsala (Theander and Westerlund, 1986; Theander and Åman, 1979) and the Englyst et al. (1982) procedures. Three parallel runs (Procedure A, B and C) were performed. The samples (125 mg if DF > 200 g kg^{-1} and 250 if DF < 200 g kg^{-1}) were weighed into 50 mg centrifuge tubes with screw caps. Acetate-buffer with $CaCl_2$ (0.1 mol l^{-1}/20 mmol L^{-1}, pH 5.0, 9.8 ml) and termostable α-amylase (Termamyl, Novo Nordisk A/S, 100 μl) were added and the samples incubated for 1 h at 100°C. During the incubation, the centrifuge tubes were mixed three times. Complete degradation of starch was done with treatment with a β-glucanase free amyloglucosidase from *Aspergillus niger* (Boehringer Mannheim GmbH, Cat No. 1202 367; 135 U ml^{-1}; 100 μl) for further 2 h at 60 °C. Soluble NSP were precipitated with four volumes of 99% (v/v) ethanol for 1 h on ice bath, the tubes centrifuged (2200 *g*, 10 min) and the supernatant discarded. The residues were washed twice with 85% (v/v) ethanol and once with acetone and dryed in a hood over night. The polysaccharides in starch free residues were treated with 12 mol l^{-1} H_2SO_4 (35°C, 60 min) and hydrolysed to monosaccharides with 1 mol l^{-1} (100°C, 120 min). To an aliquot of the hydrolysate was added an internal standard (allose, 2 mg l^{-1}) and the sugars reduced to alcohols with potassium borohydride, and acetylated using 1-methylimidazole (Connors and Pandit, 1978) to catalyse the reaction. GLC of con-

stituent sugars were performed on a Hawlett Packard 5890 fitted with a flame-ionisation detector. A 30m × 0.32 i.d. narrow-bore capillary column (Supelco SP 2380, Cat No. 2-4116) was used. The column temperature was 210°C and the injector and detector temperature 260°C. Helium was used as carrier gas. Uronic acids were measured by the colorimetric method of Scott (1979). To 0.5 ml of hydrolysate and standars (0, 12.5, 50.0, 75.0, 100.0 μg ml^{-1} of D-galacturonic acid) in 30.0 ml centrifuge tubes, was added 0.5 ml of a sodium solution-boric acid solution and the tubes mixed. Five millilitres of sulfuric acid were added, the samples vortex mixed immediately and the tubes placed in a fume-cupboard at 70°C for 40 min. After cooling 0.2 ml of dimethylphenol solution (0.1 g 3,5-$[(CH_3)_2C_6H_3OH]$ in 100 ml glacial acetic acid) was added, the samples vortex mixed and the samples measured spectrofotometrically at 400 and 450 nm after 15 min. To correct for inteferences from hexoses the reading at 400 nm was subtracted from that at 450 nm. All the constituent sugar values were corrected for losses during hydrolysis and converted to the equivalent polysaccharides values using appropiate convertion factors; 0.88 for pentoses and deoxyhexoses and 0.9 for other hexoses. Procedure B was similar to Procedure A except that the swelling of the cellulose with 12 mol l^{-1} of sulphuric acid was omitted and the non-cellulosic polysaccharides (NCP) in the starch free residue hydrolysed directly with 1 mol l^{-1} of sulphuric acid. In Procedure C the soluble NSP (S-NSP) in the starch-free residue was extracted by a phosphate buffer (Englyst et al., 1982) at neutral pH (0.2 mol l^{-1}, 100°C, 60 min, pH 7.0) and the neutral and acidic sugars in the insoluble NSP (I-NSP) analysed as described for total NSP.

Cellulose was calculated as:

$$\text{cellulose} = \text{NSP}_{\text{glucose(12 mol l}^{-1})} - \text{NSP}_{\text{glucose(1 mol l}^{-1})}, \quad (1)$$

NCP were calculated as:

$$\text{NCP} = (\text{rhamnose} + \text{arabinose} + \text{xylose} + \text{galactose} + \text{glucose} + \text{uronic acids}), \quad (2)$$

and S-NCP as:

$$\text{S-NCP} = \text{Total-NCP} - \text{I-NCP} \quad (3)$$

For the calculation of NCP average values for the individual NCP sugar residue values from Procedures A and B were used. Klason lignin was measured gravimetrically as the residue resistant to 12 mol l^{-1} H_2SO_4 (Theander and Westerlund, 1986; Theander and Åman, 1979). Klason lignin was measured separately following essentially the Procedure A except that 500 mg samples were used and the amyloglucosidase treatment was omitted.

2.3. Calculations and statistical analyses

The results are presented as average values and, if three and more samples were analysed, standard deviations (SD). The analysed value for carbohydrates and lignin (A-CHO + L) was calculated as:

$$\text{A-CHO} + \text{L} = \text{LMW-sugars} + \text{fructans} + \text{starch} + \text{total NSP} + \text{Klason lignin} \quad (4)$$

and the calculated (C-CHO + L) value as:

$$\text{C-CHO} + \text{L} = 1000 - (\text{ash} + \text{protein} + \text{fat}) \quad (5)$$

The difference between calculated and analysed values was calculated as:

$$\Delta\text{-CHO} + \text{L} = \text{C-CHO} + \text{L} - \text{A-CHO} + \text{L} \quad (6)$$

Delta CHO + L was tested statistically by a one-way analysis of variance model according to Snedecor and Cochran (1973):

$$Y_{ij} = \mu + \alpha_i + \epsilon_{ij} \quad (7)$$

where Y_{ij} is the dependent variable, μ is the overall mean, α_i the effect of feedgroups (i.e. cereals (C), cereal by-products (CB) etc.) and ϵ_{ij} is a normal distributed residues.

The correlation between dietary constituents was examined by linear regression as described by Box et al. (1978):

$$Y_i = \alpha + \beta X_i + \epsilon_i \quad (8)$$

where Y_i is the dependent variable, α is the intercept, β is the slope of the regression and ϵ_i a normally distributed residues.

3. Results

All the results are expressed as g kg^{-1} dry matter throughout the text.

3.1. Recovery of carbohydrates and lignin by the applied methods

Carbohydrates and lignin were in all but the maize gluten fraction (238 g kg^{-1}) and soybean protein concentrate (275 g kg^{-1}) the predominant dietary constituents with values in the range: cereals 787–850 g kg^{-1}; cereal by-products 674–940 g kg^{-1}; cereal substitute 895 g kg^{-1}; protein concentrates 399–728 g kg^{-1} and fibre rich materials 631–845 g kg^{-1} (Tables 1–6). In spite of the complexity of the feedstuff matrix there was a good correlation between the calculated and analysed values for carbohydrates and lignin with no systematic variations between the individual feedstuff groups. The average calculated value was 687 g kg^{-1} and the analysed value 689 g kg^{-1} and the correlation between calculated and analysed values was 0.985 ($P < 0.0001$).

A statistical analysis of the difference between the calculated and analysed values showed a tendency to a significant deviation between calculated and analysed values for the fibre rich materials. However, it was only the alfalfa meal that deviated significantly from the other samples with a delta value of -87 g kg^{-1}. The other samples of the fibre rich materials and peas, faba beans and lupin, that were among the most difficult plant materials to handle in the fibre analysis, were all within the range -54 g kg^{-1} to $+63$ g kg^{-1}.

3.2. Whole grain cereals and cereal by-products

The concentration of LMW-sugars was low in the whole grains with values in the range of 20 to 30 g kg^{-1} (Table 1). The level of LMW-sugars was in general higher in the brans, feed meal and middlings (32–75 g kg^{-1}) than in the whole grains (Table 2).

Table 1
Carbohydrate and lignin (g kg^{-1} dry matter) in whole grain cereals

	Maize		Wheat		Rye		Barley				Oats			
	Mean	SD [a]	Mean	SD	Mean	SD	Hulled		Hulless		Hulled		Hulless	
							Mean	SD	Mean	SD	Mean	SD	Mean	SD
Number of samples	3		5		7		10		6		3		4	
LMW-sugars [b]														
Monosaccharides	4	1	3	0	6	2	4	2	n.m. [c]		2	1	n.m.	
Sucrose	13	1	11	2	19	3	12	7	n.m.		11	2	n.m.	
Raffinose	2	0	4	1	4	1	5	1	n.m.		3	1	n.m.	
Stachyose	1	0	2	0	3	1	1	1	n.m.		2	1	n.m.	
Total sugars	20	2	19	1	32	3	21	7	n.m.		17	4	n.m.	
Starch	690	18	651	27	613	5	587	31	645	17	468	25	557	38
Fructan	6	2	15	3	31	2	4	1	n.m.		3	2	n.m.	
NSP [d]														
β-glucan	1	1	8	1	16	2	42	5	42	6	28	3	41	8
S-NCP [e]	9	7	25	4	42	11	56	10	50	10	40	13	54	7
Rhamnose	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Arabinose	3	2	7	2	12	2	6	1	3	1	3	1	3	1
Xylose	2	2	9	4	20	7	6	3	4	1	2	3	2	1
Mannose	2	1	2	1	2	1	2	1	1	< 1	2	1	1	1
Galactose	1	1	2	1	1	1	1	1	1	< 1	2	1	2	0
Glucose	1	1	4	3	6	4	39	7	41	8	28	5	45	7
Uronic acids	1	1	1	1	1	1	2	1	1	1	3	4	2	1
I-NCP [f]	66	11	74	6	94	9	88	10	64	11	110	9	49	10
Rhamnose	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Arabinose	19	2	22	1	24	1	22	1	17	1	15	0	10	1
Xylose	28	3	38	3	41	4	50	4	24	4	78	8	21	7
Mannose	1	1	1	1	3	1	2	1	3	0	1	0	2	1
Galactose	4	1	2	1	4	1	2	1	2	0	5	0	2	0
Glucose	9	4	7	3	20	6	8	6	17	6	5	2	11	2
Uronic acids	6	1	4	1	3	0	4	0	1	0	7	0	3	1
Cellulose	22	3	20	4	16	3	43	5	10	3	82	5	14	6
Total NSP	97	2	119	11	152	10	186	11	124	10	232	10	116	19
Klason lignin	11	2	19	2	21	2	35	3	9	2	66	9	32	6
Dietary fibre	108	4	138	10	174	10	221	13	133	12	298	19	148	23
CHO [g] and lignin:														
Analysed	823	11	823	18	850	8	834	24	n.m.		787	42	n.m.	
Calculated	830	5	814	14	849	11	823	20	n.m.		770	14	n.m.	

[a] Standard deviation.
[b] Low-molecular weight sugars.
[c] Not measured.
[d] Non-starch polysaccharides.
[e] Soluble non-cellulosic polysaccharides.
[f] Insoluble non-cellulosic polysaccharides.
[g] Carbohydrates.

In bran, LMW-sugars varied from 17 g kg^{-1} in oat bran to 76 g kg^{-1} in rye bran and in hulls from 14 g kg^{-1} in oat hull to 32 g kg^{-1} in barley hull. Sucrose was the major component of LMW-sugars accounting in most cases for 50–60% of the LMW-sugars.

Table 2
Carbohydrates and lignin (g kg^{-1} dry matter) in cereal by-products

	Maize					Wheat			
	Feed meal	Gluten fraction	Gluten feed	Flour	Bran	Flour	Bran Mean	Bran SD [a]	Middlings
Number of samples	2	1	2	2	2	2	3		1
LMW-sugars [b]									
Monosaccharides	6	2	6	4	5	1	7	1	4
Sucrose	29	2	25	6	21	8	30	6	20
Raffinose	4	1	5	1	4	3	12	3	9
Stachyose	1	1	2	0	1	3	4	0	3
Total sugars	40	6	41	10	32	17	53	9	36
Starch	566	207	282	902	376	820	222	91	575
Fructan	2	0	2	2	4	16	20	2	23
NSP [c]									
β-glucan	1	1	2	1	2	4	24	5	26
S-NCP [d]	10	6	34	8	32	16	29	15	71
Rhamnose	0	0	0	0	0	0	0	0	0
Arabinose	1	1	7	3	6	3	7	2	21
Xylose	2	1	7	3	5	7	10	6	31
Mannose	1	3	0	1	1	0	1	1	2
Galactose	1	0	3	1	2	2	2	1	3
Glucose	0	2	2	0	6	2	8	11	11
Uronic acids	4	0	15	1	12	2	2	2	3
I-NCP [e]	114	14	242	13	240	17	273	67	101
Rhamnose	0	0	0	0	0	0	0	0	0
Arabinose	32	3	61	3	66	6	83	17	27
Xylose	46	3	97	3	111	8	138	35	36
Mannose	1	0	4	0	3	1	4	1	6
Galactose	8	0	15	0	18	0	7	1	4
Glucose	10	6	14	5	10	4	27	12	21
Uronic acids	16	2	51	2	32	0	13	6	7
Cellulose	33	5	75	0	83	3	72	16	19
Total NSP	156	25	351	21	354	35	374	72	190
Klason lignin	18	0	32	4	25	0	75	18	11
Dietary fibre	174	25	383	25	379	35	449	90	201
CHO [f] and lignin:									
Analysed	783	238	708	940	791	887	704	20	836
Calculated	774	252	710	904	775	864	707	1	809

[a] Standard deviation.
[b] Low-molecular weight sugars.
[c] Non-starch polysaccharides.
[d] Soluble non-cellulosic polysaccharides.
[e] Insoluble non-cellulosic polysaccharides.
[f] Carbohydrates.

Fructan constituted 15–20 g kg^{-1} in whole grain and bran of wheat and 24–31 g kg^{-1} in rye products. The levels in maize, barley and oats were significantly lower with values in the range 1–6 g kg^{-1}.

Table 3
Carbohydrates and lignin (g kg^{-1} dry matter) in cereal by-products and substitutes

	Rye		Barley		Oats			Tapioca	
	Bran	Middlings	Dehulled	Hull meal	Feed meal	Rolled	Hull meal	Mean	SD [a]
Number of samples	2	1	1	1	2	1	1	3	
LMW-sugars [b]									
Monosaccharides	6	5	2	4	2	2	4	16	10
Sucrose	39	33	7	17	12	12	7	4	2
Raffinose	24	14	4	10	2	3	2	1	0
Stachyose	6	4	1	2	2	2	1	1	1
Total sugars	75	57	15	32	17	19	14	21	13
Starch	87	369	654	174	623	646	213	768	17
Fructan	23	22	5	7	2	1	2	0	0
NSP [c]									
β-glucan	45	37	44	16	42	42	14	0	0
S-NCP [d]	63	62	50	20	42	48	13	23	11
Rhamnose	0	0	0	0	0	0	0	0	0
Arabinose	11	17	4	3	2	4	2	1	1
Xylose	33	30	7	0	1	2	0	0	0
Mannose	1	1	1	0	2	0	1	1	1
Galactose	2	2	2	1	2	2	0	6	3
Glucose	13	10	34	13	33	38	8	5	4
Uronic acids	2	3	1	3	2	2	1	10	3
I-NCP [e]	321	199	58	267	39	37	295	33	1
Rhamnose	0	0	0	0	0	0	0	0	0
Arabinose	67	53	17	48	8	6	26	3	1
Xylose	180	89	29	184	15	11	212	7	1
Mannose	2	6	2	3	1	2	1	2	0
Galactose	10	7	0	5	1	1	9	6	1
Glucose	53	40	8	12	10	13	12	8	5
Uronic acids	8	5	2	15	3	3	35	8	1
Cellulose	39	27	19	192	8	6	196	27	6
Total NSP	422	289	127	478	89	91	505	84	12
Klason lignin	68	39	19	115	19	15	148	23	2
Dietary fibre	490	328	146	594	108	106	653	106	11
CHO [f] and lignin:									
Analysed	674	775	819	806	749	772	882	895	12
Calculated	720	768	834	786	748	766	855	885	10

[a] Standard deviation.
[b] Low-molecular weight sugars.
[c] Non-starch polysaccharides.
[d] Soluble non-cellulosic polysaccharides.
[e] Insoluble non-cellulosic polysaccharides.
[f] Carbohydrates.

Starch was the main polysaccharide of whole grain cereals with values ranging from 468 g kg^{-1} in oats and up to 690 g kg^{-1} in maize. The concentration of starch was significantly higher in hulless than in hulled barley and oats. There was also significant variation in the carbohydrate composition within the individual cereals; in barley the starch content varied from 547 g kg^{-1} to 637 g kg^{-1}, wheat from 608 g kg^{-1} to 678 g

Table 4
Carbohydrates and lignin (g kg^{-1} dry matter) in protein concentrates

	Soybean			Rapeseed				Peas			Faba beans		White lupins	
	Meal		Protein concentrate	Meal		Cake		White flowered		Coloured flowered				
	Mean	SD [a]		Mean	SD	Mean	SD	Mean	SD		Mean	SD	Mean	SD
Number of samples	6		1	4		3		3		2	6		3	
LMW-sugars [b]														
Mono-saccharides	7	1	4	8	1	4	1	9	1	9	5	2	5	2
Sucrose	70	11	0	58	2	68	7	30	4	34	27	4	24	7
Raffinose	10	1	2	4	1	3	0	5	1	3	4	1	10	2
Stachyose	47	4	14	12	3	13	1	23	3	20	16	3	53	14
Verbascose	3	2	1	0	0	0	0	22	11	37	34	9	14	2
Total sugars	137	16	21	82	1	90	7	88	9	102	86	10	104	11
Starch	27	12	69	18	16	15	8	454	43	407	407	50	14	2
NSP [c]														
S-NCP [d]	63	10	81	55	17	43	14	52	8	40	50	8	134	44
Rhamnose	1	1	1	1	1	1	1	1	0	1	1	0	2	1
Arabinose	9	2	13	12	4	13	3	19	4	16	15	2	19	4
Xylose	2	1	5	4	1	2	1	1	1	1	1	1	0	0
Mannose	5	1	2	1	1	1	0	1	1	2	1	0	4	1
Galactose	16	3	30	6	2	5	1	4	1	5	4	1	80	30
Glucose	6	3	2	9	11	3	3	5	1	2	4	2	1	1
Uronic acids	25	4	27	22	2	18	6	20	7	13	24	4	27	10
I-NCP [e]	92	9	67	123	5	103	21	76	28	73	59	45	139	21
Rhamnose	2	0	1	2	0	2	0	0	0	0	0	0	1	0
Arabinose	17	2	12	31	4	31	9	17	4	19	9	4	24	2
Xylose	17	3	7	13	3	15	5	12	1	11	11	3	36	1
Mannose	8	2	7	5	1	4	1	1	1	1	1	0	5	2
Galactose	25	3	24	13	1	15	4	3	1	4	2	1	63	16
Glucose	1	2	2	12	14	5	4	31	16	22	28	43	1	1
Uronic acids	23	3	14	39	7	32	1	12	5	17	9	5	12	5
Cellulose	62	18	30	52	3	59	11	53	9	65	81	12	131	31
Total NSP	217	27	177	220	20	205	20	180	27	178	190	50	405	54
Klason lignin	16	4	8	134	19	90	31	12	10	29	20	8	12	2
Dietary fibre	233	26	185	354	10	295	12	192	30	207	210	55	416	54
CHO [f] and lignin:														
Analysed	400	15	275	454	17	399	13	735	9	717	705	31	534	47
Calculated	416	17	277	457	12	n.m. [g]	n.m.	709	17	687	665	28	498	31

[a] Standard deviation.
[b] Low-molecular weight sugars.
[c] Non-starch polysaccharides.
[d] Soluble non-cellulosic polysaccharides.
[e] Insoluble non-cellulosic polysaccharides.
[f] Carbohydrates.
[g] Not measured.

kg^{-1}, and in oats from 443 g kg^{-1} to 492 g kg^{-1}. The variation in starch and in maize and rye was lower (~ 30 g kg^{-1}).

The concentration of starch in cereal by-products varied considerably (87–902 g kg^{-1}). The lowest level was found in the hull meals, the brans and middlings with values in the range 87–575 g kg^{-1}, whereas the flours, the dehulled fractions of barley and oats (feed meal and rolled oats) contained more starch (623–902 g kg^{-1}) than their whole grain counterparts.

Total β-glucan was found in levels of 28–45 g kg^{-1} in hulled and hulless barley and

Table 5
Carbohydrates and lignin (g kg^{-1} dry matter) in protein concentrates

	Cottonseed			Linseed meal	Coconut cake	Palm cake	Sunflower cake	Sunflower cake partly dehulled
	Cake							
	Mean	SD [a]	Meal					
Number of samples	3		1	1	1	1	2	1
LMW-sugars [b]								
Monosaccharides	2	2	3	3	7	5	5	5
Sucrose	10	6	16	28	113	17	36	33
Raffinose	39	13	35	10	2	2	14	14
Stachyose	14	7	13	2	2	0	3	5
Verbascose	1	1	2	0	0	0	0	0
Total sugars	66	12	69	42	124	24	58	56
Starch	18	11	19	27	10	11	10	17
NSP [c]								
S-NCP [d]	61	18	66	138	32	32	57	52
Rhamnose	1	1	0	6	1	0	2	1
Arabinose	16	1	11	17	5	3	8	9
Xylose	6	9	17	38	0	0	4	4
Mannose	1	0	1	1	12	16	1	1
Galactose	7	1	6	21	7	3	5	5
Glucose	6	6	14	10	3	3	5	5
Uronic acids	23	3	18	45	4	7	34	27
I-NCP [e]	103	23	127	112	336	361	136	99
Rhamnose	1	1	1	1	0	0	2	1
Arabinose	18	6	23	19	9	9	23	17
Xylose	54	21	68	28	8	31	55	38
Mannose	3	1	3	3	294	293	11	9
Galactose	5	1	6	12	18	12	8	7
Glucose	2	3	0	27	1	4	12	5
Uronic acids	22	3	27	23	6	12	33	26
Cellulose	92	30	90	53	54	73	123	89
Total NSP	257	45	283	303	422	466	315	240
Klason lignin	83	6	92	119	66	136	133	86
Dietary fibre	340	50	375	423	488	602	448	326
CHO [f] and lignin:								
Analysed	423	43	462	493	622	636	517	399
Calculated	454	47	485	501	640	688	534	439

[a] Standard deviation.
[b] Low-molecular weight sugars.
[c] Non-starch polysaccharides.
[d] Soluble non-cellulosic polysaccharides.
[e] Insoluble non-cellulosic polysaccharides.
[f] Carbohydrates.

oats, dehulled barley, oat feed meal and rolled oats and rye bran and middlings. The level in whole grain rye was 16 g kg^{-1}, in wheat bran and middling 24–26 g kg^{-1}. β-glucan was a minor constituent in whole grain maize and wheat and all maize by-products with values below 8 g kg^{-1}.

Table 6
Carbohydrates and lignin (g kg^{-1} dry matter) in fibre rich materials

	Grass meal						Alfafa	Sugar beet fibre
	First cut		Second cut		Third cut			
	Mean	SD [a]	Mean	SD	Mean	SD		
Number of samples	3		3		3		1	2
LMW-sugars [b]								
Monosaccharides	61	5	45	8	32	7	8	5
Sucrose	22	9	19	5	13	5	13	27
Raffinose	4	1	3	1	4	4	2	1
Stachyose	3	1	3	0	2	1	0	0
Total sugars	90	6	69	6	51	17	23	32
Starch	25	6	24	3	14	4	68	0
Fructan	60	16	27	8	15	10	6	0
NSP [c]								
S-NCP [d]	38	8	24	5	31	7	77	407
Rhamnose	2	1	1	1	1	1	2	6
Arabinose	5	1	3	1	4	1	7	99
Xylose	0	0	0	0	0	0	4	1
Mannose	3	1	2	1	3	1	1	0
Galactose	3	2	3	1	3	1	5	24
Glucose	2	1	1	1	5	4	11	12
Uronic acids	23	5	12	3	14	2	47	265
I-NCP [e]	165	22	192	12	173	15	113	177
Rhamnose	0	0	0	0	0	0	1	4
Arabinose	21	1	22	1	24	1	18	90
Xylose	85	22	114	13	94	10	52	13
Mannose	3	0	2	0	2	0	6	8
Galactose	8	0	7	0	9	0	10	23
Glucose	24	1	24	5	18	7	2	0
Uronic acids	24	0	23	1	25	3	25	39
Cellulose	162	25	211	15	195	17	139	195
Total NSP	366	38	426	23	398	25	329	779
Klason lignin	162	9	169	13	153	16	128	35
Dietary fibre	527	46	595	36	551	35	457	814
CHO [f] and lignin:								
Analysed	702	48	715	33	631	29	553	845
Calculated	727	56	720	35	668	45	657	805

[a] Standard deviation.
[b] Low-molecular weight sugars.
[c] Non-starch polysaccharides.
[d] Soluble non-cellulosic polysaccharides.
[e] Insoluble non-cellulosic polysaccharides.
[f] Carbohydrates.

The level of DF and NSP in whole grain cereals varied from 108 and 97 g kg^{-1}, respectively, in maize and up to 298 and 232 g kg^{-1}, respectively, in hulled oats. In the by-products the variation in DF and NSP was even bigger. The flours and the materials consisting mostly of endosperm represented the low levels (25–146 and 21–127 g kg^{-1},

respectively) and the brans and hull meals the high levels (379–653 and 354–505 g kg^{-1}, respectively).

The group of NCP was the most abundant polysaccharide constituent of NSP accounting typically for 80–90% of NSP, the exceptions being the hulled varieties of barley and oats and the hull meals, were up to 40% of NSP could be in form of cellulose. The botanical composition of the feedstuffs also had a significant impact on the ratio between I-NCP and S-NCP; in feedstuffs like hulless barley and oats, dehulled barley, oat feed meal and rolled oats there was a high percentage of S-NCP whereas the hull and bran rich fractions had relatively more I-NCP.

The predominant sugar residues of NCP were xylose, arabinose and glucose with some variation in the proportions between the cereals and between I-NCP and S-NCP. In all cases xylose and arabinose were the predominant constituents of I-NCP whereas glucose clearly outlevels these two NCP residues in S-NCP of whole grains and products of barley and oats. In rye products, however, xylose and arabinose were the two main residues also in S-NCP.

Klason lignin varied in the whole grains from 11 g kg^{-1} to 66 g kg^{-1}; maize having the lowest and hulled oats the highest level. Negligible amounts of Klason lignin were found in the maize gluten fraction and in flours of maize and wheat. In wheat and rye bran and barley and oats hull meal the level was 68–75 g kg^{-1} and 115–148 g kg^{-1}, respectively.

With the exception of the maize gluten fraction there was a significant negative correlation ($r = -0.937$, $P < 0.0001$) between the concentration of starch and dietary fibre. There was also a strong correlation between the level of cellulose and lignin ($r = +0.866$, $P < 0.0001$) and the level of β-glucan and soluble NCP ($r = +0.890$, $P < 0.0001$).

3.3. Cereal substitutes

The carbohydrate portion of tapioca amounted 862 g kg^{-1} with most of it as starch (768 g kg^{-1}) (Table 3). LMW-sugars made up only 21 g kg^{-1} and NSP 84 g kg^{-1}.

3.4. Protein concentrates

The concentration of LMW-sugars varied from 24 g kg^{-1} in palm cake and up to 137 g kg^{-1} in soya-bean meal (Tables 4 and 5). Sucrose was the main LMW-sugar component (15–91%) while the remaining part of the LMW-sugars mainly were in the form of raffinose-oligosaccharides—raffinose, stachyose and verbascose. The highest level of raffinose was found in cotton seed cake (39 g kg^{-1}), stachyose in soybean meal and lupin seeds (47–53 g kg^{-1}) and verbascose in faba beans and peas (28–34 g kg^{-1}). The starch content was low in all protein rich feedstuffs (10–30 g kg^{-1}) the exception being peas and faba beans (Table 4). In the two latter feedstuffs the starch content was 436 g kg^{-1} and 407 g kg^{-1}, respectively.

DF and NSP in the protein concentrates were in the range of 185–602 g kg^{-1} and 177–466 g kg^{-1}, respectively. Cellulose was an important constituent of the cell walls making up from 13% of NSP in coconut cake and up to 43% in faba beans. The NCP

contribution was 57–87% with a big variation in the ratio between soluble and insoluble NCP. In soybean protein concentrate, faba beans, white lupins and linseed meal the ratio between S-NCP and I-NCP was ~ 1:1 while in coconut cake and palm cake it was 1:10.

Uronic acids (25–39% of NCP), arabinose (16–25% of NCP) and galactose (6–26% of NCP) were the most important sugar residues of soya-bean meal, rape-seed meal, linseed meal, cottonseed cake, sunflower cake, peas and faba beans. In linseed meal, cotton cake and sunflower cake there was a high content of xylose (27–41% of NCP), while it was noticeable with the high level of mannose (79–83% of NCP) in coconut cake and palm cake.

Klason lignin varied from a low level (12–16 g kg^{-1}) in soybean meal, white flowered peas and white lupins and to high levels in linseed meal (119 g kg^{-1}), sunflower cake (133 g kg^{-1}), rape-seed meal and cake (134 g kg^{-1}) and palm cake (136 g kg^{-1}). The lignin content in coloured-flowered peas was 29 g kg^{-1} compared with 12 g kg^{-1} in white flowered peas.

3.5. Grass meals and dried sugar beet fibre

LMW-sugars and fructan in grass meal were 51–90 g kg^{-1} and 15–60 g kg^{-1}, respectively, with the highest levels found in grass meal from the first cut (Table 6). The level in alfalfa meal was 23 g kg^{-1} of LMW-sugars and 6 g kg^{-1} of fructans. No fructan was detected in sugar beet fibre whereas the level of LMW-sugars was 32 g kg^{-1}. There was no starch in sugar beet fibre; in grass meals the level was in the range 14–25 g kg^{-1} and 68 g kg^{-1} in alfalfa meal.

The DF level was high with values in the range 457–595 g kg^{-1} in alfalfa and grass meals and up to 814 g kg^{-1} in sugar beet fibre. Cellulose was the principal NSP polymer of grass meal and alfalfa meal making up almost 48% of NSP. Over the growing season of the grass there was a significant variation in the concentration of cellulose from 162 g kg^{-1} and up to 211 g kg^{-1}. The lowest concentration of cellulose was found in grass meal from the first cut and the highest concentration in the second cut. The main NCP sugar residues were xylose (42–54% of NCP). The same was the case in alfalfa meal which, however, contained more uronic acids and had a higher content of S-NCP.

S-NCP was the principal component of dried sugar beet fibre accounting for 52% of NSP; the remaining being almost equally distributed between I-NCP and cellulose. Uronic acids (52% of NCP) were responsible for the high level of S-NCP.

There was a high level (128–169 g kg^{-1}) of Klason lignin in grass and alfalfa meals while it was a minor constituent in sugar beet fibre (35 g kg^{-1}).

4. Discussion

The present study demonstrates that it is possible by use of well-known analytical techniques to perform a detailed chemical characterisation of the carbohydrate fraction of plant materials commonly used in animal feeding. Thus for most of the studied plant materials we obtained almost quantitative recovery as judge from the high correlation

between analysed and calculated CHO and lignin. For the whole grain cereals this is in concert with earlier studies where in principle similar analytical techniques have been applied (Theander et al., 1989). For peas and faba beans, however, it cannot be excluded that the higher analysed than calculated CHO and lignin content is due to incomplete removal of starch as found in other studies using the same enzymes to degrade starch (Theander et al., 1994). The underestimation of CHO and lignin in the alfalfa meal sample, however, is more difficult to explain.

It is at present well established that the separation of soluble and insoluble DF components is highly dependent on the extraction procedure applied (Marlett et al., 1989; Monro, 1993). In the present study we have used a phosphate buffer at neutral pH because the pH in the small intestine is about 7 after feeding (e.g. Bach Knudsen et al., 1991). For cereal products (e.g. wheat and oats) this technique also seems to give valuable informations about the bahaviour of NSP in the gastrointestinal tract in particular in relation to the degradation in the large intestine (e.g. Bach Knudsen and Hansen, 1991). However, with pectin rich materials, most of the protein rich feedstuffs and the sugar beet fibre, this method may overestimate the soluble fibre fraction. This is due to β-elimination of polygalacturonic acids during extraction at neutral pH at 100°C. As shown by Albersheim et al. (1960) there was a rapid decrease in viscosity and increase in reducing end groups when extracting pectin at 100°C in neutral solutions indicating splitting of glycosidic bonds within the pectin chain macromolecules.

Whole grain cereals and cereal by-products are used world-wide as an energy and protein source for pigs and other non-ruminant animals, in rations for high-yielding dairy cows and other intensively fed ruminants. As it appears of the present study there was a significant variation in all major carbohydrate components both within whole grain cereals and by-products. The inverse relationship between the concentration of starch and DF in cereals is primarily a consequence of the botanical composition of the grains and the distribution of polymers between the tissues. The husk (oats and barley) and the pericarp/testa (wheat, rye, maize) are mainly composed of NSP and lignin while the predominant polysaccharide of the endosperm is starch embedded in a matrix of largely protein (Fincher and Stone, 1986; Selvendran, 1984). Thus the total concentration of starch and DF will inevitably be strongly influenced by the relative proportion of husk and pericarp/testa relative to the endosperm tissues. In maize, wheat, and rye the proportion of pericarp/testa relative to the endosperm is much lower than the proportion of husk relative to endosperm in barley and oats. Consequently hulled oats and barley have a lower concentration of starch and a higher concentration of all DF components than their hull-less counterparts and maize, wheat and rye. In addition variety, location and year of harvest may have a profound effect on the carbohydrate composition of cereals. This is in agreement with other studies clearly demonstrating that whole grain barley, wheat and oats are not either chemically or nutritionally as homogeneous as earlier believed (Bach Knudsen et al., 1987; Åman, 1987; Åman, 1988; Åman et al., 1985).

The milling procedure of cereals applied when producing flours for human nutrition aims in general at separating the fibre rich aleurone, pericarp/testa and the hull tissues from the starchy endosperm. In the bran and hull fractions there is therefore a lower concentration of starch and a higher concentration of DF primarily in form of cellulose.

I-NCP and lignin than of the corresponding whole grain cereals whereas the opposite is the case with the flour fractions. Moreover, because the bran and hull fractions include cellular tissues that are metabolically active during germination—the germ, scutellum and the aleurone layer—the concentration of LMW-sugars of these fractions is higher than of whole grain cereals and flours.

The level of fructan found in this study is comparable with other investigations with barley, oats, wheat (Åman, 1987; Åman, 1988; Åman et al., 1985) and demonstrate a significant difference between the cereals. Low levels are found in whole grain and by-products of barley and oats, intermediate values in wheat and high values in rye. The nutritional importance of fructan in animal nutrition is at present unknown, but it is believed that it behaves like a soluble NSP component.

The main cell wall polysaccharides of cereals are: arabinoxylans (AX: arabinose, uronic acid and xylose residues); cellulose and β-glucan with some variation between the cereals (Fincher and Stone, 1986; Selvendran, 1984). Glucomannans are only present at low levels whereas pectin polysaccharides are not detected in the cereals analysed but is present in rice (Fincher and Stone, 1986). The husk of oats and barley and the pericarp/testa of wheat, rye and maize are mainly composed of insoluble components in form of AX, cellulose and lignin (Aspinall and Ferrier, 1957; Selvendran, 1984). Soluble and insoluble β-glucan and AX make up the aleurone and endosperm cell walls while glucomannans are found in low levels in the cell walls of the endosperm (Fincher and Stone, 1986). The endosperm, aleurone and subaleurone cell walls of barley, oats and rye have a significantly much higher content of β-glucan compared with wheat and maize (Fincher and Stone, 1986; Selvendran, 1984). This is reflected in the concentrations of β-glucan found to be highest in whole grain cereals and mill fractions of barley, oats and rye and with significantly lower values in comparable fractions of wheat and maize. From the literature it is known that the ratio between soluble and insoluble β-glucan varies. Earlier studies have shown that approximately 54% of the β-glucan was soluble in barley but 80% in oats (Åman and Graham, 1987).

Tapioca, because of the high carbohydrate content, is primarily used as a substitute for cereals when feeding pigs. The bulk of carbohydrate is present as starch in levels comparable with the flours, while the concentration of LMW-sugars and DF is low. The main NSP components are cellulose and NCP pectic substances.

By-products of soybean, rape-seed, linseed, cotton, coconut, palm, sunflower and peas, faba beans and white lupins are used as feeds for non-ruminant and ruminant animals, primarily because of their high protein and amino acid content. However, the carbohydrate fraction in these products is also an important energy source, but with a composition that is significantly different from that of cereals. While all cereals contain significant quantities of starch this polysaccharide is only present in peas and faba beans. In contrast, the protein concentrates contain the highest levels of LMW-sugars in form of raffinose oligosaccharides. In agreement with other studies (Bach Knudsen and Li, 1991) the relative proportion of the individual raffinose oligosaccharides varies between the different plants; raffinose is the predominant oligosaccharide in cotton seed meal, stachyose in soybean meal and verbascose in peas and horse beans.

Cellulose is a quantitative important cell wall constituent of all protein concentrates and is found in primary as well as secondary cell wall (Aspinall et al., 1967; Aspinall

and Cottrell, 1971; Selvendran, 1984). The predominant cell wall NCPs of the protein concentrates are rhamnogalacturonans, xylans, xyloglucans, arabinogalactans, galactomannans, arabinans, mannans and galactans (Aspinall and Cottrell, 1971; Daveby and Åman, 1993; Düsterhöft et al., 1991; Selvendran, 1984; Siddiqui and Wood, 1977; Stephan, 1983). Palm cake and coconut cake also contain mannans as intracellular compounds (Düsterhöft et al., 1991; Stephan, 1983). Moreover, in the protein concentrate there is the same relative diversity of polymeric composition of the different cellular tissues as found for the cereals. Thus soybean cotyledons contain less cellulose compared with the hull and the NCPs are neutral arabinogalactans and rhamnogalacturans, while in the hull it is galactomannans, xylan, and pectic substances similar to that found in the cotyledon fibre (Aspinall et al., 1967; Aspinall and Cottrell, 1971). The same is the case in peas where the cotyledon is rich in pectic substances, xyloglucans and cellulose whereas the walls of the hull are rich in cellulose, acidic xylans and pectic substances (Ralet et al., 1993; Selvendran, 1984). For the other protein rich materials analysed in this study we may expect a similar relative distribution of polymers between cellular tissues as described for soybean and peas.

Pectic substances are for all the protein concentrates, but coconut and palm cake the quantitatively most important NSPs. The backbone is in most cases galacturonic acid interspersed with rhamnose bearing side chains composed with galactose, arabinose, xylose and fucose (Aspinall et al., 1967; Aspinall and Cottrell, 1971; Ralet et al., 1993; Stephan, 1983). From the monomeric composition of soluble and insoluble NCPs, it appears that pectic substances represented by uronic acids, galactose and arabinose make up a significant fraction of soluble NCP while other polysaccharides e.g. xylans (xylose) and xyloglucans (xylose and glucose) typically are most abundant in the insoluble fraction. The same is the case with mannan, the predominant NSP in coconut and palm cakes (Düsterhöft et al., 1991).

The fibre rich materials have in general a low energy concentration and is therefore primarily used in diets for sows and in rations for ruminant. Grass meals contain relatively high levels of LMW-sugars with a clear decrease from first to second and third cut. The same is seen for fructan while cellulose and I-NCP run converse; increasing from first to second and third cut. These changes reflect maturation of the cell walls (Jones, 1970) which further is documented by the relative decrease in uronic acids and subsequent absolute and relative increase in cellulose and xylose residues of I-NCP. Pectic substances are always found in primary cell walls with a relative decrease when the plant cell gets older. The higher level of uronic acids in alfalfa than in grass meals is consistent with other studies (Theander and Westerlund, 1993) and suggest, together with the higher rhamnose content, that uronic acids are present in pectins rather than in acidic xylans. Moreover, in alfalfa meal there was identified starch at levels of ~ 60 g kg^{-1} clearly higher than seen for grass meals.

Sugar beet fibre has the highest DF levels of all the investigated plant materials. In agreement with other studies (Theander et al., 1989) the predominant constituents are uronic acids and arabinose residues; markers for pectic substances and the highly branched araban (Stephan, 1983).

Lignin is the cell wall component that cements and anchors together cell wall polysaccharides (Iiyama et al., 1994). In this way lignin has important implications for

the physico-chemical properties of the cell walls in vitro and in vivo and for the degradation of NSP. The term Klason lignin as used in this study and the Uppsala procedure, however, is not a well defined chemical entity but an empirical residue consisting of materials not solubilised by sulphuric acid such as e.g. condensed tannins and proteins (Carre and Brillouet, 1986; Theander et al., 1977). Compared with other studies using the Uppsala procedure the values for lignin in the present study appears to be slightly higher for whole grain wheat, barley, wheat bran, peas and soybean meal (Theander et al., 1989; Åman, 1987; Åman et al., 1985) but lower for whole grain oats (Åman, 1987) than reported previously. The reason for that is at present uncertain but the coarse grinding, protein contamination and laboratory differences are the most likely reasons. The high concentration of lignin in rapeseed cake and meals is without any doubt due to the presence of condensed tannins in these plant materials as demonstrated by Theander et al. (1977). Condensed tannins also explain the higher lignin value of coloured-flowered peas as compared to white-flowered peas (Daveby and Åman, 1993). In spite of these shortcomings, however, this study showed a wide variation in the lignin concentration within and between the different subgroups of plant materials. In whole grain cereals and by-products there is a high correlation between lignin and cellulose with the hull meals and the flours representing high and low values, respectively. This relation also seems to be valid for grass and alfalfa meals. In contrast these two dietary constituents are clearly independent in protein concentrates and sugar beet fibre.

In conclusion, the present study shows that the analytical methods can be used to perform a detailed characterisation of the carbohydrates and lignin in a broad range of plant materials used in animal feeding. It is the authors strong belief that these methods may be useful tools for nutritionists in obtaining a better understanding of the gastro-intestinal and metabolic implications of the various types of carbohydrates.

Acknowledgements

This study received financial support from the Danish Agricultural and Veterinarian Research Council. The author wish to acknowledge the technical staff at the Department of Nutrition for excellent assistance and the late Bjørn O. Eggum for his advice during the course of the work.

References

Albersheim, P., Neukom, H., Deuel, H., 1960. Splitting of pectin chain molecules in neutral solutions. Arch. Biochem. Biophys. 90, 46–51.

Aspinall, G.O., Beghie, R., McKay, J.E., 1967. Polysaccharide components of soybeans. Cereal Sci. Today 12, 225–230.

Aspinall, G.O., Cottrell, I.W., 1971. Polysaccharides of soybeans. VI: Neutral polysaccharides from cotyledon meal. Canadian J. Chem. 49, 1019–1022.

Aspinall, G.O. and Ferrier, R.J., 1957. The constitution of barley husk hemicellulose. J. Chem. Soc., 4188-4194.

Association of Official Analytical Chemists, 1975. Official Methods of Analysis. Association of Official Analytical Chemists, Washington, DC, 1094 pp.

Bach Knudsen, K.E., Hansen, I., 1991. Gastrointestinal implications in pigs of wheat and oat fractions 1. Digestibility and bulking properties of polysaccharides and other major constituents. Br. J. Nutr. 65, 217–232.

Bach Knudsen, K.E., Jensen, B.B., Andersen, J.O., Hansen, I., 1991. Gastrointestinal implications in pigs of wheat and oat fractions 2. Microbial activity in the gastrointestinal tract. Br. J. Nutr. 65, 233–248.

Bach Knudsen, K.E., Li, B., 1991. Determination of oligosaccharides in protein-rich feedstuffs by gas-liquid chromatography and high-performance liquid chromatography. J. Agric. Food Chem. 39, 689–694.

Bach Knudsen, K.E., Åman, P., Eggum, B.O., 1987. Nutritive value of danish-grown barley varieties. I. Carbohydrates and other major constituents. J. Cereal Sci. 6, 173–186.

Bailey, R.W., Ulyatt, M.J., 1970. Pasture quality and ruminant nutrition. II. Carbohydrate and lignin composition of detergent extracted residues from pasture grasses and legumes. N.Z. J. Agric Res. 13, 591–604.

Box, G.E.P., Hunter, W.G. and Hunter, J.S., 1978. Statistics for experiments. John Wiley, Toronto, 653 pp.

Carre, B., Brillouet, J.M., 1986. Yield and composition of cell wall residues isolated from various feedstuffs used for non-ruminant farm animals. J. Sci. Food Agric. 37, 341–351.

Connors, K.A., Pandit, N.K., 1978. N-methylimidazole as a catalyst for analytical acetylations of hydroxy compounds. Anal. Chem. 50, 1542–1545.

Daveby, Y.D., Åman, P., 1993. Chemical composition of certain dehulled legume seeds and their hulls with special reference to carbohydrates. Swed. J. Agric. Res. 23, 133–139.

Düsterhöft, E.M., Voragen, G.J., Engels, F.M., 1991. Non-starch polysaccharides from sunflower (*Helianthus annuus*) meal and palm kernel (*Elaeis guineenis*) meal preparation of cell wall material and extraction of polysaccharide fractions. J. Sci. Food Agric. 55, 411–422.

Englyst, H.N., Quigley, M.E., Hudson, G.J., 1994. Determination of dietary fibre as non-starch polysaccherides with gas-liquid chromatography, high-performance liquid chromatography or spectrophotometric measurements of constituent sugars. Analyst 119, 1497–1509.

Englyst, H.N., Wiggins, H.S., Cummings, J.H., 1982. Determination of non-starch polysaccharides in plant foods by gas-liquid chromatography of constituent sugars as alditol acetates. Analyst 107, 307–318.

Fincher, G.B. and Stone, B.A., 1986. Cell walls and their components in cereal grain technology. In: Y. Pomeranz (Editor). Advances in Cereal Science and Technology. American Association of Cereal Chemists, St. Paul, pp. 207-295.

Gallant, D.J., Bouchet, B., Buléon, A., Pérez, S., 1992. Physical characteristics of starch granules and susceptibility to enzymatic degradation. Euro. J. Clin. Nutr. 46 (Suppl. 2), S3–S16.

Henneberg, W., Stohmann, F., 1859. Über das Erhaltungsfutter volljährigen Rindviehs. J. Landwirtsch. 3, 485–551.

Iiyama, K., Lam, T.B.T., Stone, B.A., 1994. Covalent cross-links in the cell wall. Plant Physiol. 104, 315–320.

Jones, D.I.H., 1970. Cell-wall constituents of some grass species and varieties. J. Sci. Fd. Agric. 21, 559–562.

Larsson, K. and Bengtsson, S., 1983. Bestämning av lättilgängeliga kolhydrater i växtmaterial (Determination of readily available carbohydrates in plant material). Methods report No. 22. National Laboratory of Agricultural Chemistry, Uppsala.

Marlett, J.A., Chesters, J.G., Longacre, M.J. and Bogdanske, J.J., 1989. Recovery of soluble dietary fiber is dependent on the method of analysis. Am. J. Clin. Nutr. 50: 479-485.

McCleary, B.V., Glennie-Holmes, M., 1985. Enzymic quantification of (1-3), (1-4)-β-D-glucan in barley and malt. J. Inst. Brew. 91, 285–295.

Monro, J.A., 1993. A nutritionally valid procedure for measuring soluble dietary fibre. Food Chem. 47, 187–193.

Ralet, M.C., Saulnier, L., Thibault, J.F., 1993. Raw and extruded fibre from pea hulls. Part II: Structural study of the water-soluble polysaccharides. Carbohydr. Polymers 20, 25–35.

Reichert, R.D., 1981. Quantitative isolation and estimation of cell wall materials from dehulled pea (*Pisum satitum*) flours and concentrates. Cereal Chem. 58, 266–270.

Scott, R.W., 1979. Colorimetric determination of hexuronic acids in plant materials. Anal. Chem. 51, 936–941.

Selvendran, R.R., 1984. The plant cell wall as a source of dietary fibre: chemistry and structure. Am. J. Clin. Nutr. 39, 320–337.

Siddiqui, I.R., Wood, P.J., 1977. Carbohydrates of rapeseed: A review. J. Sci. Food Agric. 28, 530–538.

Snedecor, G.W. and Cochran, W.G., 1973. Statistical Methods. Iowa State University Press, Ames, IO. 593 pp.

Stephan, A.M., 1983. Other plant polysaccharides. In: G.O. Aspinal (Editor). The Polysaccharides, Volume 2. Academic Press, NY, pp. 97-193.

Stoldt, W., 1952. Vorschlag zur Vereinheitlichung der Fettbestimmung in Lebensmitteln (Suggestion to standardise the determination of fat in foodstuffs). Fette, Seifen, Anstrichmittel 54, 206–207.

Theander, O. and Westerlund, E., 1993. Quantitative analysis of cell wall components. In: H.G. Jung, D.R. Buxton, R.D. Hartfield and J. Ralph (Editors). Forage Cell Wall Structure and Digestibility. American Society of Agronomy, Inc., Madison, WI, pp. 83-104.

Theander, O., Westerlund, E., Åman, P., 1993. Structure and components of dietary fiber. Cereal Foods World 38, 135–141.

Theander, O., Westerlund, E., Åman, P., Graham, H., 1989. Plant cell walls and monogastric diets. Anim. Feed Sci. Technol. 23, 205–225.

Theander, O., Westerlund, E.A., 1986. Studies on dietary fiber. 3. Improved procedures for analysis of dietary fiber. J. Agric. Food Chem. 34, 330–336.

Theander, O., Åman, P., 1979. Studies on dietary fibre. 1. Analysis and chemical characterization of water-soluble and water-insoluble dietary fibres. Swed. J. Agric. Res. 9, 97–106.

Theander, O., Åman, P., 1980. Chemical composition of some forages and various residues from feeding value determinations. J. Sci. Food Agric. 31, 31–37.

Theander, O., Åman, P., Miksche, G.E. and Yasuda, S., 1977. Carbohydrates, polyphenols, and lignin in seed hulls of different colors from turnip rapeseed. J. Agri. Food Chem. 25: 270-273.

Theander, O., Åman, P., Westerlund, E., Graham, H., 1994. Enzymatic/chemical analysis of dietary fiber. J. AOAC 77, 703–709.

Van Soest, P.J., 1963. Use of detergents in the analysis of fibrous feeds. II. A rapid method for the determination of fiber and lignin. J. AOAC 46, 829–835.

Van Soest, P.J., Wine, R.H., 1967. Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell-wall constituents. J. AOAC 50, 50–55.

Åman, P., 1987. The variation in chemical composition of Swedish oats. Acta Agric. Scand. 37, 347–352.

Åman, P., 1988. The variation in chemical composition of Swedish wheats. Swed. J. Agric. Res. 18, 27–30.

Åman, P., Graham, H., 1987. Analysis of total and insoluble mixed-linked β(1-3)(1-4)-D-glucans in barley and oats. J. Agric. Food Chem. 35, 704–709.

Åman, P., Hesselman, K., Tilly, A.C., 1985. The variation in chemical composition of Swedish barley. J. Cereal Sci. 3, 73–77.