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Modification of cell-wall polymers of onion waste—Part I. Effect of pressure-cooking

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Abstract

The extraction of polymers from onion cell walls and the mechanical properties of onion tissues can be modified by heating. However, there is little information on the effects of thermal treatments on the chemistry of cell-wall polysaccharides of onion tissues. The present work reports pressure-cooking-induced changes in cell-wall polymers of onion waste. The outer fleshy scale leaves of onion (*Allium cepa* L. cv. Delta and Hysam) were subjected to a range of pressure-cooking times (0, 10, 20, 30 and 50 min, 120°C). Cell-wall material was prepared as cold-alcohol-insoluble residues and subsequently extracted with buffered phenol. The cell-wall material was then extracted sequentially with water, NaCl, imidazole, cyclohexane-*trans*-1,2-diaminetetraacetate (CDTA), Na_2CO_3 and KOH to leave a residue. The samples were analysed for their carbohydrate composition, their degree of methylesterification and the molecular size of selected soluble polysaccharides. Pressure-cooking-induced softening of onion tissue involved cell-wall swelling and cell separation. This was accompanied by an increase in water-soluble pectic polysaccharides and a decrease in the pectic polymers of the imidazole, CDTA, Na_2CO_3 and KOH-soluble fractions and insoluble residue. Pressure-cooking also resulted in a slight decrease in the peak molecular weight of water-soluble polysaccharides.

Keywords: Heat treatment; Pressure-cooking; Cell-wall polymers; Onion waste

1. Introduction

Onions (*Allium cepa* L.) are cultivated widely and a large proportion of them are processed. This yields vast quantities of waste (450 000 tonnes annually in Europe) rich in cell-wall polymers. This waste is not suitable for fodder or landfill disposal because of its characteristic strong flavour and susceptibility to phytopathogens (e.g. *Sclerotium cepivorum*). Therefore, on environmental and economic grounds, there is pressure to exploit this waste for the profitable production of non-food and food-grade products. Indeed, onions have attracted attention as a potentially valuable source of low-cost pectin which is of high quality from the standpoint of moisture, ash content, methoxyl and anhydrouronic acid values (Abdel-Fattah and Edress, 1971; Fenwick, 1985; Redgwell and Selvendran, 1986).

A detailed fractionation of cell walls from inner scale leaves of onion bulbs has already been carried out by Redgwell and Selvendran (1986). More recently, studies have demonstrated considerable variation in the carbohydrate composition of cell-wall pectic polysaccharides between tissues of onions, particularly the brown outer skin and fleshy outer and inner scale leaves (Ng et al., 1998).

In many food processes, onions are heated in order to modify their texture and flavour; heating causes softening through modification of the plant cell walls. It is likely that this will involve dissolution of pectic polymers involved in cell adhesion, probably due to β-eliminative degradation (Sajjaanantakul et al., 1993; Greve et al., 1994a and Greve et al., 1994b; Ng and Waldron, 1997a and Ng and Waldron, 1997b) and will result in cell separation (Van-Buren, 1979; Jarvis and Duncan, 1992; Parker and Waldron, 1995; Brett and Waldron, 1996). Heat treatment of onion waste may also provide the basis for modification and extraction of potentially useful cell-wall polymers. However, there is little definitive information on the effects of heat treatment on the chemistry of cell-wall polysaccharides of onion tissues.

The objective of this study has been to investigate the effects of thermal treatments on the chemistry of cell-wall polysaccharides of outer fleshy scale leaves of onions. The results have been interpreted in relation to tissue mechanical properties and changes in cell-wall morphology.

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2. Materials and methods

2.1. Materials

Onions (*Allium cepa* L. cv. Delta and Hysam) were obtained from local onion producers (Lingarden, Spalding, Lincolnshire, UK) and stored at 4°C. The two outer fleshy scale leaves of the onions (300 g) were cut into pieces (1 cm × 1 cm × 2.5 cm) and subjected to pressure-cooking in a pressure-cooker at 120°C for 0, 10, 20, 30 and 50 min. Water (600 ml) at the bottom of the vessel was collected and dialysed. The thermally-treated onion tissue was cooled briefly in air, frozen in liquid N_2, and stored at −40°C.

Unless otherwise stated, all chemicals are of AnalaR grade.

2.2. Firmness measurement

Firmness measurements of fresh and pressure-cooked onion tissues (20 g per sample, 10 samples per analysis) were determined using an Instron (Model 1122, High Wycombe, UK), with a Kramer shear cell (Kramer and Hawbecker, 1966) as described previously (Ng and Waldron, 1997a). The crosshead speed and chart drive speed on the Instron were 50 mm/min and 50 mm/min, respectively. The area under the force–displacement curve (work done) expressed in Nm was used for firmness measurement.

2.3. Light microscopy

Fresh and pressure-cooked onion tissues were fixed in 3% glutaraldehyde (Agar Scientific Ltd., Stansted, UK) in 0.05 M cacodylate (TAAB Lab., Reading, UK) buffer, pH 7.4 for 3 h. The samples were dehydrated in an ethanol (Fisons, Leicester, UK) series with three changes in 100% (v/v) ethanol, and then infiltrated with the acrylic resin LR White (London Resin Co. Ltd., Reading, UK). The samples were transferred to gelatine capsules containing fresh resin, which was polymerised for 24 h at 60°C. Sections, 1–2 μm thick, were cut with glass knives, dried down onto glass slides and stained with 1% (v/v) toluidine blue (Aldrich, Poole, UK) in 1% (v/v) borax (BDH, Poole, UK), pH 11.

2.4. Preparation of alcohol-insoluble residue (AIR)

Frozen outer scale leaves were homogenised in a Waring blender (Fischer Scientific Instrument, Loughborough, UK) with cold ethanol (85% v/v final concentration), reducing the particle size to less than 5 mm. The cold homogenate was transferred to a stainless steel beaker and homogenised with an Ystral homogeniser (Scientific Instruments Ltd., Manchester, UK) for 1 min. The homogenate was filtered through 100 μm nylon mesh (John Stannier and Co., Manchester, UK). The residue was further homogenised twice in 85% (v/v) ethanol before being extracted with phenol (BDH) buffer with Tris (250 ml, pH 7; Sigma) for 45 min (Huber, 1991). The buffered phenol was prepared by addition of 100 ml of 500 mM Tris, pH 7.5, to 200 g of phenol. The suspension was stirred and allowed to stand for 8 h and the lower layer was used. The residue was recovered by centrifugation and washed three times with ethanol (85% v/v), acetone (Fisons), and dried overnight in a fume cupboard.

The ethanol extracts were reduced by rotary evaporation, and then lyophilised. The buffered phenolic extracts were dialysed against acetic acid: water (1:1) and then water (three changes) prior to lyophilisation.

2.5. Sequential extraction of AIR

AIR (1 g) was suspended in water (100 ml, pH 5.1) and stirred for 2 h at 20°C. The water-insoluble residue was further extracted in NaCl (0.136 M, 100 ml, pH 6.5; BDH) for 2 h at 20°C. The residue was then extracted in imidazole (2 M, 100 ml, pH 7; Aldrich, Poole, UK), CDTA (Na salt, 0.05 M, 100 ml, pH 6.5; Aldrich) twice, Na_2CO_3 (0.05 M, 100 ml; containing 0.02 M $NaBH_4$; BDH) twice, at 1°C and then 20°C and KOH (0.5 M, 100 ml; containing 0.02 M $NaBH_4$) as described by Ng et al. (1998). The supernatants were filtered, neutralised where required, and dialysed exhaustively with distilled water prior to concentration and freeze drying.

2.6. Sugar analysis

Cell-wall neutral sugars and uronic acids were analysed as described previously (Parr et al., 1997). Sugars were released from cell-wall material by dispersing in 72% (v/v) H_2SO_4 (Fisons) for 3 h followed by dilution to 1 M and hydrolysing as described by Blakeney et al. (1983) using 2-deoxyglucose (Sigma) as an internal standard. Alditol acetates were quantified by gas chromatography as described in Parr et al. (1997). All samples were analysed in duplicate.

Uronic acid was determined colorimetrically by a modification of the method of Blumenkrantz and Asboe-Hansen (1973) in which each sample was dispersed in 72% (v/v) H_2SO_4 for 3 h at room temperature, diluted to 1 M H_2SO_4, and hydrolysed for 1 h at 100°C.

2.7. Methanol analysis

The degree of methylesterification (DM) was determined as described previously (Ng and Waldron, 1997a). Each sample was dispersed in distilled water (2 ml) and occasionally sonicated for 10 min. Propanol (0.4 ml, 0.2%; BDH) was added as an internal standard. The samples were de-esterified by addition of NaOH (0.8 ml, 2 M; BDH), incubated for 1 h at room temperature and then neutralised with HCl (0.8 ml, 2 M; Fisons). Methanol was quantified by isothermal GLC at 150°C on a 1.3 m × 4 mm

column packed with HayeSep ''P'' 80–100 mesh (Altech, Carnforth, UK) with argon as the carrier gas flowing at 40 ml/min.

2.8. Gel filtration chromatography

Molecular-weight profiles were determined using a Sepharose CL-4B column (Sigma) as decribed previously (Ng and Waldron, 1997a). Samples (approximately 2 mg) were eluted with imidazole buffer (1 M, pH 7, containing 0.02% v/v sodium azide) at a flow rate of 10 ml/h and collected by an LKB Bromma 2111 multirac fraction collector (15 min per fraction; LKB, St. Albans, UK). The collected fractions (2.5 ml) were assayed for total carbohydrate using the phenol/sulphuric acid method of Dubois et al. (1956). Samples were dissolved in 1 ml of buffer and dialysed against buffer before being applied to the column. Dextran (2 mg, Sigma) of size approximately 72 000 and 2 000 000, and sucrose (2 mg, Sigma) of size 342.3 were used for calibration. The bed volume of the column (V_t) was 280 ml and the void volume (V_0) was 27 ml.

2.9. Klason lignin

AIRs of fresh and processed onions were dispersed in 72% (v/v) H_2SO_4 for 3 h at 20°C followed by dilution to 1 M and hydrolysis for 2.5 h at 100°C. The residues were recovered by filtration through 35 μm nylon mesh, washed (three times with water and once with acetone) and dried overnight. The Klason lignin was then quantified gravimetrically.

2.10. Statistical analysis

Analysis of variance and means among samples prepared by various methods were calculated. Duncan's multiple range test was used to determine significant differences ($P < 0.05$).

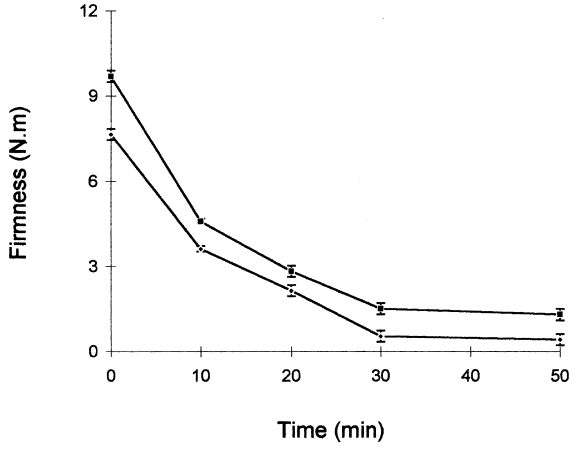

Fig. 1. Firmness of onions: textural change of the varieties Delta – • – and Hysam – ■ – during pressure-cooking.

3. Results and discussion

3.1. Instrumental firmness measurement

The instrumental firmness values of fresh tissues of Delta and Hysam onions were 7.6 and 9.7 Nm, respectively. Pressure-cooking at 120°C reduced the tissue firmness to less than 20% of the original value after 30 min (Fig. 1). Softening was complete after 50 min (Fig. 1).

3.2. Light microscopy of onion tissue

The cell walls of fresh onion tissue were thin and the cells adhered closely together [Fig. 2(a)]. After pressure-cooking for 20 min [Fig. 2(b)], the cell walls became less compact

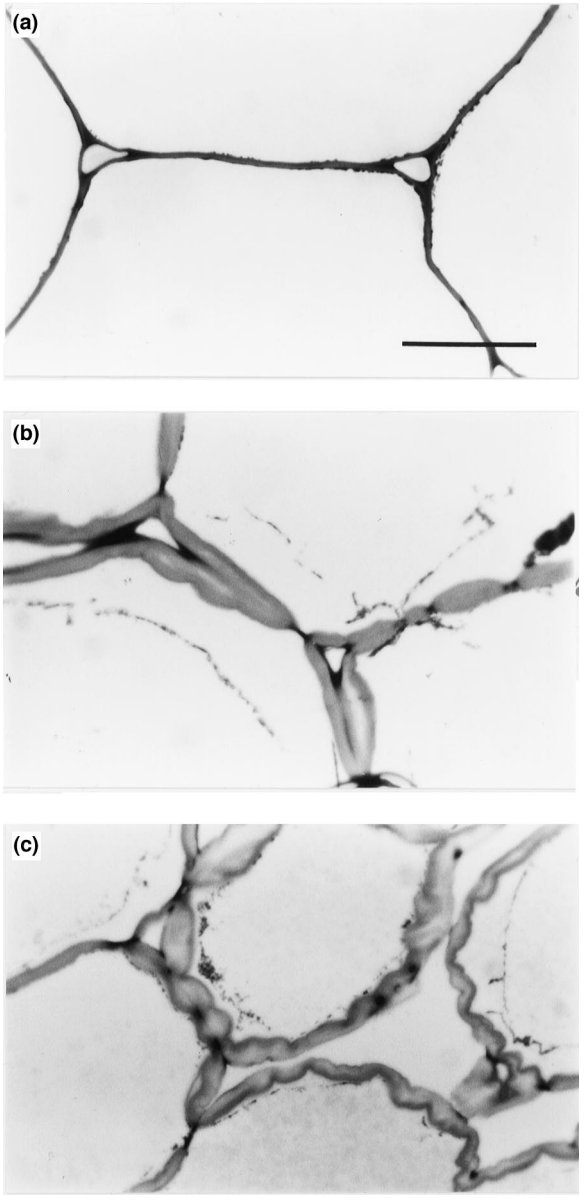

Fig. 2. Microscopy of onion (Delta) outer scale leaves: (a) fresh; (b) pressure-cooked for 20 min; (c) pressure-cooked for 50 min; (bar = 50 μm).

Table 1
Carbohydrate composition of liquor, ethanol, buffered phenol and AIR of fresh (F) and pressure-cooked (PC) onion (t indicates trace amounts)

	Yields (% Fwt)	Carbohydrate (mol%)								Total μg/mg	DM %	Ratio UA:NS
		Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA			
Liquor												
F (Delta)	–	–	–	–	–	–	–	–	–	–	–	–
F (Hysam)	–	–	–	–	–	–	–	–	–	–	–	–
PC (Delta)	1	t	t	t	t	11	5	71	12	537	–	3
PC (Hysam)	1	t	t	t	t	8	9	60	22	578	–	3
Ethanol												
F (Delta)	9	1	t	t	t	5	1	92	1	462	–	1
F (Hysam)	7	1	t	t	t	6	1	91	1	421	–	1
PC (Delta)	7	t	t	t	t	12	1	85	2	464	–	2
PC (Hysam)	4	t	t	t	t	6	2	82	8	434	–	4
Buffered phenol												
F (Delta)	0.1	t	3	3	2	11	8	21	49	148	–	5
F (Hysam)	0.1	t	1	1	t	3	5	4	84	299	–	14
PC (Delta)	0.2	1	1	1	t	1	18	1	77	512	–	4
PC (Hysam)	0.3	1	1	1	t	1	15	1	80	664	–	5
AIR												
F (Delta)	3	1	1	2	3	1	17	26	47	754	30	2
F (Hysam)	3	1	1	2	3	1	15	29	45	723	46	3
PC (Delta)	2	1	1	3	5	2	15	39	33	664	21	2
PC (Hysam)	2	1	1	3	6	2	12	43	32	659	42	3

and less-densely stained except near plasmodesmata and at edges of cell faces. Some cells showed evidence of the onset of separation in the remaining middle lamellae regions. After 50 min. (softening complete), the cell walls were highly swollen, albeit less at the plasmodesmata, and many of the larger cells below the adaxial epidermis had separated [Fig. 2(c)].

3.3. Fresh onion tissue

In order to investigate the changes of cell-wall chemistry of onion tissues during pressure-cooking, the carbohydrate composition of the cell walls of fresh and 50 min-pressure-cooked material is described.

3.3.1. AIRS—carbohydrate composition and degree of methylesterification (DM)

Fresh onion tissue was prepared as AIR and its carbohydrate composition analysed after hydrolysis in 72% (v/v) sulphuric acid (Selvendran and O'Neill, 1987). The absence of starch in the AIR was indicated by non-staining with iodine/potassium iodide and by the release of only 10% of the glucose after hydrolysis with 1 M sulphuric acid (Selvendran and O'Neil, 1987). Carbohydrate analysis of ethanol and buffered phenol fractions showed that only trace amounts of pectic polysaccharides were released, as indicated by the level of uronic acid, arabinose and galactose (approximately 2.4% and 1.2% Fwt basis, respectively; Table 1). There was only a trace of Klason lignin present in both the Delta and Hysam onions' AIRs.

The carbohydrate yields of AIR from fresh onion tissue (Delta and Hysam) were similar at 3% on a Fwt basis. Approximately 75% of the AIR comprised carbohydrate (Table 1); the remaining 25% probably contained cell-wall protein and intracellular protein which co-precipitated with the cell-wall material during extraction in ethanol, and which was not extracted in buffered phenol. The carbohydrate compositions of AIRs from both varieties were similar and contained galactose as the major neutral sugar in the pectic polysaccharides. The compositions were a little different from those reported by Redgwell and Selvendran (1986); the AIRs in this study contained higher levels of uronic acid and lower levels of galactose. The higher UA will result from the inclusion of water-soluble uronide (see below) which would not have been present in the SDS-insoluble preparation of Redgwell and Selvendran. The lower levels of galactose in this study are due to the use of outer scale leaves, which have lower levels compared with the whole onion (Ng et al., 1998). The DM of the uronic acid from Delta and Hysam onions was 30% and 46%, respectively. Similar results were obtained by Ng et al. (1998).

The material extracted in 85% (v/v) ethanol comprised most of the dry matter recovered (Table 1). This was rich in glucose and mannose which will have been derived from intracellular sucrose and the reduction of fructose from fructo-oligosaccharides yielding glucitol and mannitol. In contrast, the buffered phenol extracted only a minor quantity of material, which contained small amounts of uronic acid and glucose.

3.3.2. Sequential extraction of AIRS

The AIRs from fresh onions were extracted sequentially with water, NaCl, imidazole, CDTA, Na_2CO_3 and KOH. This approach was based on the method of Redgwell and

Table 2
Carbohydrate composition of fresh (F) and pressure-cooked (PC) onion AIR extracts and insoluble residues (defined in text)

	Yields (% AIR)	Carbohydrate (mol%)								Total μg/mg	Ratio UA:NS
		Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA		
WSP											
F (Delta)	5	t	t	2	1	3	10	9	74	782	6
F (Hysam)	5	1	1	2	1	1	8	8	72	639	7
PC (Delta)	13	1	1	4	1	1	30	11	51	957	2
PC (Hysam)	13	1	1	4	1	t	25	11	57	853	2
SSP											
F (Delta)	2	1	1	2	t	1	10	5	71	665	6
F (Hysam)	2	t	1	2	t	t	7	8	82	782	9
PC (Delta)	4	1	1	3	1	t	22	10	61	845	2
PC (Hysam)	4	1	1	3	1	t	17	10	68	943	3
ISP											
F (Delta)	3	t	1	2	1	1	10	5	80	447	7
F (Hysam)	6	t	1	1	1	1	6	8	81	242	11
PC (Delta)	6	2	1	3	1	t	24	10	58	928	2
PC (Hysam)	7	1	1	2	1	1	17	10	66	756	3
CSP-1											
F (Delta)	21	1	t	1	t	t	8	4	86	801	10
F (Hysam)	16	1	1	1	t	t	6	7	84	822	12
PC (Delta)	23	1	1	1	t	t	12	11	72	402	6
PC (Hysam)	22	1	1	2	1	t	9	10	76	344	7
CSP-2											
F (Delta)	15	t	1	1	1	1	8	4	83	190	9
F (Hysam)	21	1	1	1	t	t	7	8	82	149	10
PC (Delta)	20	1	4	1	1	8	10	8	67	47	6
PC (Hysam)	20	t	7	1	1	2	15	9	64	34	4
CIR											
F (Delta)	54	1	1	2	3	1	22	40	30	816	1
F (Hysam)	50	1	1	2	2	1	20	44	29	839	1
PC (Delta)	34	1	1	3	2	1	10	63	10	914	1
PC (Hysam)	34	1	1	3	3	1	13	68	10	935	1
NSP-2											
F (Delta)	13	1	t	1	t	t	14	4	79	840	5
F (Hysam)	10	1	t	1	t	t	13	7	77	848	6
PC (Delta)	3	1	1	5	2	1	46	12	32	85	1
PC (Hysam)	4	1	1	6	2	2	35	14	38	77	1
NSP-1											
F (Delta)	6	1	1	3	1	t	47	4	44	773	1
F (Hysam)	5	1	1	3	1	t	40	8	47	678	2
PC (Delta)	1	2	1	7	2	3	49	13	23	184	0.4
PC (Hysam)	1	2	2	10	3	5	41	15	22	216	0.4
KSP											
F (Delta)	4	1	1	4	1	t	49	4	39	618	1
F (Hysam)	2	1	1	4	1	t	48	7	32	533	1
PC (Delta)	0.4	2	1	10	3	3	43	15	23	218	0.4
PC (Hysam)	0.2	1	2	13	5	5	34	16	24	240	0.5
RES											
F (Delta)	31	1	1	3	7	2	22	60	4	689	0.1
F (Hysam)	33	1	2	4	8	3	24	55	3	668	0.1
PC (Delta)	29	t	2	2	9	3	9	71	3	691	0.3
PC (Hysam)	29	t	1	2	9	4	7	73	3	683	0.3

Selvendran (1986) with a modification in which the water-insoluble residue was extracted with NaCl and imidazole solutions in order to quantify separately the salt- (SSP), imidazole- (ISP) and CDTA-soluble polysaccharides (CSP). The procedure was designed to minimise β-eliminative degradation of pectic polymers (Waldron and Selvendran, 1992). The amounts of material extracted are based on one sequential extraction of each AIR. Previous studies by Redgwell and Selvendran (1986) indicated that relatively small amounts of polymers were released by 1 and 4 M KOH, so these were not investigated further.

The polysaccharides released by the sequential extractions were predominantly pectic in nature (Table 2). The relative yields of extracted pectic polysaccharides (sum of

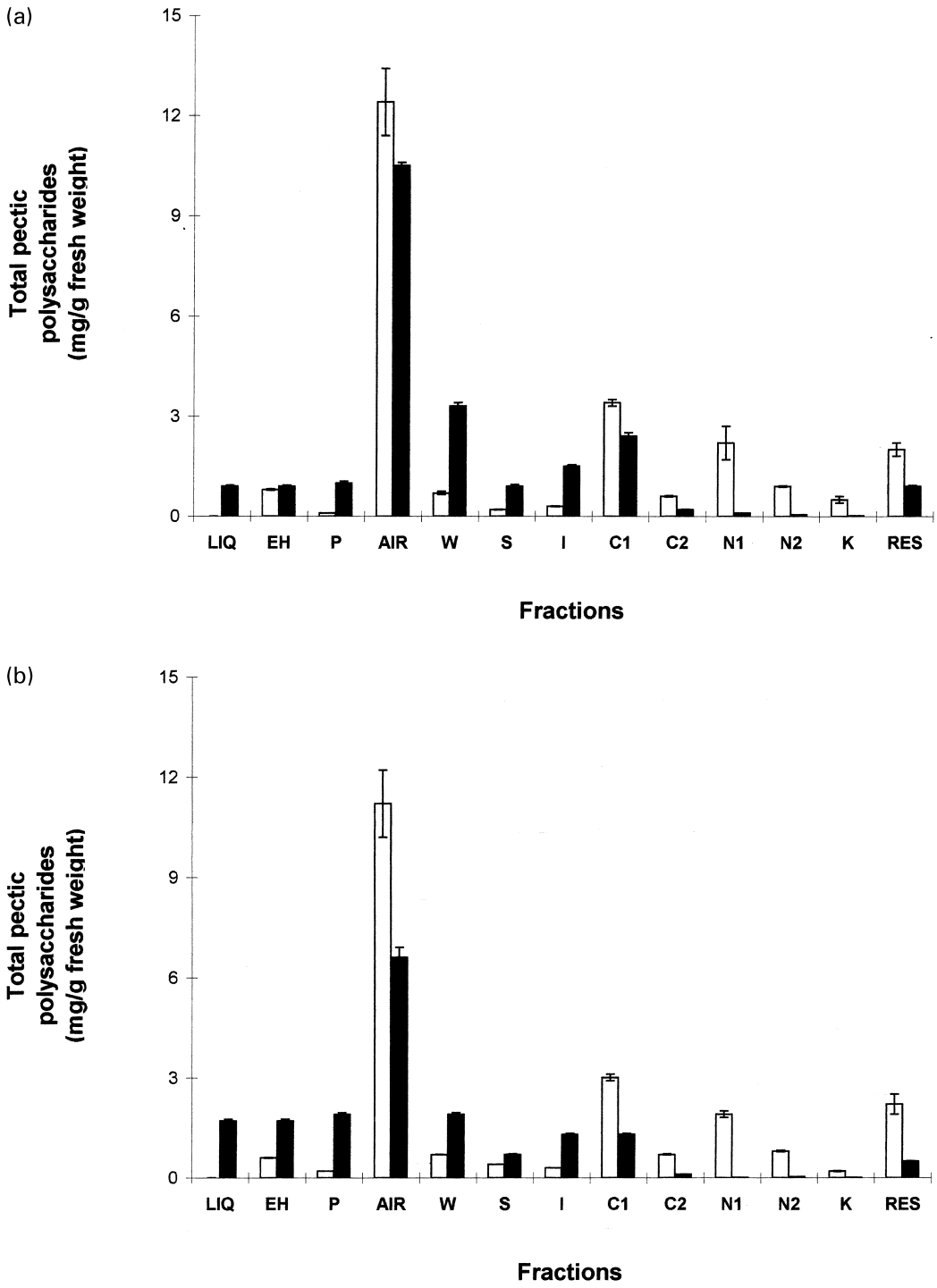

Fig. 3. Total pectic polysaccharides (mg/g fresh weight) from extracts and insoluble residues of onions: (a) effect of pressure-cooking on onion (Delta) and (b) effect of pressure-cooking on onion (Hysam) where □ denotes fresh and ■ denotes pressure-cooked. Abbreviations: LIQ = liquor; EH = ethanol; P = buffered phenol; AIR = alcohol-insoluble residue; W = water; S = salt; I = imidazole; C1 = CDTA-1; C2 = CDTA-2; N1 = Na_2CO_3-1; N2 = Na_2CO_3-2; K = KOH; RES = residue.

uronic acid, arabinose and galactose), as a function of the tissue fresh weight are shown in Fig. 3(a) and (b). This shows that the CDTA-1 and Na_2CO_3-1 treatments solubilised most of the extractable pectic polymers, whilst relatively little was released by water, NaCl, imidazole, CDTA-2, Na_2CO_3-2 or 0.5 M KOH. Similar results were obtained by Ng et al. (1998). The UA:NS (uronic acid: arabinose + galactose) ratio, was highest in CSP and Na_2CO_3-soluble polysaccharides (NSP), indicating that these were less branched than the polysaccharides extracted by water, salt, imidazole and 0.05 M KOH. Polymers extracted from AIR of Delta

and Hysam onion tissues had generally similar UA:NS values.

The yield of KOH-insoluble residues (RES) of both Delta and Hysam onions was 30% (Table 2). They were rich in glucose ($>$ 55%), the remaining carbohydrate consisting mainly of pectic components. The ratio of UA:NS of RES was lower than the AIR and probably reflects the insolubility of more highly-branched pectic polysaccharides in the RES.

3.3.3. Molecular-weight profiles

WSP, CSP-1 and Na_2CO_3-1 (NSP), 0.05 M KOH-soluble polysaccharides (KSP) of fresh onions (Delta) were investigated for molecular-weight (MW) profiles by chromatography on Sepharose CL-4B. The MW profile of WSP contained one peak with a maximum at approximately 140 000 [Fig. 4(a)]. In contrast, the CSP-1 fractions yielded two peaks with respective maxima of approximately 140 000 and 90 000 [Fig. 4(b); Table 3]. Gel filtration of NSP-1 only resolved one peak of polymers with a maximum of approximately 110 000 [Fig. 4(c)]. Gel filtration of KOH-soluble polysaccharides (KSP) contained one peak with a maximum of approximately 90 000 [Fig. 4(d)]. The yields of NaCl, imidazole and CDTA-2 extracted polymers were too small to be analysed by gel filtration. The differences in the ease of extraction and breadth of the MW profiles indicated considerable heterogeneity in the population of pectic polymers, as found in the cell walls of carrots (Ng and Waldron, 1997a) and potatoes (Ng and Waldron, 1997b).

3.4. Effect of pressure-cooking

Pressure-cooking the onion tissue at 120°C for 50 min. released a small quantity of carbohydrate into the water (LIQ) at the bottom of the vessel (Table 1). This consisted mainly of glucose, uronic acid, mannose and galactose. The

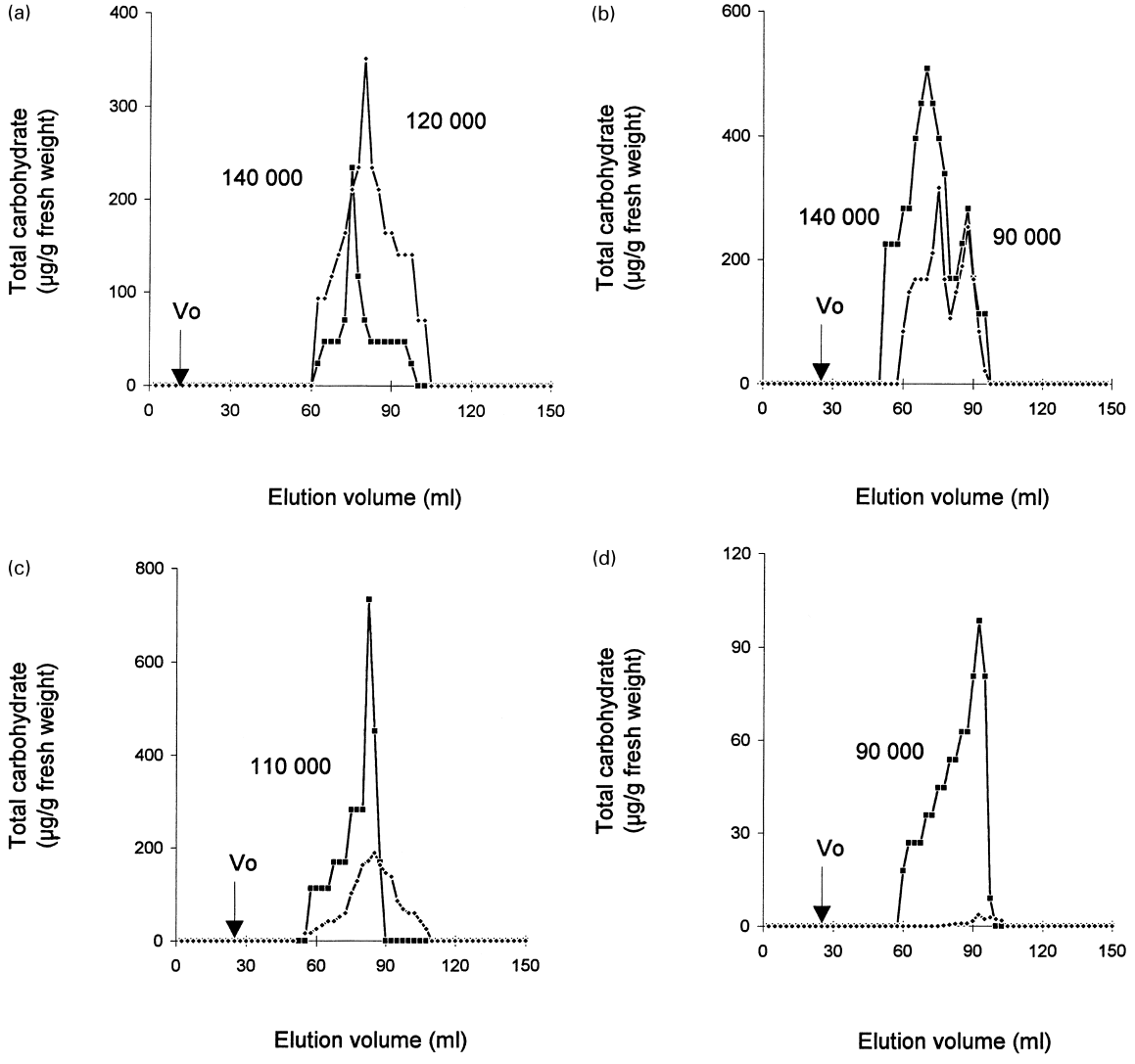

Fig. 4. Molecular-weight profiles of fresh – ■ – and pressure-cooked – ♦ – onions (Delta): (a) water-soluble polysaccharides; (b) CDTA-1-soluble polysaccharides; (c) Na_2CO_3-1-soluble polysaccharides; and (d) KOH-soluble polysaccharides.

Table 3
Carbohydrate composition of high- and low-MW fractions from CDTA-soluble polysaccharides of fresh (F) and pressure-cooked (PC) onion (Delta) AIR

	Yields (% AIR)	Carbohydrate (mol%)								Total μg/mg	Ratio UA:NS
		Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA		
High MW											
F	65	1	t	1	3	7	1	1	85	796	42
PC	77	3	t	2	2	4	3	1	85	400	17
Low MW											
F	35	3	t	1	3	2	1	1	88	760	44
PC	23	4	t	3	3	2	9	1	77	421	6

treatment also resulted in an increase in ethanol- (E) and buffered phenol-soluble (P) pectic polysaccharides, leading to a decrease in pectic polysaccharides in AIR [Fig. 3(a) and (b); $P < 0.05$]. The AIR of pressure-cooked tissues exhibited a lower DM of the UA component (Table 1).

Pressure-cooking had a major effect on the extractability of the cell-wall polysaccharides of both varieties (Fig. 3). It resulted in a substantial increase in total pectic polysaccharides of WSP, SSP and ISP; this was accompanied by a decrease in the total pectic polysaccharides solubilised by CDTA, Na_2CO_3 and 0.05 M KOH and, in particular, a relatively large decrease in the level of total pectic polysaccharides in the residue. ISP had a similar carbohydrate composition to CSP, but a relatively lower yield. These results indicate that the heat-treatment-induced modifications occur in most, if not all, pectic components in the cell wall, and are probably due to an increase in heat degradation through β-elimination resulting in base-catalysed depolymerisation (Sajjaanantakul et al., 1989; Greve et al., 1994b). They also highlight differences between ISP and CSP-polysaccharides. Heating resulted in the UA:NS ratio of most extracts and residues (Table 2), consistent with the release of UA-containing polysaccharides into the liquor (Table 1; Fig. 3). This is probably because the branched pectic polysaccharides are more highly cross-linked and were less readily solubilised.

Whilst the sequential extraction profiles of the pectic polymers from the fresh tissue of the two varieties were similar (Fig. 3), the profiles from the pressure-cooked tissues were not. Cell walls from Hysam onions were much more strongly degraded than those from the Delta variety. The greater dissolution of polymers in Hysam may be due to the higher DM value which will be one of the factors which determine the degree of β-elimination of the pectic polymers (Sajjaanantakul et al., 1993).

Pressure-cooking resulted in a slight decrease in the peak molecular weight of WSP (which increased in yield) from approximately 140 000 to 120 000 [Fig. 4(a)] and a larger decrease in the total carbohydrate of the molecular weight fractions of the polymers in the CSP, NSP and KSP extracts [Fig. 4(b)–(d)]. The changes in the CSP extract were due to losses from the larger of the two peaks [Fig. 4(b)]. Pressure-cooking-related changes in the ratios of UA:NS of the high MW and low MW component of CSP fractions (Table 3) reflected the changes in the parent extracts (Table 2).

4. General discussion

The results indicate that pressure-cooking of onion tissues results in an increase in total pectic polysaccharides of WSP, SSP and ISP, and this was accompanied by a decrease in the total pectic polysaccharides of CSP, NSP, KSP and the residues. This occurs in nearly all fractions of the cell wall, as found in carrots and potatoes (Ng and Waldron, 1997a and Ng and Waldron, 1997b), and probably involves β-eliminative degradation (Sajjaanantakul et al., 1993). Our results indicated that the carbohydrate composition of ISP and CSP were similar and rich in uronic acid, galactose and glucose. The ability to extract only a small amount of chelator-soluble polymers with imidazole is not well understood. It is conceivable that it acts as an ion-exchange agent (Ng et al., 1998).

Pressure-cooking resulted in a slight decrease in the molecular weight of WSP. Similar results were observed with the DMSO-soluble polymers of steamed potato tissues (Ng and Waldron, 1997b). Pressure-cooking also caused a large decrease in total carbohydrate of the CSP, NSP and KSP. In addition the NSP-1 and KSP fractions of pressure-cooked-onion AIRs were a lower MW compared with those from fresh onion.

The dissolution of the wall polymers is concurrent with tissue softening which involves cell separation (Ng and Waldron, 1997a). The strength of cell adhesion is likely to be dependent, to a large extent, on the strength of cell–cell interactions in the middle lamella adjacent to the intercellular spaces. Indeed, maximum tissue softening in onion only occurs after separation in this zone (see Fig. 2). This area of adhesion, which consists of the edges of cell faces, has been highlighted recently in Chinese water chestnut where it is strengthened by phenolic cross-links (Waldron et al., 1997). As a result, the cells of Chinese water chestnut fail to separate during cooking, and the tissue remains firm and crunchy.

In order to develop a greater understanding of the physico-chemical characteristics of onion cell walls on the basis of modification and extraction of potentially useful

cell-wall polymers, we have also investigated the effects of thermal treatments on the chemistry of cell-wall polysaccharides of outer fleshy scale leaves of onions as modulated by divalent cations, in Part II.

5. Conclusions

The above work has demonstrated:

1. that the chemical composition of the cell wall and extracted cell-wall polymers is similar in fresh Delta and Hysam onion tissues;
2. the heterogenous nature of the pectic polysaccharides;
3. thermal softening of onion tissue involves cell separation and is accompanied by general dissolution and depolymerisation of cell-wall pectic polymers. The pectic polymers from the pressure-cooked Hysam onions were much more strongly degraded than those from the Delta variety. This may be due to differences in the DM of the wall uronide;
4. the importance of the edges of cell faces in cell–cell adhesion.

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