

Effect of tissue type and variety on cell wall chemistry of onion (*Allium cepa* L.)

A. Ng, A. C. Smith & K. W. Waldron*

Institute of Food Research, Norwich Research Park, Colney, Norwich NR4 7UA, UK

(Received 25 July 1997; revised version received and accepted 5 November 1997)

The purpose of this study was a comparative examination of the cell wall chemistry of component tissues of different varieties of onions (*Allium cepa* L. cv Sturon, Durco, Hysam, Grano de Oro and Caribo). Cold alcohol-insoluble residues (CAIRs) were prepared and were extracted sequentially with water, imidazole, CDTA, Na₂CO₃ and 0.5 M KOH to leave a residue. These were analysed for their carbohydrate compositions. On a whole organ basis, the cell wall carbohydrate composition was similar for each variety studied, and no significant change resulted from commercial storage, with or without sprout suppressant. However, there were significant differences in the carbohydrate composition of cell walls from different tissues. Cell walls of inner leaf bases contained galactose-rich pectic polysaccharides. Outer layers had progressively less pectic galactose, and the outer brown skin contained virtually none. This was accompanied by changes in water- and CDTA-soluble polysaccharides and may be related to the dry and protective nature of the non-lignified outer skin. The differences in cell walls from different tissues provide the basis for developing processing methods for exploiting onion waste. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Onion (*Allium cepa* L.) is a ripened bulb, the edible portion being the swollen leaf bases that form the flesh. In a well ripened onion, the foliage leaves have died down and are dried up, leaving only a little shrivelled tissue at the tips of the outer fleshy scales.

Onion is one of the major vegetable crops grown in Europe. Although consumed in rather small quantities by most families, onions are used in many homes almost daily, mainly as a seasoning for a wide variety of dishes. There is a concern over the production of large quantities of industrial onion waste, and its disposal. In the European Union, 450 000 tons of onion waste are produced annually, mainly from the UK, Holland and Spain. Onion brown skin, the outer two fleshy leaves and tops and bottoms, are the major by-products after industrial peeling. The waste is not suitable for fodder, or landfill disposal due to the rapid growth of phytopathogens, e.g. *Sclerotium cepivorum* (white rot). Valorisation of the waste, particularly exploitation of the waste for the profitable production of food-grade products, will benefit the onion producers and processors.

Besides the characteristic flavorants, onions contribute to the intake of minerals and dietary fibres (Fenwick, 1985). There have been several studies on the extractable cell wall polymers of onion bulb tissues (Redgwell and Selvendran, 1986). Recently, onions have also attracted attention as a potentially valuable source of palatable, low-cost gelling pectin (Abdel-Fattah and Edrees, 1971, 1987; Alexander and Sulebele, 1973; Redgwell and Selvendran, 1986). There has also been a detailed study on the cell wall polysaccharides of peeled onions (Redgwell and Selvendran, 1986). However, there is little definitive information concerning the cell wall chemistry of different onion cultivars or of their component tissues. As part of a study, the purpose of which is to aid the exploitation of onion waste, we have investigated the carbohydrate composition and solubility of cell wall polymers of onion tissues from five commonly processed varieties in Europe, the effect of sprout suppressant and storage.

MATERIALS AND METHODS

Five varieties of mature onions (*Allium cepa*, L. cv Sturon, Durco, Hysam, Grano de Oro and Caribo) were received from local onion producers (British Onion Producers Association, UK). Different onion varieties

*To whom correspondence should be addressed. Fax: 01603 507723; e-mail: keith.waldron@bbsrc.ac.uk

used in this study were large graded (size 6 cm diameter and above) and the average weight of all onions were similar and fell into the 100–120 g range, except Durco and Grano varieties which were largest among the 160–200 g range. Since onions are largely cross-fertilized, they show some variation in the colour and shape of the bulb in different varieties. Varieties studied are the most popular intermediate globe shape. The skin colours of all onions were yellow, except brown for Sturon and reddish-yellow for Grano.

In order to investigate the effects of storage, whole mature onions were stored at 0°C (RH 60–65%) for six months.

Mature Sturon onions, with (S) or without (OS) sprout suppressant (Fazor, Maleic hydroxide), were stored at 0°C (RH 60–65%) for six months and were used to investigate the effects of sprout suppressant.

Onions were dissected into different tissue regions: (1) top and bottom (approximately 5–10 mm sliced off the top and bottom ends of the onions), (2) brown dry outer skin, (3) outer two fleshy layers of leaf bases and (4) remaining inner fleshy leaf bases (Fig. 1). They were immediately frozen in liquid nitrogen after cutting and stored at –40°C.

Unless otherwise stated, all chemicals were of Analytical grade.

Hot alcohol-insoluble residues (HAIRs)

Tissues were extracted for HAIRs as described by Martin-Cabrejas *et al.* (1994). Frozen onion tissues were homogenised in a Waring blender (Fischer, Scientific Instrument, UK) with boiled ethanol (85% v/v final concentration; Fisons), reducing particle size to less than 5 mm. The homogenate was transferred to a stainless steel beaker and homogenised with an Ystral homogeniser (Ystral GmbH, Dottingen, Germany), and boiled in a water bath for 5 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 and boiled for 1 min. The HAIR was washed with acetone (Fisons) and air-dried in a fume hood.

Cold alcohol-insoluble residues (CAIRs)

CAIR was prepared as for HAIR with a modification in which ethanol (85% v/v final concentration) at 20°C was used and boiling in a water bath was omitted.

Sequential extraction of cell wall polymers

CAIR (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 imidazole (100 ml, 2 M, pH 7; Sigma) for 24 h at 20°C. The residue was then extracted in cyclohexane-trans-1,2-diamine-*NNN'* tetra acetate (CDTA, Na salt, 0.05 M, pH 6.5; Sigma), Na₂CO₃ (0.05 M; 1°C and 20°C; BDH) and KOH (0.5 M; BDH) as described by Waldron and Selvendran (1992). The supernatants were filtered, neutralised where required, and dialysed exhaustively prior to concentration and freeze-drying.

Sugar analysis

Cell-wall neutral sugars were analysed as described previously by Coimbra *et al.* (1994). All analyses were carried out in duplicate, and the standard deviations of the data were less than 2%. Sugars were released from cell wall material by dispersing in 72% H₂SO₄ (Fisons) for 3 h followed by dilution to 1 M and hydrolysing for 2.5 h at 100°C (Saeman *et al.*, 1954). All samples were analysed in duplicate. Neutral sugars were reduced with NaBH₄ and acetylated by the method of Blakeney *et al.* (1983) using 2-deoxyglucose (Sigma) as an internal standard. Alditol acetates were quantified by gas chromatography as described in Ng and Waldron (1997a).

Uronic acids were determined colorimetrically by a modification of the method of Blumenkrantz and Asboe-Hansen (1973) in which samples were dispersed in 72% H₂SO₄ for 3 h at room temperature, diluted to 1 M H₂SO₄, and hydrolysis for 1 h at 100°C.

Methanol analysis

The degree of methylesterification (DM) was determined as described by Ng and Waldron (1997b). CAIR

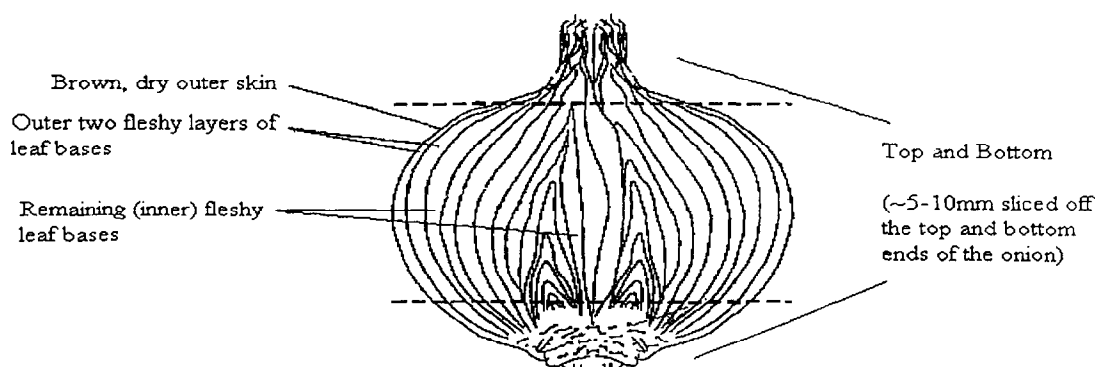


Fig. 1. Onion (*Allium cepa* L.)

(approximately 5 mg) of Sturon (S or NS) was dispersed in distilled water (2 ml) and sonicated for 10 min. Propanol (0.4 ml, 0.2%) was added as an internal standard. The sample was de-esterified by addition of NaOH (0.8 ml, 2 M; BDH) and incubated for 1 h at room temperature with occasional shaking. Subsequently, the sample was neutralised by the addition of HCl (0.8 ml, 2 M; Fisons) and allowed to equilibrate at 25°C in a water bath for 15 min. Methanol was quantified by isothermal GLC at 150°C on a 1.3 m × 4 mm column packed with HayeSep 'p' 80–100 mesh (Alltech) with argon as the carrier gas flowing at 40 ml min⁻¹. Standards of methanol and propanol gave a linear calibration.

Statistical analysis

The data of total uronic acid of CAIRs were used to interpret the significant differences between varieties and tissues by using a two-way ANOVA (Analysis of Variance).

RESULTS AND DISCUSSION

Tissue yields

Inner tissues contributed the major average weight of onions (Fig. 2). Similar results were obtained from stored onions indicating no significant loss of water during storage.

Effect of heat on quality of alcohol-insoluble residue (AIR) polysaccharides

Cell wall material is often extracted by the use of aqueous alcohol solutions at higher temperature. However, there is little information on the effect of such treatment on the integrity of cell wall polymers. Before carrying

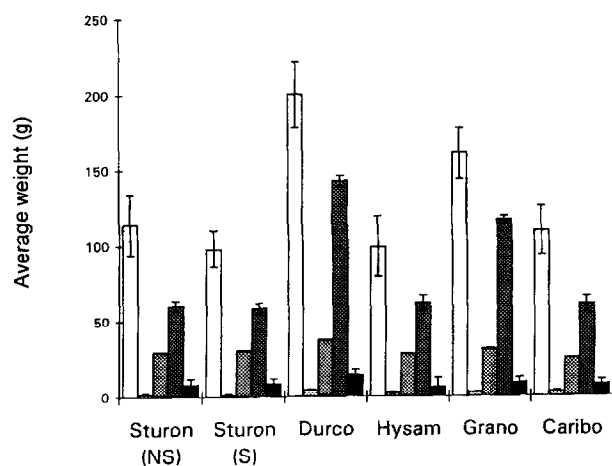


Fig. 2. Average weight of onions. Symbols: □ whole, ▨ skin, ▩ outer, ■ inner and ■ top and bottom.

out the detailed screening of onion varieties, the effect of heat, during AIR extraction of skin and outer tissues of onion (Hysam variety), on cell wall polysaccharides was monitored.

Heating had no significant effect on the AIR yield from skin or outer tissues ($p < 0.05$); likewise, heating had no significant effect on the carbohydrate composition of the AIRs (see below for detailed description). However, heating had a considerable effect on the cold water-soluble uronic acid component of AIRs from both tissues (Fig. 3). For skin tissues, heating increased the soluble uronic acid from approximately 1 to 2%. For outer tissues, heating increased the soluble uronic acid from approximately 4 to 10%. This indicated that heating was depolymerising the pectic polysaccharides, probably by β -eliminative degradation (Sajjaanantakul *et al.*, 1989). Therefore, for the purpose of this study, CAIRs were used as preparations of cell wall materials. In order to present the large amount of data clearly from so many varieties, the values for carbohydrate composition are given as the means for the varieties, with standard derivations in parentheses. The whole onions will be described, followed by tissues, varietal differences, and the effect of sprout suppressant and storage.

Carbohydrate composition of CAIRs

Whole onions

The yield of CAIR from whole onion was approximately 4% (Fwt). The bulk of the CAIR (81%) comprised carbohydrate, mainly pectic polysaccharides as inferred from the levels of uronic acid, galactose, arabinose and rhamnose, and glucose with minor quantities of xylose and mannose (Table 1). The remainder of the CAIR consisted of cell wall- or co-precipitated-intracellular protein (Martin-Cabrejas *et al.*, 1994). The compositions of onion bulbs were comparable to that reported previously for onion tissues by Redgwell and Selvendran (1986). The absence of starch from CAIRs was confirmed by lack of staining with I/I₂ and by the release of a non-cellulose (10% of the wall) glucose after hydrolysis with 1 M sulfuric acid (Selvendran and

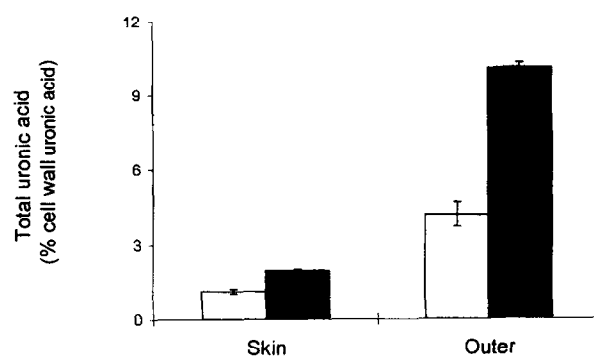


Fig. 3. Effect of heating on the solubility of total uronic acid (% cell wall uronic acid). Symbols: □ CAIR and ■ HAIR.

Table 1. Carbohydrate composition of CAIRs of fresh and stored onions

	Yields (% Fwt)	Carbohydrate (mol%)								Total $\mu\text{g mg}^{-1}$	Ratio UA:NS
		Rha	Fuc	Ara	Xyl	Man	Gal	Glc	UA		
Fresh											
Whole	4 (1)	2 (0)	1 (0)	3 (0)	4 (1)	3 (1)	10 (1)	30 (1)	47 (2)	807 (26)	4
Skin	49 (13)	2 (0)	1 (0)	1 (0)	4 (0)	2 (0)	1 (0)	32 (3)	59 (4)	828 (43)	30
Outer	3 (0)	2 (0)	1 (0)	3 (0)	4 (0)	3 (1)	12 (2)	28 (1)	48 (3)	793 (50)	3
Inner	3 (0)	2 (0)	1 (0)	4 (1)	4 (0)	3 (1)	17 (1)	29 (2)	39 (3)	816 (27)	2
Top and Bottom	13 (2)	2 (0)	1 (0)	3 (0)	6 (1)	2 (1)	4 (0)	28 (1)	53 (2)	791 (62)	8
Stored											
Skin	56 (8)	1 (0)	1 (0)	1 (0)	4 (0)	2 (0)	1 (1)	37 (1)	52 (2)	762 (40)	26
Outer	3 (0)	1 (0)	1 (0)	2 (0)	4 (1)	2 (0)	13 (2)	33 (2)	45 (3)	739 (21)	3

Values are represented as the mean of the 5 onion varieties; values in parentheses are expressed as the standard deviation of onion varieties.

Abbreviations: Rha, rhamnose; Fuc, fucose; Ara, arabinose; Xyl, xylose; Man, mannose; Gal, galactose; Glc, glucose; UA, uronic acid; UA:NS, uronic acid:neutral sugar (arabinose + galactose).

O'Neil, 1987). The DM of uronic acid (Sturon, S and OS) was approximately 45.9%.

Onion tissues

Since the inner tissues contributed most to the whole onion weight, their carbohydrate composition was, not surprisingly, broadly similar to that of the whole onions (Table 1). The key differences were that the CAIR yield was about half that of the whole onions, and the level of cell-wall galactose was approximately 75% higher. As a result, the uronic acid: neutral sugar (arabinose + galactose) (UA:NS) ratio was approximately 2 as compared to 4 for whole onion.

The surrounding outer tissues gave a similar CAIR yield and composition when compared to the inner tissues, although the level of wall galactose was approximately 30% less. Hence, the UA: (arabinose + galactose) ratio was between 2 and 3.

The outer skin tissues gave a very high yield on a dry weight basis-between approximately 40 and 70%. This corresponded to the dry nature of the fresh tissues. Interestingly, the carbohydrate composition of the skin was similar to the inner and outer tissues, except that the CAIR was almost devoid of wall galactose. This resulted in a high UA: (arabinose + galactose) ratio.

The top and bottom tissues comprised mainly a counterpart of inner, outer, and particularly skin tissues. The high skin level is reflected in the higher CAIR yield, and low levels of wall galactose.

The lower level of galactose in skin CAIR is presumably the result of galactosidase, degrading 1,4-galactan during development (Brett and Waldron, 1996). A maturation-related loss of neutral sugar side chains of onion might increase the susceptibility for association and cross-linking between pectin chains resulting in modification of its functional properties (Banker and Dara, 1982; Guillon and Thibault, 1987, 1990). This may lead to closer packing of the pectin strands and result in reduced solubility. It is interesting to speculate that the decrease in wall galactose from the

inner tissues through to the skin may be related to the water-proofing characteristic of the outer protective skin which, like the other main tissues, contained no detectable lignin.

The DM of the UA of skin, outer, inner and top and bottom tissues (Sturon, NS) onions were 45.7, 48.3, 48.8 and 47.2%, respectively. A similar result was obtained with Sturon (S) onions.

Variety and the effect of sprout suppressant

Generally, the yields and total carbohydrates of the CAIRs of whole onions and the component tissues were not affected by variety, or use of sprout suppressants (Table 1). However, for skin, Durco, Hysam and Caribo varieties had significantly lower yields than Sturon and Grano varieties ($p < 0.05$). This probably reflects the post-harvest handling, which may have differentially removed outer brown layers.

Effect of storage

The weight of six months stored onions (0 and 20°C) was similar to the fresh onions indicating that little or no water loss by evaporation occurred during storage. No fungal contamination was observed in stored onions. Stored Sturon (S and OS), Hysam and Grano varieties of skin and outer tissue were analysed for their CAIR carbohydrate compositions. The results showed that storage did not induce any significant changes in the yield, total carbohydrate and carbohydrate components of CAIRs. There were no signs of sprouting in both stored Sturon S and OS. It is possible that sprouting is inhibited during the six months storage at 0°C.

Solubility of cell-wall components

CAIRs of whole onions and the component tissues were extracted with water at 20°C. The yields ranged from

3% in skin to 6–7% in inner tissues. The bulk of the water-soluble polysaccharides comprised uronic acid (Table 2), and in all cases the level of galactose was low compared with the parent CAIRs. Hence, the UA: (arabinose + galactose) ratio was relatively high. The recovery of water-soluble polysaccharides (WSP) was significantly lower in skin resulting in relatively less solubilized uronic acid than in outer and inner tissues (Table 2; $p < 0.05$).

All the varieties studied showed a similar trend. In addition, there were no major effects of sprout suppressant or storage.

Sequential extractions of CAIRs

Because of the similarities in carbohydrate composition and WSP for all five varieties, only three were investigated further. CAIRs of whole onions and tissues of the Sturon (S), Hysam and Grano varieties were subjected to a detailed fractionation. The water-insoluble residues were extracted sequentially with imidazole, CDTA, and alkali. This approach is based on the method of Redgwell and Selvendran (1986) with a modification in which the water-insoluble residue was extracted with imidazole solutions in order to quantify the imidazole and CDTA-soluble polysaccharides (ISP and CSP) separately. The procedure is 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 CAIR. Previous studies by Redgwell and Selvendran (1986) indicated that only small quantities of polymers were extracted by 1 and 4 M KOH. These were mainly

comprised of xyloglucan hemicellulose, so were not investigated in the present study.

The polysaccharides of whole onions released by the sequential extractions were predominantly pectic in nature as shown by the high levels of UA (Table 3). In order to provide information on the ease of extraction of the cell wall uronide, the relative yields of extracted uronic acid, as a function of the total CAIR UA, are shown in Fig. 4. This shows that most of the extractable uronic acids were solubilised by the CDTA-1 and Na_2CO_3 -1, whilst relatively little was released by water, imidazole, CDTA-2, Na_2CO_3 -2 or 0.5 M KOH. Most of the arabinose was extracted in the Na_2CO_3 and KOH fractions, except for skin and top and bottom in which the majority of it was extracted in the CDTA-1 fraction (Fig. 5). Unlike arabinose, the majority of galactose remained in the KOH-insoluble residue (RES), except for skin (Fig. 6). As a result, the UA:NS ratio was lowest in Na_2CO_3 -, KOH-soluble and insoluble polysaccharides (NSP KSP and RES), indicating that these were highly-branched pectic polysaccharides (Waldron and Selvendran, 1992). Similar results were obtained by Redgwell and Selvendran (1986) in which they had demonstrated that rhamnogalacturonans were substituted to various degrees with side chains comprising galactans or arabinogalactans. They contained mainly (1→4)-linked galactose, lesser amounts of (1→4, 1→6)- and (1→2, 1→6)-linked galactose, and (1→5)-linked arabinose, and small proportions of (1→2)-linked galactose. Interestingly, ISP had a similar carbohydrate composition to CSP, but a lower yield. ISP has been proposed as an alternative extractant for CSP (Mort *et al.*, 1991; Sene *et al.*, 1994) in which imidazole can substitute for CDTA

Table 2. Carbohydrate composition of water-soluble and insoluble residues of fresh and stored onions

	Yields (%CAIR)	Carbohydrate (mol%)							Total $\mu\text{g mg}^{-1}$	Ratio UA:NS	
		Rha	Fuc	Ara	Xyl	Man	Gal	Glc			UA
Fresh											
WSP											
Whole	7 (1)	2 (0) t	2 (0) t	3 (1)	2 (0)	4 (2)	85 (4)	605 (59)	21		
Skin	3 (0)	2 (0) t	2 (0) 1 (0)	3 (1)	2 (0)	3 (1)	88 (1)	701 (65)	22		
Outer	5 (0)	1 (0) t	2 (0) t	2 (0)	4 (0)	2 (0)	86 (2)	620 (67)	14		
Inner	6 (1)	1 (0) 1 (0)	2 (0) t	5 (1)	2 (0)	5 (3)	85 (3)	720 (17)	21		
Top and Bottom	6 (1)	3 (0) t	3 (0)	1 (0)	5 (3)	2 (1)	82 (3)	565 (73)	16		
WIR											
Whole	94 (1)	1 (0)	1 (0)	3 (0)	5 (0)	1 (0)	8 (2)	34 (2)	46 (3)	821 (28)	23
Skin	97 (0)	1 (0)	1 (0)	1 (0)	5 (1)	1 (0)	1 (0)	28 (2)	62 (2)	834 (41)	31
Outer	95 (0)	1 (0)	1 (0)	3 (1)	5 (0)	1 (0)	12 (4)	31 (1)	46 (5)	802 (53)	3
Inner	94 (1)	1 (0)	1 (0)	4 (1)	6 (1)	1 (0)	19 (3)	31 (1)	37 (5)	822 (29)	2
Top and Bottom	95 (1)	1 (0)	1 (0)	3 (1)	6 (1)	2 (1)	4 (1)	33 (1)	52 (2)	803 (67)	17
Stored											
WSP											
Skin	3 (0)	1 (1) t	2 (0)	1 (0)	3 (0)	3 (1)	3 (1)	86 (1)	613 (65)	17	
Outer	5 (0)	1 (0) t	1 (0)	2 (1)	7 (4)	4 (0)	5 (1)	83 (1)	628 (51)	17	
WIR											
Skin	97 (1)	1 (0) t	1 (0)	4 (0)	2 (0)	1 (0)	41 (2)	50 (2)	762 (42)	23	
Outer	95 (1)	1 (0)	1 (0)	3 (0)	5 (0)	2 (0)	14 (2)	33 (1)	42 (3)	743 (18)	2

Values are represented as the mean of the 5 onion varieties; value in parentheses are expressed as the standard deviations of onion varieties.

For abbreviations, see text and Table 2. t, trace

Table 3. Carbohydrate composition of fresh onion CAIR extracts and insoluble residues

		Yields (%CAIR)	Carbohydrate (mol%)							Total $\mu\text{g mg}^{-1}$	Ratio UA:NS	
			Rha	Fuc	Ara	Xyl	Man	Gal	Glc			UA
ISP	Whole	5 (1)	1 (0) t	1 (0)	1 (0)	1 (0)	2 (0)	3 (0)	90 (2)	501 (18)	30	
	Skin	7 (0)	1 (0) t	1 (0)	3 (0)	3 (0)	2 (0)	4 (1)	84 (1)	519 (51)	28	
	Outer	6 (1)	1 (0) t	2 (0)	1 (0)	1 (0)	2 (0)	3 (1)	89 (2)	560 (11)	22	
	Inner	6 (0)	1 (0) t	4 (0)	4 (2)	2 (1)	2 (0)	3 (1)	83 (2)	520 (76)	14	
	Top and Bottom	8 (0)	2 (0) t	2 (1)	2 (0)	2 (0)	4 (0)	5 (2)	82 (2)	534 (11)	14	
CSP-1	Whole	13 (1)	1 (0) t	2 (0)	1 (0)	1 (0)	3 (0)	5 (1)	86 (2)	865 (35)	17	
	Skin	23 (1)	1 (0) t	2 (0)	1 (0)	3 (1)	1 (0)	4 (0)	88 (0)	868 (79)	29	
	Outer	11 (2)	1 (0) t	2 (0)	t	3 (0)	4 (0)	4 (0)	83 (1)	902 (61)	14	
	Inner	10 (1)	1 (0) t	3 (0)	t	3 (0)	5 (0)	5 (0)	83 (0)	885 (34)	10	
	Top and Bottom	18 (2)	1 (0) t	1 (0)	1 (0)	3 (1)	4 (1)	3 (0)	85 (1)	901 (72)	17	
CSP-2	Whole	16 (0)	t	t	1 (0)	t	1 (0)	4 (0)	82 (8)	196 (7)	41	
	Skin	16 (0)	t	t	1 (0)	1 (0)	3 (1)	1 (0)	2 (1)	91 (1)	46	
	Outer	14 (1)	t	t	1 (0)	1 (0)	1 (0)	1 (0)	2 (0)	93 (1)	47	
	Inner	10 (2)	t	t	1 (0)	1 (0)	1 (0)	2 (0)	1 (0)	93 (1)	31	
	Top and Bottom	15 (0)	t	t	1 (0)	1 (0)	1 (0)	2 (0)	2 (0)	92 (1)	31	
CIR	Whole	58 (2)	1 (0)	1 (0)	4 (0)	5 (1)	2 (0)	12 (2)	42 (1)	33 (2)	869 (13)	2
	Skin	51 (1)	1 (0)	1 (0)	1 (0)	4 (0)	2 (0)	1 (0)	54 (1)	35 (0)	814 (57)	18
	Outer	64 (2)	1 (0)	1 (0)	3 (2)	4 (0)	1 (0)	16 (3)	37 (1)	38 (2)	862 (75)	2
	Inner	68 (2)	1 (0)	1 (0)	5 (1)	3 (1)	1 (0)	23 (1)	37 (1)	29 (0)	836 (40)	1
	Top and Bottom	54 (2)	1 (0)	t	4 (0)	4 (0)	2 (0)	5 (0)	42 (3)	40 (2)	941 (17)	4
NSP-1	Whole	13 (0)	3 (0) t	8 (1)	1 (0)	1 (0)	11 (0)	1 (0)	74 (2)	872 (33)	4	
	Skin	14 (1)	1 (0) t	1 (0)	2 (0)	5 (1)	2 (0)	4 (1)	82 (1)	793 (23)	27	
	Outer	13 (0)	t	t	6 (0)	1 (0)	1 (0)	13 (0)	1 (0)	77 (0)	949 (2)	4
	Inner	13 (0)	1 (0) t	8 (0)	t	1 (0)	20 (2)	1 (0)	70 (2)	759 (75)	3	
	Top and Bottom	13 (1)	1 (0) t	6 (0)	1 (0)	1 (0)	3 (0)	3 (1)	84 (1)	790 (67)	9	
NSP-2	Whole	6 (1)	4 (2)	1 (0)	8 (1)	2 (0)	1 (0)	25 (0)	2 (1)	57 (4)	785 (28)	2
	Skin	5 (0)	1 (0) t	5 (1)	1 (0)	2 (0)	5 (1)	4 (0)	81 (2)	758 (42)	8	
	Outer	5 (0)	1 (0) t	3 (0)	1 (0)	1 (0)	34 (3)	5 (0)	58 (1)	836 (48)	2	
	Inner	5 (0)	1 (0) t	6 (1)	t	1 (0)	28 (3)	1 (0)	62 (4)	800 (84)	2	
	Top and Bottom	5 (0)	1 (0) t	11 (2)	t	2 (0)	7 (1)	2 (0)	76 (3)	834 (17)	4	
KSP	Whole	5 (0)	2 (0)	2 (0)	18 (1)	2 (0)	2 (0)	14 (4)	1 (0)	53 (2)	758 (25)	2
	Skin	6 (0)	1 (0)	2 (0)	2 (0)	4 (2)	5 (1)	2 (0)	3 (1)	81 (1)	750 (43)	20
	Outer	5 (0)	2 (1)	2 (0)	19 (5)	4 (0)	7 (2)	15 (3)	6 (0)	50 (3)	845 (59)	1
	Inner	4 (0)	t	t	22 (8)	2 (1)	15 (7)	15 (4)	4 (2)	41 (9)	806 (68)	1
	Top and Bottom	5 (0)	1 (0)	1 (1)	22 (1)	2 (2)	9 (0)	9 (0)	1 (0)	54 (1)	838 (32)	2
RES	Whole	31 (3)	t	t	3 (1)	4 (2)	1 (0)	19 (4)	55 (6)	20 (2)	802 (50)	1
	Skin	29 (3)	1 (0) t	1 (0)	1 (0)	3 (2)	2 (0)	t	81 (1)	13 (1)	782 (62)	13
	Outer	40 (3)	1 (0) t	2 (1)	4 (1)	2 (0)	17 (3)	56 (3)	18 (0)	890 (52)	1	
	Inner	47 (2)	t	t	2 (0)	1 (0)	2 (0)	26 (5)	53 (5)	14 (1)	824 (49)	1
	Top and Bottom	30 (3)	1 (0) t	1 (0)	5 (2)	2 (0)	4 (0)	76 (2)	10 (2)	938 (38)	2	

Values are represented as the mean of the 5 onion varieties; values in parentheses are expressed as the standard deviation of onion varieties.

For abbreviation, see text and Table 2.

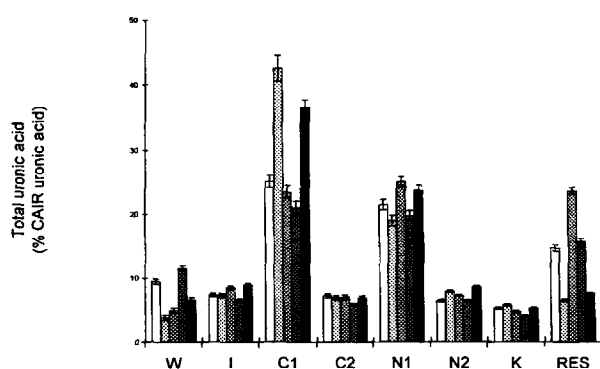


Fig. 4. Total uronic acid (% CAIR uronic acid) from extracts and insoluble residues of onions. Symbols as in Fig. 2.

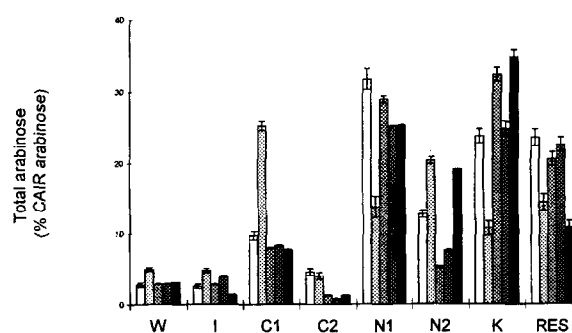


Fig. 5. Total arabinose (% CAIR arabinose) from extracts and insoluble residues of onions. Symbols as in Fig. 2.

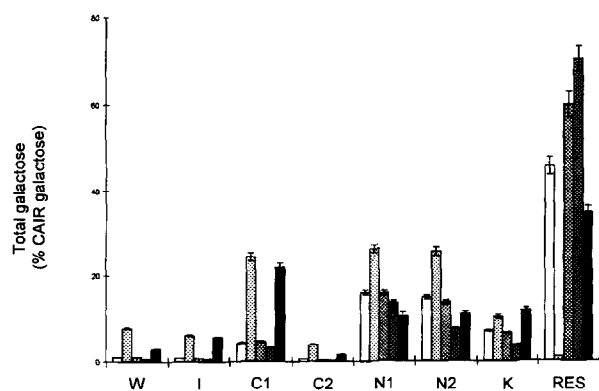


Fig. 6. Total galactose (% CAIR galactose) from extracts and insoluble residues of onions. Symbols as in Fig. 2.

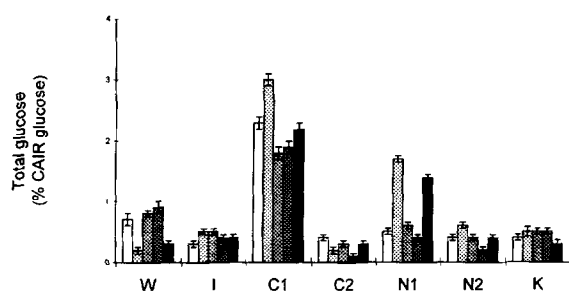


Fig. 7. Total glucose (% CAIR glucose) from extracts of onions. Symbols as in Fig. 2.

in solubilizing pectins and is readily removed by dialysis. The ability of ISP to extract a small amount of pectic polysaccharides is not well understood. Previous studies have shown that complete removal of calcium from

pectic polymers, as determined by atomic absorption spectroscopy, was, nonetheless, achieved by either dialysing with imidazole or resin. It is conceivable that imidazole acts as an ion-exchange agent.

The yields of RES of whole onions were approximately 31% (Table 3). They were rich in glucose (> 50%) and some xylose indicating the presence of a significant amount of xyloglucan (Redgwell and Selvendran, 1986). The ratio of UA: (arabinose + galactose) of RES was lower than the CAIR and probably reflects the insolubility of the more highly branched pectic polysaccharides in the RES.

Skin and top and bottom of onions contained relatively higher levels of extractable CSP with lower uronic acid remaining in the RES. This may contribute to the gelling power of onion skin pectin in which hot ammonium oxalate-extractable pectin was found to give a superior jelly grade, comparing with citrus or apple pectin in yield and quality (Abdel-Fattah and Edrees, 1971, 1987; Alexander and Sulebele, 1973).

There is a relatively small amount of glucose in all extracts as reported by Redgwell and Selvendran (1986). This may be due to small quantities of non-starch polymers, and has not been investigated further. However, extractability of glucose, to a lesser extent, bears a similarity to uronic acid (Fig. 7). There was no significant difference of the remaining cellulosic glucose between different tissues ($p < 0.05$). Furthermore, skin and outer tissues of stored Sturon (S and OS) onions were sequentially extracted and studied for the effect of storage. The results confirmed that storage had no significant effect on cell wall carbohydrate composition ($p < 0.05$; Table 4)

Table 4. Carbohydrate composition of stored onion CAIR extracts and insoluble residues

		Yields (%CAIR)	Carbohydrate (mol%)							Total $\mu\text{g mg}^{-1}$	Ratio UA:NS	
			Rha	Fuc	Ara	Xyl	Man	Gal	Glc			UA
ISP	Skin	6 (0)	1 (0) t	1 (0)	3 (0)	3 (0)	2 (0)	3 (0)	83 (1)	524 (52)	28	
	Outer	7 (1)	1 (0) t	2 (1)	1 (0)	1 (0)	2 (0)	3 (1)	90 (3)	554 (35)	23	
CSP-1	Skin	23 (1)	1 (0) t	2 (0)	1 (0)	2 (1)	1 (0)	3 (1)	90 (1)	856 (68)	30	
	Outer	15 (1)	1 (0) t	2 (0)	1 (0)	3 (1)	2 (1)	4 (0)	85 (2)	898 (76)	21	
CSP-2	Skin	16 (0)	t	t	1 (0)	1 (0)	2 (0)	1 (0)	84 (1)	195 (7)	42	
	Outer	14 (1)	t	t	1 (0)	1 (0)	1 (0)	1 (0)	85 (2)	198 (9)	42	
CIR	Skin	52 (2)	1 (0)	1 (0)	1 (0)	3 (0)	2 (0)	1 (0)	52 (2)	39 (1)	789 (46)	20
	Outer	59 (2)	1 (0)	1 (0)	3 (1)	4 (1)	1 (0)	12 (2)	37 (2)	41 (2)	812 (57)	2
NSP-1	Skin	14 (1)	1 (0)	1 (0)	1 (0)	2 (0)	2 (1)	2 (0)	3 (1)	88 (3)	714 (34)	29
	Outer	14 (1)	1 (0)	1 (0)	4 (1)	1 (0)	2 (0)	9 (1)	4 (1)	77 (2)	786 (39)	6
NSP-2	Skin	6 (1)	1 (0) t	5 (1)	1 (0)	2 (0)	5 (1)	4 (1)	82 (3)	798 (51)	8	
	Outer	6 (1)	1 (0) t	1 (0)	3 (1)	1 (0)	27 (2)	5 (1)	61 (3)	804 (45)	2	
KSP	Skin	5 (0)	1 (0) t	2 (0)	4 (1)	3 (2)	2 (0)	3 (0)	84 (2)	797 (56)	21	
	Outer	5 (1)	2 (0) t	15 (2)	4 (1)	3 (0)	10 (2)	4 (1)	61 (3)	871 (49)	2	
RES	Skin	27 (0)	1 (0) t	1 (0)	3 (1)	2 (0)	t	79 (2)	13 (1)	728 (37)	13	
	Outer	34 (0)	1 (0) t	2 (1)	3 (1)	2 (0)	14 (2)	60 (2)	12 (1)	809 (57)	1	

Values are represented as the mean of the 5 onion varieties; values in parentheses are expressed as the standard deviation of onion varieties.

For abbreviation, see text and Table 2.

CONCLUSION

The cell-wall pectic polysaccharides of onions consisted of a range of structurally related polymers which differed widely in their ease of extraction from the cell-wall complex; particularly, most of the pectic polymers were extracted by CDTA-1 and Na₂CO₃-1. The cell wall carbohydrate composition was similar in all varieties, sprout suppressant and storage conditions.

This study provides evidence that substantial variation exists in cell wall composition among tissues. The relative sizes of the arabinose and/or galactose side-chains may relate to the degree of solubility of pectic polymers, reflecting the maturity of onion tissues.

The differences in cell wall from different tissues provide the basis for developing processing methods for exploiting onion waste.

ACKNOWLEDGEMENTS

This work was funded by the UK Biotechnology and Biological Science Research Council and the European Union (FAIR-CT96-1184).

REFERENCES

- Abdel-Fattah, A. F. and Edrees, M. (1971) Chemical investigations on some constituents of pigmented onion skins. *Journal of the Science of Food and Agriculture* **22**, 298–300.
- Abdel-Fattah, A. F. (1987) Pectin from onion skins. *Indian Food Packer* **41**, 120–121.
- Alexander, M. M. and Sulebele, G. A. (1973) Pectic substances in onion and garlic skins. *Journal of the Science of Food and Agriculture* **24**, 611–615.
- Banker, D. B. and Dara, S. S. (1982) Binding of calcium and magnesium by modified onion skin. *Journal of Applied Polymer Science* **27**, 1727–1733.
- Blakeney, A. B., Harris, P. J., Henry, R. J. and Stone, B. A. (1983) A simple and rapid preparation of alditol acetates for monosaccharides analysis. *Carbohydrate Research* **113**, 291–299.
- Blumenkrantz, N. and Asboe-Hansen, G. (1973) New method for quantitative determination of uronic acids. *Analytical Biochemistry* **54**, 484–489.
- Brett, C. T. and Waldron, K. W. (1996) *The Physiology and Biochemistry of Plant Cell Walls*, 2nd edn. Chapman and Hall, London.
- Coimbra, M. A., Waldron, K. W. and Selvendran, R. R. (1994) Isolation and characterisation of cell wall polymers from the heavily lignified tissues of olive (*Olea europaea*) seed hull. *Carbohydrate Polymer* **27**, 285–294.
- Fenwick, G. R. (1985) The genus *Allium cepa*. Part 2. *CRC Critical Reviews in Food Science and Nutrition* **22**, 273–377.
- Guillon, F. and Thibault, J. F. (1987) Characterization and oxidative cross-linking of sugar beet pectins after mild hydrolysis and arabinases and galactanases degradation. *Food Hydrocolloids* **5/6**, 547–549.
- Guillon, F. and Thibault, J. F. (1990) Oxidative crosslinking of chemically and enzymatically modified sugar-beet pectin. *Carbohydrate Polymer* **12**, 353–374.
- Martin-Cabrejas, M. A. M., Waldron, K. W. and Selvendran, R. R. (1994) Cell wall changes in Spanish pear during ripening. *Journal of Plant Physiology* **144**, 541–548.
- Mort, A. J., Moerschbacher, B. M., Pierce, M. L. and Maness, N. O. (1991) Problems encountered during the extraction, purification, and chromatography of pectic fragments, and some solutions to them. *Carbohydrate Research* **215**, 219–227.
- Ng, A. and Waldron, K. W. (1997a) Effect of steaming on cell wall chemistry of potatoes (*Solanum tuberosum* cv Bintje) in relation to firmness. *Journal of Agricultural and Food Chemistry* **45**, 3411–3418.
- Ng, A. and Waldron, K. W. (1997b) Effect of cooking and pre-cooking on cell-wall chemistry in relation to firmness of carrot tissues. *Journal of the Science of Food and Agriculture* **73**, 503–512.
- Redgwell, R. J. and Selvendran, R. R. (1986) Structural features of cell-wall polysaccharides of onion (*Allium cepa*). *Carbohydrate Research* **157**, 183–199.
- Saeman, J. F., Moore, W. E., Mitchell, R. L. and Millett, M. A. (1954) Techniques for the determination of pulp constituents by quantitative paper chromatography. *TAPPI* **34**, 336–343.
- Sajjaanantakul, T., Van-Buren, J. P. and Downing, D. L. (1989) Effect of methyl ester content on heat degradation of chelator-soluble carrot pectin. *Journal of Food Science* **54**, 1272–1277.
- Selvendran, R. R. and O'Neil, M. A. (1987) Isolation and analysis of cell walls from plant material. *Methods of Biochemical Analysis* **32**, 25–153.
- Sene, C. F. B., McCann, M. C., Wilson, R. H. and Grinter, R. (1994) Fourier-transform Raman and Fourier-transform infrared and their components. *Plant Physiology* **106**, 1623–1631.
- Waldron, K. W. and Selvendran, R. R. (1992) Cell wall changes in immature Asparagus stem tissue after excision. *Phytochemistry* **31**, 1931–1940.