

Monosaccharide Composition of Sweetpotato Fiber and Cell Wall Polysaccharides from Sweetpotato, Cassava, and Potato Analyzed by the High-Performance Anion Exchange Chromatography with Pulsed Amperometric Detection Method

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The cell wall materials (CWMs) from sweetpotato (*Ipomoea batatas* cv. Kokei 14), cassava (*Manihot esculenta*), and potato (*Solanum tuberosum* cv. Danshaku) and commercial sweetpotato fiber as well as their polysaccharide fractions were analyzed for sugar composition by the high-performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD) method. The separation of arabinose and rhamnose, and xylose and mannose, by this method has been improved using a CarboPac PA 10 column. Pretreatment of the CWMs and cellulose fractions with 12 M H₂SO₄ was required for complete hydrolysis to occur. Commercial sweetpotato fiber was found to be mainly composed of glucose (88.4%), but small amounts of other sugars were also detected. Among the root crops, sweetpotato CWM had the highest amount of pectin and galacturonic acid. Fucose was detected only in cassava CWM and its hemicellulose fraction, while galactose was present in the highest amount in potato CWM. Among the polysaccharide fractions, it was only in the hemicellulose fraction where significant differences in the sugar composition, especially in the galactose content, were observed among the root crops.

Keywords: Cell wall material; monosaccharide analysis; HPAEC-PAD; dietary fiber; sweetpotato (*Ipomoea batatas*); cassava (*Manihot esculenta*); potato (*Solanum tuberosum*); hemicellulose; pectin

INTRODUCTION

The plant cell wall is mainly composed of three major classes of polysaccharides, namely, cellulose, hemicellulose, and pectin. These polysaccharides and lignin make up the dietary fiber component of plants (Southgate et al., 1978; Theander and Aman, 1979). Dietary fiber is considered important because it is found to induce a number of physiological effects which include increased fecal bulk and improved large bowel function, as well as reduced levels of blood cholesterol and sugar levels (Schneeman, 1986).

For potato, extensive studies have already been done on its dietary fiber composition (Schweizer and Mursch, 1979; Theander and Westerlund, 1986; Prosky et al., 1988) as well as its cell wall material (CWM) (Jarvis et al., 1981; Ryden and Selvendran, 1990; van Marle et al., 1997a,b). Studies on the CWM of sweetpotato and cassava have been limited. For sweetpotato, Noda et al. (1994) have done thorough investigations on its CWM. Recently, Walter and Palma (1996) studied the effect of storage on the cell wall sugars of two sweetpotato cultivars. And for cassava, no previous studies have been reported on its CWM and its polysaccharide fractions. Detailed knowledge of the major constituents

making up the cell wall is deemed important so as to control and improve the processing and utilization of several agricultural products into foodstuffs and feeds.

In this paper, we report the isolation and fractionation of CWMs from commercial sweetpotato fiber, and starch residues of sweetpotato, cassava, and potato. The CWMs and their respective polysaccharide fractions were characterized in terms of their sugar composition. The conditions for the hydrolysis of the polysaccharide fractions and for monosaccharide analysis by liquid chromatography were also studied.

MATERIALS AND METHODS

Materials. Sweetpotato (*Ipomoea batatas* cv. Kokei 14) and potato (*Solanum tuberosum* cv. Danshaku) tubers were purchased from the local market, while the cassava (*Manihot esculenta*) tubers used were from Indonesia. The sample of sweetpotato fiber was received from Kyushu Kako Co., Kagoshima, Japan. Avicel FD-101 and Avicel SF samples were donated by Asahi Kasei Co., Tokyo, Japan. The α -amylase from *Bacillus subtilis* (liquefying type) was purchased from Seikagaku Kogyo Co., Tokyo, Japan, while Termamyl 120L was from Novo Nordisk, Bagsvaerd, Denmark. The 5% HCl in methanol solution used in the methanolysis experiment was purchased from Nacalai Tesque, Inc., Kyoto, Japan. All chemicals and standard sugars used were of analytical reagent quality and were purchased from either Wako Pure Chemicals, Ind., Ltd., Osaka, Japan or Nacalai Tesque, Inc., Kyoto, Japan.

Preparation of Starch Residue. Sweetpotato, cassava, and potato tubers were peeled, sliced, and passed into a juicer. The juice containing the starch was discarded. The residue

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Table 1. Response Factors of Monosaccharides

monosaccharide	response factor ^a		monosaccharide	response factor ^a	
	PMP derivative ^b	HPLC-PAD		PMP derivative ^b	HPLC-PAD
fucose	0.97	0.86 (6.80)	mannose	1.07	0.99 (32.34)
rhamnose	0.95	0.82 (16.99)	glucose	1.00	1.00 (23.86)
arabinose	1.28	0.96 (15.49)	galactose	1.04	0.96 (19.47)
xylose	1.23	1.19 (28.86)	galacturonic acid	1.00	0.24 (39.91)

^a Calculated using glucose as the reference sugar. ^b Determined using 22% CH₃CN in 10 mM acetate buffer (pH 4.0). Values in parentheses are the retention times of the sugars in minutes.

was wrapped in four layers of gauze and washed in running water until the washings were no longer turbid. Then, it was dried in a hot-air-dryer at 50 °C and ground. The yields (g of starch residue/g of root crop × 100) of the starch residues were 36.6%, 23.3%, and 16.8% for sweetpotato, cassava, and potato, respectively.

Preparation of Cell Wall Material. CWMs from sweetpotato fiber and starch residues of sweetpotato, cassava, and potato were prepared according to the method of Noda et al. (1994). The sample (10.0 g) was first suspended in 200 mL of distilled water and heated at 100 °C for 20 min with continuous stirring. After heating, the mixture was cooled to 60 °C and treated with 50 mL of α -amylase solution from *B. subtilis* (0.2 mg/mL) in 0.1 M acetate buffer (pH 6.0) containing 0.01 M CaCl₂. This mixture was incubated at 60 °C for 30 min and was filtered with a G-3 glass filter. The whole process was repeated twice. The residue was washed successively with distilled water, methanol, and acetone and air-dried to give the CWM.

Fractionation of Cell Wall Material. The method of Shibuya and Iwasaki (1978) was adapted in the fractionation of the CWM. CWM (1.5 g) was treated with 300 mL of 0.25% (NH₄)₂C₂O₄ solution at 90 °C for 3 h. The mixture was filtered with a G-3 glass filter, and the filtrate was dialyzed against distilled water and freeze-dried to obtain the pectin fraction, while the residue was washed successively with distilled water, methanol, and acetone and air-dried. This residue was then treated with 4 M KOH containing 0.1% NaBH₄, incubated at room temperature for 24 h, and filtered. The alkaline extract was neutralized with CH₃COOH, dialyzed against distilled water, and freeze-dried to give the hemicellulose fraction. The residue was again washed with distilled water, methanol, and acetone and air-dried to give the α -cellulose fraction.

Colorimetric Assays. The total sugar content was determined by the phenol-H₂SO₄ method using glucose as standard (Dubois et al., 1956). The uronic acid content was measured by the modified carbazole method using galacturonic acid as standard (Bitter and Muir, 1962). The protein contents of the pectin and hemicellulose fractions were determined by the method of Lowry et al. (1951) using bovine serum albumin as standard.

Hydrolysis Methods. Two methods of hydrolysis were used. The first method used trifluoroacetic acid (TFA). In this method, 200 μ L of 2 M TFA was added to 1 mg of sample in a screwcapped test tube and was heated at 120 °C for 1 h (Albersheim et al., 1967; De Ruiter and Burns, 1986). TFA was removed by evaporation under reduced pressure at 40 °C. The samples were frozen until they were analyzed. In the other method, 2 mg of sample was first added to 225 μ L of 12 M H₂SO₄ and incubated at 30 °C for 1 h. After this pretreatment, distilled water was added to the mixture to give 1 M H₂SO₄ and was heated at 100 °C for 3 h. This hydrolysis method is often referred to as Saeman hydrolysis (Saeman et al., 1963; Neilson and Marlett, 1983; Garleb et al., 1989). After cooling, the hydrolyzates were neutralized with NaOH and then filtered through a 0.45 μ m membrane filter. Samples were stored at 4 °C until they were analyzed.

High-Performance Liquid Chromatography (HPLC). The sugar composition of sweetpotato fiber and microcrystalline cellulose samples (Avicel FD 101 and Avicel SF) was first determined by HPLC using the 1-phenyl-3-methyl-5-pyrazolone (PMP) derivative method by Honda et al. (1989). In this method, TFA hydrolysis was employed. After hydrolysis, TFA

was removed by evaporation, and 500 μ L of distilled water was added to the sample. The solution was then passed in a Sep-Pak cartridge, QMA Plus, Waters Corp., MA, to remove the galacturonic acid, which was found to interfere in the formation of the PMP derivatives. The solution was again evaporated to dryness. Fifty μ L of 0.3 M NaOH and 50 μ L of 0.5 M PMP in absolute methanol was then added to the sample, and the mixture was incubated at 70 °C for 30 min. After incubation, the mixture was neutralized with 150 μ L of 0.1 M HCl, and the excess reagent was removed by extraction with CHCl₃. The aqueous layer was evaporated to dryness, the residue was dissolved in 100 μ L of the HPLC eluant, and 10 μ L of this solution was injected into the HPLC column. Detection of the PMP derivatives was performed with a spectrophotometer at 245 nm. A Beckman Ultrasphere ODS column, 5 μ m (250 × 4.6 mm), was used, and its temperature was kept at 40 °C. A flow rate of 1.00 mL/min was employed. For the separation of the PMP derivatives, the conditions suggested in the original procedure were modified. Elution was carried out using two solvent systems: 22% CH₃CN in 10 mM acetate buffer (pH 4.0) and 22% CH₃CN in 10 mM citrate buffer (pH 3.1).

High-Performance Anion Exchange Chromatography (HPAEC). Chromatography of the samples was performed in a Dionex DX-500 Bio-LC system, using a CarboPac PA 10 column (250 × 4 mm) in combination with a CarboPac guard column, Dionex Corp., Sunnyvale, CA. Detection was made using a pulsed amperometric detector, with an AMMS-II anion micromembrane suppressor, Dionex Corp., Sunnyvale, CA, which used 300 mM NaOH at a flow rate of 3.0 mL/min. Potentials of $E_1 = 0.05$ V, $E_2 = 0.75$ V, and $E_3 = -0.15$ V were applied for duration times $T_1 = 0.40$ s, $T_2 = 0.20$ s, and $T_3 = 0.40$ s, respectively, at a sensitivity of 1 μ C. All determinations were carried out at room temperature using a flow rate of 0.8 mL/min. The neutral monosaccharides were eluted isocratically using 0.5 mM NaOH for 35 min, while galacturonic acid was eluted using 125 mM CH₃COONa in 200 mM NaOH for 10 min. The column was washed with 200 mM NaOH for 10 min and reequilibrated with 0.5 mM NaOH for 10 min before the next injection.

RESULTS AND DISCUSSION

Methods of Sugar Analysis. Using a standard sugar mixture composed of fucose, rhamnose, arabinose, xylose, mannose, glucose, galactose, and galacturonic acid, two methods of sugar analysis were compared. The first method was by HPLC using the PMP derivative method (Honda et al., 1989). In this study, two solvent systems, 22% CH₃CN in 10 mM citrate buffer (pH 3.1) and 22% CH₃CN in 10 mM acetate buffer (pH 4.0), were used instead of 20% CH₃CN in 0.1 M phosphate buffer (pH 5.0), which was used in the original procedure. This was necessary since arabinose and xylose were not eluted separately when the pH 4.0 buffer was used. On the other hand, when the pH 3.1 buffer was used, glucose and galacturonic acid appeared as one peak. Also, galactose was not completely separated from this peak (data not shown). The response factors of the monosaccharides were calculated using glucose as the reference sugar (Table 1). All monosaccharides were dried to constant weight under vacuum at 50 °C using

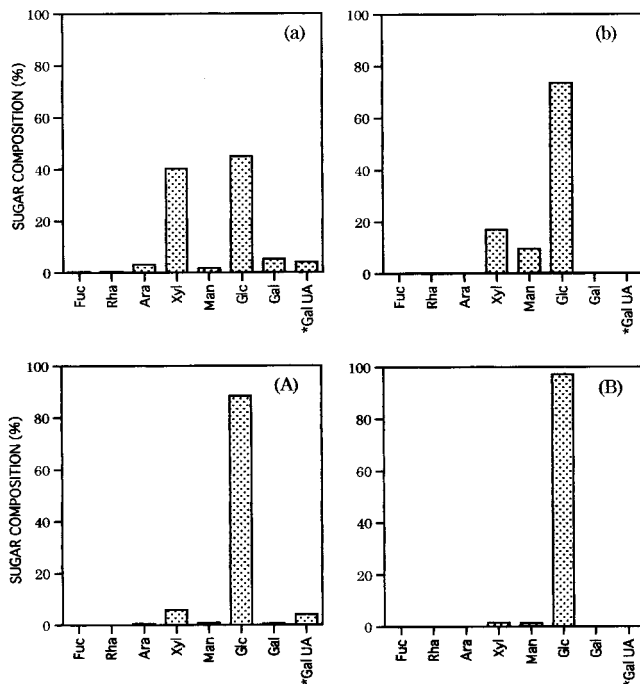


Figure 1. Sugar composition of sweetpotato fiber (a) and Avicel SF (b) determined by the PMP derivative method and the HPAEC-PAD method (A, B). Hydrolysis methods: 2 M TFA at 120 °C, 1 h for the PMP derivative method; pretreatment with 12 M H₂SO₄ at 30 °C, 1 h prior to hydrolysis with 1 M H₂SO₄ at 100 °C, 3 h for the HPAEC-PAD method. *Gal UA was determined by the modified carbazole method.

P₂O₅ prior to the determination of response factors. It can be seen that the pentoses, arabinose and xylose, gave relatively high responses (1.28 and 1.23, respectively).

The other method of sugar analysis was by HPAEC-PAD (PAD = pulsed amperometric detection). This technique has been described as a sensitive and selective means for the determination of monosaccharides (Garleb et al., 1989; Lee, 1990; Clarke et al., 1991). For this method, we initially used a CarboPac PA 1 column. With this column, we observed incomplete separation of arabinose and rhamnose, and xylose and mannose, even at various elution conditions. Another column, CarboPac PA 100, was also tested, but with this column, arabinose and rhamnose also coeluted (data not shown). When a CarboPac PA 10 column was used, a complete separation of these monosaccharides was achieved. Thus, this column was consequently used in further determinations. Shown in Table 1 are the PAD response factors of the monosaccharides used as standards for this method. Compared with the neutral sugars, galacturonic acid had a very low response at only 0.24, as previously reported (Clarke et al., 1991; De Ruiter et al., 1992).

Sugar Composition of Sweetpotato Fiber CWM.

Sweetpotato fiber is a commercially available dietary fiber obtained as a byproduct of citric acid production. It is prepared by treatment of the residue, after extraction of citric acid, with 0.25% NaOH and subsequent bleaching with NaOCl. The sugar composition of sweetpotato fiber CWM was determined with the PMP derivative and HPAEC-PAD methods (Figure 1). Microcrystalline cellulose samples (Avicel FD-101 and Avicel SF) were also subjected to the same analyses to serve as a control. Using the PMP derivative method in combination with TFA hydrolysis, sweetpotato fiber

CWM was found to contain almost equal amounts of xylose and glucose (40.2% and 44.9%, respectively) (Figure 1). For the Avicel SF sample, glucose was measured in the highest amount (73.5%), and xylose and mannose were also detected in significant amounts (Figure 1). The same results were also observed for the Avicel FD-101 sample (data not shown). The amount of glucose detected was relatively smaller than the 98% previously reported for microcrystalline cellulose (Garleb et al., 1989).

As for the HPAEC-PAD method, the Saeman hydrolysis method (Saeman et al., 1963) was used. Using this method, a greater amount of glucose was detected in all samples. For sweetpotato fiber CWM, the relative amounts of glucose and xylose were 88.4% and 5.8%, respectively (Figure 1). As for Avicel SF, glucose accounted for 97.3%, while the amounts of xylose and mannose were only about 1.4% (Figure 1). In the Avicel FD-101 sample the same amounts of sugars were detected (data not shown).

The difference in the results obtained can be attributed to the effectiveness of the hydrolysis procedure employed in each determination. After TFA hydrolysis, it was observed that considerable amounts of the samples were left undissolved, while Saeman hydrolysis resulted in the complete solubilization of the samples. The use of TFA hydrolysis has been reported to be insufficient in hydrolyzing the glycosidic linkages of cellulose or the $\beta(1,4)$ -glycosyl linkages of the xyloglucan backbone (Selvendran et al., 1979). Thus, this could explain the relatively small amounts of glucose detected in the samples hydrolyzed using this method. When H₂SO₄ hydrolysis was used in combination with the PMP derivative method, the presence of SO₄²⁻ ion has been found to interfere with the formation of the PMP derivatives. Although H₂SO₄ hydrolysis has been described as a superior hydrolysis procedure for carbohydrates (Garleb et al., 1989), the removal of SO₄²⁻ ion after hydrolysis is quite difficult. In this study, this disadvantage was remedied by neutralizing the H₂SO₄ hydrolyzate with NaOH solution without desalting before analysis by HPAEC-PAD, in addition; a suppressor was used.

The results of another experiment also revealed that hydrolysis using a low concentration of H₂SO₄ (1 M) or methanolysis combined with TFA hydrolysis did not completely hydrolyze the CWM and cellulose fraction as the amounts of glucose detected were relatively lower than expected (data not shown). The results also showed that although methanolysis combined with TFA hydrolysis is a superior hydrolysis method for uronic acid containing polysaccharides (De Ruiter et al., 1992), it is also not applicable for the hydrolysis of the CWM and cellulose fraction.

The effect of the H₂SO₄ hydrolysis method described earlier on the degradation of the standard sugars has also been checked. The hexoses had very minimal degradation, while 90% of the pentoses were retained after the hydrolysis procedure both when they were included in a mixture and when they were treated alone (data not shown). Garleb et al. (1989) also reported satisfactory recoveries of monosaccharides using this hydrolysis method.

Thus, it can be concluded that pretreatment with 12 M H₂SO₄ prior to hydrolysis with 1 M H₂SO₄ was required to completely hydrolyze sweetpotato fiber CWM and Avicel samples. The use of this hydrolysis

Table 2. Fractionation of CWMs from Sweetpotato Fiber and Starch Residues of Sweetpotato, Cassava, and Potato

sample	fraction	yield (%) ^a	total sugar (%) ^b	uronic acid (%) ^c	protein (%) ^d
sweetpotato fiber	CWM	(97.6)	75.7	4.7	nd
	pectin	2.8	1.2	0.4	0.1
	hemicellulose	7.3	5.4	0.2	0.2
	cellulose	69.1	62.0	1.9	nd
sweetpotato starch	CWM	(19.9)	80.4	31.3	nd
	pectin	32.9	34.9	22.2	0.9
	hemicellulose	9.7	8.2	1.2	0.5
	cellulose	40.1	31.8	3.0	nd
cassava starch	CWM	(7.3)	77.2	17.0	nd
	pectin	17.8	17.4	11.2	0.4
	hemicellulose	22.2	20.5	2.5	1.9
	cellulose	48.2	37.7	2.6	nd
potato starch	CWM	(30.1)	82.8	24.1	nd
	pectin	29.3	26.2	12.3	1.2
	hemicellulose	22.1	18.7	2.4	1.2
	cellulose	32.5	31.6	2.8	nd

^a Yield of CWM = (mg of CWM obtained/mg of starch residue used in the preparation) × 100; yield of fraction = (mg of fraction obtained/mg of CWM used in the fractionation) × 100. ^b (Mg of glucose/mg of CWM) × 100. ^c (Mg of galacturonic acid/mg of CWM) × 100. ^d (Mg of bovine serum albumin/mg of CWM) × 100. nd = not determined.

method in combination with the HPAEC-PAD method for sugar composition analysis also resulted in a better estimation of the true sugar composition of these samples.

Fractionation of CWM. In this experiment, CWMs from sweetpotato fiber and starch residues of sweetpotato, cassava, and potato were prepared by digestion with α -amylase derived from *B. subtilis* (Shibuya and Iwasaki, 1978; Jarvis et al., 1981; Noda et al., 1994). To determine if polysaccharides other than starch were solubilized during the heat treatment prior to the α -amylase digestion, the sugar composition of the solubilized fractions was analyzed. In these fractions, glucose was the main neutral sugar present (95–98%), with only trace amounts of arabinose, galactose, and galacturonic acid (data not shown). This may imply that although solubilization of the pectic component might have occurred during the hot water treatment (100 °C, 20 min), it was very minimal.

Sweetpotato fiber had a CWM yield (mg of CWM/mg of sweetpotato fiber × 100) of 97.6% (Table 2). The total sugar content of the CWM, expressed as glucose equivalent, was 75.7%, while the galacturonic acid content was 4.7%. In this sample, the cellulose fraction had the highest yield (mg of fraction/mg of CWM × 100) among the fractions (69.1%). The hemicellulose fraction was higher (7.3%) than the pectin fraction (2.8%). This indicates that although sweetpotato fiber is mainly composed of cellulose, other components are present as well.

Sweetpotato starch residue had a CWM yield of 19.9%. The total sugar content was measured at 80.4%, while the galacturonic acid content was 31.3%, the highest among the three root crops. In sweetpotato CWM, the cellulose fraction had the highest yield (40.1%), while the hemicellulose fraction had the lowest (9.7%). The amounts of the pectin and cellulose fractions from CWM were higher than those obtained by Noda et al. (1994), but the amount of the hemicellulose fraction was similar at about 10%.

A factory model sample of sweetpotato starch residue was also analyzed. This sample had a smaller starch

content (27.3%, measured colorimetrically) but a higher CWM yield (53.6%) than the sample prepared in the laboratory (data not shown). However, the total sugar and galacturonic acid contents of the CWM as well as the yields of the polysaccharide fractions of the two sweetpotato samples were quite similar.

Cassava starch residue had the lowest CWM yield among the root crops at only 7.3%. This can be attributed to the relatively higher starch content of the starch residue used than that of the other two root crops as determined by the method of Southgate (1969) for dietary fiber content (data not shown). Among the root crops, cassava CWM had the highest cellulose fraction yield (48.2%) but the lowest pectin fraction yield (17.8%) as well as galacturonic acid content (17%). The hemicellulose fraction also had a slightly higher yield than the pectin fraction, which is in contrast with the other two root crops.

Potato starch residue on the other hand had a CWM yield of 30.1%. The total sugar and galacturonic acid contents of this CWM were measured at 82.8% and 24.1%, respectively. The amount of galacturonic acid obtained was very close to those previously reported (Jarvis et al., 1981; Ryden and Selvendran, 1990). Although the fractionation methods employed were different, the yields of the fractions obtained were in agreement with those recently reported (van Marle et al., 1997b; Ng and Waldron, 1997).

The protein contents of the water-soluble polysaccharide fractions (pectin and hemicellulose) were also determined by the method of Lowry et al. (1951). The CWM and cellulose fraction were not subjected to the analysis because of their insolubilities. Sweetpotato fiber had almost negligible amounts of protein (Table 2). Among the root crops, sweetpotato had the lowest sum of protein contents (1.4%) while cassava and potato had almost equal amounts (2.3% and 2.4%, respectively).

Sugar Composition of the CWMs and Fractions from Sweetpotato Fiber and Starch Residues of Sweetpotato, Cassava, and Potato. Using the H₂SO₄ hydrolysis method, the sugar composition of the CWMs and fractions from the starch residues of sweetpotato, cassava, and potato was determined by the HPAEC-PAD method (Table 3). The sugar composition of the fractions derived from sweetpotato fiber was also determined. The sweetpotato fiber CWM was mainly composed of glucose residue, which is most likely to be cellulose in origin since it cannot be released by mild hydrolysis treatments (Figure 1). Its pectin and hemicellulose fractions have very similar neutral sugar compositions, although the amount of galacturonic acid measured in the pectin fraction was much greater (16.1%) than in the hemicellulose fraction (3.3%) (Table 3). However, the presence of high amounts of glucose and xylose in the pectin fraction may indicate solubilization of a part of the hemicellulose fraction during the treatment with 0.25% (NH₄)₂C₂O₄. Only very small amounts of pectic materials are actually present in the sweetpotato fiber CWM. Glucose accounted for 97.6% of the cellulose fraction.

For sweetpotato CWM, the relative quantities of neutral sugars obtained (Table 3) were similar to those of Noda et al. (1994), which are in the order glucose >> galactose > arabinose > xylose > rhamnose > mannose. However, the results obtained, especially the amount of arabinose detected, were somewhat different from

Table 3. Sugar Composition of CWMs and Polysaccharide Fractions from Sweetpotato Fiber and Starch Residues of Sweetpotato, Cassava, and Potato by the HPAEC-PAD Method

sample	fraction	sugar (%)							
		Fuc	Rha	Ara	Xyl	Man	Glc	Gal	Gal UA ^a
sweetpotato fiber	CWM	0	0	0.4	5.8	0.7	88.4	0.5	4.1
	pectin	0	0	2.5	27.9	2.7	46.8	3.9	16.1
	hemicellulose	0.3	0	1.8	35.9	1.5	55.5	1.8	3.3
	cellulose	0	0	0	0.2	0.6	97.6	0.2	1.5
sweetpotato	CWM	0	1.1	7.0	4.1	0.4	38.3	18.0	31.1
	pectin	0	2.0	9.1	0	0	0.5	28.1	60.4
	hemicellulose	0	0	12.0	23.5	0.3	38.0	15.8	10.3
	cellulose	0	0.4	2.1	1.4	0.8	84.5	5.1	5.6
cassava	CWM	0.7	0.9	4.0	9.9	1.6	43.2	22.1	17.5
	pectin	0	1.4	5.7	0.3	0.1	0.4	29.1	62.9
	hemicellulose	2.2	1.3	6.3	26.7	0	13.8	38.4	11.4
	cellulose	0	0.2	1.1	2.9	3.3	81.7	7.3	3.4
potato	CWM	0	0.9	5.6	2.2	0.9	32.8	35.2	22.4
	pectin	0	1.9	7.8	0.2	0	0.6	47.3	42.2
	hemicellulose	0	0.9	9.3	7.5	0	14.3	57.0	11.0
	cellulose	0	0.2	1.5	0.4	2.2	80.3	9.6	5.8

^a Gal UA was measured by the modified carbazole method.

those reported by Walter and Palma (1996): glucose \gg galactose $>$ xylose \gg rhamnose $>$ mannose $>$ arabinose. The pectin fraction contained high amounts of galacturonic acid (60.4%), indicating the presence of polyuronides. The presence of arabinose and rhamnose, and high amounts of galactose, may also indicate the presence of rhamnogalacturonans (McNeil et al., 1980). The pectic materials obtained from sweetpotato had a high galacturonic acid:rhamnose ratio (30:1), suggesting that they may be derived from the middle lamella region (Redgwell and Selvendran, 1986). The hemicellulose fraction obtained contained large amounts of glucose and xylose, which may suggest the presence of xyloglucans, the main hemicellulosic component of dicotyledonous plants (Redgwell and Selvendran, 1986). Noda et al. (1994) also reported the presence of significant amounts of xylan in the hemicellulose fraction of sweetpotato. The cellulose fraction of sweetpotato contained 84.5% glucose.

For cassava CWM, the relative quantities of the neutral sugars obtained were in the order glucose \gg galactose \gg xylose $>$ arabinose $>$ mannose $>$ rhamnose $>$ fucose (Table 3). Galacturonic acid accounted for 17.5%, which is the lowest among the three root crops. The pectin fraction contained high amounts of galacturonic acid and galactose residues, which were also observed in sweetpotato. Galactose, xylose, and glucose were the major neutral sugars present in the hemicellulose fraction. It can also be noted that fucose was detected in significant amounts only in this fraction (2.2%). Fucose has also been detected in the cell wall polysaccharide fractions of other plants such as rice (Shibuya and Iwasaki, 1978), gobo (Watanabe et al., 1991), cucumber (McFeeters and Lovdal, 1987), kiwi (Redgwell et al., 1988), and pear (Martin-Cabrejas et al., 1994). The cassava cellulose fraction contained mostly glucose residues (81.7%). The present study was the first report on cassava CWM and polysaccharide fractions.

Potato CWM was mainly composed of galactose and glucose residues, with a galacturonic acid content of about 22% (Table 3). The sugar composition obtained in this study conformed with those recently reported (Ng and Waldron, 1997; van Marle et al., 1997a,b). The pectic fraction was mainly comprised of galactose and galacturonic acid residues, which are present in almost equal amounts (47.3% and 42.2%, respectively). It can

also be noticed that the amount of galactose in this fraction was relatively higher than those obtained in the pectin fractions of the other two root crops. According to Jarvis et al. (1981), potato pectins are of the galactan-rich type like those of onion bulbs (Mankarios et al., 1980). Galactose was also the most abundant neutral sugar residue in the hemicellulose fraction, just like in the CWM and pectin fraction. This finding was also reported by van Marle et al. (1997b). Xyloglucan may also be the main hemicellulosic component present in the fraction. Potato hemicellulose may also contain galactoxyloglucan, a mannan or glucomannan, and an arabinogalactan (Jarvis et al., 1981). The cellulose fraction was made up of 80.3% glucose.

Among the polysaccharide fractions, it was only in the hemicellulose fraction where significant differences in the neutral sugar composition between the root crops were observed. It can be noticed that the amount of galactose detected in this fraction greatly differs in the three root crops (Table 3). However, the galacturonic acid contents were almost similar (10.3–11.4%). Glucose and xylose were the predominant neutral sugars present in sweetpotato. In cassava, glucose was replaced by galactose as the neutral sugar residue present in the highest amount. Also, fucose was detected in significant amounts only in this root crop. Potato on the other hand only had galactose as the major neutral sugar residue. The amount of arabinose was also higher than that of xylose in this sample.

Further studies are also needed on the physical properties and physiological functions of the isolated CWMs and polysaccharide fractions to improve the utilization of the root crops.

CONCLUSIONS

In this study, two methods of monosaccharide analyses were compared, namely, TFA hydrolysis and the PMP derivative method, and H₂SO₄ hydrolysis in combination with the HPAEC-PAD method. The separation of the standard sugars, arabinose and rhamnose, and xylose and mannose, by the HPAEC-PAD method has been improved using a CarboPac PA 10 column. It was also found that, for complete hydrolysis of the sweetpotato fiber CWM and Avicel samples to occur, pretreatment of these samples with 12 M H₂SO₄ was necessary prior to hydrolysis with 1 M H₂SO₄.

This study also partially characterized the polysaccharide fractions of the CWMs from sweetpotato fiber, and starch residues of sweetpotato, cassava, and potato by their extraction properties and sugar composition. Especially for cassava, this is the first report. It was revealed that although sweetpotato fiber was mainly composed of the cellulose fraction, small but significant amounts of the pectin and hemicellulose fractions were present as well. Among the root crops, sweetpotato CWM had the highest amount of the pectin fraction and consequently the highest galacturonic acid content. Cassava on the other hand had the highest amount of the cellulose fraction, and it was also in this CWM and its hemicellulose fraction where a significant amount of fucose was detected. In potato, galactose was present in the highest amount among the neutral sugar residues detected. And last, among the polysaccharide fractions, it was in the hemicellulose fraction where significant differences in the neutral sugar composition, especially in the relative amounts of galactose residues, were observed between the three root crops.

ABBREVIATIONS USED

CWM, cell wall material; HPAEC-PAD, high-performance anion exchange chromatography with pulsed amperometric detection; HPLC, high-performance liquid chromatography; PMP, 1-phenyl-3-methyl-5-pyrazolone; TFA, trifluoroacetic acid; Fuc, fucose; Rha, rhamnose; Ara, arabinose; Xyl, xylose; Man, mannose; Glc, glucose; Gal, galactose; Gal UA, galacturonic acid.

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