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Received for review May 12, 1989. Accepted September 12, 1989. This research was supported by grants from the Saskatchewan Pulse Crop Development Board, Saskatchewan Agriculture-Agriculture Development Fund, Regina, and Saskatchewan Research Council, Saskatoon.

Registry No. K^+, 7440-09-7; Ca^{2+}, 7440-70-2; Mg^{2+}, 7439-95-4; P, 7723-14-0; PA, 83-86-3; lignin, 9005-53-2; low-methoxyl pectin, 9049-34-7; water, 7732-18-5.

Changes in Nonvolatile Acids, Sugars, Pectin, and Sugar Composition of Pectin during Peach (Cv. Monroe) Maturation

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Changes in soluble sugars, nonvolatile acids, pectin content, and the sugar composition of isolated pectin were determined during Monroe peach maturation from 80 days after flowering (DAF) until about 2 weeks after the beginning of fruit drop (130 DAF). Sucrose and sorbitol showed the largest changes of all carbohydrates measured. Quinic was the major acid in immature fruit but rapidly decreased during maturation. Malic became the major acid during final growth stages, and the increase in malic acid to citric acid ratios closely paralleled the time at which sucrose reached maximum levels. Total pectin levels increased linearly in immature fruit but leveled off about the time sucrose began its second sigmoidal increase. The carbohydrate composition of pectin also changed more during the linear increase in total pectin but remained fairly constant after total amounts leveled off. The time at which sucrose levels and malic acid to citric acid ratios reached maxima and quinic acid levels were lowest could be used as reliable indices of peach physiological maturity.

Most research conducted on compositional changes during peach maturation has focused on soluble solids, total sugars, reducing sugars, and titratible acidity as reliable indices of physiological maturity (Sistrunk, 1985; Kader et al., 1982). With improved analytical techniques, individual sugars and nonvolatile acid components have been determined during maturation on a variety of peach cultivars (Ishida et al., 1985; Sandhu et al., 1983; Chalmers and van den Ende, 1975; Li and Woodroof, 1968). These studies give a more realistic approach to the biochemistry involved in fruit maturation and the relationship of the levels of sugars and acids to physiological maturity. However, there is very little information available in the literature on the changes in individual carbohydrates and nonvolatile acids relative to peach maturation in cultivars grown in the Southeastern United States. Also, information is lacking on the development of pectin content and composition during peach maturation. The purpose of this study was to monitor the changes in these components during maturation of Monroe peaches. Consistent relationships between one or more components may provide reliable indices of peach physiological maturity.

MATERIALS AND METHODS

Plant Material. Peaches were obtained from trees (cv. Monroe) grown at the University of Georgia Horticultural Farm (Watkinsville, GA). The trees were about 4 years old and received adequate rainfall and/or irrigation during the summer of 1988. Twelve peaches were hand-harvested at intervals during maturation (June 20–Aug 15), starting at 81 days after flowering (DAF) until about 2 weeks after the beginning of fruit-drop (130 DAF). Individual peach diameters (long axis) were measured with a vernier caliper to ensure sample uniformity. The average fruit weight (10–12 peaches) was also obtained.

Sugars and Nonvolatile Acid Determination. Two replicate samples of about 5–6 g of fresh mesocarp tissue were diced with a sharp knife and ground with a mortar and pestle in 75% ethanol. The tissue was allowed to extract for 10 min, brought to a final volume of 25 mL (75% ethanol), and then filtered through Whatman No. 4 filter paper. Aliquots of the extract (0.5 mL) were dried under a slow stream of dry nitrogen and sugars and nonvolatile acids determined by capillary GLC as previously described (Chapman and Horvat, 1989).

Pectin Extraction, Determination, and Carbohydrate Composition. Fresh mesocarp tissue (10–15 g) from each harvest was prepared as above and allowed to extract for 10 min in 150 mL of 75% ethanol. The extract was filtered and the pulp washed with three portions of 150 mL of 75% ethanol

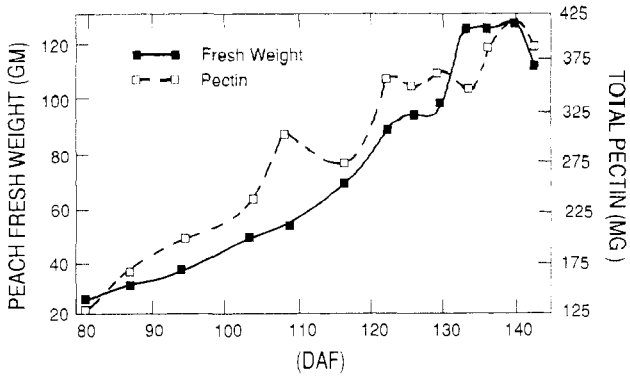

Figure 1. Changes in fresh weight and total pectin in Monroe peaches during maturation. Pectin is expressed as total amount extracted from whole peach based on fresh mesocarp tissue.

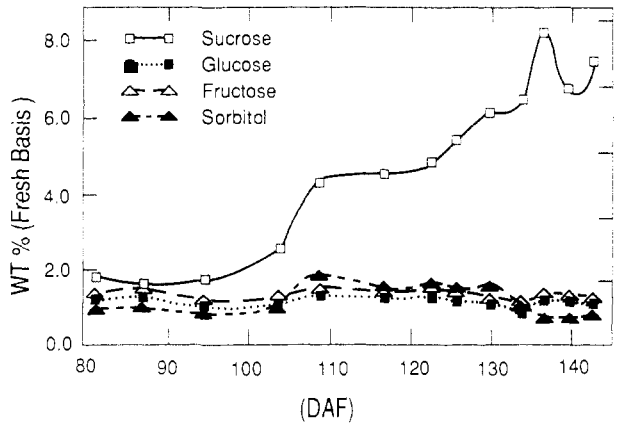

Figure 2. Changes in sugars and sugar alcohols during peach maturation.

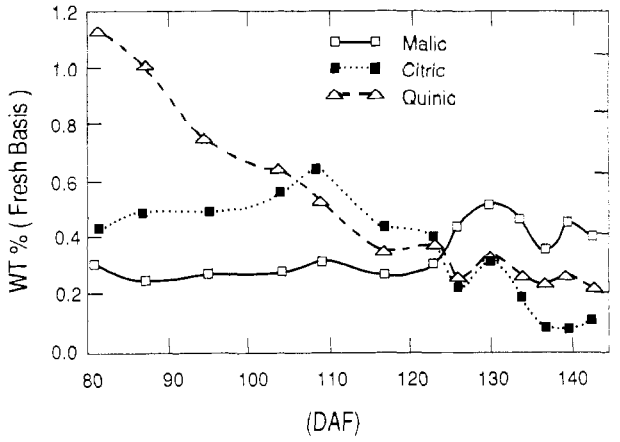

Figure 3. Changes in major nonvolatile acids during peach maturation.

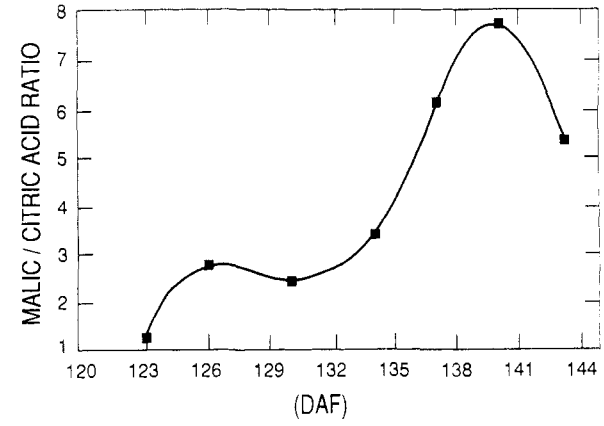

Figure 4. Changes in the malic acid to citric acid ratios during peach maturation.

with use of a coarse sintered-glass filter under vacuum to remove all soluble sugars. The washed pulp was quantitatively transferred to a small beaker and extracted with 25–30 mL of 0.03 M HCl at 85 °C for 1 h to remove peach pectin (Baig et al., 1982; Gierschner, 1981). The acidic extract was filtered through four layers of cheesecloth and the volume measured in a graduated cylinder.

A 1-mL portion of this extract was diluted to 25 mL in a volumetric flask. Pectin determinations were essentially the method of Blumenkrantz and Asboe-Hansen (1973), except volumes used for color development in these determinations were 1.0 mL of sample, 6.0 mL of H_2SO_4/0.012 M $Na_2B_4O_7$, and 0.1 mL of 0.15% 3-phenylphenol (0.5 N NaOH). Also, the tubes could be cooled in a water bath (room temperature) rather than with ice, without affecting results. The amount of peach pectin determined was based on standard curves prepared with the above reagents, citrus pectin and D-galacturonic acid (Sigma Chemical Co., St. Louis, MO).

Peach pectin for carbohydrate composition was precipitated from the acidic extracts by adding absolute ethanol to make 75% ethanol–water solutions. These solutions were refrigerated for 2 h and then centrifuged at 10400*g* for 10 min. Pellets (pectin) were initially dried in a vacuum oven at room temperature and then over a stream of nitrogen. The pectin was dissolved in 10–15 mL of 0.1 M acetate buffer (pH 4.3) for enzymatic hydrolysis. The concentrations of the pectin solutions were determined as above, and it was found that at least 2 mg/mL was necessary to obtain consistent carbohydrate composition during enzymatic reaction. *Aspergillus niger* pectinase (EC 3.2.1.15) and *Trichoderma viride* cellulase (EC 3.2.1.4; Sigma) were used for the hydrolysis of peach pectin. The former was dialyzed at 3 °C overnight against 200 volumes of 0.1 M acetate (pH 4.3) to remove significant amounts of mannose found in this preparation. Pectin (1.0 mL) was hydrolyzed by using two enzymatic systems, one with pectinase (0.2 mL, 20 units) only and the other with pectinase + cellulase (5 mg, 20 units) at 30 °C for 45–60 min. The reactions were terminated by addition of 3 mL of absolute ethanol to precipitate unhydrolyzed pectin and protein. The mixture was filtered through Whatman No. 4 filter paper and dried thoroughly with a stream of nitrogen. Individual sugars were determined as oxime–trimethylsilyl derivatives and identifications confirmed by GC/MS as described previously (Chapman and Horvat, 1989).

RESULTS AND DISCUSSION

The fresh weight increased from an average weight of 24 g (81 DAF) to 128 g at 140 DAF (Figure 1). There was a significant drop in fresh weight observed between 140 and 143 DAF. The total level of pectin increased from 81 to 123 DAF (Aug 1), then increased slightly until 140 DAF, and then decreased by 143 DAF. Approximately during the same period (123–137 DAF), sucrose levels showed the greatest rate of increase (Figure 2). This could be interpreted as the final fill-stage of Monroe peaches, since the slower increase in pectin levels may indicate the end of mesocarp cell growth; however, the cells could still be in an active fill-stage since sucrose levels increased significantly between 123 and 137 DAF (second sigmoidal; Figure 2).

The major soluble sugars and sugar alcohols found in Monroe peaches were sucrose, sorbitol, glucose, and fructose (Figure 2). Xylose, galactose, and inositol were also detected but were ≤0.1% and, therefore, not reported.

From 81 to 95 DAF, sucrose levels changed very little. The first sigmoidal increase in sucrose occurred between 95 and 109 DAF, followed by little change between 109 and 123 DAF. The second sigmoidal increase occurred between 123 and 137 DAF (Figure 2). This pattern in sucrose levels during maturation closely parallels double-

Table I. Carbohydrate Composition of Monroe Peach Pectin after Hydrolysis with Pectinase from *A. niger* during Fruit Maturation

	composition at days after flowering												
sugar[a]	81	87	95	104	109	117	123	126	130	134	137	140	143
arabinose	8.2	6.5	7.7	6.3	6.3	4.8	7.9	7.2	7.1	4.7	6.3	6.8	5.2
rhamnose	2.5	1.9	2.9	2.2	2.4	2.8	2.7	2.6	2.9	3.0	3.1	3.7	3.2
galactose	18.8	19.2	29.6	13.7	8.8	10.8	7.1	6.2	8.9	7.0	5.5	8.1	6.6
mannose	2.0	1.2	2.2	1.9	1.7	2.7	1.9	2.1	2.2	2.2	1.9	2.7	2.2
glucose	3.9	2.1	3.7	3.5	1.7	3.0	1.4	5.9	3.2	3.5	2.1	6.1	5.2
GalCOOH[b]	64.5	69.2	53.9	72.4	78.3	76.2	79.5	77.7	75.2	79.5	81.0	71.9	77.3

[a] Percent individual sugars of the total sugars obtained after hydrolysis. [b] GalCOOH = galacturonic acid.

Table II. Carbohydrate Composition of Monroe Peach Pectin after Hydrolysis with Pectinase + Cellulase (*T. viride*) during Fruit Maturation

	composition at days after flowering												
sugar[a]	81	87	95	104	109	117	123	126	130	134	137	140	143
arabinose	6.0	6.3	5.4	5.8	6.0	4.9	8.1	6.4	5.5	5.0	6.1	5.9	4.3
rhamnose	1.8	1.7	1.9	1.9	2.3	2.6	2.3	2.3	2.4	2.8	2.8	2.3	3.1
galactose	27.6	20.7	21.4	15.8	12.4	15.6	11.3	13.2	12.7	9.5	9.2	10.0	10.3
mannose	1.6	1.0	1.3	1.5	1.7	2.0	1.9	1.8	1.9	2.2	1.8	1.4	2.0
glucose	21.8	11.1	7.5	12.5	12.2	15.0	8.8	13.2	12.8	11.5	8.1	12.9	10.4
GalCOOH[b]	41.1	59.2	62.5	62.4	64.7	60.2	68.0	61.5	65.4	69.9	71.9	67.2	70.9

[a] Percent individual sugars of the total sugars obtained after hydrolysis. [b] GalCOOH = galacturonic acid.

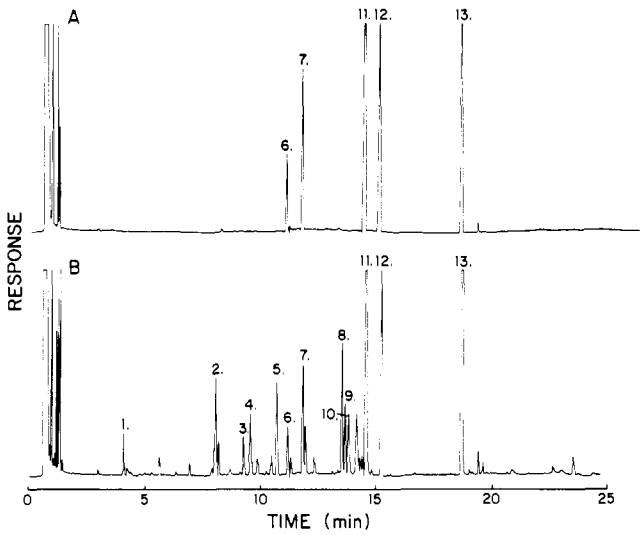

Figure 5. Gas chromatographic profile: A, oxime–trimethylsilyl derivative of authentic galacturonic acid (peaks 6–12) (peak 13 is phenylglucose, internal standard); B, oxime–trimethylsilyl sugars from enzymatic hydrolysis of Monroe peach pectin. Peak identification: 1 = UNK; 2 = arabinose; 3 = UNK; 4 = rhamnose; 5 = UNK; 6, 7 = isomeric peak of galacturonic acid; 8 = galactose; 9 = mannose; 10 = glucose; 11, 12 = galacturonic acid; 13 = phenylglucose.

sigmoidal growth curves observed in most soft and stone fruit varieties (Chalmers and van den Ende, 1975; Romani and Jennings, 1971).

Sorbitol levels increased to a maximum at about 109 DAF, remained fairly constant until 130 DAF, and then declined for the rest of the maturation period (Figure 2). Sorbitol and sucrose are thought to be biosynthesized in leaves and then translocated to the developing fruit from a variety of plants (DeVilliers et al., 1974; Bieleski and Redgwell, 1985; Ishida et al., 1985). Radiolabeling experiments also suggest that some of the sorbitol is converted into sucrose in peach mesocarp tissue (Ishida et al., 1985). Therefore, the drop in sorbitol levels we observed 130 DAF may indicate the final production of sucrose in mesocarp tissue, since sucrose levels reached maximum levels at 137 DAF and dropped significantly about 1 week later (143 DAF). The levels of glucose and fructose remained fairly constant during the entire maturation period and were almost identical in amounts.

The major nonvolatile acids quantitated were malic, citric, and quinic acids (Figure 3). Succinic acid was also found at all maturity stages, but the levels were ≤0.1% and were not reported. Initially, quinic was the major acid extracted but rapidly declined from 81 to 126 DAF and then remained constant for the rest of the growth period (Figure 3). Citric acid levels remained constant until 109 DAF and then also declined. However, citric was the major acid from 109 to 117 DAF. Malic acid levels remained fairly constant until 123 DAF, increased rapidly for the next 7 days (130 DAF), and then declined for the rest of the growth period (Figure 3). After 123 DAF, malic became the principle acid and, consequently, the malic acid to citric acid ratio steadily increased to a maximum (Figure 4). Increases in malic acid to citric acid ratios have also been observed during ripening of other peach cultivars both on and off the tree (Li and Woodroof, 1968). The time of maximum sucrose levels at 137 DAF (Figure 2) almost coincided with the maximum malic acid to citric acid ratio (Figure 4). If it is assumed that maximum levels of sucrose occur precisely at the time mesocarp cells reach full development, then these measurements could be used as a reliable index for physiological maturity in peaches.

The major sugars found in Monroe peach pectin after enzymatic hydrolysis with either enzyme system were arabinose, rhamnose, galactose, mannose, glucose, and galacturonic acid (Tables I and II). The identification of oxime–trimethylsilyl sugars in these preparations were based on GLC retention times and also confirmed by GC/MS (Chapman and Horvat, 1989). We have found that most reducing sugars yielded two GC peaks by the analytical procedure described. The peak ratios were about 4:1, with the larger peak being used for quantitation of a given reducing sugar. Galacturonic acid yielded four isomeric peaks with this procedure (Figure 5A); however, it did not interfere with the other sugars of interest (Figure 5B). The larger two peaks (11 and 12, Figure 5B) of the oxime–trimethylsilyl galacturonic acid were chosen for quantitation since their peak areas could be summed by the Hewlett-Packard 3392A integrator. Xylose and fucose have also been reported in significant levels from other fruit and plant pectins (Carpita, 1989; DeVries et al., 1981;

Baig et al., 1980). We observed these two sugars in only trace amounts from pectins isolated in this study.

At early stages of maturation (81–123 DAF), the rate of increase of pectin levels in mesocarp tissue was highest (Figure 1). During this same period, the sugar composition of pectin also showed a greater compositional change. The percentage of galactose decreased significantly, while galacturonic acid increased up to 123 DAF (Tables I and II). The percentage of glucose also decreased significantly in the dual-enzyme system (Table II). As the total amount of pectin appeared to level off (123–143 DAF, Figure 1), the sugar composition of pectin appeared to change very little during this same growth phase (Tables I and II). However, the levels of malic acid and sucrose continued to increase substantially from 123 to 143 DAF (Figures 2 and 3).

Significant differences in the sugar composition of pectin were observed when the polymer was hydrolyzed with either pectinase alone or with pectinase + cellulase. The major difference between the two hydrolytic reactions was an increase in the percentage of glucose in pectin composition in the system with both enzymes. Galacturonic acid was the major sugar hydrolyzed from pectin in either enzyme system. Galacturonic acid percentages increased from about 41 to 65% at an immature growth stage (81 DAF) to about 77.4 ± 3.0% with pectinase and 68.2 ± 3.7% with the dual-enzyme system at more mature stages (123–143 DAF, Tables I and II).

The percent hydrolysis could be computed based on measured pectin concentrations and from quantitative sugar data obtained after enzymatic hydrolysis. The average percent hydrolysis of pectin with only pectinase was about 27%, while the dual-enzyme system yielded about 47%. Several pectin samples were also hydrolyzed with 2 N trifluoroacetic acid at 130 °C for 2–3 h, but yields were consistently low (10–12%). The results would indicate that pectinase + cellulase yielded a more complete hydrolysis of pectin. Several samples of isolated peach pectin, at various growth stages, were also incubated 72 h with only cellulase. Results of several reactions revealed no significant increase in free glucose. Therefore, the hydrolysis using both enzymes may yield a more representative carbohydrate composition of Monroe peach pectin than when hydrolyzed with only pectinase.

The results also suggest that small polymers of cellulose may be covalently attached to the main polygalacturonic acid chain during early fruit development, since higher percentages of glucose were obtained after hydrolysis.

The percentages of rhamnose and mannose in pectin changed very little during maturation, and the levels liberated were nearly identical by either enzymatic system. These results could indicate that only pectinase was responsible for their release (Tables I and II). The individual sugars obtained from both hydrolytic reactions were converted to micromoles based on the total amount of pectin extracted at each maturity stage. From these data the molar ratio of galacturonic acid to rhamnose was 26:1 from 81 to 123 DAF and 21:1 from 126 DAF to the end of the maturation period. Rhamnose is thought to be incorporated periodically into the main galacturonic acid chain, and the galacturonic acid to rhamnose ratio has been reported to be 25:1 from pectins isolated from several plant sources (BeMiller, 1986). Our results substantiate these findings.

On the basis of results of this study, parenchyma cells of the mesocarp continue to increase in sucrose after cell walls cease to grow since total pectin appears to level off. Likewise, the sugar composition of pectin remains fairly constant during the final stages of peach maturation. The time during maturation when sucrose levels and the malic acid to citric acid ratio reached their maximum could be used as reliable indices of physiological maturity in this peach variety. Other components that are easy to analyze and could also be used for this purpose would be the time during maturation when quinic acid levels were lowest. Although significant changes were observed in pectin levels and its sugar composition during maturation, this component would not be suitable as an index of maturity because analytical techniques are tedious and time-consuming.

More studies are needed to determine whether maximum sucrose levels and the malic acid to citric acid ratio do indeed indicate physiological maturity in peaches. The relationship between photosynthesis, translocation, and water availability also needs to be better understood, since these are the primary factors controlling and producing changes in these components, which ultimately affect fruit maturity and quality after harvest.

ACKNOWLEDGMENT

We thank Judy B. Arthur for her able technical assistance.

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Received for review June 23, 1989. Accepted October 24, 1989. Mention of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Department of Agriculture.

Registry No. Pectin, 9000-69-5; arabinose, 147-81-9; rhamnose, 3615-41-6; galactose, 59-23-4; mannose, 3458-28-4; glucose, 50-99-7; galacturonic acid, 685-73-4; sucrose, 57-50-1; fructose, 57-48-7; sorbitol, 50-70-4; malic, 6915-15-7; citric, 77-92-9; quinic, 77-95-2.

Studies on Vegetables. Investigation of an Arabinan from Parsnip (*Pastinica sativa*)†

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An arabinan isolated from parsnip was shown by sedimentation studies to be homogeneous, and methylation revealed a highly branched structure. Hydrolysis of the fully methylated polysaccharide yielded 2,3,5-tri-*O*-methyl-L-arabinose (11 mol), 2,3-di-*O*-methyl-L-arabinose (20 mol), 3-*O*-methyl-L-arabinose (trace), 2-*O*-methyl-L-arabinose (7 mol), and L-arabinose (2 mol). The general structural features of the arabinan are discussed.

Arabinans are widely distributed in the plant kingdom, being found in, among other things, seeds, vegetables, and fruits. These polymers tend to fall into two groups: those that are associated with pectins and may be released by alkaline degradation during the isolation and fractionation procedures and those believed to be natural homoglycans such as those found in mustard, soybean, rapeseeds, and parsnip.

In order to eliminate the possibility of degradation due to β-elimination, very mild conditions were used for the removal of starch and subsequent fractionation and purification of an arabinan from parsnip. The present communication deals with the general structural features of this polysaccharide.

EXPERIMENTAL SECTION

The general experimental methods have been reported previously (Siddiqui, 1990).

Removal of Starch. The 80% ethanol insoluble residue (60 g) (Siddiqui, 1990) from parsnip in 0.2 M acetate buffer (pH 4.50) (2.5 L) was treated with (800 mg) amyloglucosidase (*Aspergillus orysae*; Sigma). The surface was layered with toluene, and the suspension was stirred for 48 h, at room temperature. The digested material was dialyzed (Spectrapore membrane tubing, diameter 32 mm, molecular weight cutoff 12 000–14 000) for 48 h against running tap water and 4 h against distilled water. The sample following concentration to a thick slurry (1.5 L) was added to ethanol (4 volumes) and allowed to settle. The clear supernatant was removed by siphoning and filtration, and the insoluble residue was washed with ethanol and acetone and air-dried for 24 h to yield a dry fluffy residue (25 g).

The clear supernatant was concentrated to a small volume and freeze-dried to yield the 80% ethanol soluble fraction (1 g). Acid hydrolysis of a portion (5 mg) with 72% sulfuric acid (general methods) showed mainly glucose and arabinose with traces of galactose, mannose, xylose, and uronic acid.

Table I. GLC and CI-MS Data for Sugars from Methylated Arabinan

compound	ret time (acetate), min	molar ratio	CI-MS [MH$^+$]	mode of linkage
2,3,5-trimethylarabinitol	0.77	11	279	L-Ara*f*-(1→
2,3-dimethylarabinitol	0.86	20	307	→5)-L-Ara*f*-(1→
2-methylarabinitol	0.93	7	335	→3,5)-L-Ara*f*-(1→
3-methylarabinitol	0.95	trace	335	→2,5)-L-Ara*f*-(1→
arabinitol	1.00	2	303	→2,3,5)-L-Ara*f*-(1→

Fractionation of Polysaccharides. The polysaccharide (~1 g, ethanol soluble fraction) was fractionated on a column (3 × 35 cm) of DEAE-cellulose (borate form) (Neiekom and Kuendig, 1965). Elution with water (600 mL), with collection of effluent in 10-mL fractions, yielded two water-eluted fractions, W_1 (tubes 15–27, negative rotation) and W_2 (tubes 29–50, positive rotation). Gradient elution with 0–0.5 M sodium metaborate (1 L) gave an acidic fraction. The neutral fractions were dialyzed (20 h against running tap water, 4 h against distilled water) and freeze-dried to yield materials W_1 (124 mg) and W_2 (154 mg). The borate fraction was acidified with acetic acid and similarly recovered following dialysis and freeze-drying to yield acidic material (180 mg).

GLC of alditol acetates prepared from the hydrolysates of W_1 and W_2 following reduction and acetylation (general methods) showed arabinose (83.2%), galactose (7.4%), glucose (8.2%), and mannose (1.2%) in the former and arabinose (16.9%), galactose (2.3%), and glucose (80%) in the latter.

Further Purification of the Arabinan. Fraction W_1 (119 mg) was fractionated on a column (2.5 × 30 cm) of Sephadex G-75 (Granath, 1965). Elution with water, with collection of effluent in 10-mL fractions, yielded fraction 1 (tubes 1–25, positive rotation) and fraction 2 (tubes 27–45, negative rotation). Fraction 2 (68 mg) was recovered following concentration and freeze-drying.

Paper chromatography of a hydrolysate revealed arabinose with a trace of glucose.

† Contribution No. 816 of the Food Research Centre, Agriculture Canada, Ottawa, Canada.

0021-8561/90/1438-0387$02.50/0 Published 1990 by the American Chemical Society