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THE MUCILAGE OF *Opuntia aurantiaca*

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ABSTRACT

The mucilage isolated from *Opuntia aurantiaca* has been shown by methylation and partial hydrolysis studies to possess a highly branched structure. The mucilage is composed of 4-linked galactosyluronic acid, 2-linked rhamnosyl, and 6-linked galactosyl residues. Most of the last-named residues carry branches at C-3 or C-4, or both C-3 and C-4. The branches are composed mainly of (1→3)-linked, (1→5)-linked, and end-group arabinofuranosyl residues, and end-group xylopyranosyl residues. The mucilage possesses both acid-stable and acid-labile galactosyluronic acid residues. The ratio of galacturonic acid to rhamnose in the degraded polysaccharide is 1 : 2.

INTRODUCTION

Mucilages isolated from various *Opuntia* species have been studied by various research groups[1–8]. In a few of these studies, only sugar compositions and methylation analyses of whole mucilages have been reported[5–8]. The presence of an alternating galacturonic acid–rhamnose backbone has been firmly established and the position of the branches in the macromolecule identified in only one of these studies[2–4]. The present study was undertaken in order to establish further structural details of the mucilage of *O. aurantiaca*.

RESULTS AND DISCUSSION

Opuntia aurantiaca (Jointed Cactus) is a low-spreading, creeping shrublet, growing up to 1 m high, which has become uncontrollable in the eastern Cape of South Africa. Eradication by means of biological control and chemical poisons has so far met with little success.

Extraction of the modified stems of *O. aurantiaca* with cold water followed by purification of the mucilage afforded fibrous polysaccharide material in 1.1% yield. Hydrolysis of the polysaccharide followed by paper-chromatographic and g.l.c.

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TABLE I

ANALYSIS OF WHOLE AND DEGRADED *Opuntia aurantiaca* MUCILAGE

Polysaccharide	*Whole*	*Degraded*
$[\alpha]_D$ (degrees)	−35.4	+24.4
N (%)	0.5	—
Constituent sugar units (mole %)		
Galactose	35	23
Arabinose	32	18
Xylose	20	17
Rhamnose	6	29
Galacturonic acid	7	13

analysis revealed the same sugars as found in the mucilage of *O. ficus-indica*[2]. The analysis for the mucilage (Table I), with the exception of the rhamnose content, is in fair agreement with that previously reported[5]. The specific rotation of the mucilage was not reported in the earlier study.

A degraded polysaccharide was prepared by partial hydrolysis of the polysaccharide under conditions essentially similar to those described for *O. ficus-indica* mucilage[2]. Paper-chromatographic and g.l.c. analysis of the acid hydrolysate of the degraded polysaccharide gave the results shown in Table I.

A comparison of these results with those obtained for the mucilage of *O. ficus-indica*[2] under almost identical conditions of partial hydrolysis suggests that *O. aurantiaca* mucilage is far more resistant to acid hydrolysis than the mucilage of *O. ficus-indica*, since the latter gave a degraded mucilage that was almost devoid of xylose and arabinose residues. However, the increase in the amount of rhamnose in the degraded mucilage clearly demonstrates that ~80% of the galactose, xylose, and arabinose residues and 60% of the galacturonic acid residues originally present in the mucilage are released during partial hydrolysis. The considerable loss of galacturonic acid from the mucilage of *O. aurantiaca* is in contrast to the situation found for the mucilage of *O. ficus-indica*[2,3] in which all of the galacturonic acid residues reside in the acid-resistant core of the mucilage. For the *O. aurantiaca* mucilage, some of the galacturonic acid residues, therefore, must be attached to labile sugars and/or occur in the side chains near the periphery of the macromolecule. Parikh and Jones[5] demonstrated that the galacturonic acid in cholla gum (from *O. fulgida*) is present in the side chains attached to position 3 of the galactosyl residues.

Examination of the non-polymeric material derived from the partial hydrolysis study revealed the presence of three oligosaccharides which were chromatographically indistinguishable from 6-*O*-β-D-galactopyranosyl-D-galactose, the polymer-homologous trisaccharide, and 5-*O*-β-D-xylopyranosyl-L-arabinose.

The degraded polysaccharide was reduced with lithium aluminium hydride, and the carboxyl-reduced, degraded polysaccharide and the degraded polysaccharide

TABLE II

METHYLATION ANALYSIS OF WHOLE AND DEGRADED MUCILAGES AND THEIR CARBOXYL-REDUCED DERIVATIVES

	Methylated whole mucilage[a]	*Methylated, reduced mucilage (mole %)*	*Methylated, degraded mucilage*	*Methylated, reduced, degraded mucilage (mole %)*
2-Me-galactose	++	4.5	+	+
2,4-Me_2-galactose	++	2.0	++	1.7
2,3-Me_2-galactose	++	8.2	++	2.7
2,6-Me_2-galactose	++	1.3		
3,6-Me_2-galactose	+	1.0		
2,3,4-Me_3-galactose	++	5.4	+++	17.5
2,3,6-Me_3-galactose	++	4.4	++	13.0
2,4,6-Me_3-galactose	++	4.8	++	2.0
2,3,4,6-Me_4-galactose	++	4.5	+++	13.6
Arabinose	++	2.4	++	1.4
3-Me-arabinose	++	3.5	+	1.2
2,5-Me_2-arabinose	++	2.6	++	5.9
2,3-Me_2-arabinose	+++	17.7	++	3.7
2,3,5-Me_3-arabinose	+++	10.7	++	4.5
2,3,4-Me_3-xylose	+++	21.1	+++	13.4
3-Me-rhamnose	++	5.2	+++	14.7
3,4-Me_2-rhamnose			++	4.8
Unidentified sugar (mono-*O*-methyl-arabinose or -rhamnose)	++	2.8		

[a]Key: +++, major; ++, minor; +, trace.

were methylated. The whole mucilage was methylated, reduced, and re-methylated. Each methylated polysaccharide was hydrolysed and the derived alditol acetates were examined by g.l.c. and g.l.c.–m.s. (Table II).

The methylation results clearly demonstrate that the degraded polysaccharide has a more complex structure than the polysaccharide obtained on graded hydrolysis of the mucilage of *O. ficus-indica*. The ratios of 2,4,6-tri-*O*-methylgalactose, 2,3,4,6-tetra-*O*-methylgalactose, and 2,3,4-tri-*O*-methylgalactose were approximately the same in both the methylated, degraded polysaccharide and the methylated, reduced, degraded polysaccharide, indicating the absence of 3-linked and end-group galacturonic acid residues in the degraded polysaccharide. By contrast, the amount of 2,3,6-tri-*O*-methylgalactose in the methylated, reduced, degraded polysaccharide was approximately four times as much as that in the methylated, degraded polysaccharide. Thus, ~75% of the 2,3,6-tri-*O*-methylgalactose is derived from reduction and methylation of 1,4-linked galacturonic acid residues in the degraded polysaccharide. The 3-*O*-methylrhamnose and 3,4-di-*O*-methylrhamnose residues in the methylated polysaccharides indicate that the rhamnose residues are 1,2-linked and branched

through position 4, as was found to be the case in the mucilage and degraded mucilage of *O. ficus-indica*. The present methylation results do not unambiguously establish the presence of a galacturonorhamnan backbone in the mucilage of *O. aurantiaca*, as was established for the degraded polysaccharide of *O. ficus-indica* and as has been inferred for a number of mucilages from other *Opuntia* species[5,6]. However, the increase in the rhamnose content of the mucilage during acid degradation and the failure to detect rhamnose (only xylose, arabinose, and galactose were detected) or rhamnose-containing saccharides amongst the fragments of low molecular mass released during the preparation of the degraded mucilage strongly suggests that the rhamnose residues are present in the backbone of the mucilage and that they are probably linked to galacturonic acid residues. In the degraded mucilage of *O. ficus-indica*[2,3], the rhamnose–galacturonic acid ratio was ~1 : 1, whereas the ratio is 2 : 1 in the present degraded-mucilage.

The other major structural feature which *O. aurantiaca* shares with *O. ficus-indica* mucilage[4] is the chains of 1,6-linked β-galactopyranosyl residues, most of which are branched at positions 3 or 4 or both positions 3 and 4. *O. aurantiaca* mucilage, in common with *O. ficus-indica* mucilage[4], possesses end-group, 1,2,5-, 1,3-, and 1,5-linked arabinofuranosyl residues, and xylopyranosyl end-groups.

The present methylation results present a more complex structure for the mucilage of *O. aurantiaca* than was previously reported[5]. In addition, the mucilage has been shown to differ from *O. ficus-indica* mucilage in the composition and structure of the backbone, and probably contains galacturonic acid in the side chains as well as in the core of the macromolecule.

EXPERIMENTAL

General and analytical methods have previously been described[2,3].

O. aurantiaca *mucilage*. — (*a*) *Isolation and purification*. Plant material (stems: 581 g) was macerated in a Waring Blendor, and the resulting mixture was centrifuged, filtered, and precipitated in ethanol (5 vol.). The crude polysaccharide was collected by decantation and centrifugation, dialysed against running water, precipitated in ethanol, washed with ether, and dried *in vacuo* at 50°, to afford the purified polysaccharide (6.38 g), $[\alpha]_D$ −35.4° (*c* 1.67, water) (Found: N, 0.46%).

(*b*) *Constituent sugars*. A hydrolysate of the polysaccharide was examined by paper chromatography (solvents *1* and *2*), and the molar ratios of the sugars were determined by g.l.c. of the alditol acetates as previously described[2]. The uronic acid was determined titrimetrically[2] (see Table I).

(*c*) *Degradation*. The polysaccharide (4 g) was hydrolysed with sulphuric acid (0.05M; 80 ml) under conditions essentially similar to those described[2] for *O. ficus-indica* mucilage, to afford degraded mucilage (1.17 g), $[\alpha]_D$ +24.4° (*c* 3.45, water); and dialysable material (2.66 g). Hydrolysates of the degraded mucilage and the dialysable material were examined by paper chromatography (solvents *1* and *2*), and the ratios of neutral sugars in the degraded polysaccharides were determined

by g.l.c. (column *3*) of the derived alditol acetates[2]. The uronic acid was determined titrimetrically.

Preparation of methylated mucilage and methylated, reduced mucilage. — The polysaccharide (190 mg) in dry methyl sulphoxide was methylated with sodium methylsulphinylmethanide and methyl iodide, followed by treatment with silver oxide and methyl iodide in *N,N*-dimethylformamide as previously described[4], to afford methylated polysaccharide (130 mg) which was reduced with lithium aluminium hydride in refluxing tetrahydrofuran. The carboxyl-reduced polysaccharide was re-methylated with methyl iodide and silver oxide in *N,N*-dimethylformamide. The methylated mucilage and methylated, reduced mucilage were converted into the methylated alditol acetates and examined by g.l.c. (columns *1*, *2*, and *3*) and g.l.c.–m.s.

Preparation of methylated, degraded mucilage and methylated, reduced, degraded mucilage. — The degraded polysaccharide (101 mg) was converted into the methyl ester with diazomethane and then reduced with sodium borohydride[10], as previously described[2], to afford carboxyl-reduced polysaccharide (90 mg). Degraded polysaccharide (54.5 mg) and reduced, degraded polysaccharide (62 mg) were separately methylated in dry methyl sulphoxide with sodium methylsulphinylmethanide and methyl iodide, and then in *N,N*-dimethylformamide with methyl iodide and silver oxide, to afford methylated, degraded (61 mg) and methylated, reduced, degraded (69 mg) polysaccharides. A portion of each methylated polysaccharide was hydrolysed with sulphuric acid (0.5M), and the derived, methylated alditol acetates were examined by g.l.c. (columns *1*, *2*, and *3*) and g.l.c.–m.s.

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