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THE ACID-LABILE, PERIPHERAL CHAINS OF THE MUCILAGE OF *Opuntia ficus-indica**

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ABSTRACT

Partial hydrolysis of the mucilage of *O. ficus-indica* affords *O*-β-D-galactopyranosyl-(1→6)-D-galactose, the polymer-homologous trisaccharide, and fourteen oligosaccharides that contain arabinose and most of which have xylosyl end-groups. *O*-β-D-Xylopyranosyl-(1→5)-L-arabinofuranose and *O*-β-D-xylopyranosyl-(1→5)-*O*-α-L-arabinofuranosyl-(1→5)-L-arabinofuranose were the oligosaccharides isolated in greatest amount. The most-important structural features found in the peripheral chains in the mucilage are discussed.

INTRODUCTION

The mucilage isolated from the modified stems of *Opuntia ficus-indica*[2,3] is composed of a group of closely related, highly branched polysaccharides. The peripheral chains, which are attached to various positions on the (1→6)-linked β-D-galactopyranosyl branches, are composed mainly of xylose and arabinose residues[3]. In order to obtain more-detailed information on the structure of these peripheral chains, the sugars liberated during the preparation of the degraded mucilage[2] have been separated and characterised.

RESULTS AND DISCUSSION

The material of low molecular weight obtained by partial hydrolysis[2] of the mucilage was fractionated first on a charcoal–Celite column and then by paper chromatography. Arabinose, xylose, and galactose were the only saccharides eluted with water. The absence of rhamnose and galacturonic acid from the hydrolysis products confirms that these sugars are confined to the acid-resistant backbone of the mucilage.

Sixteen oligosaccharides were isolated, of which eleven were completely characterised. The structures of the various oligosaccharides were assigned on the basis of

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*The Mucilage of *Opuntia ficus-indica*, Part IV. For Part III, see ref. 1.
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TABLE I

OLIGOSACCHARIDES CHARACTERISED FROM THE PARTIAL HYDROLYSATE OF THE MUCILAGE

Oligosaccharide		*Oligosaccharide*	
1	α-L-Ara*p*-(1→3)-L-Ara	**7**	β-D-Xyl*p*-(1→5)-L-Ara*f*
2	β-D-Gal*p*-(1→6)-D-Gal	**8**	β-D-Gal*p*-(1→6)-β-D-Gal*p*-(1→6)-D-Gal
3	β-D-Gal*p*-(1→3)-L-Ara	**9**	β-D-Xyl*p*-(1→3)-α-L-Ara*f*-(1→3)-L-Ara
4	β-D-Xyl*p*-(1→3)-L-Ara	**11**	β-D-Xyl*p*-(1→5)-α-L-Ara*f*-(1→3)-L-Ara
5	α-L-Ara*f*-(1→5)-L-Ara*f*	**12**	β-D-Xyl*p*-(1→5)-α-L-Ara*f*-(1→5)-L-Ara*f*
6	α-L-Ara*f*-(1→3)-L-Ara	**13**	β-D-Xyl*p*-(1→5)-α-L-Ara*f*-(1→5)-α-L-Ara*f*-(1→3)-L-Ara

the products of complete and partial hydrolysis with acid, g.l.c. of the cleavage products from the methylated derivatives of the oligosaccharides, and measurement of specific optical rotations. Since L-arabinose, D-xylose, and D-galactose are well established as the major neutral constituents of the mucilage, assignments of configuration of glycosidic linkages have been made, where possible, on the basis of molecular rotations. The oligosaccharides characterised are listed in Table I.

The isolation of 6-*O*-β-D-galactopyranosyl-D-galactose (**2**) and the polymer-homologous trisaccharide (**8**) as the only homogeneous, galactose oligosaccharides is consistent with the structure proposed[2,3] for the galactose side-chains attached to O-4 of the rhamnosyl residues in the backbone of the mucilage. The only other galactose-containing oligosaccharide isolated, 3-*O*-β-D-galactopyranosyl-L-arabinose (**3**), has been reported as a constituent of many polysaccharides, including the gum of *O. fulgida*[4] and mangle gum[5]. The presence of this structural unit in the mucilage is consistent with the observation that some galactose is cleaved during the production of the partially degraded mucilage. The arabinose residue in **3** is almost certainly present in the mucilage in the furanoid form, and the oligosaccharide is situated at or near the periphery of the macromolecule.

The configuration of the linkage in disaccharide **1**, 3-*O*-L-arabinopyranosyl-L-arabinose, is uncertain. The low, positive $[\alpha]_D$ value for **1** suggests an α-L link; however, the chromatographic mobilities of **1** in acid and basic solvents are similar to those reported for the β-linked sugar. The structural significance of **1** is difficult to assess. It appears that this disaccharide, if it does represent a genuine degradation product of *Opuntia* mucilage, must be situated within the peripheral arabinose chains, since no methyl 2,3,4-tri-*O*-methylarabinosides were detected as methanolysis products of the methylated mucilage. The isolation of **1** is the first indication of the possible presence of arabinopyranose residues in the mucilage.

5-*O*-β-D-Xylopyranosyl-L-arabinose (**7**) was the product isolated in largest amount. This disaccharide has been reported as a constituent of peach[6], cholla (*Opuntia fulgida*)[4], and *Virgilia oroboides*[7] gums. The disaccharide **1** was also produced on partial hydrolysis of trisaccharides **11** and **12** and the tetrasaccharide **13**.

A second xylosylarabinose (**4**), isolated in much smaller quantity than **7**, was

shown to be 3-*O*-β-D-xylopyranosyl-L-arabinose. The specific rotation (+15°) of **4** clearly establishes the linkage as β (*cf.* +185° for 3-*O*-α-D-xylopyranosyl-L-arabinose[8] and +33° for 2-*O*-β-D-xylopyranosyl-L-arabinose[9]). Disaccharide **4** does not appear to have been previously characterised. However, an unidentified xylosylarabinose has been isolated[10] from a partial hydrolysate of the neutral component of linseed mucilage. It formed an osazone, indicating that the linkage was not (1→2), and the specific rotation and paper-chromatographic mobility reported are identical with those for **4**. 3-*O*-β-D-Xylopyranosyl-L-arabinose was also produced on partial hydrolysis of the trisaccharide **9**.

The disaccharides **5** and **6** were isolated as a 1:4 mixture. Both have been reported as components of *V. oroboides* gum[7], and **6** has also been obtained from *O. fulgida* gum[4].

The difference between the $[M]_D$ values of trisaccharide **9** and disaccharide **4** is −130°. This is a clear indication that the linkage between the two L-arabinose residues is α and that the interior arabinosyl residue is furanoid. The above assignment can be confirmed by a comparison of the difference between the $[M]_D$ values (shown in parentheses) of the following pairs of saccharides, each of which differ by an α-L-arabinofuranosyl group: L-arabinose and 3-*O*-α-L-arabinofuranosyl-L-arabinose (−150°), L-arabinose and 4-*O*-α-L-arabinofuranosyl-L-arabinose[11] (−133°), D-glucose and 6-*O*-α-L-arabinofuranosyl-D-glucose (−156°). Values for pairs which differ by a β-L-arabinofuranosyl group are: D-glucose and 6-*O*-β-L-arabinofuranosyl-D-glucose (+134°), L-arabinose and 2-*O*-β-L-arabinofuranosyl-L-arabinose[11] (+135°), L-arabinose and 4-*O*-β-L-arabinofuranosyl-L-arabinose[11] (+92°), L-arabinose and 3-*O*-β-L-arabinofuranosyl-L-arabinose[11] (+202°). Values for pairs of sugars which differ by an α-L-arabinopyranosyl group are: D-glucose and 3-*O*-α-L-arabinopyranosyl-D-glucose (+76°), D-glucose and 4-*O*-α-L-arabinopyranosyl-D-glucose (+37°), D-glucose and 6-*O*-α-L-arabinopyranosyl-D-glucose (+81°). Values for pairs which differ by a β-L-arabinopyranosyl group are as follows: D-glucose and 2-*O*-β-L-arabinopyranosyl-D-glucose (+378°), L-arabinose and 3-*O*-β-L-arabinopyranosyl-L-arabinose (+470°), and L-arabinose and 4-*O*-β-L-arabinopyranosyl-L-arabinose (+394°). Except where otherwise indicated, $[M]_D$ values were calculated from optical rotation values in ref. 12. It is clear that α-L-arabinofuranosyl linkages are easily distinguished from β-L-arabinofuranosyl and α- and β-L-arabinopyranosyl linkages. Melton and co-workers[13] used the above approach to determine the linkages in oligosaccharides isolated from the extracellular polysaccharide from *Xanthomonas campestris*.

The difference in the $[M]_D$ values between disaccharide **7** and trisaccharide **12** (−86°) and between disaccharide **4** and trisaccharide **11** (−175°) clearly indicates the presence of an additional α-L-arabinofuranosyl group in each trisaccharide. Trisaccharide **11** has been reported[4] as a hydrolysis product of cholla gum. The additional L-arabinose in tetrasaccharide **13** can similarly be shown to be an α-L-arabinofuranosyl group by comparing its $[M]_D$ value with that of trisaccharide **11** (difference, −143°).

A fourth trisaccharide, **10**, containing xylose and arabinose in the ratio 1:2, was isolated, but only partially characterised. Partial hydrolysis failed to produce any disaccharides, while methylation analysis gave methyl 2,3,4-tri-*O*-methyl-xylosides as the only recognisable glycosides. Trisaccharide **10** formed a formazan derivative, showing that the terminal unit was not (1→2)-linked. The molecular rotation of **10** is similar to that of trisaccharide **12**, suggesting that the terminal xylopyranosyl group is β-linked to an α-L-arabinofuranosyl residue.

A further three oligosaccharides, **14–16**, were only partially characterised. Oligosaccharide **14** contains equimolar amounts of xylose and arabinose, and is probably a tetrasaccharide. It was shown to possess a terminal xylosyl group, 1,3- and 1,5-linked arabinosyl residues, and a terminal, reducing arabinose residue linked through position 3. Oligosaccharide **15** is a pentasaccharide with xylose and arabinose present in a ratio of 2:3; **7** was the only disaccharide obtained on partial hydrolysis. Methylation analysis of **15** showed xylose to be present only as non-reducing end-group, and arabinose to be present as 1,5-linked units and possibly as a branch point. Oligosaccharide **16** also possesses a terminal xylosyl group and both 1,3- and 1,5-linked arabinosyl residues, with the reducing arabinose residue linked through position 5.

The isolation of fourteen oligosaccharides containing arabinose demonstrated the complex nature of the peripheral, acid-labile chains in the mucilage. Methylation analysis of the mucilage has shown that 1-, 1,5-, 1,3-, 1,2,5-, and 1,2,3,5-linked units account for 31, 43, 9, 10, and 7%, respectively, of the arabinose residues in the mucilage. The isolation of nine oligosaccharides having 1,5-arabinofuranosyl units, the isolation of disaccharide **7** in 15 times greater quantity than the next most-prominent disaccharide, and the isolation of trisaccharide **12** in 8–24 times greater quantity than the other trisaccharides confirmed the presence of 1,5-linked arabinofuranose as a major structural feature of the mucilage. The isolation of eight oligosaccharides, albeit in small proportions, possessing 1,3-linked arabinose does not appear to be consistent with the small proportion (only 9% of the total arabinose residues) of 2,5-dimethylarabinose present in the methylated mucilage. It therefore seems that a fair proportion of the 3-linked arabinofuranosyl residues are additionally linked in the mucilage through positions 2 and 5. These additionally linked units would then, at least in part, account for the presence of unmethylated arabinose residues (7% of the total arabinose) in the methylated mucilage. The only other methylated arabinose characterised, namely, 3-*O*-methylarabinose, implies that some of the 1,5-linked arabinofuranosyl residues carry branches on position 2.

The xylose-to-arabinose ratio in the mucilage is ~1:2. If it is assumed that all of the xylose residues in the mucilage occupy terminal positions and that each xylose is linked to an arabinose residue (a reasonable assumption, since nine of the oligosaccharides isolated have xylose end-groups), then, since 31% of the arabinose residues are present as non-reducing arabinofuranosyl end-group, the average xylo-arabino chain-length must be 2. This implies that many of the branch points on the longer xyloarabinan chains must be occupied by single xylosyl groups and, in order to

satisfy all the branch points in the whole mucilage, most of the arabinofuranosyl end-groups must occur as single-unit side-chains. The isolation of oligosaccharide **15**, which was not completely characterised, but appears to be a branched-chain pentasaccharide having two xylosyl end-groups, is worthy of note.

The results presented in this and previous papers[1-3] demonstrate the complex structure of *Opuntia ficus-indica* mucilage. The peripheral chains, which are indicated as R in the partial structure previously proposed[1], consist primarily of structures **17–19**. Structure **20** is of lesser importance, and only a few of the R chains are expected to consist of, or incorporate, structure **21**. In order to account for the isolation of oligosaccharides **13** and **11**, the presence of structures **22** and **23**, respectively, as R chains is required. The broken lines indicate the positions where branching would have to occur in order to satisfy the methylation results. In order to be compatible with the xylose-to-arabinose ratio[2] in the mucilage, the branches would have to consist mainly of single xylopyranosyl groups, but some may be composed of structures **17–20**.

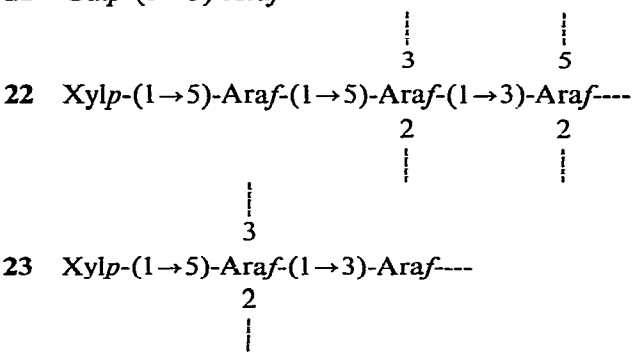
17 Ara*f*----

18 Xyl*p*-(1→5)-Ara*f*----

19 Xyl*p*-(1→5)-Ara*f*-(1→5)-Ara*f*----

20 Xyl*p*-(1→3)-Ara*f*----

21 Gal*p*-(1→3)-Ara*f*----



22 Xyl*p*-(1→5)-Ara*f*-(1→5)-Ara*f*-(1→3)-Ara*f*----

23 Xyl*p*-(1→5)-Ara*f*-(1→3)-Ara*f*----

EXPERIMENTAL

General and analytical methods have been previously described[1-3]. 2% *p*-Anisidine hydrochloride and triphenyltetrazolium chloride are sprays *a* and *b*.

Separation and identification of the oligosaccharides formed during production of degraded polysaccharide AD_3. — The combined diffusates (2.01 g) obtained as previously described[2] were fractionated on a column (450 × 30 mm) of charcoal–Celite (1 : 1) by gradient elution. Monosaccharides were eluted with water, and oligosaccharides with an ethanol gradient of 0 → 40%. Fractions (~ 16 ml) were collected, and examined by p.c. Appropriate fractions were combined, concentrated to dryness, and, where necessary, subjected to p.c. The following fractions were obtained: 1, a syrup (190 mg) that contained (p.c.; solvents *1* and *2*, spray *a*) arabinose; 2, a syrup

(409 mg) that contained arabinose, xylose, and galactose; 3, a syrup (6 mg) that contained only galactose; and 4, a syrup (8.1 mg) that contained only disaccharide **1**, $[\alpha]_D$ +76° (*c* 0.63), R_{Gal} 0.82, 0.56, and 0.80 (solvents *1–3*, respectively); **1** gave a red colour with spray *b*, and arabinose on hydrolysis with sulphuric acid (0.05M, ~100°, 2 h). A mixture[14] of **1** (2 mg), distilled *N*,*N*-dimethylformamide (0.2 ml), methyl iodide (0.2 ml), and silver oxide (200 mg) was stirred in the dark at 5°. The reaction was monitored by t.l.c. A small amount of chloroform was added, and the solution was centrifuged, filtered through cotton wool, and concentrated to dryness. The residue was treated with boiling, 2% methanolic hydrogen chloride (0.3 ml) for 6 h and the solution was injected directly into the gas chromatograph (column *4*). Peaks having the retention times of methyl 2,3,4-tri-*O*-methyl-, 2,5-di-*O*-methyl-, and 2,4-di-*O*-methyl-arabinosides were observed. Alditol acetates prepared from the methyl glycosides, when examined on column *2*, corresponded to those of 2,3,4-tri-*O*-methyl- and 2,5-di-*O*-methyl-arabinose. Thus, **1** was 3-*O*-α-L-arabinopyranosyl-L-arabinose, the α-L configuration being assigned on the basis of the optical rotation.

Fraction 5, syrup (22.4 mg), contained three components (**2–4**), which were isolated by p.c. (solvent *1*, 16 h).

Disaccharide **2** (5.7 mg), $[\alpha]_D$ +18° (*c* 0.5), had R_{Gal} 0.28 and 0.36 (solvents *1* and *3*, respectively). Hydrolysis of **2** gave only galactose, and it gave a red colour with spray *b*. Methylation analysis of **2** followed by g.l.c. of the derived methyl glycosides (column *4*) identified 2,3,4,6-tetra-*O*-methyl- and 2,3,4-tri-*O*-methyl-galactose as components of methylated **2**. Thus, **2** is 6-*O*-β-D-galactopyranosyl-D-galactose. The $[\alpha]_D$ and R_{Gal} values are in reasonable agreement with those reported[4].

Disaccharide **3** (5.7 mg), $[\alpha]_D$ +25° (*c* 0.48), had R_{Gal} 0.55 and 0.53 (solvents *1* and *2*, respectively), and gave a red colour with spray *b*. Hydrolysis of **3** gave equal proportions of galactose and arabinose. After reduction with borohydride, hydrolysis gave galactose. Methylation of **3** followed by g.l.c. of the derived methyl glycosides (column *4*) identified 2,3,4,6-tetra-*O*-methylgalactose and 2,4-di- and 2,5-di-*O*-methylarabinose as components of methylated **3**. Thus, **3** was 3-*O*-β-D-galactopyranosyl-L-arabinose; lit.[15] $[\alpha]_D$ +22°.

Disaccharide **4** (15.3 mg), $[\alpha]_D$ +15° (*c* 0.76), had R_{Gal} 0.91, 0.87, and 1.15 (solvents *1–3*, respectively), and gave a red colour with spray *b*. Hydrolysis of **4** gave equal proportions of xylose and arabinose. Reduction of **4** with borohydride followed by hydrolysis gave xylose. Methylation of **4** followed by g.l.c. of the derived methyl glycosides and alditol acetates (columns *1*, *2*, and *4*) identified 2,3,4-tri-*O*-methylxylose and 2,4-di- and 2,5-di-*O*-methylarabinose as components of methylated **4**. Thus, **4** was 3-*O*-β-D-xylopyranosyl-L-arabinose, the β-D linkage being assigned on the basis of the optical rotation.

Fraction 6, syrup (23.4 mg), contained eight components; when subjected to p.c. (solvent *2*, 48 h), fraction 6 gave **3** (2.4 mg), **4** (5.7 mg), **5** + **6** (2.7 mg), and **7** (see fraction 7). The syrupy mixture **5** + **6** had $[\alpha]_D$ −11° (*c* 0.45). R_{Gal} 1.44 and 1.77 (solvents *1* and *2*, respectively), and gave only arabinose on hydrolysis. Methylation

of **5** + **6** followed by g.l.c. of the derived alditol acetates (columns *1* and *3*) identified 2,3,5-tri-, 2,3-di-, and 2,5-di-*O*-methylarabinose as components of methylated **5** + **6**. Thus, **5** + **6** is a 1 :4 mixture of 5-*O*-α-L-arabinofuranosyl-L-arabinose (**5**) and 3-*O*-α-L-arabinofuranosyl-L-arabinose (**6**). Both **5** and **6** have been isolated[7] from *Virgilia oroboides* gum; **5** had $[\alpha]_D$ −87° and R_{Gal} 1.40 (solvent *1*); **6** had $[\alpha]_D$ 0° and R_{Gal} 1.28 (solvent *1*).

Fraction 7, syrup (215.5 mg), had $[\alpha]_D$ −53° (*c* 1.2), R_{Gal} 1.06, 1.40, and 1.42 (solvents *1–3*, respectively), gave a red colour with spray *b*, and was shown to be the same as disaccharide **7**. Hydrolysis of **7** gave xylose and arabinose in approximately equal proportions; reduction of **7** and then hydrolysis gave xylose. Methylation of **7** followed by g.l.c. of the derived methyl glycosides (column *4*) and alditol acetates (column *2*) identified 2,3,4-tri-*O*-methylxylose and 2,3-di-*O*-methylarabinose as components of methylated **7**. Thus, **7** was 5-*O*-β-D-xylopyranosyl-L-arabinose. The R_{Gal} values (solvents *1* and *3*) and $[\alpha]_D$ value are in reasonable agreement with published data[4,7].

Fraction 8, syrup (14 mg), contained two components and was fractionated by p.c. (solvent *1*, 16 h), to give **7** and trisaccharide **8** (4.8 mg), m.p. 152–155°, $[\alpha]_D$ +13° (*c* 0.48), R_{Gal} 0.09 (solvent *1*). Hydrolysis of **8** gave galactose only. Reduction of **8** with borohydride and then hydrolysis (25 min, 0.05M sulphuric acid) gave galactose and **2**. Thus, **8** was *O*-β-D-galactopyranosyl-(1→6)-*O*-β-D-galactopyranosyl-(1→6)-D-galactose; lit.[15] $[\alpha]_D$ +12.6°.

Fraction 9, syrup (9.6 mg), contained trisaccharide **9**, had $[\alpha]_D$ −21° (*c* 0.57), R_{Gal} 0.61 and 0.58 (solvents *1* and *2*, respectively), and gave a red colour with spray *b*. Hydrolysis of **9** gave xylose and arabinose in the ratio ~1 :2, and partial hydrolysis gave xylose, arabinose, and **4**. Methylation of **9** followed by g.l.c. of the derived methyl glycosides (column *4*) identified 2,3,4-tri-*O*-methylxylose and 2,4-di- and 2,5-di-*O*-methylarabinose as components of methylated **9**. Thus, **9** was *O*-β-D-xylopyranosyl-(1→3)-*O*-α-L-arabinofuranosyl-(1→3)-L-arabinose.

Fraction 10, syrup (17 mg), contained trisaccharides **10** and **11**, which were separated by p.c. (solvent *2*, 72 h).

Trisaccharide **10** (3.2 mg) had $[\alpha]_D$ −59° (*c* 0.53), R_{Gal} 0.54, 0.53, and 1.01 (solvents *1–3*, respectively), and gave a red colour with spray *b*. Hydrolysis gave xylose and arabinose in the ratio ~1 :2, but partial hydrolysis failed to afford any identifiable disaccharide.

Trisaccharide **11** (2.8 mg) had $[\alpha]_D$ −32° (*c* 0.47), R_{Gal} 1.08, 0.61, and 0.60 (solvents *1–3*, respectively), and gave a red colour with spray *b*. Hydrolysis of **11** gave xylose and arabinose in the ratio ~1 :2, and partial hydrolysis gave arabinose, xylose, and **7**. Methylation of **11** followed by g.l.c. of the derived methyl glycosides (column *4*) and alditol acetates (column *2*) identified 2,3,4-tri-*O*-methylxylose, 2,3-di-, 2,4-di-, and 2,5-di-*O*-methylarabinose as components of methylated **11**. Thus, **11** was *O*-β-D-xylopyranosyl-(1→5)-*O*-α-L-arabinofuranosyl-(1→3)-L-arabinose; lit.[4] $[\alpha]_D$ −74.2°.

Fraction 11, syrup (72 mg), contained trisaccharide **12**, had $[\alpha]_D$ −56.5°

(*c* 0.52) and R_{Gal} 0.75, 0.70, and 1.35 (solvents *1-3*, respectively), and gave a red colour with spray *b*. Hydrolysis of **12** gave arabinose and xylose in the ratio ~2:1, and partial hydrolysis gave xylose, arabinose, and **7**. Reduction of **12** with borohydride followed by partial hydrolysis gave the same products. Methylation of **12** followed by g.l.c. of the derived methyl glycosides (column *4*) and alditol acetates (column *2*) identified 2,3,4-tri-*O*-methylxylose and 2,3-di-*O*-methylarabinose as components of methylated **12**. Thus, **12** was *O*-β-D-xylopyranosyl-(1→5)-*O*-α-L-arabinofuranosyl-(1→5)-L-arabinose.

Fraction 12, syrup (35.5 mg), contained two components that were separated by p.c. (solvent *2*, 5 days), to give trisaccharide **13** and tetrasaccharide **14**.

Trisaccharide **13** (13.5 mg) had $[\alpha]_D$ −50.5° (*c* 0.77), R_{Gal} 0.40, 0.30, and 0.93 (solvents *1–3*, respectively), gave a red colour with spray *b*, and xylose and arabinose in the ratio 1:2.6 on hydrolysis. Reduction of **12** with borohydride followed by hydrolysis resulted in a decrease in the yield of arabinose, and partial hydrolysis gave xylose, arabinose, **7**, and **12**. Methylation of **13** followed by g.l.c. of the derived methyl glycosides (column *4*) and alditol acetates (columns *1* and *2*) identified 2,3,4-tri-*O*-methylxylose, 2,3-di-*O*-methylarabinose, 2,5-di-*O*-methylarabinose, and 2,4-di-*O*-methylarabinose as components of methylated **13**. Methylation analysis of reduced **13** gave 2,3-di-*O*-methylarabinose and 2,3,4-tri-*O*-methylxylose. Thus, **13** was *O*-β-D-xylopyranosyl-(1→5)-*O*-α-L-arabinofuranosyl-(1→5)-*O*-α-L-arabinofuranosyl-(1→3)-L-arabinose.

Tetrasaccharide **14**, syrup (8.8 mg), had $[\alpha]_D$ −23° (*c* 0.88), and R_{Gal} 0.40, 0.47, and 1.16 (solvents *1–3*, respectively). Hydrolysis of **14** gave xylose and arabinose in the ratio 1:1 (g.l.c. of alditol acetates, column *3*). Partial hydrolysis failed to yield any recognisable di- or tri-saccharides. Methylation of **14** followed by g.l.c. of the derived methyl glycosides identified 2,3,4-tri-*O*-methylxylose and 2,3- and 2,5-di-*O*-methylarabinose as components of methylated **14**. Reduction of **14** followed by methylation and methanolysis gave (g.l.c.) a diminished yield of 2,5-di-*O*-methylarabinose.

Fraction 13, syrup (25.4 mg), was a mixture of mainly **13** and two other oligosaccharides (**15** and **16**) which were isolated by paper p.c.

Oligosaccharide **15** (5.4 mg) had $[\alpha]_D$ −19° (*c* 0.89), R_{Gal} 0.29, 0.15, and 0.70 (solvents *1–3*, respectively), and gave xylose and arabinose in the ratio 2:3 on hydrolysis. Methylation of **15** followed by g.l.c. (column *4*) of the derived methyl glycosides revealed methyl glycosides of 2,3,4-tri-*O*-methylxylose, 2,3-di-*O*-methylarabinose, and, possibly, an *O*-methylarabinose. G.l.c. of the derived, methylated alditol acetates (column *1*) gave derivatives of 2,3,4-tri-*O*-methylxylose and 2,3-di-*O*-methylarabinose, and a peak at R_{TMG} 0.94. Partial hydrolysis of **15** gave **7**.

Oligosaccharide **16**, syrup (4.1 mg), had $[\alpha]_D$ −29° (*c* 0.69), R_{Gal} 0.44 and 0.46 (solvents *1* and *2*, respectively), and gave xylose and arabinose on hydrolysis. Methylation of **16** followed by methanolysis and g.l.c. revealed the methyl glycosides of 2,3,4-tri-*O*-methylxylose and 2,3- and 2,5-di-*O*-methylarabinose. Methylation analysis of reduced **16** gave no 2,3-di-*O*-methylarabinose.

Fraction 13, syrup (65.5 mg), contained several oligosaccharides that did not move far from the origin (solvent *2*, 8 days). Hydrolysis gave arabinose, xylose, and galactose. This fraction was not investigated further.

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REFERENCES

1 D. McGarvie and H. Parolis, *Carbohydr. Res.*, 88 (1981) 305–314.
2 D. McGarvie and H. Parolis, *Carbohydr. Res.*, 69 (1979) 171–179.
3 D. McGarvie and H. Parolis, *J. Chem. Soc., Perkin Trans. 1*, (1979) 1464–1466.
4 V. M. Parikh and J. K. N. Jones, *Can. J. Chem.*, 44 (1966) 1531–1539.
5 M. Sarkar and C. V. N. Rao, *Indian J. Chem.*, 11 (1973) 1129–1133.
6 P. Andrews, D. H. Ball, and J. K. N. Jones, *J. Chem. Soc.*, (1953) 4090–4095.
7 F. Smith and A. M. Stephen, *J. Chem. Soc.*, (1961) 4892–4903.
8 J. M. Tyler, *J. Chem. Soc.*, (1965) 5288–5300.
9 R. L. Whistler and D. I. McGilvray, *J. Am. Chem. Soc.*, 77 (1955) 1884–1892.
10 K. Hunt and J. K. N. Jones, *Can. J. Chem.*, 40 (1962) 1266–1279.
11 G. O. Aspinall and C. C. Whitehead, *Can. J. Chem.*, 48 (1970) 3850–3855.
12 R. W. Bailey, *Oligosaccharides*, Pergamon, Oxford, 1965.
13 L. D. Melton, L. Mindt, D. A. Rees, and G. R. Sanderson, *Carbohydr. Res.*, 46 (1976) 245–257.
14 Q. N. Haq and E. Percival, in H. Barnes (Ed.), *Some Contemporary Studies in Marine Science*, Allen and Unwin, London, 1966, p. 355.
15 G. O. Aspinall and V. P. Bhavanandan, *J. Chem. Soc.*, (1965) 2685–2692.