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ANALYSIS OF MIXTURES OF SOME MONO-*O*-METHYLALDOSES WITH THE COMMON ALDOSES BY G.L.C.–M.S. AFTER ISOPROPYLIDENATION

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ABSTRACT

The *O*-isopropylidene dervatives of seven naturally occurring mono-*O*-methylaldoses have been characterised by g.l.c.–m.s. G.l.c. conditions have been found under which almost complete separation of the *O*-methyl sugars and the common aldoses as their *O*-isopropylidene derivatives can be achieved. This analysis procedure has been applied to the hydrolysates of three polysaccharides that contain *O*-methyl sugars.

INTRODUCTION

O-Methylated sugars are found mainly as constituents of polysaccharides of plant[1–3], algal[4–6], soil[7–10], or bacterial[11–13] origin, but they are also present in cardiac glycosides[14] and in antibiotics[15]. Mixtures of monosaccharides can be analysed by g.l.c.–m.s. after isopropylidenation[16,17]. In this procedure, the gas chromatograms are considerably less complex than those for trimethylsilyl derivatives, and, moreover, the isopropylidene derivatives of most of the common monosaccharides give characteristic mass spectra. We now report on the g.l.c.–m.s. properties of the isopropylidene derivatives of some of the more commonly occurring *O*-methyl sugars, and the analysis of mixtures of *O*-methyl sugars and aldoses by isopropylidenation followed by g.l.c.–m.s.

RESULTS AND DISCUSSION

The following mono-*O*-methyl sugars have been investigated: 2-*O*-methyl-D-arabinose, 3-*O*-methyl-D-xylose, 2-*O*-methyl-D-xylose, 6-*O*-methyl-D-galactose, 3-*O*-methyl-D-galactose, 3-*O*-methyl-D-glucose, and 2-*O*-methyl-L-fucose. It has

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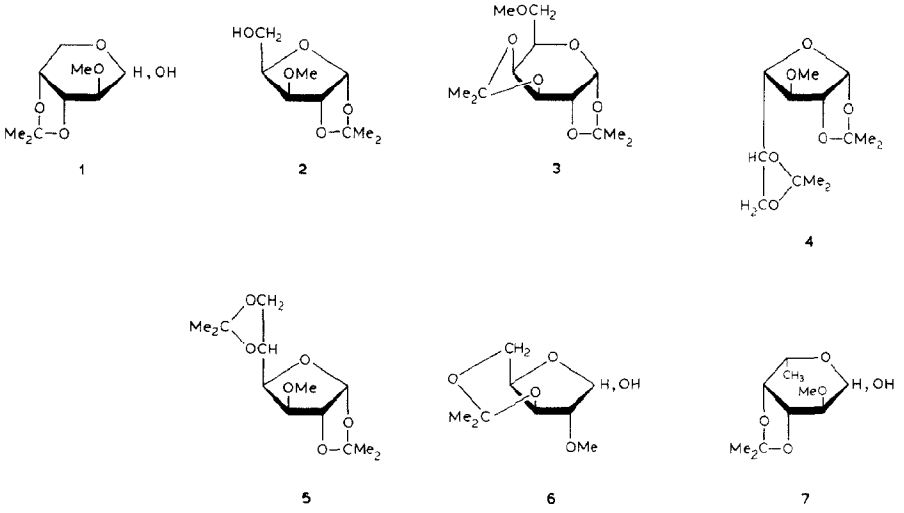
been reported that 3,4-*O*-isopropylidene-2-*O*-methyl-D-arabinopyranose[18] (**1**), 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylofuranose[19] (**2**), and 1,2:3,4-di-*O*-isopropylidene-6-*O*-methyl-α-D-galactopyranose[20] (**3**) are acetonation products of the parent *O*-methyl sugars. 3-*O*-Methyl-D-galactose and 3-*O*-methyl-D-glucose, on treatment with acetone–sulphuric acid, gave the 1,2:5,6-di-*O*-isopropylidene derivatives (**4** and **5**), identical with the compounds prepared by methylation of the 1,2:5,6-di-*O*-isopropylidene derivatives of D-galactose[21] and D-glucose[22]. 2-*O*-Methyl-D-xylose gave the 3,5-*O*-isopropylidene derivative **6**, as indicated by a peak in the mass spectrum corresponding to the loss of hydroxyl from the molecular ion[16,23,24] and by the formation of a 1,4-lactone on oxidation by silver carbonate-on-Celite[25–27] in toluene. The yield of **6** was low when 1-2% sulphuric acid in acetone was used for the isopropylidenation, but lowering of the amount of catalyst gave increased yields, a phenomenon which is not yet understood. 2-*O*-Methyl-L-fucose gave the 3,4-*O*-isopropylidene derivative (**7**), as shown by its mass spectrum and the formation of a 1,5-lactone on oxidation with silver carbonate.



G.l.c. of the isopropylidene derivatives of the *O*-methyl sugars and the aldoses on OV-225 and ECNSS-M did not give complete separation of all the derivatives (Table I). However, the sugars that gave overlapping peaks were not the same on the two stationary phases, and separation of the derivatives was markedly improved by using a mixture of OV-225 (63%) and ECNSS-M (37%). Only the derivatives of 6-*O*-methyl-D-galactose (**3**) and 2-*O*-methyl-L-fucose (**7**) gave overlapping peaks on this mixed material (Fig. 1). The peak areas were proportional to the molar concentration of the parent sugar (Table I), thereby allowing quantitative analysis of mixtures.

The e.i.-mass spectra of isopropylidene derivatives of sugars (Table II) do not usually contain molecular ions[23], but (M^+ − Me) ions are characteristic. Con-

TABLE I

CHROMATOGRAPHIC DATA FOR THE *O*-ISOPROPYLIDENE DERIVATIVES

Compound[a]	T *values*[b]			*Molar response*[d]
	OV-225	*ECNSS-M*	*Mixed material*[c]	
1	0.71	0.73	0.72	0.51 ±0.01
2	0.74	0.74	0.74	0.44 ±0.02
3	0.72	0.55	0.68	1.42 ±0.06
4	0.82	0.68	0.79	1.14 ±0.04
5	0.69	0.52	0.65	1.30 ±0.07
6	0.72	0.68	0.70	0.40[e] ±0.02
7	0.69	0.65	0.68	0.79 ±0.01

[a]**1**, 3,4-*O*-Isopropylidene-2-*O*-methyl-D-arabinopyranose; **2**, 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-xylofuranose; **3**, 1,2:3,4-di-*O*-isopropylidene-6-*O*-methyl-α-D-galactopyranose; **4**, 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-α-D-galactofuranose; **5**, 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose; **6**, 3,5-*O*-isopropylidene-2-*O*-methyl-D-xylofuranose; **7**, 3,4-*O*-isopropylidene-2-*O*-methyl-L-fucopyranose. [b]Retention time relative to that of 2,3:5,6-di-*O*-isopropylidene-D-mannose. [c]63% of OV-225 and 37% of ECNSS-M. [d]Peak areas obtained from a mixture of the parent sugars in equimolar amounts, relative to that from mannose. [e]Prepared using 0.1% sulphuric acid in acetone.

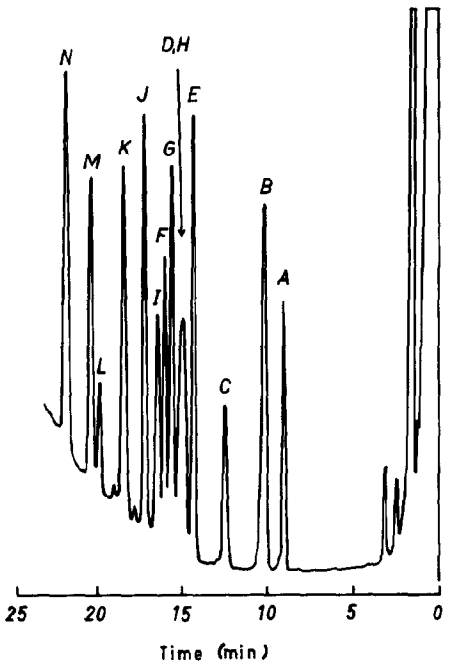


Fig. 1. Gas chromatogram on 63% of OV-225 and 37% of ECNSS-M, obtained after acetonation of a syrupy mixture of the *O*-methyl sugars and the common aldoses. The derivatives are those of A, L-fucose; B, L-arabinose; C, D-xylose; D, 2-*O*-methyl-L-fucose; E, 3-*O*-methyl-D-glucose; F, 2-*O*-methyl-D-arabinose; G, 2-*O*-methyl-D-xylose; H, 6-*O*-methyl-D-galactose; I, 3-*O*-methyl-D-xylose; J, 3-*O*-methyl-D-galactose; K, L-rhamnose; L, D-galactose; M, D-glucose; and N, D-mannose.

TABLE II

MASS-SPECTRAL DATA FOR THE *O*-ISOPROPYLIDENE DERIVATIVES[a]

m/z	*Relative intensity (%)*						
	1	**2**	**3**	**4**	**5**	**6**	**7**
259			62	36	42		
229			4				
203							6
201			9	16	15		1
189	12	58				15	
187	2					2	
173	5	48		27	10		1
171			12				
167				10	4		
159			5				
157				6	3		
145	3	4		5	3	2	4
143	3		6	2	4		7
141			18	17	8		
131	4			11	6	8	
129	9	4	5			4	
127		25	11	14	5		2
116		7				45	6
115	4	24	4	23	14	26	14
113	3	6	44	10	10	4	5
111	5					6	4
103		8		6		3	
101	15	2	11	91	87	15	6
100	23	7	66	19	11	11	19
99	6	5	7	12	7	5	33
97	6	5	7	5	5	8	
88		69					
87	96	84	8	47	26	54	90
85	49	100	39	31	27	14	71
83	6		6	10	5		15
81			39	11	6		
75		7		6	4	16	
74	28		5	6	4	64	26
73		36	6	23	16	12	9
72				30	17	32	
71	27	31	68	16	10	41	12
69	40	18	11	23	14	30	10
59	47	82	46	41	25	82	61
58	17	52	12	19	15	14	8
57	19	43	11	17	18	16	14
55	16	20	9	43	19	17	15
45	18	18	86	12	16	26	15
43	100	100	100	100	100	100	100

[a]See footnote to Table I for identities of **1–7**.

fusion may arise with rhamnose, the only naturally occurring deoxy sugar giving a mono-*O*-isopropylidene derivative, since the latter gives an (M^+ − Me) peak at *m/z* 189, as do the derivatives of mono-*O*-methylpentoses. However, there are several characteristic differences between the spectrum of the rhamnose derivative[16] and those of the *O*-methylpentoses. The latter derivatives give fragmentation patterns similar to those of their unmethylated analogues, which accords with the observation that substitution within homologous series usually does not alter the fragmentation modes[28]. This correlation has been observed for the 3-*O*-methylhexose derivatives (**4** and **5**) and 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[23], the 2-*O*-methylarabinose (**1**) and 2-*O*-methylfucose (**7**) derivatives and 3,4-*O*-isopropylidenearabinose[29], the 3-*O*-methylxylose derivative (**2**) and 1,2-*O*-isopropylidene-α-D-xylofuranose[30], and the 6-*O*-methylgalactose derivative (**3**) and 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[20]. However, the introduction of *O*-methyl groups may influence the fragmentation quantitatively, as illustrated by the peak of high intensity at *m/z* 87 in the spectra of the 2-*O*- and 3-*O*-methyl derivatives, presumably resulting from a methylated analogue of a fragment ion with *m/z* 73 formed from mono-*O*-isopropylidene sugars in substantially lower abundance[24,29,31,32]. Similarly, the fragment with *m/z* 88, formed from the 3-*O*-methylxylose derivative (**2**), could be a methylated analogue of the fragment with *m/z* 74, formed in considerably smaller proportion from 1,2-*O*-isopropylidene-α-D-xylofuranose, constituting the C-3/C-5 part of the sugar[30]. The increase in abundance of these fragments on *O*-methyl substitution is easily understood on the basis of stabilisation of the positive charges on the fragments by the methyl groups.

Mass-spectral properties do not seem to have been discussed for analogues of the 2-*O*-methylxylose derivative (**6**). Its mass spectrum contains, in addition to the peaks at *m/z* 189 (M^+ − Me), 187 (M^+ − OH), and 87, a small peak at *m/z* 129 which could be due to the loss of acetic acid from the (M^+ − Me) fragment. A prominent peak at *m/z* 116, rarely seen in spectra of *O*-isopropylidene derivatives of carbohydrates, could arise by the elimination of acetone and a subsequent loss of C-5 as formaldehyde, a fragmentation reported to occur with 1,2:3,5-di-*O*-isopropylidene-4-thio-α-D-xylofuranose[30]. A peak at *m/z* 116 is also observed in the spectrum of a methyl 3,5-*O*-isopropylidene-D-xylofuranoside[33], supporting this assumption. So-called "H-rupture"[34], common to 3,5-*O*-isopropylidenepentoses and 4,6-*O*-isopropylidenehexoses, causes a peak at *m/z* 101 in the spectrum of **6**. A fragment with *m/z* 74 is formed from **6**; since relatively prominent peaks with *m/z* 74 are observed only in the spectra of the other 2-*O*-methyl sugar derivatives (**1** and **7**), as well as in that of the methyl 3,5-*O*-isopropylidenexylofuranoside[33], this fragment presumably constitutes the C-1/C-2 part of the sugars.

The presence of a peak at (M^+ − 17) in the mass spectrum of an *O*-isopropylidene derivative of an *O*-methyl sugar is strongly indicative of 2-*O*-substitution, since only 2-*O*-methyl sugars give isopropylidene derivatives with HO-1 unsubstituted under the conditions used in this work. Furthermore, a peak of high intensity at *m/z* 45 is only expected to arise from a methoxymethyl fragment, and thus only

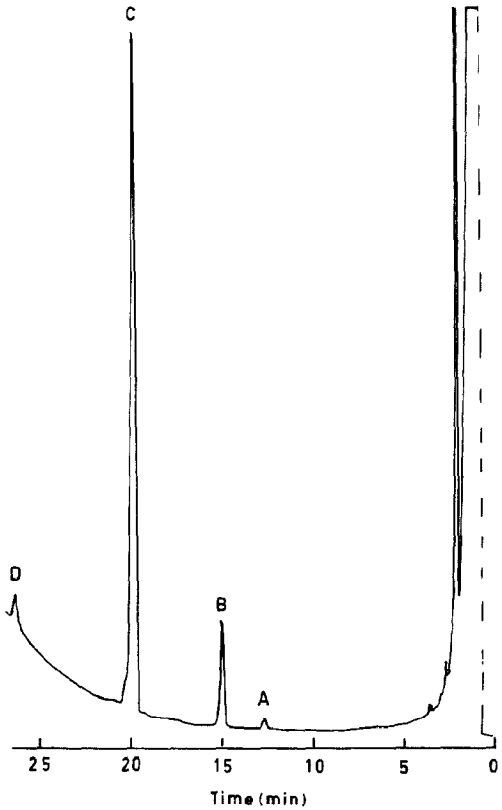


Fig. 2. Gas chromatogram on 63% of OV-225 and 37% of ECNSS-M of the *O*-isopropylidene derivatives of the monosaccharides in a hydrolysate of agar polysaccharide. The derivatives are those of A, D-xylose; B, 6-*O*-methyl-D-galactose; C, D- and L-galactose; and D, unknown (not observed after prolonged hydrolysis of the polysaccharide).

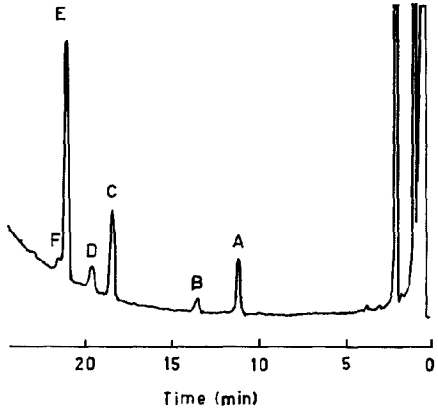


Fig. 3. Gas chromatogram on 63% of OV-225 and 37% of ECNSS-M of the *O*-isopropylidene derivatives of the neutral monosaccharides in a hydrolysate of *Ulmus glabia* polysaccharide. The derivatives are those of A, L-arabinose; B, D-xylose; C, 3-*O*-methyl-D-galactose; D, L-rhamnose; E, D-galactose; and F, D-glucose.

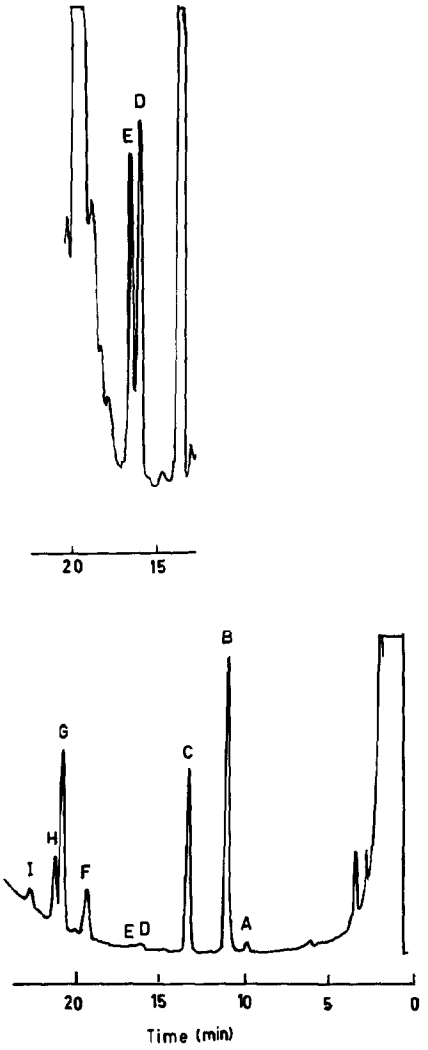


Fig. 4. Gas chromatogram on 63% of OV-225 and 37% of ECNSS-M of the *O*-isopropylidene derivatives of the neutral monosaccharides in a hydrolysate of the polysaccharide of *Papaver somniferum L.* Derivatisation with 2% (lower) and 0.1% (upper) sulphuric acid in acetone. The derivatives are those of A, L-fucose; B, L-arabinose; C, D-xylose; D, 2-*O*-methyl-L-fucose; E, 2-*O*-methyl-D-xylose; F, L-rhamnose; G, D-galactose; H, D-glucose; and I, D-mannose.

to appear in spectra of 5-*O*-methylpentose or 6-*O*-methylhexose derivatives. The diagnostic value of such peaks as those at *m/z* 88, 87, and 74 remains to be determined.

Three polysaccharides that contain *O*-methyl sugars were hydrolysed with acid, and the resulting mixtures of aldoses and *O*-methyl sugars were analysed as their *O*-isopropylidene derivatives by g.l.c.–m.s.; the materials used were an agar-

agar polysaccharide that contains 6-*O*-methyl-D-galactose[35], a polysaccharide from *Ulmus glabia* that contains 3-*O*-methyl-D-galactose[36], and a polysaccharide from *Papaver somniferum L.* that contains small proportions of 2-*O*-methyl-D-xylose and 2-*O*-methyl-L-fucose[37,38]. The agar polysaccharide also contains D- and L-galactose, 3,6-anhydro-L-galactose, and a small proportion of D-xylose. The anhydrogalactose is degraded during the hydrolysis. The two other polysaccharides contain several aldoses and also uronic acids; the latter were removed from the hydrolysates before isopropylidenation. The gas chromatograms are shown in Figs. 2–4.

Thus, mixtures of naturally occurring mono-*O*-methylaldoses and the common aldoses may be analysed by g.l.c.–m.s. of their *O*-isopropylidene derivatives. Useful information may be obtained from the mass spectra in identification of unknown *O*-methyl sugars.

EXPERIMENTAL

T.l.c. was performed on Silica gel G, using chloroform–ethanol mixtures and detection with diphenylamine–aniline–phosphoric acid[39] and (for lactones) hydroxylamine–ferric chloride[40]. G.l.c. was performed on a Perkin–Elmer F 11 gas chromatograph, equipped with a flame-ionisation detector and glass columns (6 ft. × 1.5 mm i.d.) filled with 3% of OV-225 on 100/120 Supelcoport, 3% of ECNSS-M on Gas Chrom Q 100/120, and a mixture of OV-225 (63%) and ECNSS-M (37%). The temperature programme was 4°/min from 90→190°. G.l.c.–m.s. was performed on a Varian Aerograph 2400 gas chromatograph combined with a Micromass 12 F mass spectrometer, with an ionisation energy of 70 eV, an ion-source temperature of 200°, and an accelerating voltage of 4 kV. I.r. spectra were recorded with a Perkin–Elmer spectrophotometer 597.

3-*O*-Methyl-D-glucose and 6-*O*-methyl-D-galactose were commercial materials, and 2-*O*-methyl-D-arabinose[41], 2-*O*-methyl-D-xylose[42], 3-*O*-methyl-D-xylose[18], 2-*O*-methyl-L-fucose[43], and 3-*O*-methyl-D-galactose[21] were synthesised according to reported methods. The agar-agar polysaccharide was a commercial sample, and the polysaccharide from *Ulmus glabia*[36] and a fraction of a raw polysaccharide extract from *Papaver somniferum L.* eluted from SP-Sephadex (H^+) with 0.1M acetic acid[38] were obtained from the Institute of Pharmacy, University of Oslo.

Preparation of O-*isopropylidene derivatives.* — Syrupy residues (1–10 mg), obtained by concentration of aqueous solutions of the sugars under reduced pressure and dried by evaporation of ethyl acetate, were stirred with 2% (v/v) conc. sulphuric acid in acetone (1–10 mL) for 2 h. The solutions were neutralised with solid sodium hydrogencarbonate and subjected to g.l.c.–m.s. T.l.c. and g.l.c. indicated that a single product was obtained from each *O*-methyl sugar, and t.l.c. revealed complete reaction, except for 2-*O*-methyl-D-xylose.

Identification of O-*isopropylidene derivatives.* — (*a*) The product (**4**) ob-

tained from 3-*O*-methyl-D-galactose was indistinguishable (t.l.c., g.l.c.–m.s.) from that prepared[21] by methylation of 1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose[44].

(*b*) The product (**5**) from 3-*O*-methyl-D-glucose was indistinguishable from that prepared[22] by methylation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose.

(*c*) 2-*O*-Methyl-L-fucose gave (t.l.c., g.l.c.) a single product (**7**), which was a mono-*O*-isopropylidene derivative [*m/z* 203, $(M^+ - Me)$] having HO-1 unsubstituted [*m/z* 201, $(M^+ - OH)$]. After evaporation of the acetone under reduced pressure, a solution of the residue in toluene (5 mL) was stirred at 80° with silver carbonate-on-Celite[25] (100 mg) for 1 h. T.l.c. then showed that all of the starting material had disappeared, and that a lactone (detection with hydroxylamine–ferric chloride[40]) had been formed. After filtration of the solution and removal of the solvent, the residue showed i.r. absorption ($CHCl_3$) at 1750–1755 cm^{-1}, characteristic[26,27] of 1,5-lactones. Hence, **7** was the 3,4-*O*-isopropylidene derivative.

(*d*) When 2-*O*-methyl-D-xylose (10 mg) was stirred with 0.1% sulphuric acid in acetone (20 mL) for 2 h, t.l.c. and g.l.c. of the neutralised mixture revealed the almost exclusive formation of one product (**6**). The mass spectrum showed that the compound was a mono-acetal [*m/z* 189, $(M^+ - Me)$] having HO-1 unsubstituted [*m/z* 187, $(M^+ - OH)$]. After evaporation of the acetone, the residue was oxidised with silver carbonate-on-Celite as described above. T.l.c. revealed a single product which had i.r. absorption ($CHCl_3$) at 1785–1790 cm^{-1}, characteristic[26,27] of 1,4-lactones. Thus, **6** was the 3,5-*O*-isopropylidene derivative.

Analysis of monosaccharides from hydrolysed polysaccharides. — Each polysaccharide (10 mg) was hydrolysed with M sulphuric acid at 100° for 4–6 h. The solution were neutralised with Dowex 1 (HCO_3^-) resin, filtered, and concentrated under reduced pressure. The monosaccharides were transformed into their *O*-isopropylidene derivatives as described above, and the derivatives were subjected to g.l.c. and g.l.c.–m.s.

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