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Note

Methyl ethers of L-gulose

AVRIL COOKE AND ELIZABETH PERCIVAL

Chemistry Department, Royal Holloway College (University of London), Egham, Surrey TW20 OEX (Great Britain)

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Complete methylation of uronic acid-containing polysaccharides is difficult, and it is frequent practice to reduce the uronic acid to the corresponding sugar and to methylate the derived, neutral polysaccharide. The occurrence of L-guluronic acid in alginic acid[1] and in a number of bacterial extracellular polysaccharides[2] has made it important to prepare and characterise the methyl ethers of gulose. In the present note, L-gulose was partly methylated and the derived mixture of methylated methyl L-gulosides was analysed by g.l.c. (Table I). The peaks corresponding to the respective methyl ethers were identified by comparison with those of the methyl ethers of D-glucose. An aliquot was also converted into a mixture of the corresponding alditol acetates which was analysed and characterised by g.l.c.–mass spectrometry. The relative size of the individual peaks of the alditol acetates was used to confirm the identity of the methyl L-gulosides. The retention times are given in Table I. No evidence for the formation of methyl gulofuranosides could be found. Although 2,4–

TABLE I

METHYL ETHERS OF L-GULOSE (RETENTION TIMES)

Methyl L-gulosides		*Gulitol acetates*	*Corresponding L-gulose ether*
		Column 3	
Column 1	*Column 2*		
1.53	1.37	0.96	2,3,4,6-tetra-*O*-methyl
2.1, 3.5	1.5, 2.1	1.48	2,4,6-+3,4,6-tri-*O*-methyl
2.9, 4.0	1.7, 1.93	1.65	2,3,6-tri-*O*-methyl
3.2, 4.5	1.37, 1.93	1.74	2,3,4-tri-*O*-methyl
	3.1	2.26	2,6-+4,6-di-*O*-methyl
	3.63, 3.2	2.66	3,6-di-*O*-methyl
			2,3-di-*O*-methyl
	3.2, 2.46	2.82	2,4-di-*O*-methyl
		3.1	6-*O*-monomethyl
		4.0	2-*O*-monomethyl
		4.24	4-*O*-monomethyl
		5.5	Hexa-acetate

and 3,5-di-*O*-methylgulitol acetates, 3- and 4-, and 2- and 5-mono-*O*-methyl-gulitol acetates would be expected to give the same fragmentation pattern[3] in mass spectrometry and therefore the alditols derived from furanosides would not be detected, the 5,6-di-*O*-methylgulitol acetate should give a strong primary fragment with *m/e* 89. This fragment was not given by any of the products. Furthermore, it is unlikely that the sugars in each of the above pairs would have identical retention times on g.l.c., or that methyl furanosides, if present as di- and mono-*O*-methyl sugars, would have been completely missing in the tri-*O*-methyl series. It is concluded that, under the conditions of glycosidation, the amount of furanosides formed was extremely small.

Whereas partial methylation of methyl β-D-xylopyranosides[4] by the Purdie method gave mainly the 2,4-dimethyl ether and the reactivity sequence was HO-2>HO-4>HO-3, with methyl L-guloside the 6-*O*-monomethyl sugar was present in much the largest proportion, with roughly equal amounts of the 2-, 3-, and 4-monomethyl ethers. Due to partial overlap of peaks, it was difficult to assay the di-*O*-methyl derivatives accurately, but the 2,3- and 3,6-isomers were present in least amount and the 2,4-di-*O*-methyl derivative was equal in quantity to the combined 2,6- and 4,6-di-*O*-methyl derivatives. The main tri-*O*-methyl derivative was the 2,3,6-isomer, corresponding to the combined amount of 2,4,6- and 3,4,6-compounds which, as the alditol acetates, gave an overlapping peak. The 2,3,4-tri-methyl ether was present in least amount.

EXPERIMENTAL

G.l.c.[5] of the methyl glycosides was performed on columns of acid-washed Celite coated with 15% by weight of poly(butane-1,4-diol succinate) (column 1), and 10% polyphenol ether [*m*-bis(*m*-phenoxyphenoxy)benzene] (column 2) at an operating temperature of 175°. The methylated alditol acetates were injected into a glass column (12 ft) packed with 3% OV225 on Gas Chrom Q (column 3) and fitted in a Perkin–Elmer F11 combined gas-chromatograph RMS4 mass spectrometer at 195°. The mass spectra were recorded at an inlet temperature of 200°, ionising potential of 80 eV, ionising current of 50 μamp, and a temperature of the ion source of 240°.

Chromatographically and ionophoretically pure L-gulose (50 mg from Cambrian Chemicals) was treated with 0.5% methanolic hydrogen chloride (20 ml) for 18 h under reflux; these are conditions expected to give the highest yield of methyl pyranosides. The recovered syrup was non-reducing to Fehling's solution and the Nelson reagent. Partial methylation of the derived methyl gulopyranosides was effected by the Purdie[6] procedure, using refluxing methyl iodide and silver oxide for 1 h. The derived mixture of methylated L-gulosides was analysed by g.l.c., and an aliquot was converted into the corresponding alditol acetates[7], which were analysed by g.l.c.–m.s.

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