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Note

Determination of the substituent position in mono-O-methylaldoses by oxidation with silver carbonate on Celite*

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The Fetizon reagent, silver carbonate on Celite[1], effects successive degradations from C-1 of aldoses in methanolic solution to give the series of lower aldoses[2]. At each stage of degradation, a competing oxidation to aldonolactone, or methyl aldonate, occurs. In substituted aldoses, the degradation stops when a 2-*O*-substituted aldose is formed[3,4], and this effect has been used in the identification of three reducing mono-*O*-isopropylidenegalactoses[4]. The use of silver carbonate oxidation in combination with g.l.c. for determining the position of the substituent in mono-*O*-methylaldoses is now reported prior to a study of disaccharides, and because of the increasing number of naturally occurring mono-*O*-methylaldoses. The procedure has been applied[5] in the identification of 2-*O*-methyl-D-xylose, a constituent of a pectin-type polysaccharide.

2-*O*-, 3-*O*-, and 6-*O*-Methyl-D-galactose, 3-*O*-, 4-*O*-, and 5-*O*-methyl-D-glucose, 4-*O*-methyl-D-mannose, and 2-*O*-methyl-D-fucose were treated separately with silver carbonate on Celite in methanol at 58–60° for 5 and 20 min. Borohydride reduction of the resulting *O*-methylaldoses or aldonic esters gave *O*-methylalditols, which were trimethylsilylated and subjected to g.l.c. The number of peaks was diagnostic of the number of degradation steps undergone by the parent *O*-methylaldose, and hence of the position of the methyl group.

The differentiation between 5-*O*- and 6-*O*-methylaldohexoses cannot be achieved from the number of peaks in the gas chromatograms, because of the very small amount of 2-methoxyethanol derived from the 6-*O*-methylaldose and its poor resolution from peaks for reagents. 2- and 1-*O*-Methylglycerol derived from a 5- and 6-*O*-methylhexose, respectively, exhibit retention times sufficiently different to allow differentiation to be made.

The gas chromatograms of the products derived from 2-, 3-, 4-, and 6-*O*-methylhexoses are shown in Fig. 1. In Fig. 1D, the small peak between those (7 and 8) of the trimethylsilylated *O*-methylglycerols and *O*-methyltetritols was identified by

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*Oxidation of Carbohydrate Derivatives with Silver Carbonate on Celite: Part XIV.

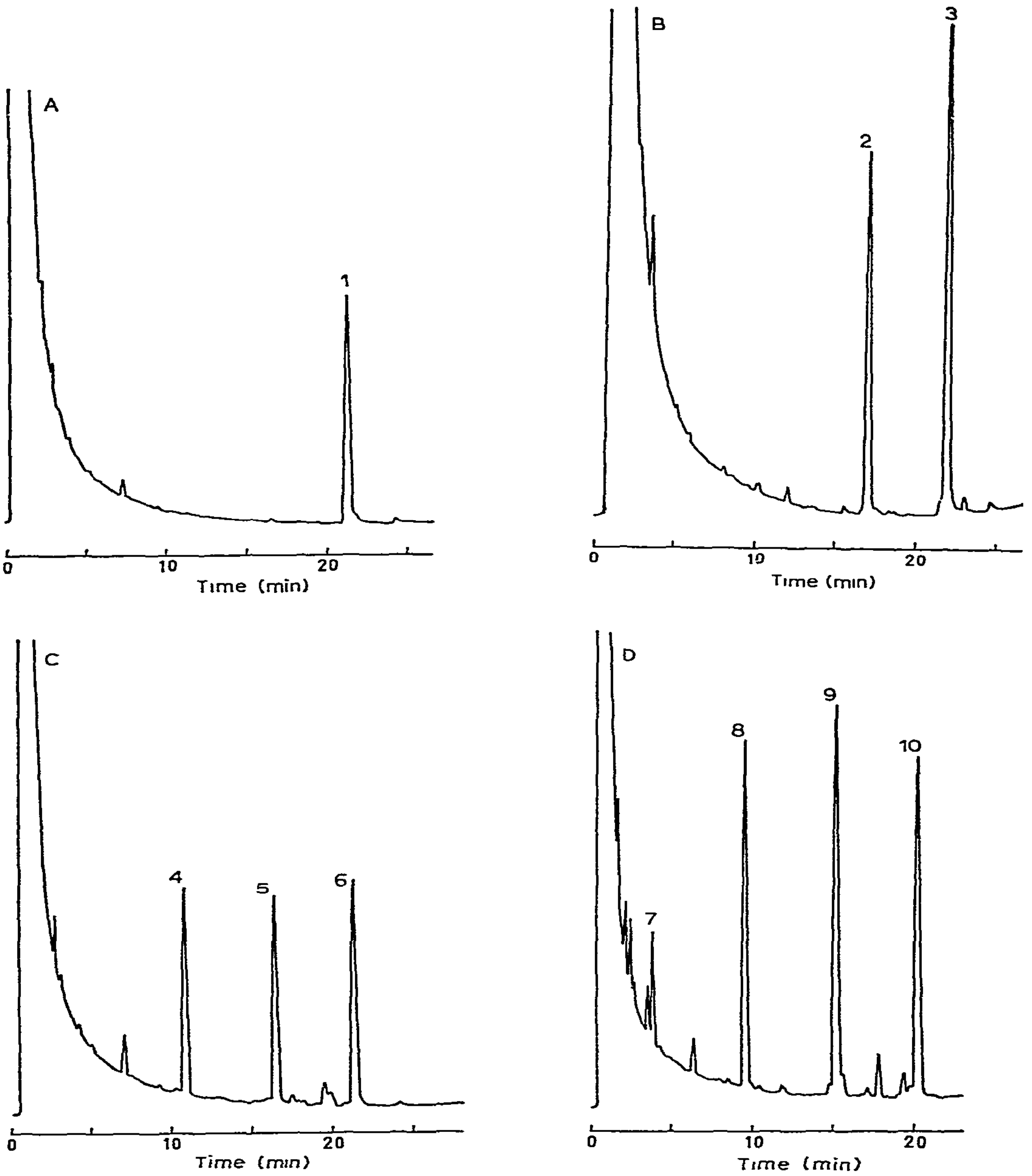

Fig. 1. Gas chromatograms of the trimethylsilylated *O*-methylalditols derived from A, 2-*O*-methyl-D-galactose (1, 2-*O*-methyl-D-galactitol); B, 3-*O*-methyl-D-glucose (2, 2-*O*-methyl-D-arabinitol; 3, 3-*O*-methyl-D-glucitol); C, 4-*O*-methyl-D-mannose (4, 2-*O*-methyl-D-erythritol; 5, 3-*O*-methyl-D-arabinitol; 6, 3-*O*-methyl-D-mannitol); D, 6-*O*-methyl-D-galactose (7, 1-*O*-methyl-L-glycerol; 8, 1-*O*-methyl-D-threitol; 9, 1-*O*-methyl-D-arabinitol; 10, 1-*O*-methyl-L-galactitol).

g.l.c.–m.s.[6] as trimethylsilylated glycerol. The origin of the glycerol is not clear, but it could have arisen from contaminant aldoses in the samples of the *O*-methylaldoses.

Mass-spectral data for the various trimethylsilylated *O*-methylalditols are given in Table I. The fragmentation patterns are similar to those of trimethylsilylated alditols[6], with the modifications expected for the *O*-methyl groups present. The location of the methyl group was usually based on the presence or absence of fragments having *m/e* 205 and 307, indicative, respectively, of two and three contiguous carbons bearing hydroxyl groups. The analogous fragment (*m/e* 409) expected from 1-*O*-methylpentitols was not observed, in accordance with the finding that this peak has a very low intensity in the spectra of the trimethylsilylated alditols[6]. A more intense peak at *m/e* 319 (409—Me_3SiOH) was observed in the spectra of trimethylsilylated alditols. This fragmentation cannot be used to distinguish between 1- and 2-*O*-methylpentitols, since a fragment at *m/e* 319 is formed from all the *O*-methylpentitols, presumably due to loss of methanol from the fragment arising from terminal C–C cleavage [M^+—CH_2OSiMe_3].

Periodate[7] and lead tetra-acetate[8] have been used in the stepwise degradation of reducing sugar derivatives, but, for the purposes noted in this paper, the use of silver carbonate on Celite is more advantageous, since it does not effect glycol cleavage.

The silver carbonate oxidation–g.l.c. combination is a simple method, not involving mass spectrometry, for locating the substituent in mono-*O*-substituted aldoses. However, for mixtures of these compounds, the use of g.l.c.–m.s. is necessary after, for example, borodeuteride reduction followed by acetylation[9] or trimethylsilylation[10].

EXPERIMENTAL

G.l.c. was performed on a Perkin–Elmer F 11 gas chromatograph, equipped with a flame-ionization detector and a glass column (2 m × 1.5 mm i.d.) filled with 2.5% of SE 30 on Chromosorb G AW DMCS (80–100 mesh). The temperature was programmed at 5°/min from 100 → 225°. Mass spectra (70 eV) were recorded with a Micromass 12 F mass spectrometer.

6-*O*-Methyl-D-galactose was obtained commercially, 4-*O*-methyl-D-glucose was a gift from Dr. J. K. Wold (University of Oslo), and the following *O*-methyl sugars were prepared by literature methods: 2-*O*-methyl-D-fucose[11], 2-*O*-methyl-D-galactose[12], 3-*O*-methyl-D-galactose[13], 3-*O*-methyl-D-glucose[14], and 5-*O*-methyl-D-glucose[15]. 4-*O*-Methyl-D-mannose was prepared by borohydride reduction of methyl (methyl 4-*O*-methyl-α- and β-D-mannopyranosid)uronate followed by acid hydrolysis.

Oxidation reactions. — A solution of each *O*-methyl sugar (1–3 mg) in methanol (2 ml) was stirred for a few min with a small amount of Dowex-1 (HCO_3^-) resin (to remove any traces of acid), filtered, and then stirred at 58–60° with silver carbonate on Celite (25 mg). Samples (0.8 ml) were withdrawn after 5 and 20 min. To the combined samples, a solution of sodium borohydride (30 mg) in water (2 ml) was added. After 2 h, the solution was treated with Dowex-50 W (H^+) resin, filtered, and concentrated to

TABLE I

G.L.C. AND M.S. DATA FOR TRIMETHYLSILYLATED *O*-METHYLALDITOLS

Compound	T^a	*Relative intensities (%)*																	
		m/e	*319*	*307*	*261*	*249*	*219*	*218*	*217*	*206*	*205*	*159*	*147*	*133*	*129*	*117*	*103*	*73*	*45*
1-*O*-Methyl-D-arabinitol	0.75		8	13	7	20	10	7	23	—	23	16	43	17	11	8	60	100	9
2-*O*-Methyl-D-arabinitol	0.76		11	17	—	19	24	24	38	—	29	11	36	9	20	12	66	100	—
3-*O*-Methyl-D-arabinitol	0.78		5	—	8	6	10	9	22	33	73	9	34	18	10	14	22	100	—
2-*O*-Methyl-D-lyxitol	0.77		11	15	—	11	13	21	31	—	21	7	29	6	14	7	60	100	—
		m/e	*307*	*249*	*219*	*217*	*205*	*159*	*147*	*133*	*117*	*116*	*103*	*73*	*45*				
1-*O*-Methyl-D-threitol	0.48		9	13	8	19	28	13	53	21	18	34	48	100	9				
2-*O*-Methyl-L-erythritol	0.51		—	12	10	21	37	19	37	8	17	6	42	100	—				
		m/e	*218*	*205*	*148*	*147*	*117*	*103*	*89*	*73*	*45*								
1-*O*-Methyl-L-glycerol	0.215		—	44	12	84	15	9	16	100	19								
2-*O*-Methylglycerol	0.23		28	—	14	57	—	20	41	100	—								

[a] Retention times relative to that of trimethylsilylated 3-*O*-methyl-D-glucitol.

dryness. Boric acid was removed by distillation of methanol (twice) from the residue, which was then heated at 65° for 30 min with pyridine–hexamethyldisilazane–chlorotrimethylsilane (0.3:0.1:0.05, 0.5 ml). Samples were injected directly on the gas chromatograph.

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