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Note

Indirect, anodic oxidation of D-glucitol in aqueous calcium iodide

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The anodic oxidation of aldoses in aqueous solution, using platinum electrodes, yields lower aldoses, and it has been assumed that progressive degradation proceeds through the corresponding aldonic and aldulosonic acids until the monosaccharide is completely converted into carbon dioxide[1–5].

Such degradation occurs even in non-aqueous media and, although aldonic acids were not detected, their formation was presumed to be the first step[6]. However, when a platinum anode was used in a phosphate buffer (pH 7.4) in the potential range −0.75 to +0.20 V, D-gluconic acid was formed from D-glucose and was not further oxidised, but was adsorbed on the electrode surface, thereby hindering the oxidation process[7]. Since ozone is produced in the electrolysis of aldoses[1], α-keto compounds may be formed[8] and subsequently α-ketoaldonic acids which can undergo decarboxylation to the next lower aldose.

Indirect electro-oxidation of aldoses to the corresponding aldonic acids was described by Isbell and Frush[9]. Aldoses were oxidised with hypobromite (formed by electro-oxidation of bromide), to give aldonic acid anion and a bromide ion. Calcium carbonate was present to maintain an almost neutral medium and the hypobromite was continuously regenerated. We have applied this method to D-glucitol and D-mannitol, using calcium iodide, in order to determine if the α-keto group is formed before or after the carboxyl group.

Paper chromatography of the products of the electro-chemical reaction of D-glucitol and detection with orcinol revealed ketohexoses (red spots) and aldoses (blue spots). Aniline hydrogen phthalate also revealed aldohexoses and aldotetroses. G.l.c. of the product mixture after trimethylsilylation revealed glucose, gulose, fructose, sorbose, arabinose, xylose, erythrose, threose, and glyceraldehyde.

G.l.c.–m.s. of the product mixture after trimethylsilylation or isopropylidenation was used to investigate the other products (**1–9**).

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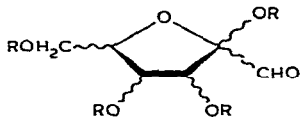

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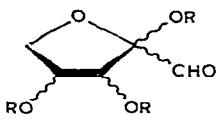

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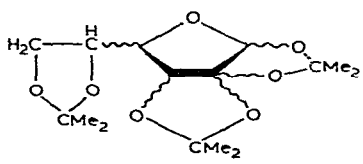

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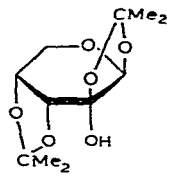

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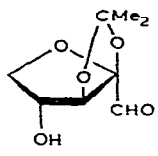

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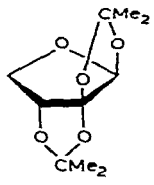

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TABLE I

MASS SPECTRA (70 eV) OF THE *O*-TRIMETHYLSILYL DERIVATIVES OF THE OSULOSES

m/z	**1** *and* **2** (%)	**3** *and* **4** (%)	m/z	**1** *and* **2** (%)	**3** *and* **4** (%)
466	0.25		230	6.00	
451	1.21		217	56.80	20.10
437	1.81		205	2.10	
408	0.20		204	3.13	5.30
393	0.27		201	2.10	
379	25.50		191	6.86	13.30
364		6.60	189	10.78	6.60
363	0.58		177	2.70	
361	0.98		175	1.80	1.10
349		46.00	169	2.94	2.10
348	0.96		161	3.13	
335		9.10	159	4.70	6.10
333	1.53	12.66	157	6.27	
319	1.87	20.00	147	23.50	26.60
305	2.80	17.30	143	7.60	
291	17.40	16.00	133	19.60	
275	1.80	8.00	131	8.00	
271	4.70		129	14.70	15.30
259		6.60	117	6.90	9.60
257	31.30		103	20.60	
246		8.10	89	13.80	12.30
245	3.70	11.00	75	40.10	
243	2.84	0.60	73	100.00	100.00
231	3.90	6.60	69	4.60	5.20

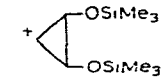
The 2,3,4,6-tetra-*O*-trimethylsilyl-2-hexosulo-2,5-furanoses (**1** and **2**) gave peaks (Table I) at *m/z* 466 ($M^{+\cdot}$), 451 ($M^+ - CH_3$), 361 ($M^+ - CH_3 - Me_3SiOH$), and 271 ($M^+ - CH_3 - 2\ Me_3SiOH$), which confirmed the molecular weight[10]. The fragments *m/z* 437 ($M^+ - CHO$) and 348 ($M^+ - CHO - Me_3SiO$) confirmed the presence of a -CHO group[10]. The fragments *m/z* 363 ($M^+ - Me_3SiOCH_2$), 333

TABLE II

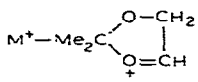
MASS SPECTRA (70 eV) OF THE *O*-ISOPROPYLIDENE DERIVATIVES OF THE OSULOSES

m/z	5 *and* 6 (%)	7 (%)	8 (%)	9 (%)
317	0.01			
301	3.00			
258	0.30			
245		19.80		
243	3.60			
231		25.00		
229	2.10	18.10		
217				0.20
215	0.60			
202			25.00	
201	0.70			0.30
200	1.80	28.20		
187	0.20	61.10	1.90	
185	16.00			
173	0.70	68.00	0.30	0.30
171	1.70	80.10	2.50	
159		8.10	0.50	
156			0.20	
145				5.40
144		98.80	5.30	
143	3.20		2.10	8.00
141				1.60
129	2.90	48.40	1.60	1.40
127		31.20	0.40	2.10
125	4.20			
117	7.00			0.80
115	7.30			0.80
113	5.10	30.80	2.20	0.70
101	23.10		2.10	1.82
100		70.60	4.10	1.80
99	2.10	30.30	2.20	14.50
97	8.60			
85	12.40	65.20	6.10	15.20
73			2.10	3.00
72	12.50			
71		62.50	7.20	2.80
69	15.30	16.50	2.80	
59	37.10	87.80	20.70	30.20
57	12.00	25.30	9.00	
55	14.50	13.10	8.50	8.00
43	100.00	100.00	100.00	100.00

($M^+ - Me_3SiOCH_2CHOH$), 133 (Me_3SiOCH_2CHOH), and 103 (Me_3SiOCH_2) confirmed the presence of a Me_3SiOCH_2 group[11], and the fragments *m/z* 217 and 204 ($[Me_3SiOCH{=}CHOSiMe_3]^+$) confirmed a furanoid ring[11].



m/z = 217



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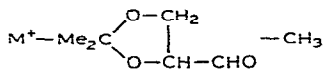

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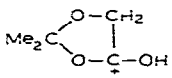

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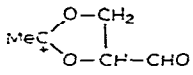

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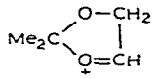

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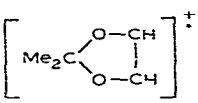
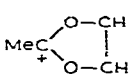
The structures of the 2,3,4-tri-*O*-trimethylsilyl-2-pentosulo-2,5-furanoses (**3** and **4**) were confirmed by the fragments (Table I): *m/z* 349 ($M^+ - CH_3$), 291 ($M^+ - Me_3Si$), 275 ($M^+ - Me_3SiO$), 259 ($M^+ - CH_3 - Me_3SiOH$), and 169 ($M^+ - CH_3 - 2\ Me_3SiOH$), which confirmed the molecular weight[10]. The fragments *m/z* 335 ($M^+ - CHO$) and 246 ($M^+ - CHO - Me_3SiO$) confirmed the presence of a -CHO group[10], and the fragments *m/z* 217 and 204 ($[Me_3SiOCH{=}CHOSiOMe_3]^+$) are characteristic of a furanoid ring[11].

The 1,2:2,3:5,6-tri-*O*-isopropylidene-2-hexosulo-1,4-furanoses (**5** and **6**) gave peaks (Table II) at *m/z* 317 ($M^+ + 1$), 301 ($M^+ - CH_3$), 258 ($M^+ - CH_3COCH_3$), 243 ($M^+ - CH_3 - CH_3COCH_3$), 200 ($M^+ - 2\ CH_3COCH_3$), 185 ($M^+ - CH_3 - 2\ CH_3COCH_3$), and 125 ($M^+ - CH_3 - 2\ CH_3COCH_3 - CH_3COOH$), which confirmed[12–14] a molecular weight of 316. The fragments at *m/z* 99 and 97 may be indicative of a furanoid ring[12,15,16], and those at *m/z* 215, 171, 117, 115, and 101,



m/z = 100



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together with the results for the hexadeuterioacetone derivatives, confirm a tri-*O*-isopropylidene derivative containing a 1,4-furanoid ring[12–15].

The 1,2:3,4-di-*O*-isopropylidene-2-pentosulo-1,5-pyranose (**7**) gave fragments (Table II) at *m/z* 231 ($M^+ - CH_3$), 173 ($M^+ - CH_3 - CH_3COCH_3$), 113 ($M^+ - CH_3 - CH_3COCH_3 - CH_3COOH$), which are indicative[12–14] of a molecular weight of 246. The fragments at *m/z* 245 ($M^+ - H$), 187 ($M^+ - H - CH_3COCH_3$), 229 ($M^+ - OH$), and 171 ($M^+ - OH - CH_3COCH_3$) correspond[17] to a free hydroxyl group on C-1 or C-2. Moreover, the fragments at *m/z* 100 and 85, together with the absence of fragments at *m/z* 117, 115, and 101, confirm this assignment[13,18].

The 2,3-*O*-isopropylidene-2-pentosulo-2,5-furanose (**8**) gave fragments (Table II) at *m/z* 187 ($M^+ - H$), 173 ($M^+ - CH_3$), 171 ($M^+ - OH$), 159 ($M^+ - CHO$), 129 ($M^+ - H - CH_3COCH_3$), 101 ($M^+ - CHO - CH_3COCH_3$), 100, and 85, which confirm the assignments of structures as in the compounds noted above.

The 1,2:2,3-di-*O*-isopropylidene-*glycero*-2-tetrosulo-1,4-furanose (**9**) gave fragments (Table II) at *m/z* 217 ($M^+ + 1$), 201 ($M^+ - CH_3$), 143 ($M^+ - CH_3 - CH_3COCH_3$), 141 ($M^+ - CH_3 - CH_3COOH$), and 85, which are indicative of this structure.

The structure assignments based on the mass spectra were verified by comparison with the fragmentation patterns of compounds prepared in conventional ways[11, 19–21]. The same mass spectra were obtained in the following cases: compounds **1** and **2** and the *O*-trimethylsilyl derivatives of D-*arabino*-2-hexosulose and L-*xylo*-2-hexosulose: compounds **3** and **4** and the *O*-trimethylsilyl derivatives of D-*erythro*-2-pentosulose and L-*threo*-2-pentosulose; compounds **5** and **6** and isopropylidene derivatives of D-*arabino*-2-hexosulose and L-*xylo*-2-hexosulose; compound **7** and the *O*-isopropylidene derivative of D-*erythro*-2-pentosulose; compound **8** and the *O*-isopropylidene derivative of L-*threo*-2-pentosulose; and compound **9** and the *O*-isopropylidene derivative of D-glyceraldehyde. Compounds having the same mass spectra were distinguished by g.l.c. (see Experimental).

After electrolysis of D-mannitol under conditions similar to those described for D-glucitol, the following compounds were identified: D-fructose, D-glucose, D-arabinose, D-erythrose, DL-glyceraldehyde, and **1**, **3**, **5**, **7**, and **9**, which accord with the molecular symmetry of mannitol. D-Glucitol is not symmetrical, so that pairs of isomers are produced on oxidation (*e.g.*, oxidation at C-1 yields D-glucose, whereas oxidation at C-6 yields L-gulose, *etc.*). Both isomers of each pair give the same mass spectrum. For D-mannitol, the molecular symmetry means that oxidation gives only one isomer (*e.g.*, oxidation at C-1 or C-6 yields D-glucose).

The first step in the anodic oxidation of alditols is the formation of aldoses and ketohexoses. When D-fructose or L-sorbose was electrolysed under the same conditions, aldopentoses were not formed, and D-glucose and D-mannitol gave the same results. On the other hand, for aldose degradation, the osuloses detected suggest that the α-keto group is formed before the carboxyl group.

EXPERIMENTAL

Electrolysis. — A stirred solution of D-glucitol (7.29 g, 0.04 mol) and calcium iodide (1.47 g, 0.005 mol) in water (75 ml) was contained in a refrigerated cell without a separator diaphragm. Current was supplied from an Arrosu rectifier (5 A, 100 V). The anode and cathode were platinum. Electrolysis was performed at a constant current of 2 A for 5 h with a potential of 22 V. The current density was 0.17 A/cm^2 and the temperature was kept at 20°. The solution was then concentrated and the residue was dried by distillation of methanol therefrom.

General methods. — All evaporations were carried out at 30–40° under reduced pressure.

Descending paper chromatography was performed on Whatman No. 1 paper with 1-butanol–acetone–water (2:7:1) (R_{Rha} values: gulose, 0.55; glucose, 0.56; fructose, 0.73; sorbose, 0.75; arabinose, 0.76; xylose, 0.78; erythrose, 1.24; threose, 1.30), 1-butanol–pyridine–water (6:4:3). 1-butanol–acetic acid–water (4:1:5), and 2-propanol–acetic acid–water (7:2:1). Detection was effected with aniline hydrogen phthalate in 1-butanol, orcinol–HCl, or orcinol–Cl_3C COOH.

Trimethylsilylation of the dry, syrupy products of electrolysis was performed by the usual method[19]. Isopropylidenation was performed as follows: a mixture of syrup (1 g), dry acetone (36 ml), and conc. sulphuric acid (0.7 ml) was shaken for 8 h, cooled, neutralised with anhydrous sodium carbonate, filtered, and concentrated to dryness. Deuterated acetone was also employed when a confirmation of fragment assignations in m.s. was required.

G.l.c. was performed on a Perkin–Elmer Chromatograph Model 3920 B with a column (4 m × 0.125 in.) packed with SE-52 on Chromosorb W (80–100 mesh): initial temperature, 80°; temperature programme, 2°/min to 250° and then isothermal. The retention times and configurations of the products accorded with those of standards. *T* values of *O*-trimethylsilyl derivatives: glucitol, 1.00; glucose, 1.03 and 0.94; gulose, 0.86; fructose, 0.82; sorbose, 0.88; arabinose, 0.71; xylose, 0.77; erythrose, 0.38, threose, 0.45; and glyceraldehyde, 0.15. *T* values (relative to that of the corresponding derivative of glucitol) and configurations for **1**–**9**: (*a*) trimethylsilyl derivatives, **1** (D-*arabino*) 0.69, **2** (L-*xylo*) 0.68, **3** (D-*erythro*) 0.61, **4** (L-*threo*) 0.63; (*b*) tri-*O*-isopropylidene derivatives, **5** (D-*arabino*) 1.16, **6** (L-*xylo*) 1.17, **7** (D-*erythro*) 0.76, **8** (L-*threo*) 0.73, and **9** (DL-*glycero*) 0.36.

Mass spectra (70 eV) were obtained with a Hewlett–Packard gas chromatograph Model 5710 A coupled to a mass spectrometer Model 5980 A.

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