

Table 3. Recovery of iodine in % after incineration of Na<sup>131</sup>I with addition of alkali carbonate.

Carbonate added	Vessel	Iodide		1 h	Recovery, %		
		m.p.°C	b.p.°C		2 h	6 h	24 h
1 ml 4 N K <sub>2</sub> CO <sub>3</sub>	Ni crucible	723	1 420	—	92	79	71
1 ml 4 N Na <sub>2</sub> CO <sub>3</sub>	do.	651	1 300	81	75	70	49
1 ml 4 N K <sub>2</sub> CO <sub>3</sub>	Pyrex tube	723	1 420	98	92	87	87
1 ml 4 N Na <sub>2</sub> CO <sub>3</sub>	do.	651	1 300	100	92	87	64

Table 4. Effect of calcium on iodine recovery in % after alkaline incineration of Na<sup>131</sup>I.

Ca conc. mg/100 ml	K <sub>2</sub> CO <sub>3</sub> incineration		Na <sub>2</sub> CO <sub>3</sub> incineration	
	Batch 1	Batch 2	Batch 1	Batch 2
15 800	94 92	96	70 72	85
158	82 84	79	43 42	55
15.8	88 85	82	81 81	75
1.58	90 91	88	89 89	81
0	94 96	97	90 88	87

about the same in the physiologic range, but in higher concentrations the loss was much more pronounced in the Na<sub>2</sub>CO<sub>3</sub> series.

It is obvious that the presence of greater concentrations of cations, the iodides of which have low meltingpoints, may result in considerable errors in the quantitative determination of iodine in organic material. The use of K<sub>2</sub>CO<sub>3</sub> instead of Na<sub>2</sub>CO<sub>3</sub> on incineration will result in a more complete recovery of iodine.

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## The Oxidation of Glycosides

### X. \* Reduction of Some Methyl D-Oxo-glucopyranosides

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The reduction of oxo-*cyclo*-hexane ring compounds has been widely studied and it is well known that the proportion of axial to equatorial hydroxyl groups formed is dependent upon the type of reduction, and that hindered oxo groups afford axial alcohols. The effect of hindrance is particularly strong in catalytic hydrogenation (for summary and references see Barton<sup>1</sup>). There is usually considered to be good conformational analogy between pyrane- and *cyclo*-hexane-rings. Raymond recently<sup>2</sup> reported the results of borohydride reduction of *myo*-inosose-2 (I) and *epi*-inosose-2 (II) and compared the ratio of the inositol isomers formed with the results previously obtained by Posternak, using catalytic hydrogenation (Pt-catalyst) and reduction

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Table 1. Reduction of methyl D-oxo-glucopyranosides (Percentage of equatorial (glucoside) and axial (mannoside, alloside) epimers formed).

Method of reduction	Methyl $\beta$ -2- -oxo-glucoside		Methyl $\beta$ -3- -oxo-glucoside		Methyl $\alpha$ -3- -oxo-glucoside	
	glucoside	mannoside	glucoside	alloside	glucoside	alloside
H <sub>2</sub> /Pt (ca. pH 6 and room temperature)	6	94	23	77	14	86
Raney nickel (ca. pH 6 and 78°)	26	74	38 *	62 *	9	91
Sodium amalgam (pH 6 and room temperature)	47	53	34	66	37	63
Borohydride (pH 9.5 and room temperature)	35 **	65 **	51 **	49 **	4	96

\* A 500 mg-scale experiment gave an 85 % yield of sugars, containing glucose (35 %), allose (57 %) and 1,6-anhydro-allose (8 %).

\*\* These figures are more accurate than those previously <sup>4</sup> given.

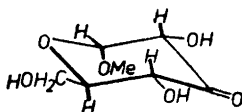
with sodium amalgam. The *myo*-inosose-2, having no axial hydroxyl groups, gave a large proportion of the axial epimer on catalytic hydrogenation, and a ratio of axial to equatorial epimers of about 4:3 on reduction with borohydride and sodium amalgam. The second compound (II), in which the oxo group is hindered by an axial hydroxyl group in  $\beta$ -position, gave the axial epimer only, on catalytic hydrogenation or borohydride reduction and an axial to equatorial ratio of about 6:2 on reduction with sodium amalgam. The results obtained with compound II show that the axial hydroxyl group  $\beta$  to the oxo group has a considerable effect on the approach of the borohydride ion.

In the present investigation methyl  $\beta$ -D-2-oxo-glucopyranoside (III), methyl  $\beta$ -D-3-oxo-glucopyranoside (IV) and methyl  $\alpha$ -D-3-oxo-glucopyranoside (V) were reduced catalytically with Pt- and Raney nickel-catalyst, with sodium amalgam and with borohydride and the proportions of the methyl glycosides obtained were estimated. It was shown by paper chromatography that the resulting glycosides contained only small amounts of unreacted oxo-glucoside and only traces of other compounds. The ratios of epimeric glycosides obtained were determined by quantitative analysis of the sugars obtained on hydrolysis of the reduction product. The analytical

figures (Table 1) were corrected for sugar decomposition during hydrolysis and for the formation of 1,6-anhydro-D-allose <sup>3</sup>.

In comparing the four types of reducing agents, it must be borne in mind that one of them (Raney nickel) was used at a higher temperature and one (borohydride) at a higher pH than the others. As in the case of the two inososes none of these reducing agents gave products in which the most stable, equatorial isomer (the methyl glucoside) predominated. In general the effect of hindrance was most marked in the Pt-catalysed reduction and least using sodium amalgam. The reduction with Raney nickel catalyst gave ratios of the methyl glycoside epimers closer to those obtained with sodium amalgam and borohydride than to those obtained using H<sub>2</sub>/Pt. Methyl  $\alpha$ -3-oxo-glucoside (V), with an axial, bulky methoxyl group  $\beta$  to the oxo-group, was similar to *epi*-inosose-2, and gave a large proportion of the axial isomer on reduction with borohydride, as was expected, and also with Raney nickel.

*Experimental.* The oxo-glucosides were prepared as described previously <sup>5,6</sup> and 20 mg samples of the compounds were reduced in 1 % solution. Reduction over platinum catalyst was done in unbuffered aqueous solution at pH 6 for 4 h using Adams catalyst and with Raney nickel according to the procedure of Karabinos

Methyl- $\alpha$ -D-3-oxo-glucopyranoside.

and Ballun<sup>7</sup>, by refluxing the oxo-glucoside for 3 h in unbuffered aqueous ethanol (30 % water) at pH 6. They were reduced with sodium amalgam (2.5 % sodium) for 4 h in aqueous solution buffered to pH 6. The amalgam was added at intervals over 4 h and the pH was kept at 6 by the addition of small amounts of acetic acid, the product was then deionised. The borohydride reduction was done in aqueous solution buffered to pH 9.5 for 5 h and the product was then deionised.

The reduction products were hydrolysed with 0.5 N sulphuric acid for 16 h at 100°, neutralised with Amberlite IR-4B (free base) and the solution obtained was concentrated. The sugars were separated by paper chromatography and a quantitative quadruple estimation was made using the procedure of Saeman *et al.*<sup>8</sup>. Schleicher and Schüll No. 2043a papers were used and the chromatograms were eluted with ethyl acetate-acetic acid-water, 3:1:3 (upper phase).

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## Some Remarks about the Shape of Gaussian Error Curve of Absorption Bands

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As it is well known in literature, the Gaussian error curve is often a good approximation of absorption band shape for transition group complexes<sup>1</sup>. In the theory of electronic transitions in molecules<sup>2</sup> this behaviour can be understood as the projection of the (squared) vibrational wavefunction of the electronic groundstate on the potential curve of the excited electronic state. If the electronic groundstate has a parabolic potential curve as function of the internuclear distance, and if the temperature is so low that only the groundstate ( $n=0$  in  $E = (n + \frac{1}{2})h\nu_0$ ) of the harmonic oscillator is populated, the Gaussian shaped wavefunction will produce a nearly Gaussian shaped absorption band (by projection on a linear potential curve of the excited electronic state) viz.

$$\varepsilon = \frac{\sigma}{\sigma_0} \varepsilon_0 \exp \left[ -\frac{(\sigma - \sigma_0)^2}{\delta^2} \right] \ln 2 \quad (\text{I})$$

where the indices zero on the wavenumber  $\sigma$  and extinction coefficient  $\varepsilon$  refer to a point near to the band maximum. The

factor  $\frac{\sigma}{\sigma_0}$  explains partly that fact<sup>1</sup> that  $\delta(-) < \delta < \delta(+)$ , where  $\delta(-)$  and  $\delta(+)$  are the halfwidths of two halves of non-corrected Gaussian curves towards smaller and larger  $\sigma$ . Dr. Klixbüll Jørgensen has pointed out that in this approximation, the maximum occurs at  $\sigma = \sigma_0 + \frac{\delta^2}{\sigma_0 2 \ln 2}$  and the ratio between the two half-widths is  $\frac{\delta(+)}{\delta(-)} \cong 1 + \frac{\delta}{\sigma_0 \ln 2}$ . Reasonable values for the slope of the excited state's potential curve, as implied from ligand field theory<sup>3-5</sup>, agree well with the observed values of  $\delta$ .