Carbohydrate Research, 49 (1976) 69–77

BROMINE OXIDATION OF METHYL α- AND β-PYRANOSIDES OF D-GALACTOSE, D-GLUCOSE, AND D-MANNOSE*†

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(Received October 3rd, 1975; accepted for publication, October 9th, 1975)

ABSTRACT

Methyl α- and β-pyranosides of D-galactose, D-glucose, and D-mannose have been oxidized with bromine in aqueous solution at various pH values. The resulting keto glycosides were converted into their more-stable *O*-methyloxime derivatives which were characterized by spectroscopy and chromatography. Oxidation at a ring carbon atom where the hydrogen is axial is hindered by bulky substituents in *syn* (*i.e.*, a 1,3) diaxial relationship. Thus, the aglycon group in the α anomers protects position 3, the axial HO-4 in galactopyranosides protects position 2, and the axial HO-2 in mannopyranosides protects position 4 from oxidation.

INTRODUCTION

Keto glycosides are intermediates in the biosynthesis[1] and chemical synthesis[2–4] of other sugars and are also formed from cellulose and other polysaccharides during bleaching or oxidative treatments[5]. Consequently, improved methods for their chemical synthesis and characterization are important. Various oxidising agents have been used for the preparation of dicarbonyl sugars and their derivatives. The specific oxidation of secondary hydroxyl groups usually requires partly protected derivatives[2,4,6]. Labile glycosiduloses may be partly destroyed when the protecting groups are removed in the syntheses of keto glycosides having free hydroxyl groups.

Alternatively, the isomeric carbonyl glycosides may be isolated by chromatography of the mixture obtained after oxidation of the unprotected glycoside. This procedure is often time-consuming and the yields of individual compounds are usually rather low. However, some keto pentopyranosides have been prepared in rather high yields by platinum-catalyzed oxidation of unprotected glycosides; axial hydroxyl groups[7] are preferentially oxidised.

We have previously studied the chlorine oxidation of glycosides and polysaccharides at various pH values[8]. Oxidation in aqueous, acid solution involves a

*Dedicated to the memory of Professor Edward J. Bourne.
†The oxidation of Glycosides: Part XIX. Part XVIII: H. F. G. Beving and O. Theander, *Acta Chem. Scand.*, *B*, 29 (1975) 641–646.

combination of a slow ionic, and a more-rapid radical, mechanism. We have now studied the oxidation of methyl glycosides with bromine. Previous reports[9–11] on the bromine oxidation of carbohydrates have mainly described the acidic products or the analytical determination of carbonyl and carboxyl content.

RESULTS AND DISCUSSION

On treatment of methyl α-D-glucopyranoside with bromine in aqueous solution, oxidation at pH 5 was observed to be slow (*cf.* ref. 12). At higher pH values, the reaction was faster, but the keto glycosides were degraded at pH >7. Thus, the optimal pH is 7. With ~2 mol of bromine (as 0.1M bromine) per mol of glycoside at 30°, the oxidant was generally consumed after 4–6 h in daylight or in the dark, thereby indicating an ionic reaction.

Keto glycosides are extremely sensitive compounds[2,4] and it is difficult to analyse accurately the mixtures of reaction products obtained by oxidation of glycosides. The possibility of stabilising the products as *O*-methyloxime derivatives was therefore investigated. When the anomeric methyl D-*ribo*-hexopyranosid-3-uloses and methyl α-D-*arabino*-hexopyranosiduloses, respectively, were treated with methoxyamine hydrochloride[13], the *O*-methyloximes were obtained in quantitative yields. In contrast to the parent keto glycosides, these derivatives were stable towards alkali[14] and could be trimethylsilylated[15], acetylated, and methylated under alkaline conditions without degradation.

The reaction mixtures obtained by bromine oxidation of the methyl α- and β-pyranosides of D-galactose, D-glucose, and D-mannose, respectively, were converted into their *O*-methyloxime derivatives. Where authentic reference samples were not available, the purified products were identified by elemental analysis, n.m.r. spectroscopy, and g.l.c.–m.s. of their trimethylsilyl derivatives. The position of the carbonyl function was generally deduced from n.m.r. data. The *O*-methyloximes derived from the glucosides and mannosides were obtained as mixtures of *syn* and *anti* forms, detectable by n.m.r. spectroscopy. The configurational assignment of *syn* and *anti* forms of oximes based on n.m.r. data has been described[16], but is beyond the scope of this investigation. The proportions of various trimethylsilylated *O*-methyloximes in particular reaction mixtures were determined by g.l.c. It was assumed that all derivatives gave the same response in g.l.c., as did the trimethylsilylated *O*-methyloxime of methyl β-D-*xylo*-hexopyranosid-4-ulose (Table I).

Bromine oxidation of methyl α-D-glucopyranoside yielded mainly the 2- and 4-uloses (**1** and **6**, respectively); no 3-ulose could be detected. Oxidation of the corresponding β-D-glucoside was less specific, the three possible uloses (**2**, **3**, and **7**, respectively) being obtained in comparable amounts. Oxidation of methyl α-D-galactopyranoside yielded the 4-ulose **6**, whereas the β-D anomer gave the 3- and 4-uloses (**4** and **7**, respectively) together with small amounts of methyl β-D *erythro*-hexopyranosid-3,4-diulose. Likewise, methyl α-D-mannopyranoside yielded the 2-ulose (**1**), and the β-D anomer gave the 2- and 3-uloses (**2** and **5**, respectively). The

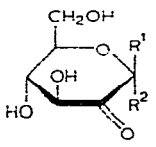
TABLE I

KETO GLYCOSIDES FROM BROMINE-OXIDISED GLYCOPYRANOSIDES, ANALYSED AS TRIMETHYLSILYLATED *O*-METHYLOXIME DERIVATIVES

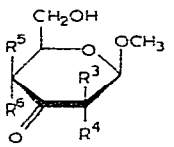
Oxidised glycoside	*Yields* (%)[a]							*Unreacted material* (%)
	1	**2**	**3**	**4**	**5**	**6**	**7**	
Methyl α-D-glucopyranoside	17(0.77)[b]					26(0.73)		35(0.83)
Methyl β-D-glucopyranoside		11(0.74)[c]	9(0.71)				17(0.74)[c]	24(0.86)
Methyl α-D-galactopyranoside						31(0.73)		34(0.81)
Methyl β-D-galactopyranoside				10(0.76)			19(0.74)	36(0.83)
Methyl α-D-mannopyranoside	29(0.77)[c]							44(0.77)[c]
Methyl β-D-mannopyranoside		24(0.74)			6(0.71)			43(0.80)

[a]The yields are calculated against *myo*-inositol, which is added as an internal standard. [b]The values in brackets are the retention times relative to trimethylsilylated *myo*-inositol. [c]Determined from the proportions of the fully acetylated (Ac_2O/pyridine) *O*-methyloxime derivatives.

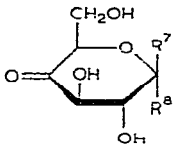
yield of **5** was very low and its identification was based mainly on the similarity of the mass spectrum of its trimethylsilylated *O*-methyloxime to those of the corresponding derivatives of **3** and **4**. The combined yield of hexosiduloses was ~30% in the foregoing oxidations. The presence of diketo compounds in most of the product mixtures was indicated by electrophoresis in hydrogen sulfite and by n.m.r. data, but no 6-aldehydoglycosides could be detected.



1 $R^1 = H, R^2 = OMe$
2 $R^1 = OMe, R^2 = H$



3 $R^3 = H, R^4 = OH$
$R^5 = H, R^6 = OH$
4 $R^3 = H, R^4 = OH$
$R^5 = OH, R^6 = H$
5 $R^3 = OH, R^4 = H$
$R^5 = H, R^6 = OH$



6 $R^7 = H, R^8 = OMe$
7 $R^7 = OMe, R^8 = H$

Aldehydo derivatives are probably rapidly oxidized to the uronic acids that were detected by electrophoresis and paper chromatography in all the reaction mixtures. Contrary to the results from the oxidation of glycosides with aqueous chlorine[8], no significant amounts of aldonic acids, corresponding to the parent sugars, were detected, and the yields of keto glycosides were considerably higher. However, it is likely that the latter compounds are partly oxidized to dicarboxylic acids that have not been characterized. Such products were previously found in the bromine oxidation of methyl α-D-mannopyranoside[9] and amylose[10].

The foregoing results indicate that steric factors affect the bromine oxidation of methyl glycopyranosides. Oxidation at position 3 of a methyl D-glycopyranoside is prevented by an axial MeO-1 (α-series). Additionally, in the mannopyranosides, the axial HO-2 protects position 4, and in the galactopyranosides, the axial HO-4 protects position 2. Several mechanisms for the bromine oxidation of secondary alcohols have been proposed, but it is generally agreed that the rate-determining step is the removal of a secondary hydrogen with its electron pair[17,18]. The present investigation indicates that a hydroxyl or methoxyl group which is in 1,3-*cis*-axial relationship to the hydrogen which is to be eliminated hinders the approach of the oxidising agent. For other reactions at ring carbon atoms in pyranoside or cyclohexane derivatives, similar steric factors have been reported[19,20].

Bromine oxidation of aqueous solutions of glycopyranosides having suitably oriented ring substituents appears to be a useful and simple method for the preparation of carbonyl derivatives of unprotected glycosides. The quantitative conversion of the keto glycosides into the more stable *O*-methyloxime derivatives simplifies purification by chromatography. The parent carbonyl compound can be regenerated in a good yield by treatment with weak acid.

EXPERIMENTAL

General methods. — Melting points are corrected. Solutions were concentrated at reduced pressure below 40°. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter and n.m.r. spectra with a Varian HA-100 D spectrometer. G.l.c. was conducted with a Varian model 2700 instrument, fitted with a flame-ionization detector. Separations were performed on glass columns (240 × 0.15 cm) containing (*a*) 3% of OV-1 on Varaport 30 (100–120 mesh) at 100–275° (6°/min) for the trimethylsilylated derivatives, and (*b*) 3% of OV-225 on Gas Chrom Q (100–120 mesh) at 190° for the acetylated derivatives. For quantitative g.l.c., an Autolab minigrator was used. G.l.c.–m.s. was performed with a Varian CH 7 gas chromatograph–mass spectrometer. P.c. was carried out on Whatman No. 1 paper with ethyl acetate–acetic acid–water (3:1:1). Electrophoresis was performed on Whatman No. 1 paper with *A* 0.1M sodium hydrogen sulfite buffer (pH 4.7) at 40° (for carbonyl glycosides) and *B* 0.5M sodium acetate buffer (pH 4.5) at 25° (for uronic acids). Detection was effected with *p*-anisidine hydrochloride and silver nitrate–sodium hydroxide.

General analytical procedure for determination of the products from bromine-oxidised methyl glycopyranosides. — A solution (0.1M) of bromine (2.4 g) in water (150 ml) was adjusted to pH 7.0. A solution of the methyl glycopyranoside (1.2 g) in water (25 ml) was added and the mixture was kept at 30°. The appropriate pH value was maintained by automatic addition of 0.5M sodium hydroxide, using a Metrohm E 300B pH-meter. The consumption of oxidant was followed by thiosulphate titration of acidified aliquots containing excess of potassium iodide. When the oxidant was consumed (after 4–6 h), the pH was adjusted to 5.0, and the mixture was concentrated to 100 ml. An aliquot was analysed qualitatively for carbonyl glycosides by p.c. and electrophoresis (buffer *A*). Another aliquot was hydrolysed (0.25M H_2SO_4, 100°, 24 h), then neutralized with barium carbonate, and analysed for uronic acids by p.c. and electrophoresis (buffer *B*). A third aliquot (50 ml) was concentrated to 25 ml and added to a solution of methoxyamine hydrochloride (1 g) in water (15 ml) adjusted to pH 4.0 with 2M sodium hydroxide. The reaction temperature was kept at 50° and the pH was maintained at 4.0 by the automatic addition of 0.1M sodium hydroxide. After 2.5 h, the pH was raised to 7.0 and the volume was adjusted to 50 ml. Aliquots (3 ml), to which *myo*-inositol (5 mg) was added as an internal standard, were concentrated to dryness and the residues were trimethylsilylated or acetylated. The yields of trimethylsilylated *O*-methyloximes were determined by g.l.c. (Table I). The detection responses for the trimethylsilylated derivatives of 7 and methyl α-D-glucopyranoside were determined by reference to a constant amount of trimethylsilyated *myo*-inositol. The same detector responses (0.50 and 0.62, respectively) were assumed for the other trimethylsilylated *O*-methyloximes and methyl glycopyranosides. A second aliquot (25 ml) was concentrated to dryness, the residue was trimethylsilylated, and the n.m.r. spectrum in carbon tetrachloride was recorded. It was sometimes possible to determine the proportions of *O*-methyloximes in the reaction mixtures by using n.m.r. data.

Bromine oxidations. — (*a*) *Methyl α-D-glucopyranoside.* On oxidation of 1.25 g of methyl α-D-glucopyranoside, methyl α-D-*arabino*-hexopyranosidulose (**1**), methyl α-D-*xylo*-hexopyranosid-4-ulose (**6**), and methyl α-D-glucopyranosiduronic acid were obtained, as determined by p.c., electrophoresis, and g.l.c.–m.s. The reaction mixture was processed and treated with methoxyamine hydrochloride as described above, and then concentrated to dryness, and the residue was extracted with chloroform (5 × 10 ml). The product in the extract was eluted from a column of silica gel with chloroform–pyridine–ethanol (94:5:1) and the fractionation was monitored by t.l.c. Yields were not optimised and only pure fractions from each oxime were collected. The products were recrystallized from chloroform.

The *O*-methyloxime of **1** (53 mg) had m.p. 101–105° and 122–126° (*syn* and *anti* mixture), $[\alpha]_{578}^{20}$ +78° (*c* 0.4, ethanol).

Anal. Calc. for $C_8H_{15}NO_6$: C, 43.4; H, 6.8; N, 6.3. Found: C, 43.9; H, 6.9; N, 5.9.

The m.s. of the trimethylsilylated *O*-methyloxime of **1** had, *inter alia*, peaks at *m/e* 73 (100%), 74 (8), 75 (32), 89 (12), 103 (15), 133 (25), 147 (9), 203 (8), 204 (4), 217 (3), 218 (3), 274 (9), 422 (2), and 437 (5, M^+).

The *O*-methyloxime of **6** (146 mg) had m.p. 69–75° and $[\alpha]_{578}^{20}$ +66° (*c* 0.3, ethanol).

Anal. Found: C, 43.3; H, 6.9; N, 5.9.

The m.s. of the trimethylsilylated *O*-methyloxime of **6** had, *inter alia*, peaks at *m/e* 73 (100%), 74 (18), 75 (21), 89 (22), 101 (6), 103 (16), 117 (5), 131 (5), 133 (30), 142 (5), 146 (7), 147 (15), 188 (17), 191 (13), 204 (4), 229 (3), 244 (3), 287 (7), 346 (4), 347 (2), and 437 (2, M^+).

The n.m.r. data of the trimethylsilylated *O*-methyloximes of **1** and **6** are given in Table II.

(*b*) *Methyl β-D-glucopyranoside.* On oxidation of 2.55 g of methyl β-D-glucopyranoside, methyl β-D-*arabino*-hexopyranosidulose (**2**), methyl β-D-*ribo*-hexopyranosid-3-ulose (**3**), methyl β-D-*xylo*-hexopyranosid-4-ulose (**7**), and methyl β-D-glucopyranosiduronic acid were obtained. The *O*-methyloxime derivatives were prepared and isolated as described above.

The *O*-methyloxime of **2** (147 mg) had m.p. 112–115°, $[\alpha]_{578}^{20}$ +41.5° (*c* 0.2, ethanol).

Anal. Calc. for $C_8H_{15}NO_6$: C, 43.4; H, 6.8; N, 6.3. Found: C, 43.0; H, 6.8; N, 5.9.

The m.s. of the trimethylsilylated *O*-methyloxime of **2** gave, *inter alia*, peaks at *m/e* 73 (100%), 74 (10), 75 (24), 89 (13), 103 (18), 133 (30), 147 (14), 191 (6), 203 (8), 217 (11), 218 (7), 219 (3), 256 (6), 274 (11), 346 (2), and 437 (6, M^+).

The *O*-methyloxime of **3** (121 mg) was a syrup, $[\alpha]_{578}^{20}$ −69.5° (*c* 0.3, ethanol).

Anal. Found: C, 41.3; H, 6.5; N, 6.6.

The m.s. of the trimethylsilylated *O*-methyloxime of **3** gave, *inter alia*, peaks at *m/e* 73 (100%), 74 (12), 75 (13), 85 (8), 89 (14), 103 (13), 129 (7), 131 (5), 133 (25), 146 (10), 147 (9), 191 (6), 207 (3), 214 (5), 217 (4), 218 (10), 274 (10), and 275 (3).

TABLE II

^{1}H-N.M.R. SPECTRAL DATA OF TRIMETHYLSILYLATED *O*-METHYLOXIME DERIVATIVES OF CARBONYL GLYCOSIDES

Parent compound	**1**	**2**[b,d]		**3**[d]		**4**[b]	**6**[b]	**7**[b]
Chemical shifts (p.p.m.)								
H-1	5.58 s	4.77 d	5.38 s	4.60 d	4.66 d	4.02 d	4.60 d	4.03 d
H-2	—	—	—	4.33 d	3.97 d	4.20 d	3.68 dd	3.62 dd
H-3	4.20–4.35[c]	4.50 dd	3.85–4.05[c]	—	—	—	4.09 d	3.92 d
H-4	3.50–3.65[c]	4.08 dd		4.77 d	4.27 d	5.02 d	—	—
H-5		3.32 m	3.30–3.50[c]	3.20–3.80[c]		3.25 m	4.79 dd	4.67 dd
H-6	3.60–3.75[c]	3.80 dd	3.50–4.00[c]			3.65 dd	3.80 dd	3.75 d
H-6′						3.55 dd	3.52 dd	3.70 d
C-OCH_3	3.33 s	3.68 dd	3.39 s	3.40 s	3.37 s	3.45 s	3.38 s	3.43 s
N-OCH_3	3.85 s	3.88 s	3.86 s	3.85 s	3.87 s	3.89 s	3.86 s	3.86 s
Coupling constant (Hz)								
$J_{1,2}$				5.8	2.9	7.5	2.0	6.0
$J_{2,3}$							5.3	3.0
$J_{3,4}$		5.7						
$J_{4,5}$		7.1				1.4		
$J_{5,6}$		4.4				8.0	6.5	3.5
$J_{5,6'}$		3.8				5.2	3.1	7.2
$J_{6,6'}$		−10.7				−9.5	−10.9	−10.5
$J_{1,3}$		0.7						
$J_{2,4}$				0.7	0.9			

[a]In CCl_4. [b]Analysis confirmed by spectral simulation using the Varian 995128-OOB program. [c]Unresolved. [d]Signals from the *syn* and *anti* forms.

The *O*-methyloxime of **7** (361 mg) had m.p. 137–139°, $[\alpha]_{578}^{20}$ +40° (*c* 0.4, ethanol).

Anal. Found: C, 43.9; H, 6.9; N, 6.1.

The m.s. of the trimethylsilylated *O*-methyloxime of **7** gave, *inter alia*, peaks at *m/e* 73 (100%), 74 (13), 75 (16), 89 (19), 101 (5), 103 (16), 116 (6), 131 (5), 133 (30), 142 (5), 146 (8), 147 (16), 188 (11), 191 (14), 204 (5), 229 (5), 287 (7), 346 (5), 422 (2), and 437 (3, M^+).

The n.m.r. spectra of the trimethylsilylated *O*-methyloximes of **2**, **3**, and **7** are given in Table II.

(*c*) *Methyl* α-D-*galactopyranoside.* On oxidation of methyl α-D-galactopyranoside, methyl α-D-*xylo*-hexopyranosid-4-ulose (**6**) and methyl α-D-galactopyranosiduronic acid were obtained, as determined by p.c., electrophoresis, and g.l.c.–m.s. of the trimethylsilylated *O*-methyloxime derivative.

(*d*) *Methyl β-D-galactopyranoside.* Oxidation of 2.5 g of methyl β-D-galactopyranoside yielded methyl β-D-*xylo*-hexopyranosid-3-ulose (**4**), methyl β-D-*xylo*-hexopyranosid-4-ulose (**7**), small amounts of methyl β-D-*erythro*-hexopyranosid-3,4-diulose, and methyl β-D-galactopyranosiduronic acid. The reaction mixture was processed, and the *O*-methyloximes were prepared. The *O*-methyloxime of **4** (93 mg) had m.p. 124–126°, $[\alpha]_{578}^{20}$ +6° (*c* 0.5, ethanol).

Anal. Calc. for $C_8H_{15}NO_6$: C, 43.4; H, 6.8; N, 6.3. Found: C, 43.2; H, 6.8; N, 6.1.

The m.s. of the trimethylsilylated *O*-methyloxime of **4** gave, *inter alia*, peaks at *m/e* 73 (100%), 74 (9), 75 (9), 89 (12), 103 (14), 129 (4), 133 (34), 134 (4), 146 (4), 147 (14), 191 (9), 217 (5), 218 (10), 214 (3), 219 (3), 255 (1), 274 (9), 275 (3), and 346 (2).

The analytical data for the *O*-methyloxime of **7** were in agreement with those given for the compound described in (*b*), and the n.m.r. data for the trimethylsilylated *O*-methyloxime of **4** are given in Table II.

The *O*-methyloxime of the 3,4-diulose was identified by n.m.r. spectroscopy. N.m.r. data (CD_3OD): δ 4.62 (d, $J_{1,2}$ 6.3 Hz, H-1), 4.44 (d, H-2), 4.87 (dd, $J_{5,6}$ 5.5, $J_{5,6'}$ 2.8 Hz, H-5), 3.79 (d, $J_{6,6'}$ −10.5 Hz, H-6), 3.84 (d, H-6'), 3.52 (s, C-OMe), 3.97 (s, N-OMe).

The analysis was confirmed by spectral simulation.

(*e*) *Methyl α-D-mannopyranoside.* Oxidation of methyl α-D-mannopyranoside yielded methyl α-D-*arabino*-hexopyranosidulose (**1**) and methyl α-D-mannopyranosiduronic acid, as determined by p.c., electrophoresis, and g.l.c.–m.s. of the trimethylsilylated *O*-methyloxime derivatives.

(*f*) *Methyl β-D-mannopyranoside.* Oxidation of methyl β-D-mannopyranoside (112 mg) yielded methyl β-D-*arabino*-hexopyranosidulose (**2**), small amounts of methyl β-D-*arabino*-hexopyranosid-3-ulose (**5**), and methyl β-D-mannopyranosiduronic acid, as determined by p.c., electrophoresis, and g.l.c.–m.s.

The m.s. of the trimethylsilylated *O*-methyloxime derivative of **5** gave, *inter alia*, peaks at *m/e* 73 (100%), 74 (9), 75 (11), 89 (14), 103 (14), 133 (21), 146 (56), 147 (19), 191 (7), 217 (3), 218 (6), 219 (3), 274 (7), 281 (2), and 346 (2).

Regeneration of the parent carbonyl glycoside from the O*-methyloxime derivative.* — In a typical experiment, to a solution of the *O*-methyloxime of **7** (40 mg) in water (20 ml), Dowex-50(H^+) resin (2 g) was added, and the mixture was stored at 22°. The reaction was monitored by t.l.c. (chloroform–pyridine–ethanol, 88:10:2). When no starting material remained (1 h), the mixture was filtered and concentrated to give **7** (35 mg), m.p. 61–65°, $[\alpha]_{578}^{20}$ −29° (*c* 0.4, water). N.m.r. data (D_2O): δ 4.86 (d, $J_{1,2}$ 7.3 Hz, H-1), 3.82 (dd, $J_{2,3}$ 9.8 Hz, H-2), 4.01 (d, H-3), 4.01 (dd, $J_{5,6}$ 2.5, $J_{5,6'}$ 7.5 Hz, H-5), 4.47 (dd, $J_{6,6'}$ −12.2 Hz, H-6), 4.29 (dd, H-6'), 4.09 (s, C-OMe). The analysis was confirmed by spectral simulation.

ACKNOWLEDGMENTS

We thank Docent Kjell Olsson for valuable discussion, Dr. A. N. de Belder for a generous gift of methyl α-D-*ribo*-hexopyranosid-3-ulose, Mr. Rolf Andersson for recording the n.m.r. spectra, and Mr. Gunnar Hesselius for the elemental analysis.

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