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THE REACTIONS OF OH RADICALS WITH D-RIBOSE IN DEOXYGENATED AND OXYGENATED AQUEOUS SOLUTION*

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ABSTRACT

Aqueous solution of D-ribose (10^{-2}M) saturated with N_2O and N_2O/O_2 (4/1) were γ-irradiated (dose rate: 3.85×10^{18} eV.g^{-1}.h^{-1}) at room temperature. The following products were identified: D-ribonic acid (**1**), D-*erythro*-pentos-2-ulose (**2**), D-*erythro*-pentos-4-ulose (**3**), D-*erythro*-pentos-3-ulose (**4**), D-*ribo*-pentodialdose (**5**), 2-deoxy-D-*erythro*-pentonic acid (**6**), 2-deoxypentos-3-ulose (**7**)(?), 4-deoxypentos-3-ulose (**8**), 3-deoxypentos-4-ulose (**9**), 3-deoxypentos-2-ulose (**10**), 5-deoxypentos-4-ulose (**11**), erythrose (**12**), *erythro*-tetrodialdose (**13**), erythronic acid (**14**), threose/erythrulose (**15**), threonic acid (**16**), 2-deoxytetrose (**17**), and glyceraldehyde (**18**). In deoxygenated solutions, **13**, **14**, and **16** were absent. In the presence of oxygen, the formation of **6**–**11** and **17** was suppressed. From quantitative measurements, *G*-values were calculated for both deoxygenated and oxygenated conditions. Five different, primary, ribosyl radicals are formed which, in deoxygenated solution, undergo disproportionation reactions (to give **1**–**5**), and transformations such as elimination of water and carbon monoxide followed by disproportionation reactions (to give **6**–**12**, **17**). Material-balance considerations indicate the formation of dimers (not measured). In oxygenated solutions, oxygen rapidly adds to the primary ribosyl radicals, thus preventing the transformation reactions, and the main products are **1**–**5** and **13**. Possible mechanistic routes are discussed. The attack of HO radicals on D-ribose involves C-1, ~20%; C-2 and C-4, ~35%; C-3, ~20%; and C-5, ~25%.

INTRODUCTION

The reaction of OH radicals with carbohydrates in aqueous solutions can be studied most conveniently by using high-energy radiation. The γ-radiolysis of water (reaction *1*) yields OH radicals, solvated electrons (e_{aq}^-), and H atoms as primary free-radical species.

$$H_2O \longrightarrow \gamma \rightarrow {}^{\bullet}OH, e_{aq}^-, {}^{\bullet}H, H_2, H_2O_2, H^+, HO^- \qquad (1)$$

$$e_{aq}^- + N_2O \rightarrow {}^{\bullet}OH + N_2 + HO^- \qquad (2)$$

*Radiation Chemistry of Carbohydrates: Part XI.

The solvated electrons are converted into OH radicals by saturating the solution with N_2O (reaction *2*). The reactivity of carbohydrates towards the solvated electron is too low[1] to compete with this reaction at the concentrations (10^{-2}M) of D-ribose used in these experiments. The system then consists of ~90% of OH radicals and ~10% of H atoms. Both species abstract carbon-bound hydrogen atoms from D-ribose, giving rise to five different, primary, ribosyl radicals.

In the absence of oxygen, these primary ribosyl radicals undergo a series of reactions leading to secondary radicals and eventually to end-products. In the presence of oxygen, oxygen adds to the ribosyl radicals, giving rise to the corresponding peroxyl radicals. Their chemistry determines the structure of the products in oxygenated solutions. The radiation chemistry of D-ribose has received some attention[2-4], and that of its 5-phosphate has been extensively studied[5-10] in order to elucidate the mechanisms of the OH-radical-induced scission of the nucleic acid strands.

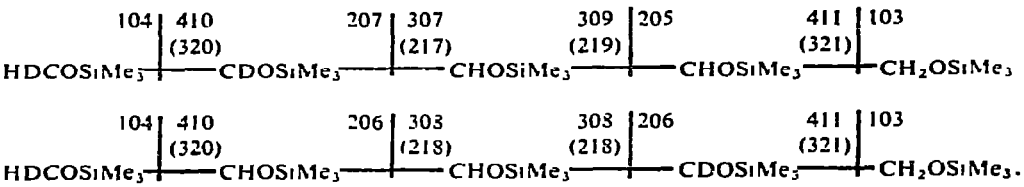
We now report a detailed analysis of the products from D-ribose, and present mechanistic considerations.

RESULTS

Aqueous solutions of D-ribose (10^{-2}M) were saturated with oxygen-free N_2O or with N_2O/O_2 (80:20), and were γ-irradiated ($0.8–3.9 \times 10^{19}$ eV.g^{-1} at a dose rate of 3.85×10^{18} eV.g^{-1}.h^{-1}). The irradiated samples were reduced with $NaBD_4$, trimethylsilylated, and analysed by g.l.c.–m.s. Fig. 1 shows a typical gas chromatogram. The mass spectra were interpreted on the basis of established fragmentation patterns for this class of compound[11]. Some products were isolated by column chromatography, and were identified (g.l.c.–m.s.) after methoximation and trimethylsilylation. The data are given in Table I.

Ribonic acid (**1**) was identified as the 1,4-lactone after separation from most of the other material by column chromatography. The residual material of this fraction was converted by methoximation into compounds that were eluted much earlier and thus did not interfere with the determination of **1**.

Pentos-2-ulose (**2**) and pentos-4-ulose (**3**), on reduction with $NaBD_4$, each gave arabinitol and ribitol. The mass spectrum of Me_3Si-arabinitol (Fig. 1, peak 12) contained prominent fragments at *m/e* 103 (25%), 104 (23%), 205 (14%), 206 (20%), 207 (15%), 217 (10%), 218 (18%), 219 (8%), 307 (3%), 308 (5%), 309 (2%), 320 (3%), 321 (3%), and 334 (< 1%); base peak, *m/e* 73. The ions at *m/e* 205, 206, 207, 307, 308, and 309 are consistent with the presence of arabinitol-*1,2-d*$_2$ and arabinitol-*1,4-d*$_2$, which would fragment as follows:



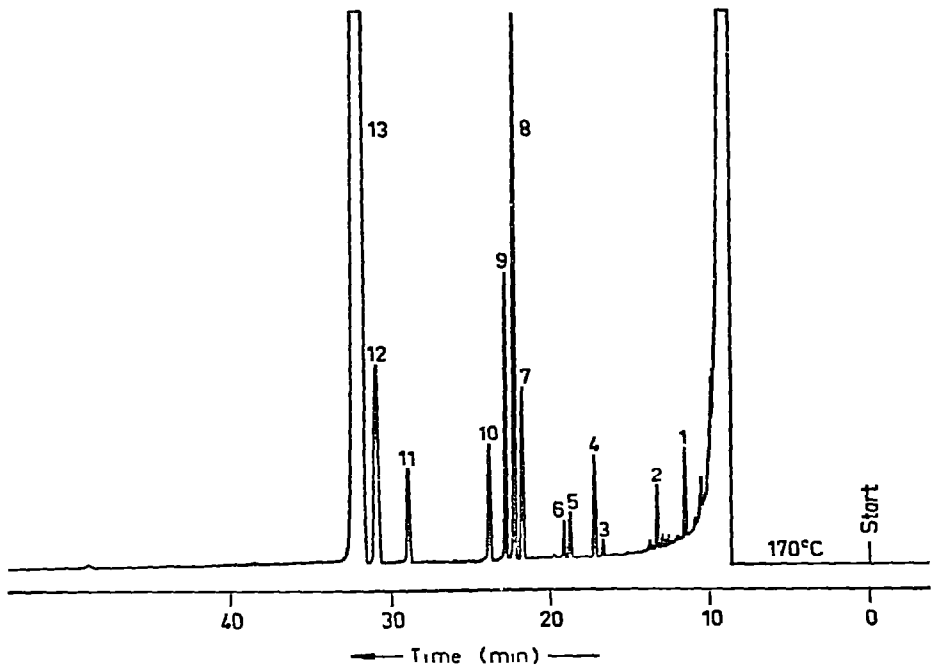


Fig. 1. Gas chromatogram of a $NaBH_4$-reduced and trimethylsilylated sample of D-ribose γ-irradiated in N_2O-saturated, aqueous solution: 130-m glass-capillary column; Dexsil 300; 170 isothermal. For numbers, refer to the text.

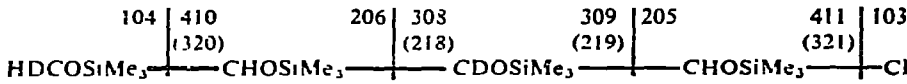
TABLE I

PRODUCTS IN THE γ-RADIOLYSIS[a] OF DEOXYGENATED AND OXYGENATED, N_2O-SATURATED, AQUEOUS SOLUTIONS OF D-RIBOSE

Product	*Determined as*	G-*values*	
		N_2O	N_2O/O_2
D-Ribonic acid (1)	Me_3Si ether of its lactone	0.05	1.0
D-*erythro*-Pentos-2-ulose (2)	Arabinitol-*1,2-d*$_2$ (Me_3Si ether)	0.7	1.8
D-*erythro*-Pentos-4-ulose (3)	Arabinitol-*1,4-d*$_2$ (Me_3Si ether)		
D-*erythro*-Pentos-3-ulose (4)	Xylitol-*1,3-d*$_2$ (Me_3Si ether)	0.2	1.0
D-*ribo*-Pentodialdose (5)	Methoxime–Me_3Si derivative	0.15	0.8
2-Deoxy-D-*erythro*-pentonic acid (6)	2-Deoxy-D-*erythro*-pentitol-*1,1-d*$_2$ (Me_3Si ether)	0.55	absent
2-Deoxypentos-3-ulose (7) (?)	Methoxime–Me_3Si derivative	0.30	absent
4-Deoxypentos-3-ulose (8)	2-Deoxy-*threo*-pentitol-*3,5-d*$_2$		absent
3-Deoxypentos-4-ulose (9)	3-Deoxypentitol-*1,4-d*$_2$	0.40	absent
3-Deoxypentos-2-ulose (10)	3-Deoxypentitol-*1,2-d*$_2$		absent
5-Deoxypentos-4-ulose (11)	5-Deoxypentitol-*1,4-d*$_2$	0.10	absent
Erythrose (12)	Erythritol-*1-d*$_1$	0.05	uncertain
erythro-Tetrodialdose (13)	Methoxime–Me_3Si derivative	absent	0.45
Erythronic acid (14)	Erythritol-*1,1-d*$_2$	absent	
Threose/erythrulose (15)	Pentitol-*1-d*$_1$/*2-d*$_1$	0.01	uncertain
Threonic acid (16)	Threitol *1,1-d*$_2$	absent	0.04
2-Deoxytetrose (17)	2-Deoxytetritol-*1-d*$_1$	0.03	absent
Glyceraldehyde (18)	Glycerol-*1-d*$_1$	0.06	0.02

[a]25°; dose, $(0.8–3.9) \times 10^{19}$ eV.g^{-1}; dose rate, 3.85×10^{18} eV.g^{-1}.h^{-1}.

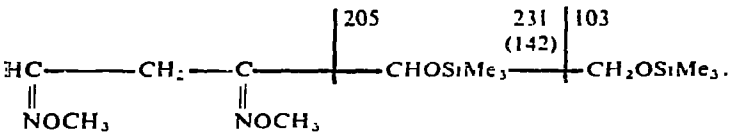
Pentos-3-ulose (**4**) was identified as Me_3Si-xylitol-*1,3-d*$_2$, the mass spectrum of which showed ions at *m/e* 103 (23%), 104 (30%), 205 (13%), 206 (15%), 218 (19%), 219 (14%), 308 (8%), 309 (9%), 320 (2%), and 321 (2%); base peak, *m/e* 73; indicative of the fragmentation:



ribo-Pentodialdose (**5**) was identified after methoximation and trimethylsilylation of a column-chromatographic fraction. *xylo*-Pentodialdose served as reference material in mass spectrometry.

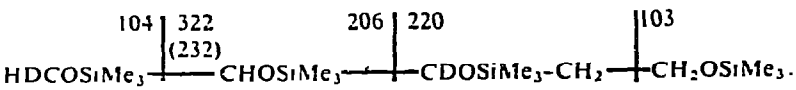
2-Deoxy-*erythro*-pentonic acid (**6**) was identified as 2-deoxy-D-*erythro*-pentitol-*1,1-d*$_2$ after reduction with $NaBD_4$ and trimethylsilylation of a column-chromatographic fraction.

Methoximation and trimethylsilylation of a column-chromatographic fraction led to a product whose mass spectrum contained ions at *m/e* 103 (4%), 117 (10%), 142 (22%), 155 (M−90−89; 2%), 205 (10%), 213 (M−31−90; 8%), 231 (32%), 244 (M−90; 1%), 303 M−31; <1%), and 319 (M−15; 2%); base peak, *m/e* 73. This mass spectrum could indicate 2-deoxypentos-3-ulose (**7**).

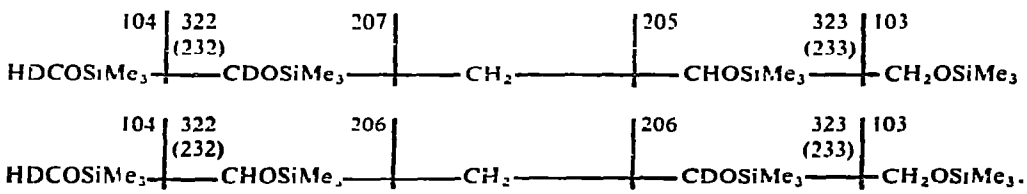


Alternatively, the mass spectrum could be interpreted as being due to the methoxime Me_3Si derivative of 3-deoxypentos-2-ulose (**9**).

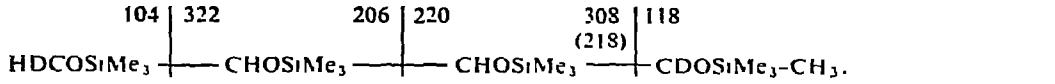
4-Deoxypentos-3-ulose (**8**) was isolated by column chromatography. The product obtained by reduction with $NaBD_4$, followed by trimethylsilylation, gave a mass spectrum which contained ions at *m/e* 103 (100%), 104 (15%), 206 (5%), 220 (30%), 232 (3%), 246 (1%), 321 (<1%), and 322 (<1%). The ions at *m/e* 104, and 220 show that deuterium atoms are incorporated both at C-1 and C-3:



3-Deoxypentos-2-ulose (**9**) and 3-deoxypentos-4-ulose (**10**), on reduction with $NaBD_4$, gave two stereoisomeric polyhydric alcohols (peaks 9 and 10, Fig. 1). The mass spectra of the Me_3Si derivatives of these alcohols are similar and contain ions at *m/e* 103 (4%), 104 (2%), 205 (10%), 206 (18%), 207 (8%), 232 (30%), 233 (32%), 246 (1%), 322 (<1%), and 323 (<1%); base peak, *m/e* 73. These ions are consistent with the presence of 3-deoxypentitol-*1,2-d*$_2$ and 3-deoxypentitol-*1,4-d*$_2$:

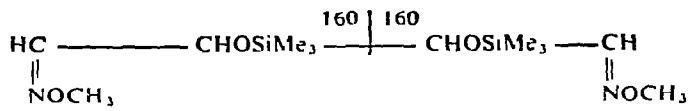


5-Deoxypentos-4-ulose (**11**), on reduction with $NaBD_4$, gave two polyhydric alcohols. The mass spectra of their Me_3Si ethers (peaks 5 and 6 in Fig. 1) are identical and contained ions at *m/e* 103 (22%), 104 (20%), 118 (50%), 157 (1%), 206 (5%), 218 (6%), 220 (10%), 231 (5%), 308 (5%), 321 (M − 15 − 90; 1%), 322 (< 1%), and 336 (< 1%): base peak, *m/e* 73. These data are consistent with the presence of deuterium at C-1 and C-4:



In the absence of oxygen, a g.l.c. peak due to Me_3Si-erythritol (peak 4 in Fig. 1) is preceded by a smaller peak for Me_3Si-threitol (peak 3 in Fig. 1). Each compound contains one deuterium atom. Whereas the precursor of most of the erythritol is erythrose (**12**), the precursor of the threitol might be threose and/or erythrulose (**15**).

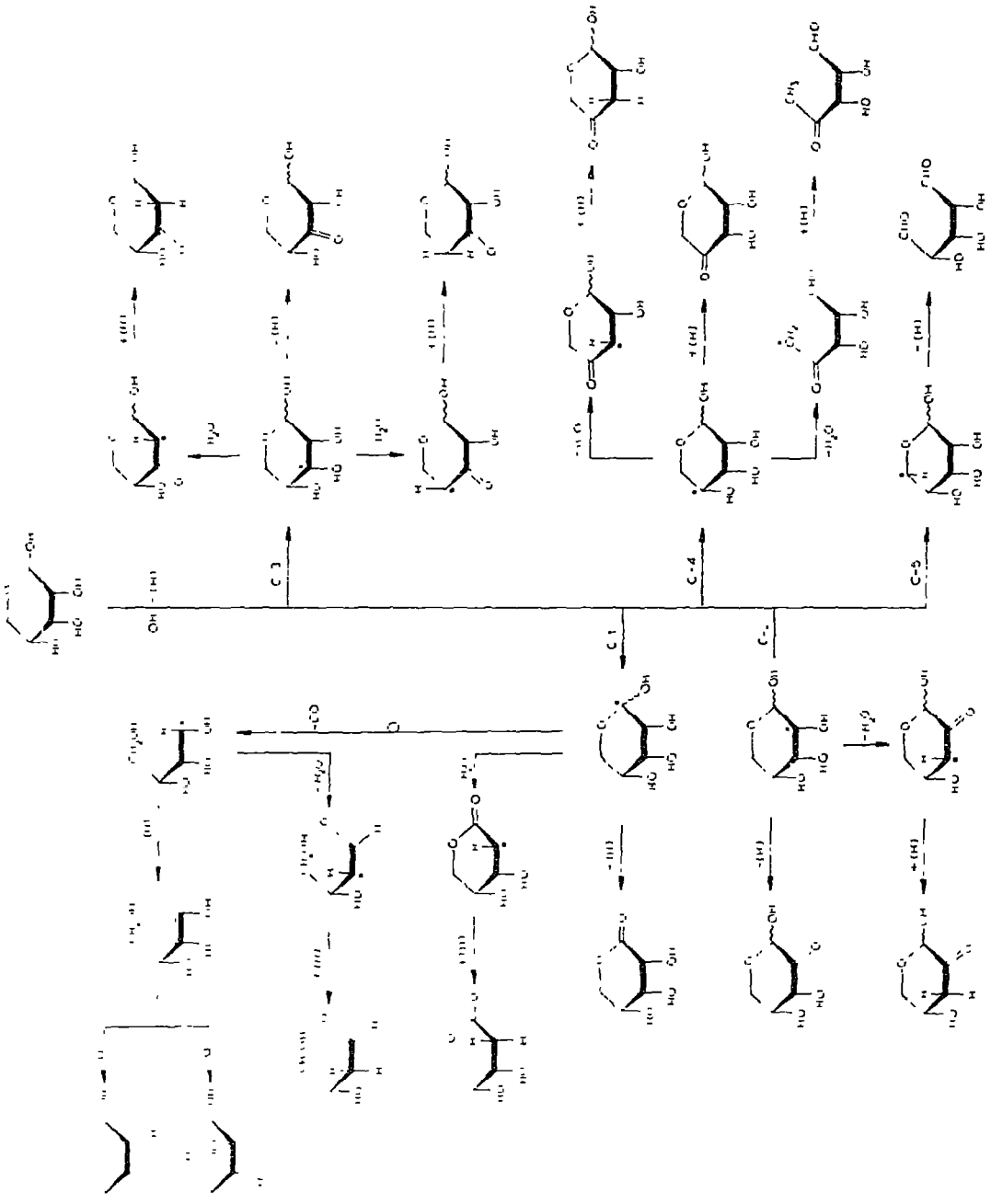
erythro-Tetrodialdose (**13**) was identified after methoximation followed by trimethylsilylation. The mass spectrum contained ions at *m/e* 73 (97%) 160 (100%), 215 (M − 15 − 90; 1%), 231 (M − 89; < 1%), 243 (M − 31 − 31; < 1%), 274 (M − 31; < 1%), and 305 (M − 15; < 1%) consistent with the following fragmentation:



This product was also identified as erythritol-*1,4*-d_2. Erythronic acid (**14**) and threonic acid (**16**) were identified as erythritol-*1,1*-d_2 and threitol-*1,1*-d_2, respectively. The presence of minor amounts of erythrose, erythrulose, and threose cannot be excluded from the series of products obtained from oxygenated solutions.

2-Deoxytetrose (**1**) was identified as 2-deoxytetritol-*1*-d_1 (peak 2 in Fig. 1), as described previously[12]. For quantitative analysis of the reduced samples, rhamnitol was used as an internal standard, and ribitol for the methoximated samples. Reduction of the pentosuloses **2**–**4** gave ribitol and another stereoisomer. Only the latter was determined, and its yield was arbitrarily multiplied by two (Table I). The yields of products on reduction of hexosuloses with $NaBH_4$ is usually near to equimolar, but in one case (*ribo*-hexos-3-ulose) a ratio of 1:1.75 was found.

The quantitative determination of *ribo*-pentodialdose was carried out *via* its methoxime Me_3Si-derivatives. The g.l.c. peaks corresponding to the *syn* and *anti* forms were identified by using ribose 5-phosphate irradiated in oxygenated, aqueous solutions as reference material, which gives *ribo*-pentodialdose as the only major phosphate-free product containing five carbon atoms[7]. These samples also allowed determination of the sum of the products **2**–**5**. In N_2O-saturated solutions, a *G*-value of 1.2 was obtained in agreement with the values in Table I. The g.l.c. response factor of the methoxime Me_3Si-derivatives was calculated on an increment basis[13]. The *G*-values obtained in these experiments are thought to be correct to ± 20%, although the reproducibility was usually better (± 10%).



Scheme 1. γ-Radiolysis of D-ribose in deoxygenated aqueous solutions; (H) denotes a hydrogen atom transferred in a disproportionation reaction.

DISCUSSION

For aqueous solutions of D-ribose, the OH radicals and H atoms generated by the radiolysis of water abstract carbon-bound hydrogen atoms from D-ribose to give five different, primary, ribosyl radicals (Scheme 1), which undergo a series of reactions. The types of reactions are similar to those observed for 2-deoxy-D-*erythro*-pentose[14,15], cellobiose[16,17], D-glucose[18], and D-fructose[19]. They are as follows.

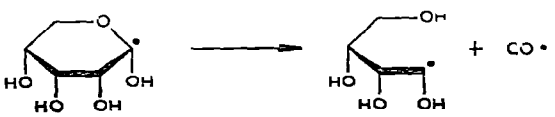
The elimination of water from α,β-dihydroxyalkyl radicals:

$$-\dot{C}OH-CHOH- \rightarrow -CO-\dot{C}H- + H_2O. \qquad (3)$$

The corresponding reaction involving an O–R group:

$$-\dot{C}OH-CHOR- \rightarrow -CO-\dot{C}H- + HOR. \qquad (4)$$

Elimination of CO and $CO + H_2O$ from radicals of the types $-CHOH-\dot{C}O-$, and $-CHOH-\dot{C}(OH)_2-$ and its ring-closed carbohydrate analogues:



(5)

Rearrangement involving the ring oxygen:

(6)

Disproportionation reactions of the primary radicals:

$$2\,-\dot{C}OH-CHOH- \rightarrow -CO-CHOH- + -CHOH-CHOH- \qquad (7a)$$

$$2\,-\dot{C}OH-CHOH- \rightarrow -COH{=}COH- + -CHOH-CHOH-. \qquad (7b)$$

Enols[20] are expected to be, in part, intermediates in the formation of the carbonyl compound (reaction *7b*). The reduced product of reaction *7* can thereby lose its original configuration[21]. Dimerisation reactions of these radicals appear to be of minor importance.

Radicals of the $-CO-\dot{C}H-$ type formed in reaction *3* are either reduced by the radicals of the $-\dot{C}OH-CHOH-$ type (reaction *8*) or dimerize (reaction *9*). The oxidation of these radicals has not been observed so far in carbohydrate free-radical chemistry.

$$-CO-\dot{C}H- + -\dot{C}OH-CHOH- \rightarrow -CO-CH_2- + -CO-CHOH- \qquad (8)$$

$$2\,-CO-\dot{C}H- \rightarrow \begin{matrix} -CO-CH- \\ \quad\quad | \\ -CO-CH- \end{matrix} \qquad (9)$$

In the presence of oxygen, the primary radicals add O_2:

$$-\dot{C}OH-CHOH- + O_2 \rightarrow -\underset{\underset{O-O^\bullet}{|}}{COH}-CHOH- . \qquad (10)$$

At the O_2 concentration used in these experiments, this process competes successfully with those of reactions *1–6*.

The fate of the peroxyl radicals is not yet fully understood. However, there is increasing evidence[22–24] that α-hydroxyl peroxyl-radicals eliminate $HO_2^{\bullet -}$ in a fast reaction:

$$\underset{\underset{O-O^\bullet}{|}}{-COH-CHOH-} \rightarrow -CO-CHOH- + HO_2^{\bullet -} . \qquad (11)$$

The scission of C–C bonds has been attributed[7,25] to bimolecular reactions with other peroxyl radicals:

$$\underset{\underset{O-O^\bullet}{|}}{-COH-CHOH-} + RO_2^{\bullet} \rightarrow \underset{\underset{O^\bullet}{|}}{-COH-CHOH-} + O_2 + RO^\bullet \qquad (12)$$

$$\underset{\underset{O^\bullet}{|}}{-COH-CHOH-} \rightarrow -\underset{\underset{O}{\|}}{C}-OH + \dot{C}HOH . \qquad (13)$$

The most likely peroxy radical ($RO_2^{\bullet}$) to give this reaction may[13] be the $HO_2^{\bullet}$ ($O_2^{\bullet -}$) radical, because of its long lifetime and hence its high steady-state concentration. The p*K* value of the $HO_2^{\bullet}$ radical is 4.8. The solutions turn slightly acidic during radiolysis because of the formation of ribonic acid (**1**). Therefore, both $O_2^{\bullet -}$ and $HO_2^{\bullet}$ can play a role.

The hydroperoxyl radicals $HO_2^{\bullet}$ ($O_2^{\bullet -}$) largely disproportionate to give H_2O_2 and oxygen.

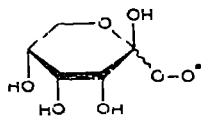
Deoxygenated solutions

In Scheme 1, the mechanism of the formation of the major products containing up to 5 carbon atoms is given for deoxygenated solutions. The dimers suggested to be formed according to equation *9* could not be analysed. Analysis has been possible so far only for the smaller analogues ethylene glycol[26] and erythritol[12]. The rearrangement according to reaction *6* is not observed with D-ribose in aqueous solution. However, the expected product, 5-deoxyribonic acid, was found when D-ribose was irradiated in the crystalline state[27]. In aqueous solution, the elimination of water from the C-1 radical (ultimately giving rise to 2-deoxy-D-*erythro*-pentonic acid) appears to be faster than the rearrangement (reaction *6*). In aqueous solutions, the furanose forms of D-ribose are present to only a small percentage[28], and are disregarded in Scheme 1. On the basis of the combined *G*-value of OH radicals and H atoms, which is ~6, oxidized products (from the disproportionation reaction *7*) and dimers would be expected to be formed with half of this yield, *i.e.*, ~3. The sum of the oxidized

products is only ~1.1, which indicates that many products escaped detection and might have been present in the dimer fraction which was not analyzed.

Oxygenated solutions

In oxygenated solutions, products containing the structural unit $-CH_2-CO-$ are absent. This is due to the fast addition of molecular oxygen to the primary sugar radicals, which is virtually a diffusion-controlled process[24].



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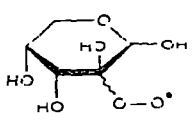

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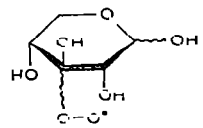

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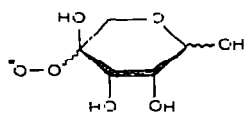

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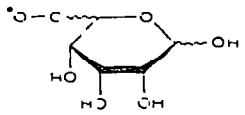

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The lifetime of the primary peroxyl radicals **19–22** is thought to be short because of the fast reaction *11*. The peroxyl radical at C-5 (**23**) might be more stable to unimolecular decay and hence have the chance to undergo a bimolecular fragmentation reaction (reactions *12* and *13*). *erythro*-Tetrodialdose (**13**) is expected to be, and is, the major fragmentation product.

In the presence of oxygen, most of the hydrogen atoms are scavenged by oxygen, and only the OH radicals give rise to the primary ribosyl radicals ($G \sim 5.5$). G (**1–5**) = 4.6 and G (**1–5, 13**) = 5.05 approach this value within experimental error. The better material balance with respect to deoxygenated solutions is thought to be due to the lack of dimer formation. The quantitative data (Table I) allow calculations on the probabilities of attack by OH radicals at the various positions of D-ribose. It is estimated that there is ~20% attack at C-1 (to give **1**), ~35% at C-2 and C-4 (to give **2** and **3**), ~20% at C-3 (to give **4**), and ~25% at C-5 (to give **5** and **13**).

EXPERIMENTAL

Materials. — 2-Deoxy-D-*erythro*-pentonic acid was synthesized by oxidation[29] of 2-deoxy-D-*erythro*-pentose with bromine. *xylo*-Pentodialdose was obtained by oxidation of 1,2-*O*-isopropylidene-α-D-glucofuranose[30] with periodic acid.

Irradiation and preparation of samples. — 0.01M D-Ribose was saturated with oxygen-free N_2O for 30 min prior to irradiation, or with N_2O/O_2 (80:20) during irradiation. Irradiations were performed in a Nuclear Engineering Ltd. panorama ^{60}Co-γ-source (dose rate, 3.85×10^{18} eV.g^{-1}.h^{-1}) at room temperature. Doses

ranged from $0.77\text{–}3.85 \times 10^{19}$ eV.g^{-1}. Separation of the products by column chromatography, the reduction with $NaBH_4$ ($NaBD_4$), derivatisation, g.l.c., and g.l.c.–m.s. were carried out essentially as described previously[7,16].

Quantitative determinations[31]. — A known amount of the standard (rhamnose) was added to an aliquot of the irradiated solution, and the solution was reduced with $NaBH_4$. The product mixture was then trimethylsilylated and subjected to g.l.c. A correction factor of 1.0 was determined for the polyhydric alcohols with respect to rhamnitol. D-Ribonic acid was determined as the Me_3Si derivative of its lactone. Methoxylamine was added to obtain a good separation from other material, which is thereby converted into the methoxime–Me_3Si derivatives. Ribitol was the internal standard, and a correction factor of 1.3 was determined for ribono-1,4-lactone with respect to ribitol.

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