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RADICAL-INDUCED DEAMINATION OF 2-AMINO-2-DEOXY-D-GLUCOSE IN AQUEOUS SOLUTION*

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ABSTRACT

2-Amino-2-deoxy-D-glucose (10mM) as the free base (pH 8.5) and the hydrochloride (pH 5) were γ-irradiated in aqueous solution under deoxygenated (N_2O-saturated) and oxygenated [N_2O/O_2(4:1)-saturated] conditions. Ammonia and 18 nitrogen-free products were identified and their *G*-values determined. Mechanisms for the radical-induced deamination are proposed. The radicals centered at C-1, C-2, C-3, and the nitrogen are suggested as initiators in the deamination processes.

INTRODUCTION

The biological importance of certain amino sugar-containing biopolymers and their known susceptibility to ionising radiation[1] have led to investigation of the radiation behaviour of the amino sugars in general. We have shown[2] that, on irradiation, 2-acetamido-2-deoxy-D-glucose does not readily eliminate the acetamido group. However, Kochetkov *et al.*[3,4] have shown that deamination occurs with 2-amino-2-deoxy-D-glucose, as they have isolated D-arabinose as a major product. We now report a more detailed study of the radical-induced deamination of this substance.

Ammonia yields were measured, and neutral products obtained on γ-irradiation of protonated and unprotonated 2-amino-2-deoxy-D-glucose in aqueous solution were isolated and identified. Solutions were saturated with N_2O or with a 4:1 mixture of N_2O and O_2. Under these conditions, the primary reactive species consist of ~90% OH radicals and ~10% H atoms.

The OH radicals (and the H atoms in deoxygenated solution) react with the solute molecules by abstracting carbon-bound hydrogen atoms:

$$RH + HO\cdot\ (H\cdot) \rightarrow R\cdot + H_2O\ (H_2) \qquad (1)$$

These radicals then undergo further reactions before ending up as products. In the presence of oxygen, peroxyl radicals ($RO_2\cdot$) formed by oxygen addition are the product precursors.

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EXPERIMENTAL

Irradiation. — Solutions (10mM) of 2-amino-2-deoxy-D-glucose hydrochloride (Merck) (recrystallised from ethanol) in triply distilled water were irradiated at pH 5 or after adjustment to pH 8.5 using freshly prepared, aqueous sodium hydroxide. Samples were purged with N_2O or N_2O/O_2 (4:1) for 30 min before irradiating in a Co-60-γ source to doses between 0.7 and 2.8 $\times$ 10^{19} $eV.g^{-1}$ at a dose rate of 3.5 $\times$ 10^{18} $eV.g^{-1}.h^{-1}$. Some irradiations were carried out in D_2O.

Samples. — Aliquots of the irradiated solutions were reduced with sodium borohydride or sodium borodeuteride. The solutions were then treated with Dowex W X8 (H^+) resin (200–400 mesh), which removed Na^+ ions and compounds containing the amino group. Further treatment and g.l.c.–m.s. were performed as described earlier[5]. For unreduced samples, aliquots of irradiated solution were treated with Dowex W X8 for 1 h before evaporation and trimethylsilylation. It was found that a strongly basic ion-exchanger was more efficient in removing all basic material, but was responsible for decomposition of some of the products.

Analysis. — The quantitative determination of the carbohydrate products was effected as previously described[5]. Ammonia determinations were carried out using a Conway microdiffusion cell[6], and Nessler's reagent[7]. Carbon monoxide and carbon dioxide yields were determined by g.l.c.[8], and formaldehyde[9] and formic acid[10] by colorimetric procedures.

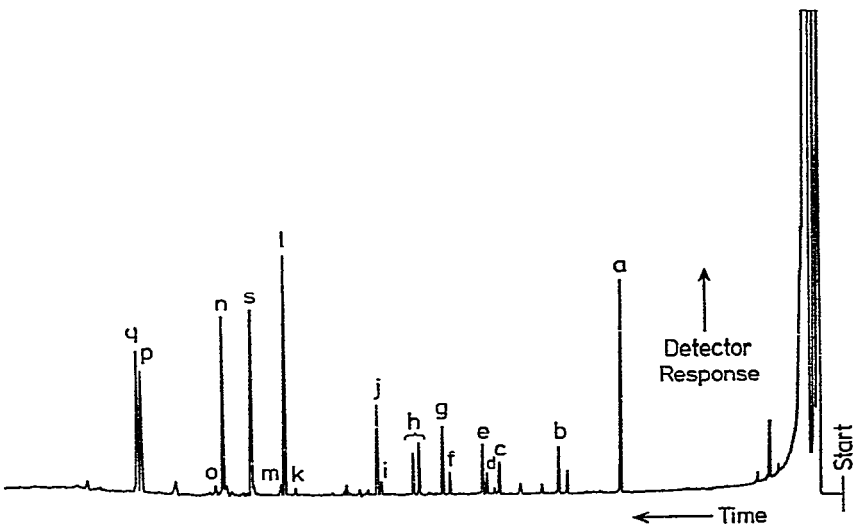


Fig. 1. Gas chromatogram of trimethylsilylated, reduced derivatives of neutral products from a γ-irradiated, N_2O-saturated, aqueous solution of 2-amino-2-deoxy-D-glucose (10mM, pH 8.5) (99-m, SF-96 glass-capillary column; 100–240°, 4° per min): a, glycerol; b, 3-deoxytetritol; c, 2,3-dideoxy-*cis*-2-pentenitol; d, 2,3-dideoxypentitol; e, 2,3-dideoxy-*trans*-2-pentenitol; f, threitol; g, erythritol; h, 1-deoxypentitol; i, 2-deoxy-*threo*-pentitol; j, 2-deoxy-*erythro*-pentitol; k, xylitol; l, arabinitol; m, ribitol; n, 2-deoxy-*arabino*-hexitol; o, 2-deoxy-*ribo*-hexitol; p, mannitol; q, glucitol; s, standard (6-deoxymannitol).

RESULTS

Fig. 1 shows a gas chromatogram of the neutral products ($NaBH_4$ reduced, Me_3Si derivatives) of γ-irradiation of 10mM 2-amino-2-deoxy-D-glucose (pH 8.5, N_2O). Most of the reduced derivatives were recognised by peak matching in g.l.c. Their precursors were identified by g.l.c.–m.s., using $NaBD_4$ as reducing agent in order to label carbonyl groups with deuterium atoms[11]. G.l.c.–m.s. was also used to determine the location of deuterium atoms incorporated in products formed on irradiation in D_2O.

Peak *a*, *f*, *g*, *j*, and *l* were assigned to the Me_3Si derivatives of reduced glyceraldehyde, threose, erythrose, 2-deoxy-D-*erythro*-pentose, and D-arabinose, respectively. Peak *b* was assigned to 3-deoxytetritol-*1,2-d*$_2$, for which the precursor is 3-deoxytetrosulose (**14**). One further deuterium atom was incorporated at C-3 if irradiation was carried out in D_2O.

Compounds *c* and *e* gave identical mass spectra. Their precursors were identified as the *cis* and *trans* isomers of 2,3-dideoxy-D-*glycero*-2-pentenose (**11**) by g.l.c.–m.s. of a reduced ($NaBD_4$) and trimethylsilylated sample. The mass spectra showed prominent ions at *m/e* 73 (100%), 103 (3), 133 (5), 143 (8), 147 (50), 156 (5), 232 (50), 244 (1), and 245 (2), corresponding to

$$CHDOSiMe_3\text{–}CH = CH\text{–}\underset{232}{CHOSiMe_3}\text{–}\underset{103}{CH_2OSiMe_3}.$$

Authentic **11** was obtained by autoclaving aqueous solutions of 2-deoxy-D-*erythro*-pentose[12]. The ^{1}H-n.m.r. spectrum of **11** (D_2O) gave the following signals: δ 3.59 (m, 2 H, H-5), 4.47 (d, 1 H, H-4), 6.27 (q, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 15.5 Hz, H-2), 7.01 (q, 1 H, H-3), and 9.39 (d, 1 H, H-1). The large value of $J_{2,3}$ indicates that the *trans* isomer is formed by autoclaving. The acyclic structure is verified by the low-field signal for the aldehydic proton.

The mass spectrum of *d* corresponds to the Me_3Si derivative of 2,3-dideoxypentitol-*1,4-d*$_2$, whose precursor is 2,3-dideoxypentos-4-ulose[13]. The corresponding product from D_2O-irradiated solutions contained a deuterium atom at C-2 or C-3.

The mass spectra of the two compounds at *h* were assigned to the Me_3Si ethers of reduced 1-deoxy-D-*erythro*-pentulose (**9**).

$$CH_3\text{–}\underset{118}{CDOSiMe_3}\text{–}\underset{307}{\overset{220}{\overset{(130)}{CHOSiMe_3}}}\text{–}\underset{205}{\overset{322}{\overset{(231)}{CHOSiMe_3}}}\text{–}\underset{103}{CH_2OSiMe_3}$$

The large fragment ion at *m/e* 118 (70%) is typical[11] of a 1-deoxy compound having deuterium substitution at C-2. Other prominent peaks are at *m/e* 103 (40%), 205 (8), 217 (18), 220 (12), 231 (7), and 307 (8). If irradiation was carried out in D_2O, three deuterium atoms were incorporated at the methyl group.

The small peak at *i* is recognisable as the *threo* isomer of its larger neighbour *j*

(2-deoxy-D-*erythro*-pentitol Me_3Si ether). The mass spectra of *i* and *j* are identical, so 2-deoxy-D-*threo*-pentose is expected to be the precursor of *i*. The small peaks at *k* and *m* correspond to the Me_3Si ethers of xylitol-*1,4*-d_2 and ribitol (no m.s.); *s* is the internal standard 6-deoxymannitol.

The mass spectrum of *n* corresponds to the Me_3Si ether of 2-deoxy-D-*arabino*-hexitol-*1,1*-d_2. The precursor is 2-deoxy-D-*arabino*-hexonolactone[11]. The mass spectrum corresponding to the small, neighbouring peak *o* was recognisable as that of the Me_3Si ether of reduced 2-deoxy-D-*erythro*-hexos-3-ulose[11].

Compounds *p* (Me_3Si-mannitol-*1,2*-d_2) and *q* (Me_3Si-glucitol-*1,2*-d_2) gave identical mass spectra, and are derived from D-*arabino*-hexosulose[14].

Irradiation of 2-amino-2-deoxy-D-glucose under other experimental conditions (see Table I) did not yield any additional products in noticeable yield, as analysed by g.l.c.–m.s. Attempts to make satisfactory analyses of samples containing aminated sugars by the above technique have, until now, been unsuccessful.

Fig. 2 shows the dose dependence of the *G*-values of ammonia and some other major products from irradiated 2-amino-2-deoxy-D-glucose. The products and their

TABLE I

G-VALUES OF DEAMINATED PRODUCTS AND AMMONIA FROM γ-IRRADIATED, AQUEOUS SOLUTIONS OF 2-AMINO-2-DEOXY-D-GLUCOSE (10 mM)

Product	G-*values*			
	N_2O pH 8.5	*N_2O pH 5.0*	*N_2O/O_2 pH 8.5*	*N_2O/O_2 pH 5.0*
1 2-Deoxy-D-*arabino*-hexonic acid	0.18	0.30	absent	absent
2 2-Deoxy-D-*erythro*-hexos-3-ulose	0.01	0.02	absent	absent
3 D-*arabino*-Hexosulose	0.30	0.03	0.45	0.10
4 D-Arabinose	0.18	0.04	1.00	0.53
5 D-*threo*-Pentos-4-ulose	0.01	0.01	0.15	0.08[a]
6 D-Ribose[b]	0.01	0.005	0.05	0.05
7 2-Deoxy-D-*erythro*-pentose	0.09	0.05	absent	absent
8 2-Deoxy-D-*threo*-pentose	0.01	absent	absent	absent
9 1-Deoxy-D-*erythro*-pentulose	0.10	absent	absent	absent
10 2,3-Dideoxypentos-4-ulose	0.02	absent	absent	absent
11 2,3-Dideoxy-D-*glycero*-2-pentenose	0.08	absent	absent	absent
12 D-Erythrose	0.07	0.05	0.15	0.13
13 D-Threose	0.02	0.005	0.04	0.02
14 3-Deoxytetrosulose	0.05	absent	absent	absent
15 Glyceraldehyde	0.30	0.18	0.20	0.13
16 Ammonia	2.8	1.6	2.4	[c]
17 Formic acid	0.2	[c]	0.8	0.3
18 Formaldehyde	0.17	0.22	0.17	0.13
19 Carbon monoxide	0.02	0.03	[a]	[c]
20 Carbon dioxide				absent

[a]Determined only as xylitol. [b]Determined only as ribitol. [c]Not determined.

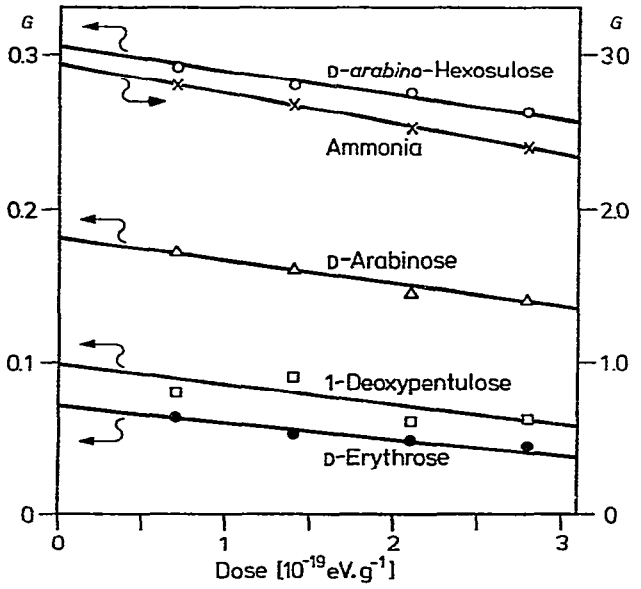


Fig. 2. Dose dependence of G-values of products in the γ-radiolysis of N_2O-saturated, aqueous solutions of 2-amino-2-deoxy-D-glucose (10mM) at pH 8.5. $G(NH_3)$ right-hand scale.

G-values (extrapolated to zero dose) are listed in Table I.

Treatment with $NaBH_4$ did not cause any significant deamination of any possible amine-containing products, as shown by ammonia determinations of irradiated solutions before and after reduction.

DISCUSSION

2-Amino-2-deoxy-D-glucose was used in the form of its hydrochloride. Chloride ions and OH radicals are in a fast equilibrium with $[HOCl]^{\cdot-}$. The equilibrium lies well to the side of the OH radicals and chloride ions[15]. As observed for various solutes[16,17] in the pH range of our study, the presence of chloride ions does not change the rate of attack on the substrate. The rate constant of the reaction of OH radicals with 2-amino-2-deoxy-D-galactose hydrochloride[18] is 1.77×10^9 l.mol^{-1}. sec^{-1}. The rate constant of the reaction with 2-amino-2-deoxy-D-glucose hydrochloride is expected to be similar.

Deoxygenated solutions

The pK value of 2-amino-2-deoxy-D-glucose is[19] 7.8 at 20°. Thus, at pH 8.5, the OH radicals essentially react with the free base, and at pH 5.0 with the protonated form. E.s.r. studies on protonated amino-alcohols[20] revealed that OH radicals preferentially abstract a hydrogen atom from the carbon atom β to the ammonium

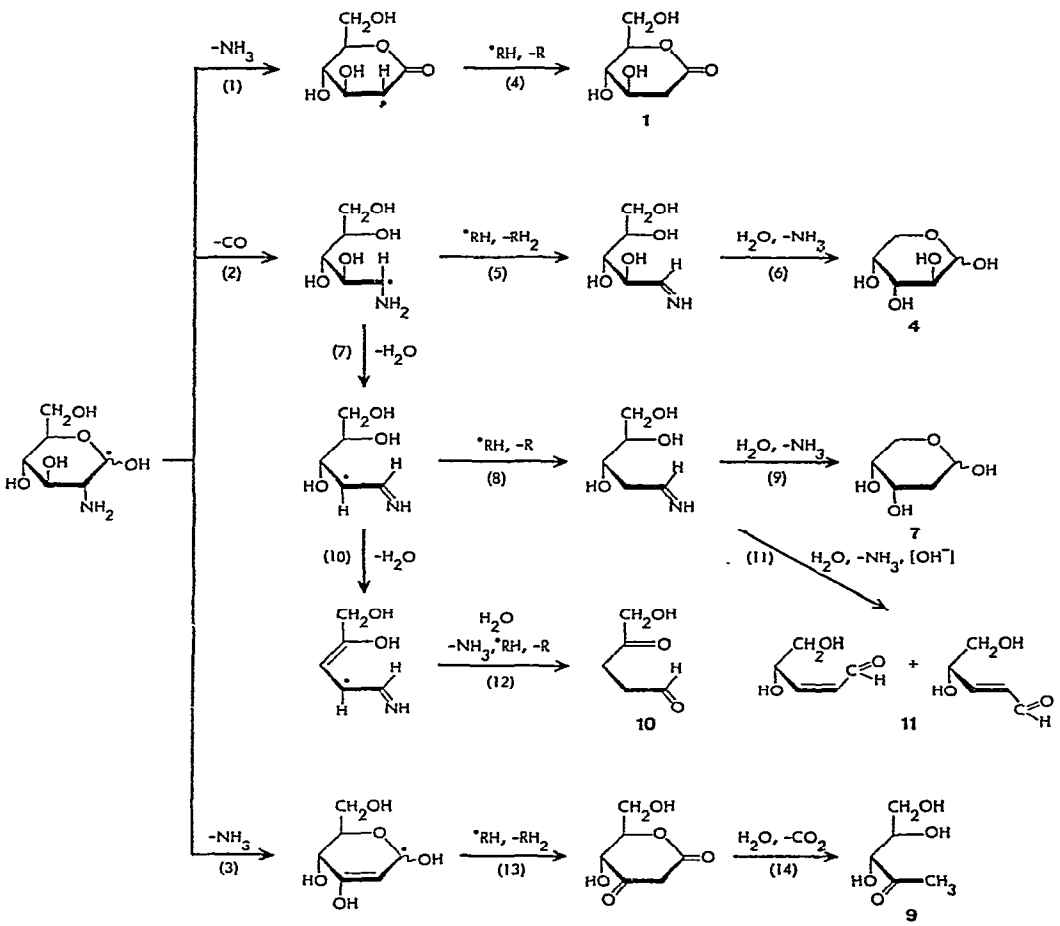
group. Following deprotonation, these radicals undergo an NR_2H-elimination (R = H or alkyl):

$$\overset{+}{H}R_2\overset{\cdot}{N}\text{-}CH_2\text{-}\dot{C}HOH \rightarrow H^+ + HR_2N + \cdot CH_2\text{-}CHO \qquad (2)$$

Reaction *2* is similar to the well-documented[21] water elimination from 1,2-dihydroxyalkyl-(1) radicals.

Whereas no radicals centered at the carbon α to the amino group, or at the nitrogen in protonated amino-alcohols, have been reported, α-ammoniumalkyl radicals have been observed by e.s.r. in a series of amino acids[22]. There, under favourable conditions, an *N*-centered radical has also been observed with a deprotonated amino acid[22]. The general non-detectability of *N*-centered radicals was attributed to their fast reaction with the substrate to give *C*-centered radicals[22].

In the present study, only the radical-induced deamination of 2-amino-2-



Scheme 1. Deamination reactions starting from the radical at C-1 of 2-amino-2-deoxy-D-glucose.

deoxy-D-glucose has been studied. Therefore, only the radicals at C-1 to C-3, and possibly that at the nitrogen, are expected to play a role. The reactions of OH radicals are thought to be not very selective (*cf.* D-glucose[14]: abstraction at C-1 and C-2, each ~20%; C-3 to C-5, each ~10–15%; and C-6, ~30%).

In Scheme 1, the possible routes are depicted for deamination from the radical at C-1 as precursor. The sequences are written for the free base, but most of the reactions possibly also occur with the protonated form. However, the yields of the products are different (see Table I), because the preferred site of attack of the electrophilic[23] OH radicals will change according to the state of protonation of the substrate. Thus, it is more likely that abstraction occurs at C-1 and C-3 from the protonated form, whereas C-2 and possibly the amino group are more-active sites in the free base.

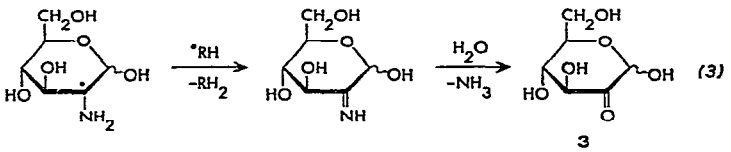
Reactions from the radical at C-1. — Route (1) followed by route (4) in Scheme 1 gives rise to 2-deoxy-D-*arabino*-hexonic acid (**1**); the routes (2), (5), and (6) to D-arabinose (**4**); and (2), (7), (8), and (9) to 2-deoxy-D-*erythro*-pentose (**7**). These products were also obtained from D-glucose[21], and the free-radical part of the reaction sequence is formulated in a similar way. D-Arabinose and 2-deoxy-D-*erythro*-pentose are expected to be formed from the hydrolysis of the corresponding imine intermediates. The postulated imine intermediates are thought to have a similar stability against hydrolysis as the glycosylamines. Some may have even a lower stability, because stabilizing cyclic forms are missing. Isbell and Frush[24] have shown that glycosylamines hydrolyse with a maximum rate at our experimental conditions. From their data, we estimate that, after our irradiation and work-up time, hydrolysis of the imine intermediates should be complete. The route to product **11** has no such analogy. On autoclaving neutral 2-deoxy-D-*erythro*-pentose solutions at 120°, the trans isomer of **11** is formed (see above). In the radiolysis of 2-amino-2-deoxy-D-glucose at pH 8.5, the trans:cis ratio of **11** is ~3:2. In alkaline solutions (pH 10), 2-deoxy-D-*erythro*-pentose itself does not form any measurable quantities of **11**, and cannot therefore be its precursor. However, there is a possibility that its imine intermediate undergoes a base-catalysed elimination [route (11) in Scheme 1]. At pH 5.0, no **11** has been detected. It is noteworthy that these compounds absorb in the near u.v. (λ_{max} ~230 nm) and may contribute to absorptions observed with irradiated sugars. Usually, this type of absorption is attributed to malonaldehyde[25].

The β-γ elimination of water to give allyl radicals is known from other carbohydrate-derived radicals[26,27], notably in 2-acetamido-2-deoxy-D-glucose[2]. A β-γ water elimination is also expected to occur in the formation of 2,3-dideoxypentos-4-ulose (**10**) [route (10) in Scheme 1].

The precursor of the 1-deoxypentulose **9** is likely to be 2-deoxy-D-*erythro*-hex-3-ulosonic acid [routes (3) and (13) in Scheme 1]. Such β-keto acids readily eliminate CO_2 [route (14) in Scheme 1]. On formation from samples irradiated in D_2O, three deuterium atoms are incorporated at the methyl group. The hydrogen atoms of the deoxy group in the acid precursor are activated by the two flanking carbonyl groups and undergo a thermal exchange with the solvent. A further deuterium is gained on decarboxylation.

A rearrangement from the radical at C-5 to C-1 (formation of a carbonyl group at C-5) would be expected to give rise, after deamination, to 2-deoxyhexos-5-ulose [*cf.* Ref. 21, and routes (1) and (4) in Scheme 1]. This compound has not been found as a product. Possibly, other reactions[21] compete favourably with such a process. Similarly, for D-ribose[28], an expected reaction was fully suppressed in aqueous solution by a competing process, but has been found to occur in the solid state.

Reactions from the radicals at C-2 and C-3. — The only product attributable to the radical at C-2 as precursor is D-*arabino*-hexosulose (**3**). This product could be formed *via* an imine intermediate:



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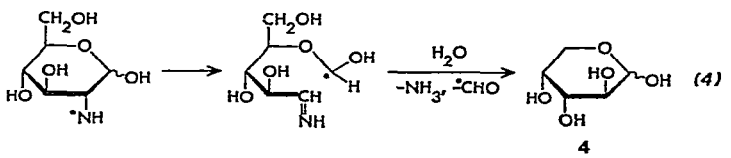
This type of reaction has previously been postulated for the formation of α-keto acids in the γ-radiolysis of amino acids[29,30]. An alternative precursor is the *N*-centered radical (see below). Both are expected to be formed more readily from the free base. In accordance with this, $G(3) = 0.3$ at pH 8.5, but only 0.03 at pH 5.0. 2-Deoxy-D-*erythro*-hexos-3-ulose (**2**) originates from the radical at C-3 following ammonia elimination (*cf.* route to **1** in Scheme 1).

Reactions from the N-*centered radical.* — The OH radical has only a slight tendency to abstract oxygen-bound hydrogen atoms from alcohols[31]. However, because of its electrophilic nature, it might react more readily with the unprotonated amino group either by hydrogen-atom abstraction or by electron transfer followed by proton elimination. Therefore, in contrast to neutral carbohydrates, the primary radicals at the hetero atom should also be considered. A substantial part of the D-arabinose, and possibly also of the D-*arabino*-hexosulose, may have the *N*-centered radical as precursor. The formation of D-arabinose might then proceed *via* a β-fragmentation.



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Although only an approximate value of $G(CO)$ is obtained, it appears to be too low to explain the formation of the products containing five carbon atoms exclusively by the reactions as given in Scheme 1. Furthermore, the yield of D-arabinose is markedly lower at pH 5.0 than at pH 8.5. The yield of 2-deoxy-D-*arabino*-hexonic acid shows the reverse behavior. This could reflect the different probabilities of the sites of attack, at C-1 and at the amino group, respectively. In the protonated 2-amino-2-deoxy-D-glucose, the attack at the amino group will be negligible com-

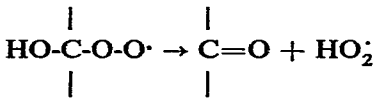
pared to that at C-1, whereas in the free base it could gain importance at the cost of that at C-1.

There are a number of further products containing less than six carbon atoms. Most prominent is glyceraldehyde (**15**). However, no mechanisms are foreseen at present.

Oxygenated solutions

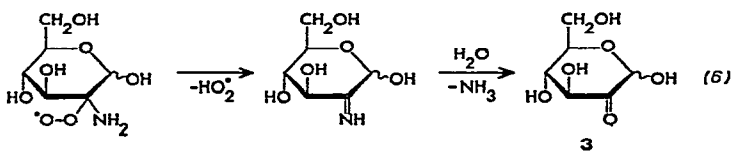
In the presence of molecular oxygen, rapid addition of oxygen to the primary sugar radicals leads to peroxyl radicals, which are the precursors of the products in oxygenated solutions. It has been shown recently[14] that carbohydrate peroxyl radicals undergo both HO_2 eliminations [reaction *5* (first order in peroxyl radicals)] and C–C bond fragmentations. The latter are caused by their reaction with long-lived peroxyl radicals, e.g. $HO_2^{\cdot}$ ($O_2^{\cdot-}$) (second order in peroxyl radicals). Product distribution is, therefore, dose-rate dependent.

The first-order process (base catalyzed[14,32]) is the elimination of $HO_2^{\cdot}$ ($O_2^{\cdot-} + H^+$) from the α-hydroxyalkyl peroxyl radicals (reaction *5*).



(*5*)

D-*arabino*-Hexosulose (**3**) is thought to be formed *via* such a mechanism (reaction *6*).



(*6*)

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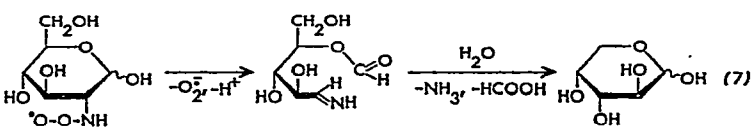
A possible precursor of D-arabinose is the *N*-centered peroxyl radical, which could undergo a reaction (*7*) similar to that proposed for the formation of D-*xylo*-hexos-5-ulose from D-glucose[14].



(*7*)

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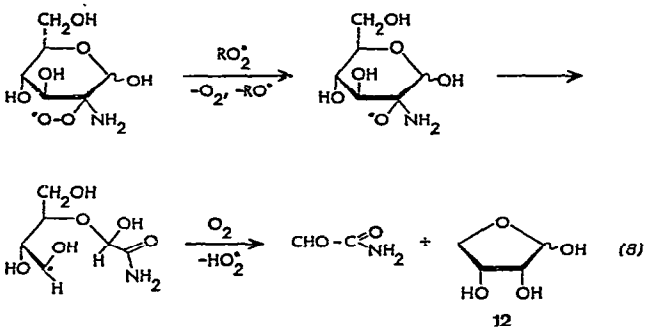
In competition to reaction *6*, the peroxyl radical at C-2 could give, on reaction with other peroxyl radicals, e.g. $HO_2^{\cdot}$ ($O_2^{\cdot-}$), D-erythrose (**12**) (reaction *8*).
A similar reaction leading to D-arabinose from the peroxyl radical at C-1 is excluded. The rate of $HO_2^{\cdot}$ ($O_2^{\cdot-}$) elimination from this radical ($k > 7 \times 10^3$ sec^{-1} at pH 5, faster at higher pH[33]) is too fast to allow for a reaction with $HO_2^{\cdot}$ radicals at the given dose rate.



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The marked effect of pH on the *G*-values of the various products (see Table I) is tentatively explained as follows. On protonation, the rate of reaction *6* is reduced, thereby enhancing the lifetime of the peroxyl radical at C-2 which is then more likely to undergo the second-order reaction sequence (*8*), *i.e.*, formation of D-erythrose (**12**). However, the probability of OH attack at C-2 is also reduced on protonation. Consequently, the *G*-values of the sum of these products are lowered, but that of **3** more markedly, because of the shift towards D-erythrose formation.

A similar influence of protonation is expected for the *N*-centered radical. Indeed, on protonation of 2-amino-2-deoxy-D-glucose, *G*(D-arabinose) is halved.

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