Radiation Chemistry of Carbohydrates, X*

γ-Radiolysis of Crystalline D-Glucose and D-Fructose

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GC–MS, G-Values, Radical Reactions, Chain Reaction

α-D-Glucose and β-D-fructose were γ-irradiated in the solid (polycrystalline) state at room temperature at doses of \(3.5 \cdot 10^{20} \text{-} 4.2 \cdot 10^{21} \text{eV g}^{-1}\) (dose rate \(1.16 \cdot 10^{9} \text{eV g}^{-1} \text{min}^{-1}\)). Carbohydrate products containing \(\leq 6\) carbon atoms were identified and their G-values (in parentheses) measured.

Glucose: Dihydroxyacetone (1) \((0.05)\), 3-deoxy-tetrose (2) \((0.01)\), 1,4-dideoxy-2-pentulose (3) \((0.05)\), 2,4-dideoxy-pentose (4) \((0.08)\), 2,4-dideoxy-pentonic acid (5) \((0.02)\), 3,4-dIDEOXY-PENTOSANOSULOSE (6) \((0.03)\), threose (7), erythrose (8), erythronic acid (10) \((0.04)\), 1-deoxy-2-pentulose (11) \((0.005)\), 2-deoxy-ribose (12) \((0.25)\), 3-deoxy-2-pentulosanose (13) \((0.02)\), 2,3-dideoxy-hexonic acid (14) \((0.02)\), 3,5-dideoxy-hexonic acid (15) \((0.01)\), arabinose (16) \((0.25)\), ribose (17), ribonic acid (18) \((0.02)\), 2-deoxy-2-C-hydroxymethyl-pentonic acid (19) \((0.01)\), 5-deoxy-gluconic acid (20), 2-deoxy-5-keto-glucose (21), 2-deoxy-gluconic acid (22), 2-deoxy-3-keto-glucose (23), 3-deoxy-glucose (24), 3-deoxy-gluconic acid (25), 3-deoxy-4-keto-glucose (26), 3-deoxy-mannonic acid (27) \((0.04)\). Identified but not measured quantitatively were glucosone (28), 3-keto-glucose (29), 4-keto-glucose (30), 5-keto-glucose (31) and gluconic acid (32). G(H₂) = 5.75; G(CO₂) = 0.7.

Fructose: 7-9 \((0.65)\), 3-deoxy-pentonic acids (37), 3-deoxy-pentulosanose (38) \((0.03)\), ribulose (39) \((0.1)\), 18 \((0.05)\), 6-deoxy-2,5-hexodiulose (40) \((0.03)\). Identified but not measured quantitatively were glyceraldehyde (34), butanone-(3)-diol-(1,2) (35) and 2- and 3-deoxy-hexodiuloses. G(H₂) = 4.75, G(CO₂) = 0.05.

Reaction schemes are proposed to account for the formation of the products. The scission of the hemiacetal bond and of the C-H and C-C bonds next to it appears to be typical for solid state irradiations. The formation of deoxy-compounds is observed both in the solid state and in aqueous solution. The formation of dideoxy-compounds is only prominent in the solid state. In polycrystalline fructose a chain reaction is induced leading to 6-deoxy-2,5-hexodiulose (40).

Introduction

There is a general interest in the radiation chemistry of carbohydrates since ionizing radiation provides a powerful tool for food sterilisation. In the last years the studies on the radiation chemistry of carbohydrates have largely been carried out in dilute aqueous solutions. Under these conditions the radiation energy is absorbed by the solvent water and the water radicals (OH and H) attack the sugar molecules by abstracting hydrogen atoms. The products are then formed in the subsequent free radical reactions of the sugar radicals. If solid carbohydrates are irradiated, the energy of the ionizing radiation is absorbed by the carbohydrates themselves and further reactions not encountered in solution are expected to occur. Recently it has been shown that in α-lactose H₂O 2-3, 2-deoxy-D-ribose 6 and D-fructose 5-7,8, chain reactions are initiated by γ-irradiation opening up new interesting preparative routes 5,6,8. The chain reactions are restricted to only a few compounds and do not

* Part IX in this series is ref. 30.

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reflect the general behaviour of the radiation chemistry of crystalline carbohydrates. Therefore, it seemed worthwhile to have a closer look into the irradiation products of D-glucose. This compound shows apparently no chain reaction, and its irradiation products might be compared with the non-chain products of D-fructose. This comparison will enable the indication of some radiation induced reactions typical for carbohydrates in the solid state.

Results

Radiation products were concentrated by column chromatography, reduced with NaBD₄ to the corresponding polyalcohols, trimethylsilylated, and gas-chromatographed using glass capillary columns. They were identified by GC–MS as has been done in previous work⁹,¹⁰. The MS assignments are supported by the GC retention indices¹¹.

α-D-Glucose: Fig. 1 shows an original gas chromatogram of the derivatized products. A small number of products which were not sufficiently separated from glucose in the enrichment process have not been analyzed for and an assignment of some of the products as detected by GC (Fig. 1) is missing. On the other hand, a series of products (in their reduced form: mannitol, allitol, galactitol and iditol) could be identified by this procedure. Without the pre-enrichment process these products were concealed by a huge glucitol peak stemming from the starting material, glucose.

A large number of products was identical with those obtained in the γ-radiolysis of aqueous solution of cellobiose⁹ and glucose¹⁰ and the discussion of their mass spectra will not be repeated here. They belong to the peaks No. 1, 6, 7, 9, 13, 16, 17 in Fig. 1. Polyalcohols containing deoxy groups are readily identified if deuterated at the positions where a carbonyl group has been prior to reduction. Identification is more difficult and in many cases ambiguous if the deoxy group is missing¹². Therefore aldoses and the epimeric ketoses cannot be distinguished by this technique with certainty and hence these products are given in parentheses in Tab. I.

In the following section the mass spectra of the material corresponding to various GC-peaks are discussed. If not stated otherwise m/e 73 is the base peak. Some of the GC-separation is lost by the link between the gas chromatograph and the mass spectrometer and both overlapping and coinciding peaks yield mass spectra from more than one compound. For the interpretation of these spectra the knowledge from previous work⁹,¹⁰ was used where extended column chromatography enabled a firmer assignment of the individual components.

![Fig. 1. Gas chromatogram of a γ-irradiated, NaBD₄ reduced and trimethylsilylated sample of α-D-glucose. Glass capillary column, 63 m, OV-101, temperature programmed 120–200 °C, 2°/min, carrier gas 1 at H₂.](image-url)
GC-Peak No. 2. The most prominent fragment ions were \( m/e \) 103 (100%), 104 (15%), 206 (2%), 219 (30%) and 233 (1%). The mass spectrum is ascribed to the TMS-ether of butanetriol-1,2,4-d-1, its precursor being 3-deoxytetrose (2).

\[
\begin{align*}
104 & \quad 206 \\
HDCOTMS & \quad CHOTMS \quad CH_2 \quad CH_2\text{OTMS} \\
& \quad 219 \\
& \quad 103
\end{align*}
\]

GC-Peak No. 3. The most prominent fragment ions were \( m/e \) 103 (100%), 118 (30%), 158 (5%), 219 (30%), 232 (1%), 247 (M-90; < 1%). The mass spectrum is ascribed to the TMS-ether of 1,4-dideoxy-pentitol-2-d, its precursor being 1,4-dideoxy-2-pentulose (3).

\[
\begin{align*}
104 & \quad 219 \\
H_2COTMS & \quad CH_2 \quad CHOTMS \quad CDOTMS \quad CH_3 \\
& \quad 118
\end{align*}
\]

GC-Peak No. 4. The mass spectrum is due to two components. They were identified on the basis of their typical fragment ions. Both contained \( m/e \) 103 (60%) and 219 (10%). They differed in \( m/e \) 104 (30%), 105 (30%), 157 (20%), 158 (10%), 220 (5%), 221 (5%), 232 (< 1%), 233 (< 1%), 247 (< 1%), 248 (< 1%), 252 (< 1%) and 332 (< 1%).

This composite mass spectrum may be explained assuming a mixture of the TMS-ethers of 2,4-dideoxy-pentitol-1-d, and 2,4-dideoxy-pentitol-1,1-d. The precursors are 2,4-dideoxy-pentose (4) and 2,4-dideoxy-pentonic acid (5).

\[
\begin{align*}
104 & \quad 207 \\
HDCOTMS & \quad CH_2 \quad CHOTMS \quad CH_2 \quad CHOTMS \\
& \quad 219 \\
& \quad 103
\end{align*}
\]

GC-Peak No. 5. The most prominent fragment ions were \( m/e \) 103 (5%), 144 (85%), 158 (2%), 206 (1%), and 234 (7%). The mass spectrum is assigned to the TMS-ether of 2,3-dideoxy-pentitol-4-d. The precursor is 2,3-dideoxy-4-pentulose (6).

\[
\begin{align*}
103 & \quad 234 \\
H_2COTMS & \quad CH_2 \quad CH_2 \quad CDOTMS \quad CH_2\text{OTMS} \\
& \quad 206 \\
& \quad 103
\end{align*}
\]

GC-Peak No. 8. The most prominent fragment ions were \( m/e \) 103 (30%), 118 (65%), 205 (10%), 217 (17%), 220 (10%), 246 (1%), 307 (15%) and 335 (1%). The mass spectrum is ascribed to the TMS ether of 1-deoxy-pentitol-2-d. The precursor is 1-deoxy-2-pentulose (11).

\[
\begin{align*}
118 & \quad 220 \\
CH_3 \quad CDOTMS & \quad CHOTMS \quad CHOTMS \quad CH_2OTMS \\
& \quad 307 \\
& \quad 205 \\
& \quad 103
\end{align*}
\]

GC-Peak No. 10. The most prominent fragment ions were \( m/e \) 103 (2%), 104 (2%), 156 (2%), 205 (20%), 207 (20%), 232 (40%), 233 (40%), 246 (1%) and 336 (< 1%). The mass spectrum is assigned to the TMS-ether of 3-deoxy-pentitol-1,2-d. The precursor is 3-deoxy-pentosulose 13.

\[
\begin{align*}
104 & \quad 207 \\
HDCOTMS & \quad CDOTMS \quad CH_2 \quad CHOTMS \quad CH_2\text{OTMS} \\
& \quad 322 \quad (232) \\
& \quad 323 \quad (233)
\end{align*}
\]

GC-Peak No. 11. The most prominent fragment ions were \( m/e \) 103 (85%), 105 (20%), 170 (5%), 207 (1%), 219 (25%), 245 (10%), 260 (10%), 323 (< 1%) and 335 (< 1%). The mass spectrum is ascribed to the TMS-ether of 3,5-dideoxy-hexitol-1,1-d. The precursor is 3,5-dideoxy-hexonic acid (14).

\[
\begin{align*}
105 & \quad 207 \\
D_2COTMS & \quad CHOTMS \quad CH_2 \quad CH_2\text{OTMS} \\
& \quad 219 \\
& \quad 103
\end{align*}
\]

GC-Peak No. 12. The most prominent fragment ions were \( m/e \) 103 (30%), 105 (10%), 145 (40%), 205 (10%), 219 (10%), 235 (5%) and 247 (2%). The mass spectrum is assigned to the TMS-ether of 2,3-dideoxy-hexitol-1,1-d. The precursor is 2,3-dideoxy-hexonic acid (15).
GC-Peak No. 14. GC retention time indicates the TMS-ether of ribitol. The mass spectrum is due to two components. They can be distinguished on the basis of their typical fragment ions. Both contain m/e 103 (30%), 205 (20%), 217 (18%), 307 (8%) and 319 (5%). They differ in m/e 104 (18%), 105 (7%), 206 (10%), 207 (6%), 308 (5%), 309 (3%), 320 (5%) and 321 (3%). This composite mass spectrum is explained as resulting from a mixture of the TMS-ethers of ribitol-1-d and ribitol-1,1-d₂.

GC-Peak No. 15. The products contained in this peak apparently do not belong to the straight chain products observed so far in the γ-radiolysis of carbohydrates. Information on their nature was obtained by comparing the mass spectra of the TMS-ethers of the polyalcohols formed by reduction with NaBH₄ and NaBD₄ respectively. In the case of NaBH₄ reduction the most prominent fragment ions were m/e 103 (15%), 129 (100%), 155 (3%), 167 (1%), 205 (5%), 217 (5%), 221 (< 1%), 231 (2%), 243 (8%), 257 (1%), 307 (< 1%), 321 (5%), 331 (< 1%), 333 (1%) and 347 (< 1%). In the case of NaBD₄ reduction these were m/e 103 (12%), 104 (2%), 105 (7%), 129 (80%), 130 (15%), 131 (77%), 155 (3%), 157 (3%), 168 (1%), 169 (1%), 205 (8%), 217 (5%), 218 (2%), 219 (1%), 221 (1%), 232 (2%), 233 (3%), 244 (5%), 245 (4%), 258 (1%), 259 (1%), 307 (< 1%), 332 (8%), 334 (1%), 335 (1%), 347 (< 1%) and 348 (< 1%). The prominent fragment ions at m/e 129 (80%; H₂C=C=CH=O+ -TMS) and 131 (77%; D₂C=C=CH=O+ -TMS) are thought to be formed from the ion at m/e 323 by loss of OTMS and of D₂C-OTMS, and of H₂C-OTMS, resp.

The mass spectra are assigned to the TMS-ethers of the branched polyalcohols 2-deoxy-2-C-hydroxymethyl-pentitol and 2-deoxy-2-C-hydroxymethyl-pentitol-1,1-d₂, respectively.

The precursors are the two stereoisomeric 2-deoxy-2-C-hydroxymethyl-pentonic acids (19). All fragments were accounted for in our proposed structural assignment.

GC-Peak No. 18. The mass spectrum is due to three components. Two of them have already been identified in the earlier work. Common fragment ions were m/e 103 (10%), 205 (5%), 233 (50%), 243 (3%), 323 (< 1%) and 333 (2%). The components differed in m/e 104 (2%), 105 (2%), 206 (18%), 207 (10%), 217 (5%), 218 (4%), 244 (5%), 245 (3%), 258 (1%), 259 (1%), 307 (< 1%), 308 (< 1%) and...
This composite mass spectrum is explained as a mixture of the TMS-ethers of 3-deoxy-glucitol-1,2-$d_2$, 3-deoxy-glucitol-1,4-$d_2$ and 3-deoxy-glucitol-1,1-$d_2$.

The precursors are 3-deoxy-gluconic acid (25), 3-deoxy-4-keto-glucose (26), identified earlier and 3-deoxy-gluconic acid (25).

GC-Peak No. 19. The mass spectrum is due to two components. Both contain $m/e$ 103 (12%), 104 (25%), 205 (8%), 233 (30%), 244 (2%), 245 (2%), 325 (1%) and 334 (1%). They differ in 206 (15%), 217 (5%), 218 (5%), 221 (15%) and 307 (4%), 308 (<1%). They are assigned to a mixture of the TMS-ethers of 4-deoxy-glucitol-3,6-$d_2$ and 2-deoxy-allitol-1,3-$d_2$.

4-Deoxy-glucitol-3,6-$d_2$ is the stereoisomer of 3-deoxy-glucitol-1,4-$d_2$ the latter already identified as its TMS-ether in GC peak 18. The stereoisomer of 2-deoxy-allitol-1,3-$d_2$, namely 2-deoxy-glucitol-1,3-$d_2$ should have appeared as TMS-ether in GC peak 17 but could not be traced there, possibly because of low concentration. The precursors are 3-deoxy-4-keto-glucose (26) and 2-deoxy-3-keto-glucose (23).

GC-Peak No. 20. The composite mass spectrum is most probably due to the TMS-ethers of 3-deoxy-mannitol-1,2-$d_2$ and 3-deoxy-mannitol-1,1-$d_2$. Their precursors are 3-deoxy-gluconic acid (24) and 3-deoxy-mannonic acid (27). These are the stereoisomers of 3-deoxy-glucitol-1,2-$d_2$ and 3-deoxy-glucitol-1,1-$d_2$, respectively. Their mass spectra have been reported in the discussion of GC-peak 18.

In the enrichment process products have been isolated giving glucitol, mannitol, allitol, galactitol and iditol, after NaBD$_4$ reduction. They are expected to have the corresponding keto-glucoses 28-31 as their precursors. However, they could not be identified unambiguously.

Gluconic acid (32) was identified as the TMS-ethers of its $\gamma$- and $\delta$-lactones. Hydrogen 33 is the major volatile product. Carbon monoxide has been recognized as a product but its yield was too low to be determined quantitatively. Acidic products (carbonic acids and enolizable compounds) have been titrated after adding an excess of base. $G$ (acids) has been found to be around 9.

$\beta$-D-Fructose: The gas chromatogram of an irradiated, reduced and trimethylsilylated sample is given in Fig. 2. The mass spectra of the products corresponding to the GC peaks No. 1-5 and 8-12 have already been reported earlier$^9,10$ and in the glucose section.

GC-Peaks No. 6. The mass spectra appear to be
due to two components. They are very similar in structure. However, their relative amounts vary somewhat which was expected since NaBD₄ reduction yields the stereoisomeric alcohols with unequal yields. Both components contain m/e 103 (3%), 205 (20%), 207 (18%), 233 (30%), and 323 (<1%). They differ in m/e 104 (2%), 105 (1%), 231 (30%), 232 (9%) and 322 (<1%). They are assigned to the TMS-ethers of 3-deoxy-pentitol-1,1-d₂ and 3-deoxy-pentitol-1,2-d₂.

Their precursors are 3-deoxy-threo-pentonic acid and 3-deoxy-erythro-pentonic acid (37) and 3-deoxy-pentosulose (38).

GC-Peak No. 7. The retention time of this peak corresponds to that of TMS ether of arabinitol. Most prominent fragment ions were m/e 103 (35%), 105 (19%), 205 (20%), 207 (17%), 217 (18%), 218 (15%), 219 (7%), 307 (10%), 309 (12%), 319 (5%) and 321 (4%). The mass spectrum corresponds to that of the TMS-ether of arabinitol-1,1-d₂.

Its precursor is arabonic acid (39).

GC-Peaks No. 13. This group belongs to the series of TMS-ethers of 2- and 3-deoxy-hexitols. In the case of glucose, it has been possible to analyze for this group of compounds. However, in the case of fructose the corresponding precursors are expected to be deoxy-hexodiuloses. On reduction, each of these products gives up to four stereoisomeric polyalcohols giving in all a complex mixture which could not be separated by GC. No assignments could be arrived at from the MS data.
Discussion
The radiation chemical studies of carbohydrates in aqueous solutions and in the crystalline state have revealed a series of free radicals reactions which are typical of this class of compounds. Hence mechanistic proposals for likely routes of formation can now be put forward for most of the products observed in this work. They are represented for \( \alpha \)-D-glucose in Schemes 1 and 2, for \( \beta \)-D-fructose in Scheme 3. The most relevant free radical reactions recognized so far are as follows:

1. Disproportionation of the \( \alpha \)-hydroxyalkyl radicals. In carbohydrates \( \alpha \)-hydroxyalkyl radicals are the primary radicals formed in hydrogen abstraction reactions. In the disproportionation reaction the carbonyl compound may either be formed by the transfer of the oxygen bound hydrogen (reactions 1 and 17 in Scheme 1, reactions 3, 6, 9, 27)

Scheme 1. Routes for products from the radical centered at C-1 of glucose. \( \text{(H)} \) denotes a hydrogen atom transferred in a disproportionation and/or hydrogen abstraction reaction.
and 12 in Scheme 2, reactions 1 and 11 in Scheme 3) or by the transfer of a neighbouring carbon bound hydrogen\(^{13}\). In the latter case an enol is formed as an intermediate (reactions 2 and 15 in Scheme 1, reactions 2 and 10 in Scheme 3). In the Schemes only one of the possibilities is depicted. Dimerisations of the bulky \(\alpha\)-hydroxyalkyl radicals seem to be less likely and appear to be important only in the case of the simplest ones, e.g. hydroxymethyl and \(\alpha\)-hydroxyethyl\(^{14}\).

2. Elimination of water from \(\alpha\,\beta\)-dihydroxyalkyl radicals (reactions 5 and 19 in Scheme 1, reactions 1, 4, 7 and 11 in Scheme 2, reaction 15 in Scheme 3). This is a well documented process\(^{10-15-23}\). It also plays a role in the propagation of some chain reactions\(^{4,19,24}\). The resulting radicals of the type \(-\text{CO}-\text{CH}-\) then abstract hydrogen atoms from the starting material and regenerate \(\alpha\,\beta\)-dihydroxyalkyl radicals.

3. Elimination of ROH from \(\alpha\)-hydroxy-\(\beta\)-alkoxy-alkyl radicals\(^{25}\). This reaction is analogous to the water elimination process. A very similar reaction is a propagating step in the radiation induced chain reaction occurring in crystalline \(\beta\)-D-fructose\(^8\) (reactions 1 and 2).

4. Fragmentation of radicals of the type \(\geq \text{C-O-CR}_3\) according to reaction 3 yielding a carbonyl function and an alkyl radical\(^{4-6,22,26,27}\) reaction 7 in scheme 1, reaction 10 in Scheme 2).

\[\geq \text{C-O-CR}_3 \rightarrow \geq \text{C}=\text{O} + \text{CR}_3\]  

(3)

In two cases chain reactions have been observed where the resulting alkyl radicals propagate the chains by abstracting a hydrogen atom from the starting material\(^{4-6}\).

5. Decarbonylation of \(\beta\)-hydroxyalkyl formyl radicals or elimination of carbon monoxide and water from their hydrated forms\(^{28}\). Analogously, in reaction 14 in Scheme 1 and reaction 9 in Scheme 3. CO and HOR are eliminated.

6. Water elimination involving the OH group in \(\beta\)- or \(\gamma\)-position to the radical site (reaction 9, 21 and 23 in Scheme 1, reaction 5 and 17 in Scheme 3). This process gives rise to allyl radicals which may lead to quite a number of products (6, 13, 24, and 27 in Scheme 1. 35, 37 and 38 in Scheme 3).

Scheme 2. Routes for products from the radicals centered at C-2, C-3, C-4 and C-5 of glucose. (H) denotes a hydrogen atom transferred in a disproportionation and/or hydrogen abstraction reaction.
It appears that this process is more prominent in the crystalline state than in aqueous solution. Except for minor products in the γ-radiolysis of aqueous deoxygenated solutions of ribose-5-phosphate and N-acetyl glucosamine it has not been encountered before in the free radical chemistry of carbohydrates in aqueous solution.

7. Formation of carbon dioxide. The mechanism by which CO₂ is formed during irradiation of glucose is not yet properly understood. One product, 2,4-dideoxy-pentose (4), may shine some light on the mechanism. Scheme 4 presents a mechanistic proposal. The radiation induced scission of the O–H bond next to C-1 gives an oxyl radical. Oxyl radicals are known to be prone to fragmentation (reaction 1 in Scheme 4). Elimination of water and hydrogen abstraction (reaction 2 and 3 in Scheme 4) are feasible processes as well as the CO₂ elimination and hydrogen abstraction reactions (reactions 4 and 5 in Scheme 4) which finally would give
product 4. In fructose a sequence of this kind will not give rise to CO$_2$ and, indeed, G(CO$_2$) is comparatively negligible. In the formation of the branched acid 19 CO$_2$ or CO$_2^-$ may play a role as a carboxylating agent, but too little is known about the free radical chemistry in solids to present an acceptable mechanism.

**Quantitative Aspects**

With both glucose and fructose, hydrogen appears to be the major gaseous product. The values found by us are considerably higher than the ones reported in the literature. The yield of hydrogen from α-D-glucose has been reported to be $G(H_2) = 3.8^{32,33}$ whereas we find $G(H_2) = 5.75$ (Table I). $G(H_2)$ from β-D-fructose has been determined to be 4.75. In any case, $G(H_2)$ from glucose is significantly higher than that of fructose. With fructose a large number of products originate from the radical which arises from the scission of the C-1-C-2 bond (Scheme 3). Thus it appears that bonds next to the lactol group (C-1-H in glucose, C-2-C-1 in fructose) are among the most likely to break. In glucose C-1-H bond scission would be equivalent to the C-1-C-2 scission in fructose. This would imply a higher yield of hydrogen in the case of glucose which is in agreement with the experiment.

However, the modes of hydrogen formation are far from being understood. From O-deuterated carbohydrates mainly H$_2$(>90%) has been obtained$^{33}$, whereas from (liquid) O-deuterated alcohols (a not too distant model compound for O-deuterated carbohydrates) mainly H$_2$O has been obtained$^{33}$. Thus it appears that bonds next to the lactol group (C-1-H in glucose, C-2-C-1 in fructose) are among the most likely to break. In glucose C-1-H bond scission would be equivalent to the C-1-C-2 scission in fructose. This would imply a higher yield of hydrogen in the case of glucose which is in agreement with the experiment.

### Table I. γ-Ray Radiolysis of crystalline D-glucose. Products and their G-values. GC-peak numbers refer to Fig. 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Product</th>
<th>Determined as TMS ether after reduction with NaBD$_4$</th>
<th>GC-peak</th>
<th>G-value No.</th>
<th>G-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dihydroxyacetone</td>
<td>Glycerol-2-d$_1$</td>
<td>1</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3-Deoxy-x-tetrose</td>
<td>Butanetriol-1,2,4,1-d$_1$</td>
<td>2</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1,4-Dideoxy-2-pentulose</td>
<td>1,4-Dideoxy-pentitol-2-d$_1$</td>
<td>3</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2,4-Dideoxy-pentose</td>
<td>2,4-Dideoxy-pentitol-1-d$_1$</td>
<td>4</td>
<td>0.085</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2,4-Dideoxy-pentonic acid</td>
<td>2,4-Dideoxy-pentitol-1,1-d$_2$</td>
<td>5</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2,3-Dideoxy-pentose-4-ulos</td>
<td>2,3-Dideoxy-pentitol-1,4-d$_2$</td>
<td>6</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(Threose)</td>
<td>Treitol; 1 D incorporated</td>
<td>7</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>(Erythrolulose)</td>
<td>Erythritol; 1 D incorporated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(Erythrole)</td>
<td>Erythritol-1-d$_2$</td>
<td>10</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Erthronic acid</td>
<td>1-Deoxy-pentitol-1-d$_2$</td>
<td>11</td>
<td>0.25</td>
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<td>11</td>
<td>1-Deoxy-2-pentulose</td>
<td>1-Deoxy-pentitol-2-d$_1$</td>
<td>12</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2-Deoxy-ribose</td>
<td>2-Deoxy-ribitol-1-d$_1$</td>
<td>13</td>
<td>0.025</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>3-Deoxy-pentosulose</td>
<td>3-Deoxy-pentitol-1,2-d$_2$</td>
<td>14</td>
<td>0.024</td>
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<td>14</td>
<td>3,5-Dideoxy-hexonic acid</td>
<td>3,5-Dideoxy-hexitol-1,1-d$_2$</td>
<td>15</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2,3-Dideoxy-hexonic acid</td>
<td>2,3-Dideoxy-hexitol-1,1-d$_2$</td>
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<tr>
<td>16</td>
<td>Arabinose</td>
<td>Arabinitol-1-d$_1$</td>
<td>17</td>
<td>0.25</td>
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<tr>
<td>17</td>
<td>Ribose</td>
<td>Ribitol-1-d$_1$</td>
<td>18</td>
<td>0.02</td>
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<tr>
<td>18</td>
<td>Ribonic acid</td>
<td>Ribitol-1,1-d$_2$</td>
<td>19</td>
<td>0.024</td>
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<td>19</td>
<td>2-Deoxy-2-C-hydroxymethylpentonic acid</td>
<td>2-Deoxy-2-C-hydroxymethyl-pentitol-1,1-d$_2$</td>
<td>20</td>
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<td>20</td>
<td>5-Deoxy-gluciconic acid</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
<td>21</td>
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<tr>
<td>21</td>
<td>2-Deoxy-5-keto-glucose</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
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<td>5-Deoxy-glucitol-1,1-d$_2$</td>
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<td>(2-Deoxy-5-keto-glucose)</td>
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<td>25</td>
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<td>25</td>
<td>3-Deoxy-gluciconic acid</td>
<td>3-Deoxy-glucitol-1,1-d$_2$</td>
<td>26</td>
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<td>26</td>
<td>3-Deoxy-sulfonate</td>
<td>3-Deoxy-glucitol-1,1-d$_2$</td>
<td>27</td>
<td>0.19</td>
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</tr>
<tr>
<td>27</td>
<td>5-Deoxy-sulfonic acid</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
<td>28</td>
<td>0.19</td>
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<td>28</td>
<td>5-Deoxy-sulfonate</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
<td>29</td>
<td>0.19</td>
<td></td>
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<td>29</td>
<td>5-Deoxy-sulfonic acid</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
<td>30</td>
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<td>30</td>
<td>5-Deoxy-sulfonic acid</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
<td>31</td>
<td>0.19</td>
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<td>31</td>
<td>5-Deoxy-sulfonic acid</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
<td>32</td>
<td>0.19</td>
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<tr>
<td>32</td>
<td>5-Deoxy-sulfonic acid</td>
<td>5-Deoxy-glucitol-1,1-d$_2$</td>
<td>33</td>
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<tr>
<td>33</td>
<td>Hydrogen</td>
<td>Hydrogen</td>
<td></td>
<td>5.75</td>
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</table>

* Not determined.
carbohydrates) HD is the major radiolysis product (HD > 75%)\(^\text{39}\). The radiolysis and photolysis of the alcohols appears to be fairly well understood\(^\text{35-38}\). A fair amount of tritium is incorporated at unexchangeable sites (i.e. becomes carbon bound) if O-tritiated carbohydrates are irradiated. An exchange mechanism as depicted by DOLE and CRACCO\(^\text{39}\) for deuterium exchange in \(\gamma\)-irradiated polyethylene could account, in part, for this finding. The reported G-values for tritium incorporation in glucose are 0.7\(^\text{40}\) and 1.8\(^\text{33}\) and fructose about 2.3\(^\text{33}\). For 2-deoxy-ribose a value of 2.66 has been given\(^\text{40}\).

It is of interest to quote the high yield of \(\alpha\)-D-glucose destruction of approximately \(G = 20\)\(^\text{41}\) (a value of 9.3 has also been reported\(^\text{42}\), but as compared to G (acid formation) = 13\(^\text{42}\) (present work: G (acid) \(\approx 9\)) this value appears to be too low). Although quite a number of carbohydrate products have been identified in the present work and some volatile products in an earlier study\(^\text{43}\), the material balance is poor. The high \(H_2\) yield is not balanced by carbohydrate products(cf. Tables I and II). This is mainly thought to be due to the fact that the radicals of the type \(-CO-CH-\) dimerize if they do not find a suitable hydrogen donor\(^\text{23,29}\). We, therefore, believe that the major part of carbohydrate products is of the \(-CO-CH-\) dimer type\(^\text{19,21}\). Carbon dioxide is a general product in the \(\gamma\)-radiolysis of crystalline aldoses (ribose, \(G(CO_2) = 1.144\); arabinose, \(G(CO_2) = 1.254\), xylose, \(G(CO_2) = 0.654\); \(\alpha\)-D-glucose, \(G(CO_2) = 0.744\), 2.54, \(\alpha\)-D-glucose \(\cdot H_2O\), \(G(CO_2) = 0.633\). It is formed even if the samples are freed from oxygen by evacuating the sample tubes prior to irradiation. In contrast to the aldoses, the radiolysis of ketoses leads to only negligible amounts of \(CO_2\) (fructose, \(G(CO_2) = 0.054\), nil\(^\text{45}\), sorbose \(G(CO_2) = 0.015\)). A possible mechanism for the \(CO_2\) formation in glucose has been suggested above. However, the quantitative data show that its free radical counterpart must undergo further reactions and other routes to \(CO_2\) formation may also occur.

### Experimental

Samples (\(\approx 2\) g) of \(\alpha\)-D-glucose and D-fructose (Merck) were placed in a tube fitted with a stopcock and evacuated prior to irradiation. Irradiations were at room temperature at a dose rate of 1.16 \(\cdot 10^{18}\) eV g\(^{-1}\) min\(^{-1}\). Doses were from 3.5\(\cdot 10^{20}\) to 4.2 \(\cdot 10^{21}\) eV g\(^{-1}\). Dosimetry was carried out using the Fricke dosimeter. No corrections were made for the different electron densities of the Fricke dosimeter and the carbohydrates. The error introduced is negligible (\(\approx 4\%) and would tend to reduce the G-values given in this paper accordingly. The isolation and determination of the carbohydrate products was in principle the same as described in our previous work\(^\text{8-10}\). Since most of the hydrogen and carbon dioxide formed was buried in the solid it was necessary to suck deoxygenated water into the evacuated and irradiated sample container before purging the gases from it into the gas-chromatograph\(^\text{46}\).

### Table II. \(\gamma\)-Radiolysis of crystalline D-fructose products and their G-values. GC-peak numbers refer to Fig. 2.

<table>
<thead>
<tr>
<th>No.</th>
<th>Product</th>
<th>Determined as TMS ether after reduction with NaBD(_4)</th>
<th>GC-peak G-value No.</th>
</tr>
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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>Glyceraldehyde</td>
<td>Glycerol-1-d(_1)</td>
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<tr>
<td>35</td>
<td>Butanone-(3)-diol-(1,2)</td>
<td>Butanetriol-1,2,3-3-d(_1)</td>
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<tr>
<td>36</td>
<td>2-Deoxy-tetrose</td>
<td>Butanetriol-1,2,4-1-d(_1)</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>(Threose)</td>
<td>Treitol (1 D incorporated)</td>
<td>4</td>
</tr>
<tr>
<td>8</td>
<td>(Erythrose)</td>
<td>Erythritol (1 D incorporated)</td>
<td>5</td>
</tr>
<tr>
<td>37</td>
<td>3-Deoxy-pentonic acids</td>
<td>3-Deoxy-pentitol-1,1-d(_2)</td>
<td>6</td>
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<tr>
<td>38</td>
<td>(3-Deoxy-pentosulose)</td>
<td>(3-Deoxy-pentitol-1,2-d(_2)</td>
<td>7</td>
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<tr>
<td>39</td>
<td>Arabinonic acid</td>
<td>Arabinitol-1,1-d(_2)</td>
<td>8</td>
</tr>
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<td>41</td>
<td>Ribonic acid</td>
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<td>40</td>
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<td>2- and 3-Deoxy-hexitols</td>
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<tr>
<td>33</td>
<td>Hydrogen</td>
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</tr>
</tbody>
</table>

* Not determined.

---

1 Bibliography on the radiation chemistry of carbohydrates. Radiation Chemistry Data Center, Radiation Laboratory, University of Notre Dame, Notre Dame 1971.
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