154. *Radiation Chemistry of Carbohydrates. Part III.* The Effect of gamma-Radiation on Aqueous Solutions of* D-*Fructose.*

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The degradation of D-fructose in aqueous solution by ^{60}Co γ-radiation has been examined by measuring the changes in acidity, absorption spectra, and optical rotation with dose. Hydrogen peroxide and carbon dioxide formation have also been measured. Paper chromatographic and radioactive tracer methods revealed that the main products were glucosone, 2-oxogluconic acid, oxalic acid, and two-carbon aldehydic fragments. Isotope dilution and absorption spectra indicate the formation of three-carbon aldehydic fragments.

By following the yield–dose curves for the main products, the primary and secondary products are identified. These products are considered to arise from at least three types of degradation process: (*a*) oxidation of the primary alcohol group at position 1 to form glucosone, which is then converted into 2-oxogluconic acid (there is also evidence of a similar process occurring at position 6); (*b*) direct scission between $C_{(2)}$ and $C_{(3)}$ to form two- and four-carbon aldehydic fragments which are subsequently oxidised; (*c*) symmetrical scission of the molecule to form glyceraldehyde and glycerosone.

The chemical action of ionising solutions on D-fructose has received only scant attention. No study has been reported of the products. Khenokh [1] observed an absorption maximum

* Part II, 1958, 3534.

[1] Khenokh, *Doklady Akad. Nauk S.S.S.R.*, 1955, **104**, 746.

at 265 mμ for solutions of D-fructose exposed to gamma-radiation. Other changes accompanying the irradiation of D-fructose solutions have, however, not been described. Combrisson and Uebersfeld [2] detected a characteristic paramagnetic resonance spectrum in solid D-fructose after irradiation with pile-neutrons, and it was observed by Williams, Geusic, Wolfrom, and McCabe [3] that the paramagnetic resonance spectra of β-D-fructopyranose and L-sorbose were similar. In the present work the chemical changes accompanying gamma-irradiation of dilute aqueous solutions of D-fructose are reported.

Results and Experimental

The ^{60}Co source, irradiation vessels, dosimetric techniques, and the chromatographic, spectroscopic, and isotope dilution methods were similar to those previously described.[4] Two dose rates were employed in the investigation. In the large cell (vol. 150 ml.) the dose rate was $1{\cdot}43 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$, and in the small cell (vol. 40 ml.) $1{\cdot}03 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$.

Chromatographic Analysis of Irradiated Solutions.—A 0·055M-solution (150 ml.) of D-fructose was irradiated to a total energy input of 3×10^{22} ev, and then chromatographed with butan-1-ol–acetic acid–water (4 : 1 : 5). The chromatogram showed some streaking when sprayed with *p*-anisidine but this feature was not as marked as with D-glucose.[4] Four spots were apparent; pink, R_F 0·15; brown, R_F 0·18, glucosone; yellow, R_F 0·23, fructose; brown-yellow, R_F 0·30.

A solution (150 ml.) of [^{14}C]fructose (7·73 millimoles and specific activity 6·45 μc/millimole) was irradiated in oxygen to a total dose of $24{\cdot}6 \times 10^{22}$ ev. After chromatography in butan-1-ol–acetic acid–water, the autoradiographs showed two further spots, at R_F 0·34 and 0·42, not previously revealed with *p*-anisidine.

Rate of Formation of Acid: Initial Rate.—The rate of formation of acid in oxygenated solutions showed a gradual rise with energy input, and the yield was independent of concentration over a ten-fold range. If the acid is assumed to be monobasic, the initial rate corresponds to *G*(acid) 1·1. For evacuated fructose solutions ($5{\cdot}5 \times 10^{-2}$M to $5{\cdot}5 \times 10^{-3}$M), the acid yield was lower than in oxygen, and the initial rate corresponds to *G*(acid) 0·4. The results are shown in Fig. 1.

Acid Yields at High Energy Inputs.—0·055M-Solutions (150 ml.) of fructose were irradiated to doses varying from 2 to $20{\cdot}5 \times 10^{20}$ ev/ml. Volatile acid was measured by vacuum-distillation of the solutions at $<35°$ and collection of the distillate in a receiver cooled in liquid air. The residue after distillation was examined for non-volatile acid. Total acid was estimated on a portion of the whole irradiated solution. The results are shown in Fig. 2. Very small amounts of volatile acid are formed at doses less than 2×10^{20} ev/ml., whereas at 20×10^{20} ev/ml. volatile acid constitutes about 37% of the total acid.

Rate of Carbon Dioxide Formation.—The gas stream leaving the irradiated solution was passed through barium hydroxide solution, and the amount of carbon dioxide formed determined as barium carbonate. The threshold energy input for formation of carbon dioxide appears to be in the region of 4×10^{20} ev/ml. Thereafter its rate of formation increases with dose (Fig. 2).

Absorption Spectra of Irradiated Solutions.—A typical ultraviolet absorption spectrum for fructose solutions (40 ml.) irradiated in oxygen is shown in Fig. 3, with a maximum absorption at 285—290 mμ, which on addition of potassium hydrogen carbonate shifts to 295 mμ but does not increase in intensity. The minimum at 245 mμ, on addition of potassium hydrogen carbonate, does not change in either position or intensity. Addition of hydrochloric acid to the irradiated solution does not affect the position or intensity of the maxima or minima. However, fructose solutions (40 ml.) irradiated *in vacuo* show maximum absorption at 265 mμ and a minimum at 225 mμ, and there is little change on addition of alkali (Fig. 3).

The rate of formation of the absorbing substances with energy input was measured in oxygen and in a vacuum (Fig. 4). For the same energy input, the peak at 265 mμ is formed faster than at 290 mμ. In oxygen and in a vacuum there was evidence of a slow post-irradiation process, and the absorption maxima continued to increase for several days after irradiation had ceased (Table 1).

[2] Combrisson and Uebersfeld, *Compt. rend.*, 1954, **238**, 1397.
[3] Williams, Geusic, Wolfrom, and McCabe, *Proc. Nat. Acad. Sci., U.S.A.*, 1958, **44**, 1128.
[4] Phillips, Moody, and Mattok, *J.*, 1958, 3522.

TABLE 1. *Change in absorption spectrum after irradiation.*

Condition of system	Energy input (10^{21} ev)	Optical density At end of the irradiation	After 170 hr.
Evacuated	1·3	(265 mμ) 1·15	1·54
Oxygenated	3·7	(290 mμ) 0·30	0·38

FIG. 1.

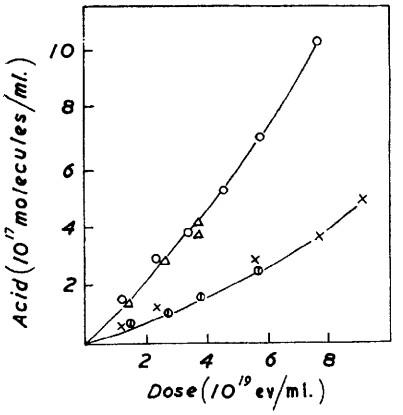


FIG. 2.

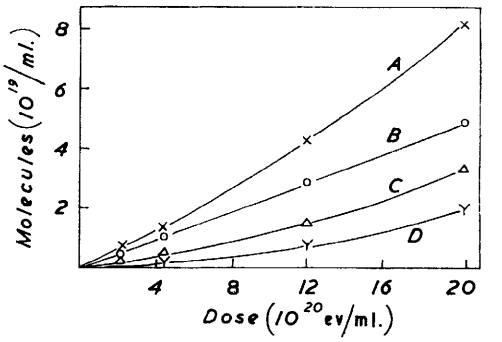


FIG. 1. *Acid production during irradiation of* D-*fructose solutions. Dose rate* 1·03 × 10^{17} ev min.$^{-1}$ ml.$^{-1}$
In oxygen: ○, 5·5 × 10^{-3}M; △, 5·5 × 10^{-2}M.
In a vacuum: ×, 5·5 × 10^{-3}M; ⓘ, 5·5 × 10^{-2}M.

FIG. 2. *Production of acid and carbon dioxide during irradiation of* D-*fructose solutions* (5·5 × 10^{-2}M) *in oxygen.*
A, Total acid; B, non-volatile acid; C, volatile acid; D, carbon dioxide.

FIG. 3.

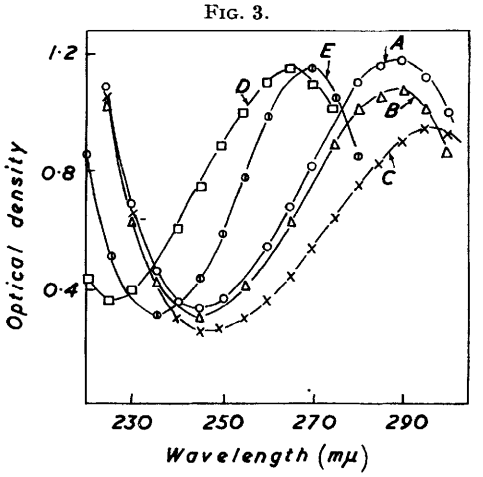


FIG. 4.

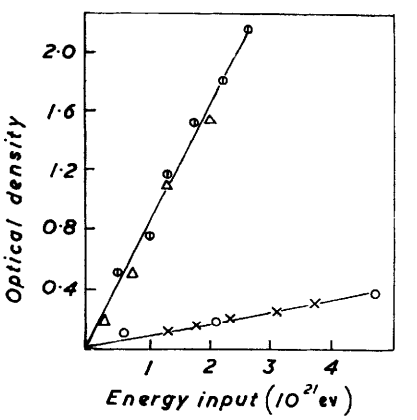


FIG. 3. *Ultraviolet absorption spectra of irradiated* D-*fructose solutions*
A (○), *In oxygen; energy input* 3·0 × 10^{22} ev. *B* (△), *Irradiated solution with added hydrochloric acid. C* (×), *Irradiated solution with added potassium hydrogen carbonate. D* (□), In vacuo; *energy input* 1·3 × 10^{21} ev. *E* (ⓘ), *Irradiated solution with added potassium hydrogen carbonate.*

FIG. 4. *Increase in ultraviolet absorption with energy input during irradiation of* D-*fructose solutions* (*ml.*). *Dose rate* 1·03 × 10^{17} ev. min.$^{-1}$ ml.$^{-1}$.
ⓘ 5·5 × 10^{-3}M, △ 5·5 × 10^{-2}M } in vacuo *at* 265 mμ.
× 5·5 × 10^{-3}M, ○ 5·5 × 10^{-2}M } *in oxygen at* 290 mμ.

Formation of Hydrogen Peroxide.—The rate of formation of hydrogen peroxide with energy input was measured by the colorimetric method [5] for oxygenated fructose solutions (40 ml.). Initially the rate of formation was constant up to a dose of *ca.* 3×10^{19} ev/ml. (Fig. 5). The initial rate corresponds to $G(H_2O_2)$ 2·0. When irradiation ceased, the peroxide decreased at a rate of 4×10^{13} molecules $min.^{-1}$ $ml.^{-1}$ until no peroxide could be detected.

Changes in Optical Rotation.—During irradiation of oxygenated fructose solutions (150 ml.) the optical rotation increases with energy input (Table 2).

TABLE 2. *Change in optical rotation for oxygenated fructose solutions* ($5{\cdot}5 \times 10^{-2}$M).

$[\alpha]_D$ initial = −92·5° (2 dm. tube).

Dose (10^{20} ev/ml.)	2	4·3	8·5	11·8	20·5
$[\alpha]_D$	−77·4°	−61·8°	−42°	−37·2°	−18·2°
Hours of post-irradiation	52	48	—	72	72
$[\alpha]_D$	−72°	−57°	—	−34°	−16·1°

Estimation of the Products by Isotope Dilution.—To estimate the products, isotope dilution was applied directly to the untreated irradiated solutions. In a typical experiment, an aqueous solution (150 ml.) of fructose (7·81 millimoles) of specific activity 5·06 μc/millimole was irradiated

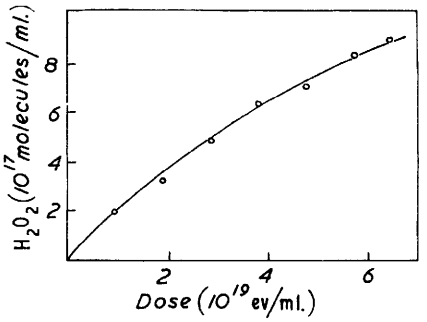


FIG. 5. *Formation of hydrogen peroxide during irradiation of* D-*fructose solutions* ($5{\cdot}5 \times 10^{-3}$M) *in oxygen; dose rate* $1{\cdot}03 \times 10^{17}$ ev. $min.^{-1}$ $ml.^{-1}$.

at a dose rate of 1·43 ev $min.^{-1}$ $ml.^{-1}$ in oxygen for 24 hr. The following constituents were estimated:

Fructose. (*a*) As D-fructosazone. Carrier D-fructose (0·86 millimole) was added to the irradiated solution (10 ml.) together with phenylhydrazine (2 ml.) and acetic acid (1·5 ml.), and the whole was boiled for 40 min. The solid, after being washed with benzene (50 ml.) and recrystallised seven times from ethanol, had m. p. 199—200° and constant specific activity 1·72 μc/millimole.

(*b*) As 1,2:4,5-di-*O*-isopropylidene-D-fructopyranose.[6] The irradiated solution (5 ml.) was distilled under reduced pressure at <35°, and the distillate collected in a vessel cooled in liquid air. The residue, after drying over phosphoric oxide, was treated with carrier fructose (1·22 millimoles), dry acetone (6 ml.), and concentrated sulphuric acid (0·02 ml.), and the mixture was shaken for 24 hr. The acetone was removed under reduced pressure, and the residue extracted three times with ether. Each ether extract was washed successively with dilute sulphuric acid (1 : 10) and dilute sodium hydroxide, then dried (Na_2SO_4) and evaporated. The residue, recrystallised seven times from light petroleum (b. p. 60—80°), had m. p. 112—113° and constant specific activity 0·73 μc/millimole.

Formaldehyde. Half the distillate obtained from the estimation of di-isopropylidene-fructose was treated with carrier formaldehyde (0·233 millimole) and 10% dimedone solution (5 ml.). After 24 hr. the precipitate was filtered, and after recrystallising twice from ethanol had m. p. 189° and specific activity $2{\cdot}5 \times 10^{-3}$ μc/millimole.

Glucosone. Carrier glucosone (0·3 millimole), phenylhydrazine (1·5 ml.), and acetic acid (1 ml.) were added to the irradiated solution (10 ml.). After 2 hr. the precipitate was filtered off and washed with benzene (50 ml.); after six recrystallisations from ethanol it had m. p. 200° and specific activity 0·34 μc/millimole.

Glyoxal. The irradiated solution (10 ml.) was treated with phenylhydrazine (1·5 ml.),

[5] Eisenburg, *Ind. Eng. Chem., Analyt.*, 1943, **15**, 327.

[6] Bates, "Polarimetry, Saccharimetry and the Sugars," U.S. Govt. Printing Office, Washington, 1942, p. 483.

acetic acid (1 ml.), and carrier glyoxal (1·85 millimoles). Eight recrystallisations from benzene gave glyoxal bisphenylhydrazone, m. p. 169°, and constant specific activity 0·037 μc/millimole.

D-*Arabinose.* The irradiated solution (10 ml.) and carrier D-arabinose (0·585 millimole) were refluxed for 30 min. with diphenylhydrazine (0·5 ml.) in ethanol (5 ml.).[7] After 24 hr. the solution was filtered, and the solid recrystallised seven times from ethanol to give arabinose diphenylhydrazone, m. p. 198° and specific activity 5×10^{-3} μc/millimole.

1,3-*Dihydroxyacetone.* The irradiated solution (10 ml.) with carrier 1,3-dihydroxyacetone (1·17 millimoles) was boiled with phenylhydrazine (1·5 ml.) and acetic acid (1 ml.) for 5 min.

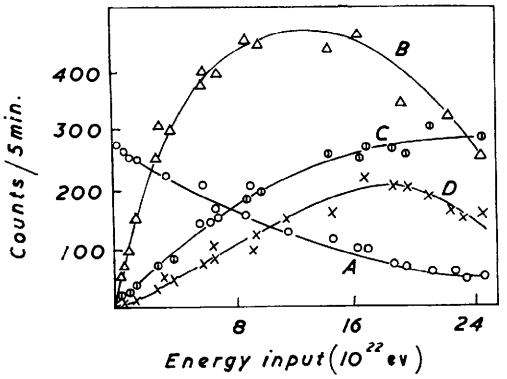


FIG. 6. *Rate of formation of products during the irradiation of* D-*fructose solutions in oxygen.*

A (○), D-*Fructose* ($\times 10^{-2}$); *B* (△), D-*glucosone*; *C* (ⓘ), *product of* R_F 0·30 (*yellow-brown*); *D* (×), *product of* R_F 0·15 (*pink*).

FIG. 7.

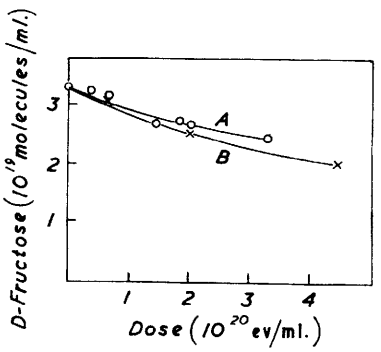


FIG. 8.

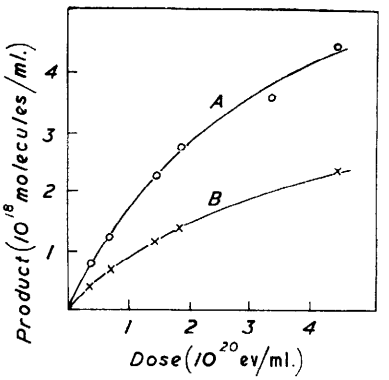


FIG. 7. *Rate of destruction of* D-*fructose in irradiated oxygenated solutions; dose rate* $1·03 \times 10^{17}$ ev. min.$^{-1}$ ml.$^{-1}$.

D-*Fructose, estimated as* (*A*) *osazone, and* (*B*) *as* 1,2:4-5-*di-isopropylidenefructose.*

FIG. 8. *Rate of formation of products during irradiation of* D-*fructose solution in oxygen.*

A, Two-carbon fragment; B, D-*glucosone.*

The solid, after six recrystallisations from benzene, had m. p. 128° and constant specific activity 0·065 μc/millimole.

Oxalic acid. In an independent experiment an aqueous solution (150 ml.) of fructose (7·73 millimoles and specific activity 6·45 μc/millimole) was irradiated in oxygen to a total dose of $24·6 \times 10^{22}$ ev. The irradiated solution (5 ml.) was freeze-dried and carrier oxalic acid (0·96 millimole) added. Eight recrystallisations from hot water gave pure oxalic acid, m. p. 101° and constant specific activity 0·06 μc/millimole.

D-*Glucuronolactone.* Another portion of the above solution (10 ml.) was freeze-dried, and carrier D-glucuronolactone (0·8 millimole) added; eight recrystallisations from hot water gave pure D-glucuronolactone, m. p. 175° and specific activity 1×10^{-4} μc/millimole. Table 3 shows the yields of products at two different energy inputs under fully oxygenated conditions.

Rate of Formation of Products.—Accurately known amounts of irradiated [^{14}C]fructose

[7] Neuberg and Wohlgemuth, *Z. physiol. Chem.*, 1902, **35**, 31.

solution (150 ml.; 7·73 millimoles) of specific activity 6·45 μc/millimole which had received progressively increasing doses of radiation (dose rate $1{\cdot}43 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$) were chromatographed in butan-1-ol–acetic acid–water (4 : 1 : 5), and the activities of the spots were measured. The rate of decomposition of the fructose with energy input was measured, and also the rate of formation of glucosone, R_F 0·18, and the unidentified products with R_F 0·15 and 0·30 severally. The results are shown in Fig. 6.

Individual estimations by means of the isotope dilution method were carried out for the two-carbon fragment (as glyoxal bisphenylhydrazone), glucosone, and unchanged fructose after varying doses. Fructose solution (240 ml.; 13·31 millimoles) of specific activity 7·2 μc/millimole was irradiated in six 40 ml. portions, each to a successively increasing dose in the range 2·39—44·9 $\times 10^{19}$ ev/ml. The dose rate was $1{\cdot}03 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$. At each dose level fructose, glucosone, and the two-carbon fragment were estimated by applying the isotope dilution method to the untreated irradiated solution. These compounds were estimated as 1,2:4,5-di-isopropylidenefructose and fructosazone, glucosazone, and glyoxal bisphenylhydrazone. The results are shown in Figs. 7 and 8.

Discussion

When aqueous solutions of D-fructose are irradiated with gamma radiation, chromatography indicates several products. In butan-1-ol–acetic acid–water the following spots were detected with *p*-anisidine; pink, R_F 0·15; brown, R_F 0·18; yellow, R_F 0·23; yellow-brown, R_F 0·30. The spot at R_F 0·23 is due to unchanged fructose. Two further products shown by autoradiography had R_F 0·34 and 0·42 severally. It is probable that the two compounds with R_F 0·15 and 0·18 are formed by oxidation of the primary alcohol group at $C_{(1)}$ in fructose, the former being due to 2-oxogluconic acid and the latter to glucosone. The chromatographic behaviour of these compounds is identical with the two spots under consideration (R_F 0·15 and 0·18). The presence of glucosone was confirmed by isotope dilution (Table 3), and further evidence provided by comparison of the values obtained for fructose estimated as di-*O*-isopropylidenefructose and as fructosazone. Any glucosone present would contribute to the latter value only, since it forms the same osazone as fructose, and at 3×10^{20} ev (Table 3*a*) and $24{\cdot}6 \times 10^{20}$ ev (Table 3*b*) the difference between the two values compares favourably, within experimental limits, with the direct estimation of glucosone. After its formation there is doubtless rapid conversion of glucosone into 2-oxogluconic acid, particularly when oxygen is passing through the solution. The overall shapes of the yield–dose curves (Fig. 6) for glucosone and the product responsible for the spot R_F 0·15 on the chromatogram also support the view that these products are inter-related in this way. Glucosone behaves as a primary product and as it is degraded the compound with R_F 0·15 is formed, and its molecule suffers extensive degradation only at high energy inputs. We consider, therefore, that the spot at R_F 0·15 is due to 2-oxogluconic acid. Oxidation of the primary alcohol group at position 6 would lead in a similar fashion to 5-oxo-L-gulonic acid, which may be responsible for the spot of R_F 0·30 detected with *p*-anisidine. Previously [4] it was shown that 5-oxogluconic acid had R_F 0·28 in butan-1-ol–acetic acid–water, and this compound might reasonably be expected to behave similarly to 5-oxo-L-gulonic acid which has yet to be examined directly. Moreover, the amounts of 2- and 5-oxogluconic acid available are insufficient for application of the isotope dilution method of estimation. Figs. 1 and 2, however, indicate that acid formation is an important feature of the radiation degradation of fructose solutions. During initial stages of the degradation the main acid fraction is non-volatile, but production of carbon dioxide and volatile acid increases at high doses. It appears accordingly that formic acid and carbon dioxide are not produced in the primary process, and thus comprise lower degradation products.

A further product appears to be a two-carbon aldehydic fragment which was estimated by isotope dilution as glyoxal bisphenylhydrazone. Glyoxal and glycollaldehyde give rise to the same osazone,[8] and their separate detection is not possible by this method alone.

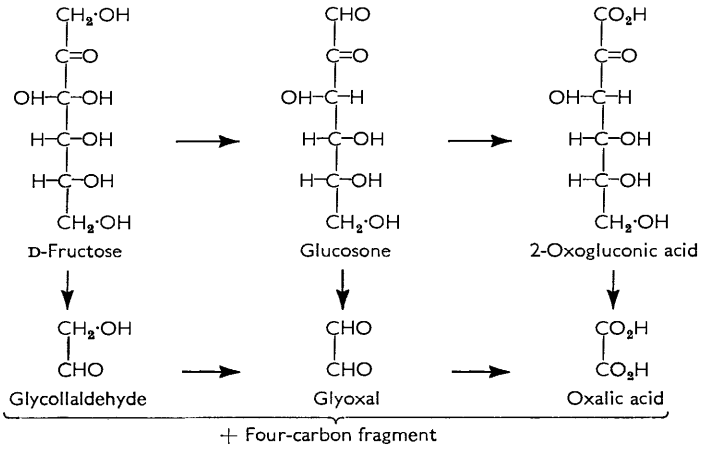
[8] Wohl and Neuberg, *Ber.*, 1900, **33**, 3095.

TABLE 3. *Products formed on irradiation of aqueous solutions of* D-*fructose with gamma-radiation in oxygen.*

(*a*) Initial fructose 7·81 millimole; Energy input 3·0 × 10^{22} ev. (Volume 150 ml.)			
Product	Carrier (millimoles)	Specific activity (μc/millimole)	Yield (millimoles)
Fructose			
(i) Di-*O*-isopropylidenefructose...	1·22	0·73	6·18
(ii) Fructosazone ...	0·86	1·72	6·57
D-Glucosone	0·3	0·34	0·32
D-Arabinose.....	0·585	0·005	0·01
1,3-Dihydroxyacetone	1·17	0·065	0·45
Glyoxal	1·85	0·037	0·62
Formaldehyde	0·233	0·0025	0·04

(*b*) Initial fructose 7·73 millimoles; Energy input 24·6 × 10^{22} ev. (Volume 120 ml.)			
Product	Carrier (millimoles)	Specific activity (μc/millimole)	Yield (millimoles)
Fructose			
(i) Di-*O*-isopropylidene fructose	1·17	0·516	1·22
(ii) Fructosazone ...	0·89	0·77	1·46
D-Glucosone	0·30	0·3	0·17
D-Arabinose	0·94	0·01	0·04
1,3-Dihydroxyacetone	1·01	0·15	0·59
D-Glucurone	0·80	1·0 × 10^{-4}	1·2 × 10^{-4}
Glyoxal	2·18	0·045	0·56
Formaldehyde	0·233	0·046	0·12
Oxalic acid	0·96	0·06	0·62

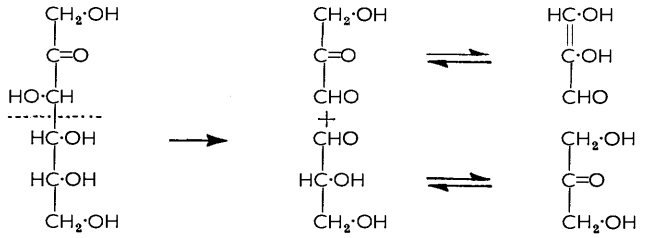
It is likely that both compounds are present, with glycollaldehyde predominating initially owing to direct scission between $C_{(2)}$ and $C_{(3)}$ of the fructose. In the later stages a further amount may be formed through scission of the 2,3-bond in glucosone. Subsequent degradation of 2-oxogluconic acid in a similar fashion leads to oxalic acid, the presence of which was established by isotope dilution (Table 3). Oxalic acid may also be formed by further oxidation of the two-carbon aldehydic fragments. On the basis of these considerations the following inter-related degradation processes may be distinguished at this stage:



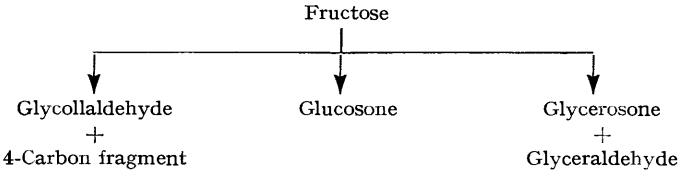
The yield–dose for the two-carbon fragment (Fig. 8) shows features similar to that obtained with glucosone, and indicates that it is mainly formed by a primary process, thus leading to the formation of a four-carbon fragment at an early stage. Although a four-carbon fragment has not been identified, there is some paper chromatographic evidence (spot R_F 0·42) that it is formed. Appreciable amounts of erythrose were not observed in the irradiated solutions, and isotope dilution estimations of this compound proved unsatisfactory.

The small amount of formaldehyde produced at low energy inputs indicates that there is no direct scission between $C_{(1)}$ and $C_{(2)}$ by a primary process. The amount of formaldehyde increases at high doses, as would be expected if it were a lower degradation product. The amount of D-arabinose formed is negligible.

The ultraviolet absorption spectrum of fructose solutions irradiated in oxygen is more complex than that of similarly irradiated glucose solutions. The peak at 285—290 mμ in the spectrum of the fructose solutions moves to higher wavelengths on addition of alkali. The complexity of the spectrum arises from the contributions of the several absorbing products in the solution. The presence of three-carbon fragments was revealed by isotope dilution assays involving the addition of carrier 1,3-dihydroxyacetone and estimation as glycerosazone. This osazone may be formed from glycerosone, reductone, glyceraldehyde, or dihydroxyacetone, all of which may be present in the irradiated solution. The last compound (formed by isomerisation of glyceraldehyde) shows absorption at 265 mμ and proved to be the main constituent responsible for the absorption spectrum of irradiated glucose solutions.[4] Glucosone, in alkali, also shows an absorption maximum at this wavelength, while 2-oxogluconic acid, in alkali, enolises and the solution shows an absorption maximum at 275 mμ. In irradiated fructose solutions, however, the spectra of these compounds are masked owing to the presence of other products which absorb at higher wavelengths. One product which may account for this behaviour and be formed by scission between $C_{(3)}$ and $C_{(4)}$ in fructose may be reductone. This compound exhibits a strong absorption maximum at 287 mμ in alkali.[4] Thus two major absorbing constituents may be formed by symmetrical scission of the fructose molecule:



For the decomposition of fructose, calculated from the values given in Fig. 7, G is 4·0, which is of the same order as the rate of consumption of glucose (G 3·5) under comparable conditions.[4] The primary degradation pattern which has been elucidated may therefore be summarised:



Another primary process may involve oxidation of the primary alcohol at position 6 to form 5-oxo-L-gulonic acid, since there is now accumulating evidence, from glucose,[4] D-sorbitol,[9] and D-mannitol [10] that the primary alcohol groups are more reactive than secondary alcohol groups towards free radicals formed by the action of radiation on water. The detailed mechanism of these processes will be considered later.

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