## 155. *Radiation Chemistry of Carbohydrates. Part IV.*[1] *The Effect of gamma-Radiation on Aqueous Solution of Sucrose.*

By G. O. Phillips and G. J. Moody.

Yield–dose curves obtained from isotope dilution and paper chromatographic methods reveal that glucose and fructose are primary products of γ-irradiation of aqueous sucrose solutions, together with smaller amounts of glucosone and gluconic acid. Glucuronic acid, 2-oxogluconic acid, arabinose, and two- and three-carbon aldehydic fragments arise in secondary processes. In the final stages carbon dioxide and formic acid are formed. Hydrogen peroxide is produced continuously.

The amounts of volatile and non-volatile acid formed, and changes in optical rotation and absorption spectra, were determined. Thus, the degradation of sucrose is related to two types of oxidative scission of the disaccharide linkage.

Hydrolysis occurs during irradiation of sucrose in aqueous solution and acid is produced.[2] Changes in the ultraviolet absorption spectrum have also been noted,[3] and the overall change in optical rotation was proposed by Wright as a pile-radiation dosimeter.[4] However, except recently by Wolfrom, Binkley, and McCabe,[5] the chemical effects of irradiation of sucrose have not been investigated. These workers irradiated 50% concentrated sucrose solutions in open aluminium containers without oxygenation. Previous papers in this Series described the radiative degradation of dilute aqueous glucose [6] and fructose.[1] The study is now extended to sucrose, under comparable conditions, which is of particular interest in respect of the sterilisation of food.[7] The products have been identified and estimated by paper chromatographic and radioisotopic tracer methods, and yield–dose curves for the main products have enabled primary and secondary products to be recognised.

### Results and Experimental

The source of gamma-radiation, and experimental and dosimetric techniques, were described in Part I. The dose rate into the large irradiation cell (150 ml.) was $1{\cdot}43 \times 10^{17}$, and into the small cell (40 ml.) was $1{\cdot}03 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$.

*Chromatographic Analysis of Irradiated Solutions.*—A solution (150 ml.; $2{\cdot}9 \times 10^{-2}$M) of sucrose was irradiated in oxygen at a dose rate of $1{\cdot}43 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$ for 120 hr.; the pH fell to 2·2 and $[\alpha]_D$ from $+66{\cdot}5°$ to $+29°$. The irradiated solution, chromatographed in butan-1-ol–acetic acid–water (4 : 1 : 5) and sprayed with *p*-anisidine revealed three spots in addition to unchanged sucrose $R_F$ 0·14, yellow-brown. These had $R_F$ 0·18 (brown), 0·23 (yellow-brown), and 0·28 (brown). When the solution after irradiation at high energy inputs (*ca.* $16 \times 10^{22}$ ev) was similarly examined, the spot of $R_F$ 0·14 due to sucrose was tinged slightly pink.

*Rate of Acid Formation: Initial Rate.*—The rate of acid formation was similar to that for glucose and fructose and showed a gradual increase with energy input (Fig. 1). The yield was independent of sucrose concentration in the range $2{\cdot}9 \times 10^{-3}$ to $2{\cdot}9 \times 10^{-2}$M and independent of dose rate within the range $1{\cdot}03$—$1{\cdot}43 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$. On the assumption that the acid is monobasic, $G$(acid) in oxygen is 1·2—1·3. For evacuated solutions $G$(acid) is 0·4—0·5 (Fig. 1).

*Acid Yields at High Energy Inputs.*—Oxygenated sucrose solutions in 150 ml. portions were irradiated to doses ranging from 6 to $18{\cdot}4 \times 10^{20}$ ev/ml. At successive increasing energy inputs,

[1] Part III, Phillips and Moody, preceding paper.
[2] Reinhard and Tucker, *Radiology*, 1929, **12**, 151.
[3] Khenokh, *Doklady Akad. Nauk. S.S.S.R.*, 1955, **104**, 746.
[4] Wright, *Discuss. Faraday Soc.*, 1952, **12**, 60.
[5] Wolfrom, Binkley, and McCabe, *J. Amer. Chem. Soc.*, 1959, **81**, 1442.
[6] Phillips, Moody, and Mattok, *J.*, 1958, 3522.
[7] Proc. U.N. Food and Agricultural Organisation Food Irradiation Conference 1958, in the press.

the total, volatile, and non-volatile acid were estimated in the irradiated solutions as described previously for fructose.[1] The results are shown in Fig. 2. Only very small quantities of volatile acid were produced below $2 \times 10^{20}$ ev/ml., but the amounts increased at higher doses. At $18{\cdot}4 \times 10^{20}$ ev/ml. the volatile acid constituted 34% of the total acid (Fig. 2).

TABLE 1. *Change in optical rotation of oxygenated sucrose solution* ($2{\cdot}9 \times 10^{-2}$M) *on irradiation.*

$[\alpha]_D = +66{\cdot}5°$ initially.

| Energy input ($10^{20}$ ev/ml.) | 6 | 8·35 | 10·3 | 18·4 |
|---|---|---|---|---|
| $[\alpha]_D$ | +44·0° | +31·0° | +29·0° | +11·5° |

TABLE 2. *Change in absorption spectrum after irradiation.*

| System | Energy input ($10^{21}$ ev) | Optical density at 275 mμ after irradiation | after 180 hr. |
|---|---|---|---|
| Oxygenated | 19·6 | 0·35 | 0·74 |

*Carbon Dioxide.*—Carbon dioxide produced during irradiation was estimated as barium carbonate. Fig. 2 shows also the rate of formation of carbon dioxide with increasing dose.

*Changes in Optical Rotation.*—A portion of the irradiated solution used for acid estimations was used to follow the change in optical rotation with dose (see Table 1). At the end of an irradiation to a total energy input of $8{\cdot}35 \times 10^{20}$ ev/ml., the optical rotation continues to fall during 168 hr. from $[\alpha]_D$ +31° to +25°.

FIG. 1.

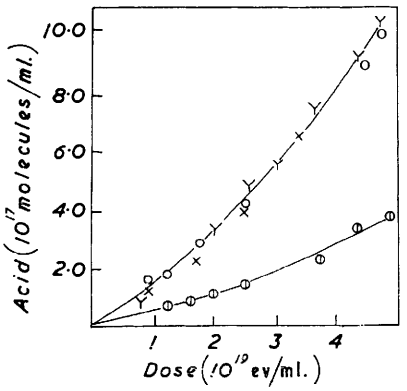



FIG. 2.

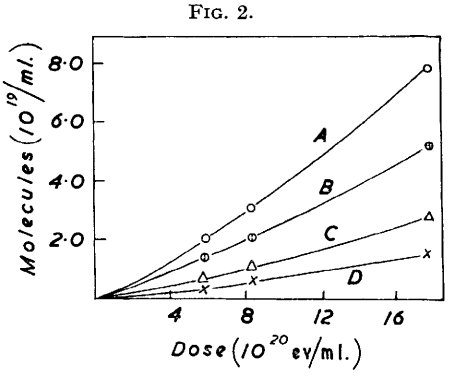



FIG. 1. *Acid production during irradiation of sucrose solutions.*

Ⓘ In vacuo ($2{\cdot}9 \times 10^{-3}$M) } dose rate
Y *In oxygen* ($4{\cdot}9 \times 10^{-3}$M) } $1{\cdot}03 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$
○ *In oxygen* ($2{\cdot}9 \times 10^{-3}$M) } dose rate
× *In oxygen* ($2{\cdot}9 \times 10^{-2}$M) } $1{\cdot}43 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$

FIG. 2. *Formation of acid and carbon dioxide during the irradiation of oxygenated sucrose solutions* ($2{\cdot}9 \times 10^{-2}$M); *dose rate* $1{\cdot}43 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$.

*A* (○), *Total acid*; *B* (Ⓘ) *non-volatile acid*; *C* (△) *volatile acid*; *D* (×) *carbon dioxide.*

*Ultraviolet Absorption Spectra of Irradiated Solutions.*—When irradiated in oxygen the solution showed a selective absorption maximum at 275 mμ, and a minimum at 245 mμ. On addition of potassium hydrogen carbonate solution, the maximum moved to 295 mμ and increased in intensity; the minimum did not change its position (Fig. 3). Addition of hydrochloric acid moved the absorption maximum to 265 mμ (Fig. 3). Sucrose solutions irradiated *in vacuo* showed an absorption maximum at 265 mμ (Fig. 3). The rate of increase of the absorption maxima with energy input for oxygenated and evacuated solutions is shown in Fig. 4. The change in ultraviolet absorption after irradiation had ended (Table 2) indicates the existence of a post-irradiation process in oxygen.

*Formation of Hydrogen Peroxide.*—The rate of formation of hydrogen peroxide with dose is

shown in Fig. 5. The yield was independent of concentration within a ten-fold range, and the rate of formation remained initially constant. The rate decreased after the formation of

FIG. 3.

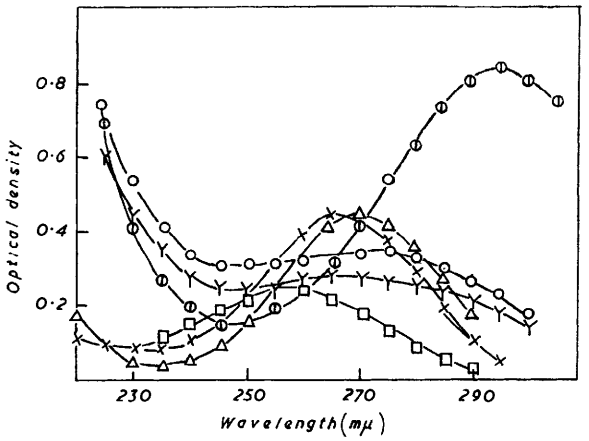



FIG. 4.

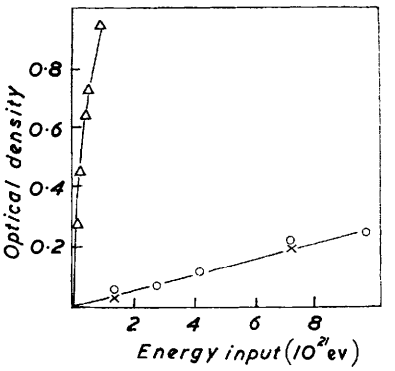



FIG. 3. *Ultraviolet absorption spectra of irradiated sucrose solutions.*

○ *In oxygen* (*energy input* 19·6 × $10^{21}$ ev; 2·9 × $10^{-3}$M); ⊕ *irradiated solution with added potassium hydrogen carbonate*; Y *irradiated solution with added hydrochloric acid*; × in vacuo (*energy input* 2·4 × $10^{20}$ ev; 2·9 × $10^{-2}$M); △ *irradiated solution with added potassium hydrogen carbonate*; □ *irradiated solution with added hydrochloric acid.*

FIG. 4. *Increase in ultraviolet absorption at* 275 *and* 265 mμ *during irradiation by aqueous sucrose; dose rate* 1·03 × $10^{17}$ ev $min^{-1}$ $ml.^{-1}$.

○ *In oxygen* (2·9 × $10^{-3}$M) *at* 275 mμ. × *In oxygen* (2·9 × $10^{-2}$) *at* 275 mμ. △ In vacuo (2·9 × $10^{-2}$M) *at* 265 mμ.

FIG. 5.

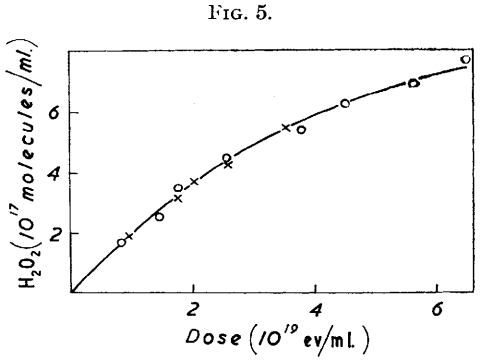



FIG. 6.

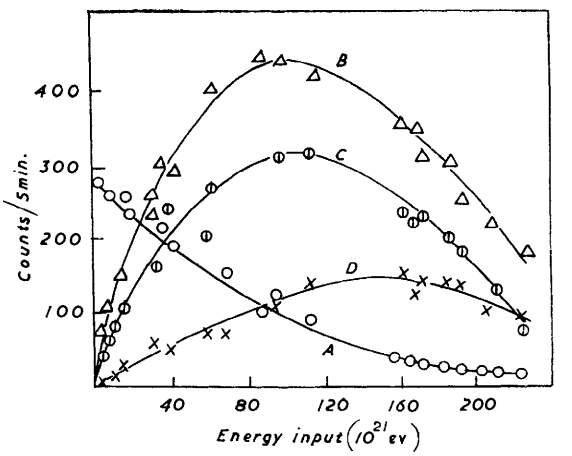



FIG. 5. *Formation of hydrogen peroxide during irradiation of sucrose solutions; dose rate* 1·43 × $10^{17}$ ev $min.^{-1}$ $ml.^{-1}$.

○, 2·9 × $10^{-2}$M; ×, 2·9 × $10^{-3}$M.

FIG. 6. *Rate of formation of products during the irradiation of oxygenated sucrose solutions.*

A (○), *Sucrose* (×10-²); B (△), D-*glucose* + D-*glucosone*; C (⊕), D-*fructose*; *D* (×), *product of* $R_F$ 0·28.

2 × $10^{17}$ molecules/ml., and at high energy inputs the rates of degradation and formation were similar. The initial rate corresponds to $G(H_2O_2)$ 2·0. A post-irradiation decrease in concentration of hydrogen peroxide was observed; the rate was 2 × $10^{13}$ molecules $ml.^{-1}$ $min.^{-1}$.

*Rate of Formation of Products.*—Accurately known amounts (0·05 ml.) of oxygenated [$^{14}$C]sucrose solution (4·19 millimoles; specific activity 10·5 μc/millimole in 150 ml.) which had received progressively increasing doses of radiation were chromatographed in butan-1-ol–acetic acid–water (4 : 1 : 5) and the radioactivity of the spots was measured. The rate of formation with energy input was measured for fructose at $R_F$ 0·23, combined glucose and glucosone at $R_F$ 0·18, and the brown spot of $R_F$ 0·28. The rate of decomposition of sucrose with energy input was also measured. The results are shown in Fig. 6. At the end of the irradiation, after a total energy input of 22·5 × $10^{22}$ ev (dose rate 1·43 × $10^{17}$ ev min.$^{-1}$ ml.$^{-1}$)

FIG. 7.

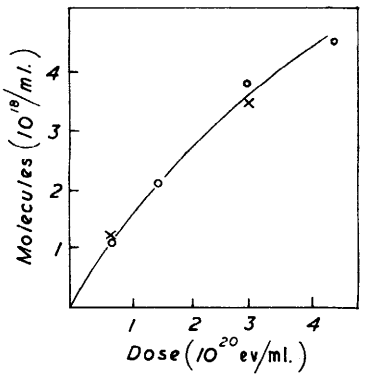



FIG. 8.

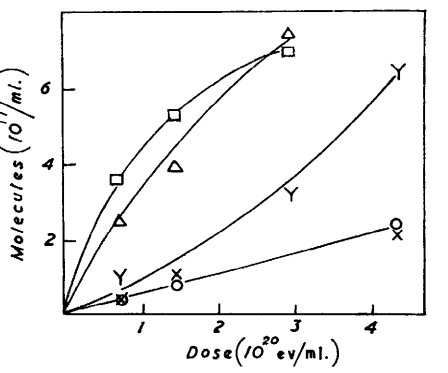



FIG. 7. *Rate of formation of* D-*fructose and* D-*glucose in oxygenated sucrose solutions; dose rate* 1·03 × $10^{17}$ ev min.$^{-1}$ ml.$^{-1}$.

○, D-*Glucose*; ×, D-*fructose*

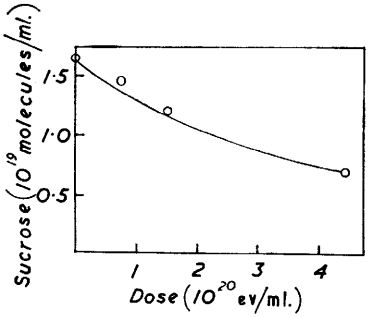
FIG. 8. *Rate of formation of products in oxygenated sucrose solutions; dose rate* 1·03 × $10^{17}$ ev min.$^{-1}$ ml.$^{-1}$.

□ D-*Glucosone*; △ D-*gluconic acid*; ○ D-*arabinose*; × D-*glucuronic acid*; Y *glyoxal.*

the concentration of degradation products was measured in the whole irradiated solution by isotope dilution analysis. The full analysis, which is typical of similar measurements reported in this paper is given below.

*Glucose.* The irradiated solution (10 ml.) was freeze-dried, carrier glucose (1·0 millimole), acetic anhydride (1 ml.), and sodium acetate (0·1 g.) were added, and the mixture was heated at 100° for 2 hr. Addition of ice-water (5 ml.) deposited impure penta-*O*-acetate which after

FIG. 9. *Rate of destruction of sucrose during irradiation of its solutions; dose rate* 1·03 × $10^{17}$ ev min.$^{-1}$ ml.$^{-1}$.




ten recrystallisations from ethanol had m. p. 134° and constant specific activity 1·54 × $10^{-1}$ μc/millimole.

*Glucosone.* The irradiated solution (5 ml.) was treated with carrier glucusone (0·3 millimole), phenylhydrazine (1 ml.), and acetic acid (0·5 ml.) and left for 2 hr. The yellow-brown precipitate was filtered, washed with benzene (50 ml.), and recrystallised six times from ethanol to give glucosazone, m. p. 201° and constant specific activity 1·33 × $10^{-1}$ μc/millimole.

*Fructose.* The procedure detailed in the preceding paper gave 1,2:4,5-di-*O*-isopropylidene fructose, m. p. 113—114°, and constant specific activity 0·057 μc/millimole.

*Formaldehyde.* The distillate obtained from the estimation of fructose was treated with 10% dimedone solution (5 ml.) and carrier formaldehyde (0·233 millimole). Working up as in the preceding paper gave the dimedone derivative, m. p. 188°, and specific activity $1·9 \times 10^{-2}$ μc/millimole.

D-*Gluconolactone.* The irradiated solution (5 ml.) was treated with carrier gluconolactone (1·14 millimoles) and excess of calcium carbonate, and filtered after three days. Calcium gluconate was precipitated with ethanol and removed. Eight such precipitations gave pure gluconate of constant specific activity $1·06 \times 10^{-1}$ μc/millimole.

D-*Glucurone.* The irradiated solution (5 ml.) was freeze-dried and treated with carrier glucurone (0·54 millimole). Nine recrystallisations from hot water gave pure D-glucurone, m. p. 175°, and constant specific activity $1·7 \times 10^{-2}$ μc/millimole.

D-*Arabinose.* The irradiated solution (5 ml.) and carrier arabinose (0·47 millimole) were refluxed for 30 min. with diphenylhydrazine (0·5 ml.) in ethanol (5 ml.).[8] Next morning the solid was separated and on recrystallisation eight times from ethanol gave pure arabinose diphenylhydrazone, m. p. 197°, of constant specific activity $1·17 \times 10^{-2}$ μc/millimole.

*Glyoxal.* The irradiated solution (5 ml.) with carrier glyoxal (2·08 millimoles) was treated with phenylhydrazine (1·5 ml.) and acetic acid (1 ml.). Eight recrystallisations of the product from benzene gave glyoxal bisphenylhydrazone, m. p. 170° and constant specific activity $3·1 \times 10^{-2}$ μc/millimole.

*Dihydroxyacetone.* The irradiated solution, carrier dihydroxyacetone (0·9 millimole), phenylhydrazine (1 ml.), and acetic acid (0·5 ml.) were boiled for 10 min. After 24 hr. glycerosazone was collected; recrystallised seven times from benzene it had m. p. 129° and constant specific activity $7·2 \times 10^{-2}$ μc/millimole.

*Total hexose.* The irradiated solution (5 ml.), carrier fructose (0·9 millimole), phenylhydrazine (1 ml.), and acetic acid (0·5 ml.) were boiled for 40 min. The glucosazone which separated after 15 hr., when washed with benzene (100 ml.) and recrystallised eight times from ethanol, had m. p. 202° and constant specific activity $2·2 \times 10^{-1}$ μc/millimole.

The results are shown in Table 3.

TABLE 3. *Products formed by gamma-irradiation of oxygenated solutions of sucrose.*

Initial sucrose ..... 4·19 millimoles. Energy input ..... $22·5 \times 10^{22}$ ev.

| Product | Carrier (millimoles) | Specific activity (μc/millimole) | Yield (millimoles) | Product | Carrier (millimoles) | Specific activity (μc millimole) | Yield (millimoles) |
|---|---|---|---|---|---|---|---|
| Fructose ..... | 1·2 | $5·7 \times 10^{-2}$ | 0·31 | D-Arabinose ..... | 0·47 | $1·17 \times 10^{-2}$ | 0·03 |
| Glucose ..... | 1·0 | $1·54 \times 10^{-1}$ | 0·36 | Dihydroxyacetone | 0·96 | $7·2 \times 10^{-2}$ | 0·65 |
| Glucosone ..... | 0·3 | $1·33 \times 10^{-1}$ | 0·19 | Glyoxal ..... | 2·08 | $3·1 \times 10^{-2}$ | 0·86 |
| D-Glucurone ... | 0·54 | $1·7 \times 10^{-2}$ | 0·04 | Formaldehyde ... | 0·233 | $1·9 \times 10^{-2}$ | 0·12 |
| D-Gluconic acid | 1·14 | $1·06 \times 10^{-1}$ | 0·28 | Total hexose ..... | 0·9 | $2·2 \times 10^{-1}$ | 0·94 |

Paper-chromatographic estimation showed the presence of 0·22 millimole of sucrose.

*Estimation of Initial Rates of Formation of Products.*—For this purpose four portions of [$^{14}$C]sucrose (1·09 millimoles in 40 ml. of water; specific activity 9·16 μc/millimole) were irradiated separately in oxygen to total energy inputs of 2·84, 5·8, 11·72, and $17·6 \times 10^{21}$ ev (dose rate $1·03 \times 10^{-1}$ ev min.$^{-1}$ ml.$^{-1}$), then analysed for glucosone, glucose, fructose, D-arabinose, glyoxal, formaldehyde, D-glucurone, and D-gluconolactone without preliminary treatment as described above. In addition, sucrose was estimated as octa-*O*-acetate by the method of Tatlow *et al.*[9] A typical analysis after an energy input of $2·84 \times 10^{21}$ ev is given.

The irradiated solution (4 ml.) was freeze-dried, carrier sucrose (0·80 millimole) added, together with a cold mixture of glacial acetic acid (0·75 ml.) and trifluoroacetic anhydride (2·5 ml.). After 5 hr. in the cold and 3 days at room temperature, saturated sodium hydrogen carbonate solution was poured into the mixture, and the whole extracted three times with chloroform (20 ml.). The combined extracts were dried ($MgSO_4$) and evaporated to a syrup, which readily crystallised. Eight recrystallisations from ethanol gave octa-*O*-acetylsucrose, m. p. 86—87° and constant specific activity 1·0 μc/millimole.

The results are shown in Figs. 7, 8, and 9.

[8] Neuberg and Wohlgemuth, *Z. physiol. Chem.*, 1902, **35**, 31.
[9] Tatlow, Bourne, Stacey, and Tedder, *J.*, 1949, 2977.

## Discussion

The degradation products formed when sucrose is irradiated in dilute aqueous solution were readily detected by paper chromatography in butan-1-ol–acetic acid–water. The streaking produced on spraying with *p*-anisidine is considerably less than is observed with irradiated glucose solutions,[6] and four constituents were detected: yellow-brown, $R_F$ 0·14, sucrose; brown, $R_F$ 0·18, glucose; yellow-brown, $R_F$ 0·23, fructose; brown, $R_F$ 0·28. The autoradiographs revealed no further products, and the pattern was identical with that of the sprayed chromatograms. After irradiation to higher energy inputs ($>16 \times 10^{22}$ ev) the spot at $R_F$ 0·14 due to sucrose became more pink, probably owing to the presence of 2-oxogluconic acid which runs identically with sucrose in this solvent. We also observed that the [$^{14}$C]sucrose (supplied by the Radiochemical Centre, Amersham) contained small amounts of glucose and fructose owing to self-decomposition. Similar self-decomposition has been observed with several [$^{14}$C]sugars by us and other workers,[10] and we are investigating these processes. By counting of paper chromatograms the hexose content was shown to comprise less than 0·5% of the total sample. Nevertheless, since our experiments involved assaying small amounts of these hexoses by isotope dilution, every sample of [$^{14}$C]sucrose was purified by paper chromatography before use, and the [$^{14}$C]sucrose recovered by elution and freeze-drying.

In view of these precautions our results indicate definitely that hydrolysis to fructose and glucose is an important feature of the action of radiation on aqueous sucrose solutions. Wolfrom, Binkley, and McCabe [5] also observed hydrolysis when more concentrated sucrose solutions (50%) were irradiated, and found that the extent of apparent hydrolysis increased with increasing dose and varied with the temperature. The irradiations were carried out in open aluminium containers at ambient temperatures without oxygenation, and the degree of apparent hydrolysis measured by the copper reduction method of Somogyi.[11] The only products detected by these workers were D-fructose and D-glucose, the former by paper chromatography and the latter as the penta-acetate. Beyond these general observations, it is not possible to make a closer comparison of our results and those of Wolfrom *et al.*[5] in view of the different experimental conditions.

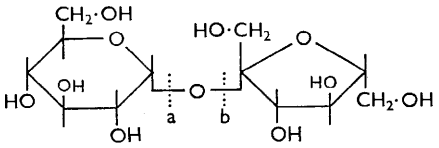
In our experiments the yield–dose curves for fructose and glucose were computed by isotope dilution (Fig. 7) and counting of paper chromatograms (Fig. 6); they indicate that fructose and glucose are primary products formed at comparable rates. The isotope dilution results give initial $G$ values for glucose and fructose as 1·5—1·6, and for fructose there is reasonable agreement between the two methods, since the initial $G$(fructose) is 1·4 from paper-chromatogram counts. For glucose, however, the initial $G$ values given by the two methods do not agree. The paper-chromatogram counts (Fig. 6) show a higher rate of formation than does isotope dilution (Fig. 7), which indicates that another product is formed which has the same $R_F$ as glucose. We consider that the presence of glucosone ($R_F$ 0·18 in butan-1-ol–acetic acid–water) in the irradiated solution is responsible for the divergence, and its presence was confirmed by isotope dilution (Table 3). The yield–dose curve for this compound obtained from individual isotope dilution experiments (Fig. 8) shows that it is a primary product with initial $G$ value 0·6. When allowance is made for its presence of this compound in the composite spot at $R_F$ 0·18, the initial $G$(glucose) from paper-chromatogram counts is 1·5, in excellent agreement with isotope-dilution value.

The other products detected in small amounts in irradiated sucrose solutions are gluconic acid, glucuronic acid, arabinose, and two-carbon and three-carbon aldehydic fragments. The yield–dose curve for these products which are present in small amount indicate that gluconic acid is the only primary product (initial $G$ 0·4) among them. The remainder appear to be secondary products formed by degradation of fructose and glucose liberated in the initial step. Their rates of formation increase sharply with dose at a stage where there is observable degradation of the primary products. The pattern of radiation

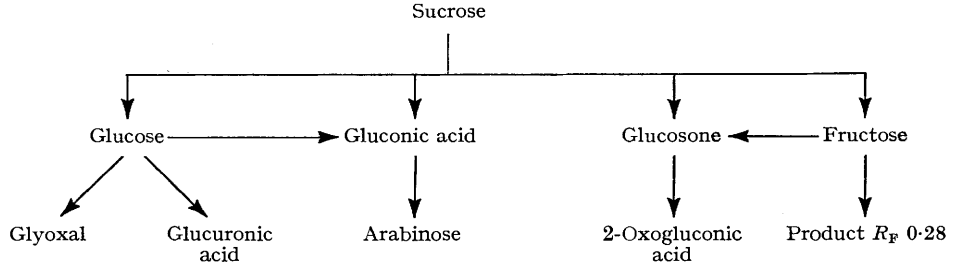
[10] Personal communication, Professor E. J. Bourne, Dr. H. Weigel, and Dr. R. J. Bayly.
[11] Somogyi, *J. Biol. Chem.*, 1952, **22**, 195.

degradation of these hexoses [1,6] described previously supports this view. Although a detailed yield–dose curve for the three-carbon fragment is not presented, the previous results with glucose and fructose support the view that it is a secondary product.

The primary formation of gluconic acid and glucosone simultaneously with glucose and fructose may be accounted for by two types of oxidative scission of the disaccharide linkage at a and b. The former leads to fructose and gluconic acid, and the latter to glucose and glucosone. A similar type of process may be envisaged for the degradation of aqueous dextran with gamma-radiation.[12] If the two types of scission occurred to a comparable extent, the amounts of the four main products would be of the same order. The results show, however, that while comparable amounts of gluconic acid and glucosone are formed, the proportions of glucose and fructose are higher. It appears, therefore, that hydrolysis is the dominant process but accompanied, to a smaller extent, by the oxidative scission already described. During the later stages of the degradation gluconic acid and glucosone are probably also formed by secondary attack on the primary products, glucose and fructose respectively. For gluconic acid particularly, the yield–dose curve at high




doses (Fig. 8) indicates an appreciable contribution to the yield from glucose. From the detailed degradation patterns of these hexoses [1,6] it is probable that glyoxal, glucuronic acid, and arabinose are also secondary products from glucose. The unknown spot of $R_F$ 0·28 and 2-oxogluconic acid, previously identified as degradation products from fructose, are probably derived from this source in the present system. On the basis of the present results, therefore, the over-all degradation pattern for sucrose may be formulated as follows:




The yield–dose curves (Fig. 2) for carbon dioxide and volatile acid support the view [1] that carbon dioxide and formic acid are final products in the degradation.

The absorption spectrum of sucrose solutions irradiated in oxygen shows features similar to those for irradiated fructose solutions. The absorption maximum appears at 275 mμ and moves to 295 mμ on addition of alkali (Fig. 3). Addition of acid, however, to the irradiated sucrose causes the peak to shift to 265 mμ; and this behaviour has not previously been observed for irradiated fructose solutions. Although the spectrum is complex owing to the presence of several constituents, the similarities between the spectra and those of irradiated glucose and fructose solutions indicate that secondary products formed from these hexoses are mainly responsible.

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[1] Phillips and Moody, *J.*, 1958, 3534.