680. *Radiation Chemistry of Carbohydrates. Part VI.* Action of Gamma-radiation on Aqueous Solutions of* D-*Mannose in Oxygen.*

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Paper-chromatographic and radioactive-tracer methods showed that gamma-irradiation of oxygenated D-mannose solutions gives D-mannuronic acid, D-mannonic acid, D-arabinose, D-erythrose, two-carbon aldehydic fragments, formic acid, and carbon dioxide. Changes in acidity, absorption spectra, and the rate of formation of hydrogen peroxide were measured.

Primary and secondary products are distinguished by reference to the yield–dose curves which were obtained from isotope dilution analysis and paper chromatography; there is good agreement between the two methods.

Experiments using D-[1-^{14}C]mannose indicate directly that the primary degradation processes are (*a*) oxidation at $C_{(6)}$ and $C_{(1)}$ to give mannuronic acid and mannonic acid respectively, (*b*) direct scission between $C_{(1)}$ and $C_{(2)}$ to form D-arabinose and formaldehyde, and (*c*) scission between $C_{(2)}$ and $C_{(3)}$ to give D-erythrose and a two-carbon aldehydic fragment with, simultaneously, direct conversion of the hexose molecule into three two-carbon aldehydic fragments. These account for 80% of the initial amount of D-mannose degraded (*G* 3·5).

The results also indicate secondary formation of D-arabinose, D-lyxose, oxalic acid, formic acid, and carbon dioxide.

This study of the effect of gamma-radiation on aqueous D-mannose in oxygen follows our work on D-glucose.[1] Our preliminary note [2] stated that in dilute solution mannuronic acid was formed. Our later work revealed several other products. These were identified and estimated by chromatographic, spectroscopic, and isotope dilution methods. As far as we are aware, no other chemical study of the effect of ionising radiations on D-mannose solutions has been reported.

Results and Experimental

The ^{60}Co source and techniques used in this investigation are similar to those described previously.[1] Two dose rates were employed. In the large cell (100 ml.) the dose rate was $1{\cdot}60 \times 10^{17}$ and in the small (vol. 40 ml.) was $1{\cdot}07 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$.

Chromatographic Analysis of Irradiated Solutions.—A solution of D-mannose (5·56 millimoles) in water (100 ml.) was irradiated to a total energy input of $6{\cdot}65 \times 10^{22}$ ev, and chromatographed with butan-1-ol–acetic acid–water (4 : 1 : 5) with *p*-anisidine as spray reagent. The following spots were revealed: brown, R_F 0·21, mannose; pink, R_F 0·04 (faint); pink, R_F 0·11; pink, R_F 0·15; pink, R_F 0·21; bright yellow, R_F 0·42. When silver nitrate was used as a spray

* Part V, preceding paper.

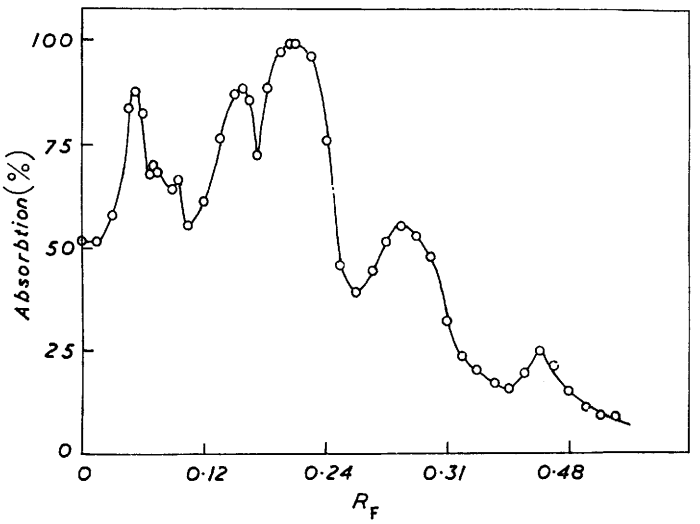
[1] Phillips, Moody, and Mattok, *J.*, 1958, 3522.
[2] Phillips, *Nature*, 1954, **173**, 1044.

reagent the spot of R_F 0·04 was very pronounced, indicating the presence of a non-reducing acid in addition to the reducing component revealed by *p*-anisidine. When the irradiated solution was concentrated by freeze-drying a further spot was observed at R_F 0·08, and at high energy inputs (*ca.* 1·3 × 10^{23} ev) a pink spot of R_F 0·25 was detected, corresponding to lyxose.

The irradiated solution was treated with phenylhydrazine and acetic acid at 100° for 30 min., and the precipitated osazones were separated by circular paper chromatography.[3] This method indicated the presence of mannosazone (glucosazone), R_F 0·04, and erythrosazone, R_F 0·50.

A solution (100 ml.) of [1-^{14}C]mannose (5·56 millimoles, *ca.* 25 μc) was irradiated to a total energy input of 6·7 × 10^{22} ev. After chromatography, the autoradiographs showed a pattern similar to that revealed by spray reagents. The autoradiographs were scanned by using a Hilger photoelectric densitometer, and Fig. 1 shows the intensities of the individual spots,

FIG. 1. *Density of spots on autoradiograph, giving a measure of* ^{14}C *concentration along the paper chromatogram.*



giving a direct measure of the ^{14}C concentration along the paper chromatogram. The high background confirms the pronounced streaking indicated by spray reagents. Table 1 shows the main organic constituents indicated by paper chromatography and autoradiography in the irradiated solution.

TABLE 1. *Constituents in* D-*mannose solution after irradiation.*

Autoradiograph	Colour	R_F	Product
I	Faint pink	0·04	Mannonic and mannuronic acid
II, III	Pink	0·10—0·12	Mannurono-δ-lactone and possibly 2-oxogluconic acid
IV	Pink	0·15	Mannono-δ- and -γ-lactone
V	Brown	0·21	Mannose and arabinose
VI	—	0·31	Mannono-γ-lactone
VII	Bright yellow	0·42	Erythrose

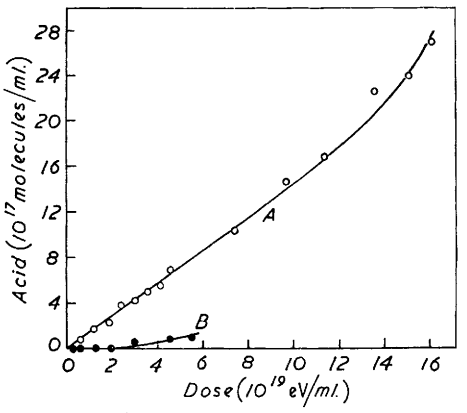
The distillate from the irradiated solution was trapped in a receiver cooled in liquid air, and treated with excess of ammonia solution. After removal of the solvent under reduced pressure, the solid was chromatographed in 95% ethanol–ammonia (*d* 0·88) (100 : 1).[4] Spraying with Bromocresol Green in absolute ethanol [5] revealed a blue spot on a yellow background, of R_F 0·31, which corresponded to ammonium formate, and indicated the presence of formic acid in the irradiated solution.

Acid Formation.—On the assumption that the acids formed are monobasic, Fig. 2 shows

[3] Barry and Mitchell, *J.*, 1957, 4020.
[4] Kennedy and Barker, *Analyt. Chem.*, 1951, **23**, 1033.
[5] Block, Durrum, and Zweig, "Paper Chromatography and Paper Electrophoresis," Academic Press, New York, 1955, p. 160.

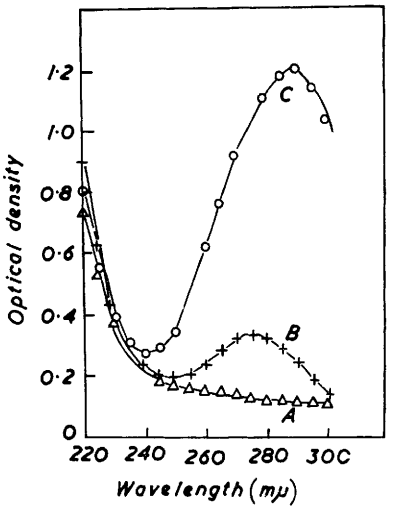
the rate of acid formation with energy input, indicating initial G(acid) 1·6. No variation in G value was observed within a ten-fold variation in mannose concentration. The fall in pH with energy input is shown in Table 2. The rate of formation of volatile acid with energy input is also shown in Fig. 2.

FIG. 2. *Acid formation during irradiation of* D-*mannose solutions in oxygen.*



A, Total acid; B, volatile acid (×10).

FIG. 3. *Ultraviolet absorption spectra of irradiated* D-*mannose solutions* (40 ml.).



A, Unirradiated D-*mannose; B,* D-*mannose after energy input of* 2·5 × 10^{21} ev; *C, as B but with added* $KHCO_3$.

FIG. 4. *Increase in ultraviolet absorption at* 275 mμ *during irradiation of aqueous* D-*mannose solution* (40 ml.).

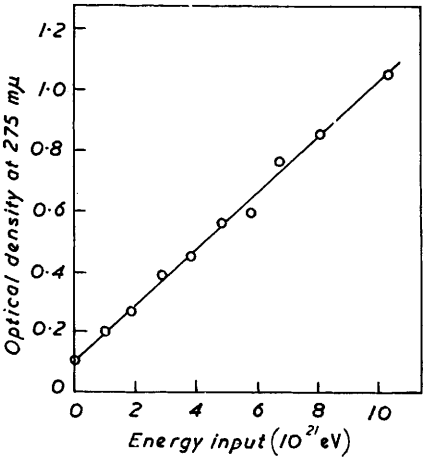
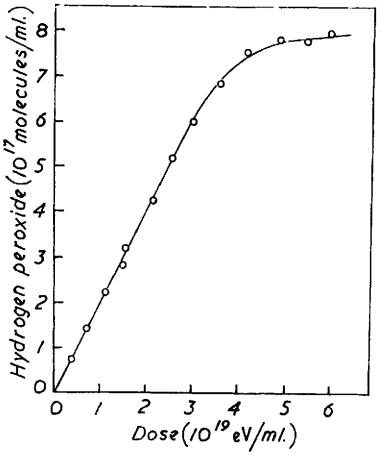


FIG. 5. *Formation of hydrogen peroxide during irradiation of* D-*mannose solutions.*



Absorption Spectra of Irradiated Solutions.—A typical ultraviolet absorption spectrum of an irradiated mannose solution is shown in Fig. 3, in comparison with an unirradiated solution. Addition of potassium hydrogen carbonate modifies the spectrum considerably. Fig. 4 shows the increase in ultraviolet absorption with energy input.

Hydrogen Peroxide Formation.—Hydrogen peroxide was estimated by using titanium

TABLE 2. *Change in* pH *during irradiation of* D-*mannose solutions.*

Dose (10^{19} ev ml.$^{-1}$)	0·6	1·2	2·4	3·6	4·8	6·0	13·2	21·0	27·6
pH	6·25	6·15	5·90	5·70	5·65	5·55	5·25	5·15	5·00

sulphate solution,[6] and the results are shown in Fig. 5. After an initial constant rate of formation with initial G value 1·9, there is extensive degradation of hydrogen peroxide, and equilibrium is established at *ca.* 5×10^{19} ev ml.$^{-1}$. We observed a post-irradiation fall in hydrogen peroxide concentration at a rate of $3{\cdot}2 \times 10^{13}$ molecules ml.$^{-1}$ min.$^{-1}$.

Estimation of Products by the Isotope Dilution Method.—The main products were estimated by application of isotope dilution analysis directly to the untreated irradiated solutions. In a typical experiment, an aqueous solution (100 ml.) of D-mannose (5·56 millimoles) of specific activity 3·6 μc/millimole was irradiated at a dose rate of $1{\cdot}60 \times 10^{17}$ ev ml.$^{-1}$ min.$^{-1}$ in oxygen for 39 hr. The following constituents were estimated:

Mannose. Mannose phenylhydrazone was prepared according to Bourquelot and Hérissey's directions.[7] The irradiated solution (5 ml.) was treated with carrier D-mannose (1·08 millimoles), acetic acid (0·5 ml.), and phenylhydrazine (1·0 ml.). After 8 hr. at 5°, the solid hydrazone which separated was recrystallised five times from aqueous ethanol and gave pure mannose phenylhydrazone, m. p. 185°, constant specific activity 0·50 (μc/millimole).

Arabinose. The irradiated solution (5 ml.) and carrier D-arabinose (1·12 millimoles) were refluxed for 30 min. with ethanol (15 ml.) and diphenylhydrazine.[8] After 24 hr. a solid was separated, which on six recrystallisations from ethanol gave pure arabinose diphenylhydrazone, m. p. 196°, constant specific activity (0·058 μc/millimole).

Lyxose. The irradiated solution (5 ml.) was heated with carrier D-lyxose (1·0 millimole), acetic acid (1·0 ml.), and phenylhydrazine (2·0 ml.) at 100° for 20 min. Water (5 ml.) was added, and the solid which separated was chromatographed in ethanol on a column of calcined aluminium oxide. Continued elution with ethanol removed the lyxosazone band. This material was again chromatographed and twice recrystallised from benzene, giving lyxosazone, m. p. 159°, constant specific activity (0·01 μc/millimole).

Two-carbon aldehydic fragments. The irradiated solution (5 ml.) was treated with carrier glyoxal (2·0 millimoles), acetic acid (1·0 ml.), and phenylhydrazine (2·0 ml.). The product, after eight recrystallisations from benzene, gave pure glyoxal bisphenylhydrazone, m. p. 170°, constant specific activity (0·015 μc/millimole).

1,3-*Dihydroxyacetone.* The irradiated solution (10 ml.) was heated with carrier 1,3-dihydroxyacetone (1·23 millimoles), acetic acid (1·0 ml.), and phenylhydrazine (2·0 ml.) for 10 min. The solid which separated on addition of water (5 ml.) was recrystallised eight times from benzene, to give glycerosazone, m. p. 129°, constant specific activity (0·007 μc/millimole).

Formaldehyde. The irradiated solution (5 ml.) was distilled under reduced pressure and the distillate trapped in liquid air. Carrier formaldehyde (0·226 millimole), 10% ethanolic dimedone (10 ml.), and ethanol (50 ml.) were added to the distillate. After 48 hr. the dimedone complex was separated and crystallised from ethanol until it had m. p. 189° and constant specific activity (0·018 μc/millimole).

Oxalic acid. The syrup obtained during the formaldehyde estimation was treated with carrier oxalic acid (1·00 millimole) and dissolved in water (2·0 ml.). Eight recrystallisations gave pure oxalic acid, m. p. 99°, constant specific activity (0·001 μc/millimole).

Mannonic acid. In an independent experiment an aqueous solution (30 ml.) of mannose (1·66 millimoles) of specific activity 3·5 μc/millimole was irradiated for 24 hr. at a dose rate of $1{\cdot}07 \times 10^{17}$ ev min.$^{-1}$ ml.$^{-1}$. The irradiated solution (5 ml.) was treated with carrier D-mannono-γ-lactone (0·6 millimole) and excess of freshly precipitated calcium carbonate. The solution was filtered after 24 hr., then evaporated to 1 ml., and hot ethanol was added to precipitate calcium mannonate. Ten recrystallisations were necessary to give pure calcium mannonate with constant specific activity of 0·14 μc/millimole.

Mannuronic acid. Attempts to prepare suitable crystalline derivatives of mannuronic acid for isotope dilution analysis were unsuccessful. Estimations were attempted with the limited amounts of barium mannuronate which were available as carrier. However, no values can be quoted since pure barium mannuronate of constant specific activity was not isolated even after twelve recrystallisations.

Table 3 shows the yields of products at two energy inputs ($3{\cdot}7 \times 10^{22}$ and $2{\cdot}25 \times 10^{23}$ ev) under fully oxygenated conditions.

Rate of Formation of Products.—In order that accurate initial G values could be evaluated

[6] Eisenberg, *Ind. Eng. Chem., Analyt. Ed.*, 1943, **15**, 327.
[7] Bourquelot and Hérissey, *Compt. rend.*, 1899, **129**, 339.
[8] Neuberg and Wohlgemut, *Z. physiol. Chem.*, 1902, **35**, 31.

for the main products, individual estimations by the isotope dilution method were carried out at varying energy inputs. For this purpose D-[1-^{14}C]mannose solutions (30 ml.) with specific activities 3·5—3·6 μc/millimole were independently irradiated at a dose rate of $1·07 \times 10^{17}$

TABLE 3. *Products when aqueous* D-*mannose is irradiated with gamma-radiation in oxygen.*

(*a*) Initial mannose, 5·6 millimoles.

Energy input, $3·7 \times 10^{22}$ ev (vol. 100 ml.).

Product	D-Mannose	D-Arabinose	D-Lyxose	Glyoxal	1,3-Dihydroxy-acetone	$H_2C_2O_4$	CH_2O
Carrier (millimoles)	1·08	1·12	1·00	2·00	1·23	1·00	0·23
Specific activity (μc/millimole)	0·50	0·058	0·01	0·015	0·007	0·001	0·018
Yield (millimoles)	3·5	0·44	0·06	0·40	0·05	0·04	0·18

Sugar acids estimated from paper chromatography	0·46 millimole
Erythrose estimated from paper chromatography	0·12 millimole
Carbon dioxide determined gravimetrically	0·03 millimole
Formic acid determined as volatile acid by titration	0·22 millimole

(*b*) Initial D-mannose, 5·48 millimoles.

Energy input, $2·25 \times 10^{23}$ ev.

Product	D-Mannose	D-Arabinose	D-Lyxose	Glyoxal	1,3-Dihydroxy-acetone	$H_2C_2O_4$	CH_2O
Carrier (millimoles)	1·0	1·03	0·95	2·22	1·13	1·60	0·22
Specific activity (μc/millimole)	0·048	0·062	0·040	0·057	0·038	0·093	0·033
Yield (millimoles)	0·16	0·26	0·17	1·40	0·31	0·74	0·18

Sugar acids estimated from paper chromatography	0·57 millimole
Erythrose estimated from paper chromatography	0·69 millimole
Carbon dioxide determined gravimetrically	2·33 millimole
Formic acid determined as volatile acid by titration	6·34 millimole

ev min.$^{-1}$ ml.$^{-1}$, doses varying from $2·2 \times 10^{19}$ to $13·2 \times 10^{19}$ ev ml.$^{-1}$. Mannose, arabinose, lyxose, glyoxal, oxalic acid, and formaldehyde were estimated at varying dose levels by applying the isotope dilution method to the untreated irradiated solution as described above. The results are shown in Figs. 6 and 7. Initial *G* values calculated from these curves are as follows: mannose (rate of consumption) 3·5; arabinose 0·5; formaldehyde 0·3; glyoxal 0·64.

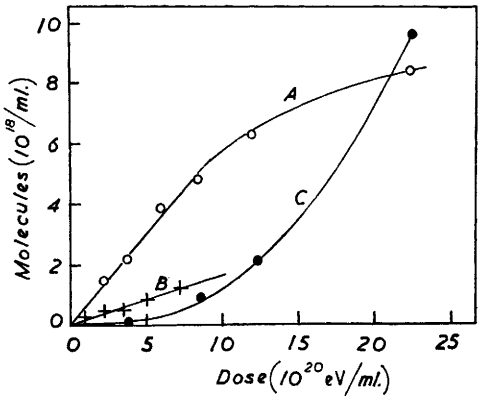
Experiments were carried out with D-[1-^{14}C]mannose to provide information about the mechanism of formation of formaldehyde and glyoxal. [1-^{14}C]Mannose solutions (30 ml.) with specific activity of 3·65 μc/millimole were irradiated at a dose rate of $1·07 \times 10^{17}$ ev. min.$^{-1}$ ml.$^{-1}$, doses ranging from 1·0 to $7·1 \times 10^{20}$ ev ml.$^{-1}$. [^{14}C]Glyoxal and [^{14}C]formaldehyde were estimated by isotope dilution. The results are shown in Figs. 6 and 7. [1-^{14}C]Arabinose was also estimated, but the diphenylhydrazone isolated proved to be inactive, indicating that scission occurs at the 1,2-bond to form [^{14}C]formaldehyde and inactive arabinose. The carbon dioxide formed during the irradiation was determined by passing the oxygen stream escaping from the irradiation cell through barium hydroxide, the carbonate precipitated being weighed (Fig. 8).

Formic acid was determined by direct titration of the distillate from the irradiated solution after it had been trapped in a receiver cooled in liquid air (Fig. 2).

Yield–dose curves for several of the products were obtained by paper chromatography. Accurately known amounts of irradiated D-[^{14}C]mannose solution which had received progressively increasing doses of radiation were chromatographed and the radioactivity of the spots measured (Fig. 9). The rate of formation with energy input was measured for erythrose, which runs as an independent spot and for the total amount of sugar acids running at positions I, II, III, and IV (Table 1) since these acids and lactones cannot be conveniently separated as independent spots. When these measurements were carried out, mannono-γ-lactone (VI) had not been detected by autoradiography, and is not therefore included. Fig. 1 indicates, however, that this lactone represents up to 20% of the total sugar acids present. Since mannose and

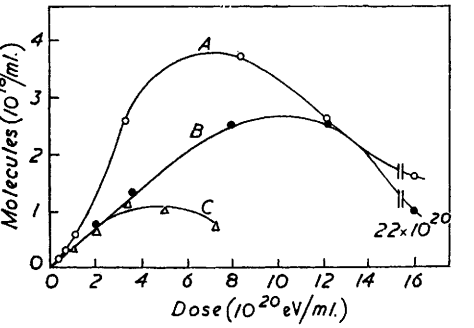
arabinose run at the same position on paper chromatograms in butan-1-ol–acetic acid–water we have measured the over-all change in radioactivity resulting from a fall in mannose concentration and the formation of arabinose (Fig. 9). The individual yield–dose curves for disappearance of arabinose and mannose are accurately known from isotope dilution measurements (Fig. 6 and 7); correlation is therefore possible between the two methods. Thus we calculate initial G (arabinose) from paper chromatography to be 0·6 (based on G 3·5 for disappearance of

FIG. 6. *Rate of formation of products in oxygenated* D-*mannose solutions determined by isotope dilution.*



A, Two-carbon aldehydic fragments; B, two-carbon aldehydic fragments from D-[1-^{14}C]*mannose; C, oxalic acid.*

FIG. 7. *Rate of formation of products during irradiation of oxygenated* D-*mannose solutions, determined by isotope dilution.*



A, D-*Arabinose; B, formaldehyde; C, formaldehyde from* D-[1-^{14}C]*mannose.*

FIG. 8. *Rate of formation of carbon dioxide from oxygenated* D-*mannose solutions* (100 ml.).

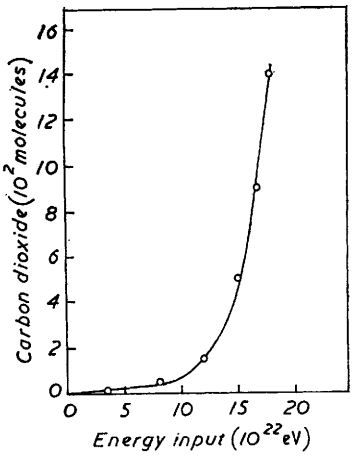
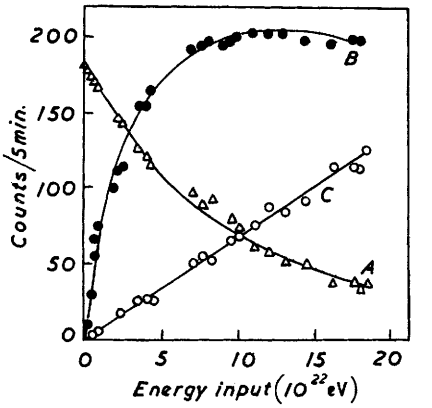


FIG. 9. *Rate of formation of products during irradiation of oxygenated* D-*mannose solution* (100 ml.), *determined by paper chromatography.*



A, D-*Mannose +* D-*arabinose* ($\times 10^{-1}$); *B, sugar acids + lactones; C,* D-*erythrose.*

mannose). The comparable value from isotope dilution is 0·5. On a similar basis we calculate G(sugar acids) from paper chromatography to be 1·4, which is to be compared with the direct value 1·6 from titration. Initial G(erythrose) is 0·18 from paper chromatography.

Discussion

Paper chromatography and isotope dilution analysis indicate that a number of products are formed when D-mannose solutions are irradiated in oxygen. Table 3 shows the nature and amounts of the main products after total energy inputs of $3{\cdot}7 \times 10^{22}$ and $2{\cdot}25 \times 10^{23}$

ev. In these analyses, the sum of the products and unchanged mannose account for 85% and 72% by weight respectively of the original mannose present. It is evident that at high energy inputs part of the complexity of the system is due to secondary degradation of the primary products. Therefore, to elucidate the nature of the primary degradation, particular attention was given to the yield–dose curves for the main products at low energy inputs.

The formation of acid (Fig. 2) is a primary process and the acid yield is independent of mannose concentration, indicating that the radiation energy is absorbed by the water, and that chemical reactions are initiated by the reactive species formed. Since the rate of acid formation increases with energy input, it appears that acids are also formed by secondary processes, possibly formic acid. Initially negligible amounts of this acid are present (Fig. 2) but at high energy inputs the proportion is appreciable (Table 3*b*). From paper-chromatographic evidence it is probable that mannonic and mannuronic acid are formed. Presence of the former was confirmed by isotope dilution analysis, but as previously noted difficulties were encountered in preparing pure samples of mannuronic acid derivatives for combustion. From paper chromatography, initial G for acid formation is 1·4, which is in reasonable agreement with the value from titration (G 1·6) particularly when it is recalled that the paper chromatographic value is approximately 20% low because the amount of mannono-γ-lactone was not estimated. Isotope dilution gives initial G for mannonic acid 0·6—0·7, but this value is calculated from only one measurement and is thus subject to error. Autoradiographs (Fig. 1) and radioactive measurements support the view that mannuronic acid represents the major portion of the remainder of the acid which is formed initially.

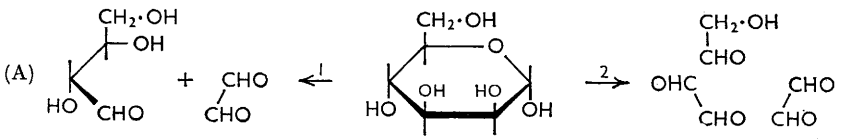
Arabinose is the main pentose formed during irradiation. Isotope-dilution and paper-chromatographic measurements reveal that it is a primary product with initial G 0·5—0·6. The rate of formation increases at higher energy inputs, indicating that arabinose is formed by a secondary process also. During the irradiation of D-glucose solutions in oxygen [1] a similar yield–dose curve was obtained for arabinose, it being concluded that this pentose was a secondary product only. The more accurate measurements now reported for irradiated D-mannose solutions, particularly at low energy inputs, support the view that arabinose is formed by primary and by secondary processes. The primary formation arises as a result of the scission of the 1,2-bond, while decarboxylation of mannonic acid may account for the secondary formation.

The primary scission of the 1,2-bond to form arabinose probably also leads to formaldehyde, which our results indicate is a primary product with initial G 0·3. The lower initial yield of formaldehyde than of arabinose may be accounted for by the loss of formaldehyde in the oxygen stream. Our experiments with D-[1-^{14}C]mannose confirm the view that formaldehyde formed during the primary degradation comes by direct scission of the 1,2-bond. Initially the yield–dose curve for formaldehyde from D-[1-^{14}C]mannose and D-[^{14}C]mannose (generally labelled) are identical, but at increased energy inputs the apparent yield of formaldehyde from D-[1-^{14}C]mannose decreases (Fig. 7). Since in the latter estimation only [^{14}C]formaldehyde is measured, the fall in concentration probably results from dilution by formaldehyde formed from the remaining inactive portion of the mannose molecule. We have also confirmed that arabinose formed in [1-^{14}C]mannose experiments is inactive.

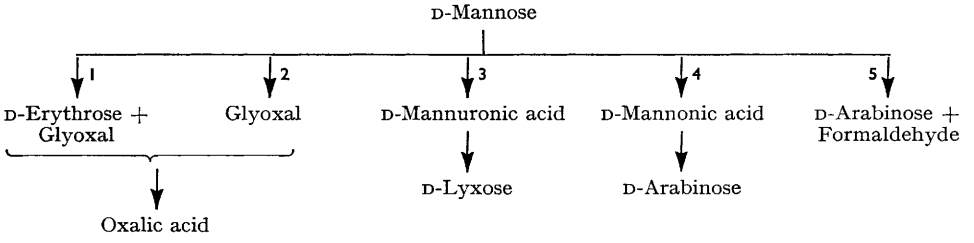
D-Lyxose, the remaining pentose detected in the irradiated solution, was present only in small amount at high energy inputs. It may therefore be formed by decarboxylation of mannuronic acid by a secondary process.

Our results indicate that primary scission of the hexose molecule into four- and two-carbon aldehydic fragments occurs. Although erythrose and glyoxal are the most probable products from a scission of this type, our estimations by isotope dilution analysis do not distinguish between them and other similar fragments which form identical osazones on treatment with phenylhydrazine in acetic acid. The yield–dose curve for two-carbon

fragments is shown in Fig. 6, giving an initial G value 0·64. Experiments with D-[1-^{14}C]-mannose allow a more detailed description of this process. This method measures the primary formation of two-carbon fragments which contain [^{14}C] and thus are formed by scission of the 2,3-bond; this process should lead also to simultaneous formation of a four-carbon fragment. Initial G value for two-carbon fragments derived from ^{14}C measurements is 0·2, which is in reasonable agreement with initial G(erythrose) 0·18, calculated from paper-chromatogram measurements. The appreciable difference between these values and the overall formation of two-carbon fragments (G 0·64) leads to the conclusion that such fragments must be formed by two primary processes which may be represented as in (A). Further oxidation of glyoxal to form oxalic acid occurs (Fig. 6), but this appears to be a secondary process.



Symmetrical scission of the hexose molecule into three-carbon fragments only occurs to a small extent (Table 3) and is less than we observed for irradiated D-glucose solution in oxygen.[1] This rather different behaviour may be related to the fact that maximum absorption for irradiated mannose solutions occurs at 275 mμ, and on addition of alkali moves to 290 mμ with pronounced increase in intensity. Glucose solutions show maximum absorption at 265 mμ, which we previously related to the presence of 1,3-dihydroxyacetone which absorbs at this wavelength in acid solution. However, it is possible that more than one constituent may account for the resultant absorption spectrum. Enediols in general would be expected to absorb strongly in this region,[9] and in particular reductone, a possible constituent present in irradiated mannose solution, absorbs at 290 mμ in alkali.[10] The overall consumption of mannose during irradiation shows initial G 3·5, in excellent agreement with glucose irradiations (G 3·5), and in broad outline the patterns of degradation for the two hexoses are similar. For mannose the degradation may be accounted for by the processes shown in the chart. Reactions 1 and 2 together proceed with combined initial



G 0·64, the initial rate of formation of the two-carbon aldehyde fragments; D-erythrose is produced simultaneously with initial G 0·18. We have observed two primary processes leading to acid formation (reactions 3 and 4), and the total initial acid yield is G 1·4—1·6, the former being derived from paper chromatography and the latter by direct titration. Isotope dilution indicates that mannonic acid (reaction 4) is produced with initial G 0·6—0·7. The initial formation of arabinose occurs by scission of the 1,2-bond (initial G 0·5—0·6) and is accompanied by formation of formaldehyde. Thus the primary process

[9] Grant and Ward, *J.*, 1959, 2871.
[10] von Euler, Hasselquist, and Hanshoff, *Arkiv Kemi*, 1953, **6**, 471.

which we have identified proceeds with initial G 2·84. In comparison with the rate of consumption of mannose, therefore, it appears that we have accounted for the main degradation processes, although a further degradative path is not precluded.

UNIVERSITY COLLEGE, CARDIFF. [*Received, February 18th*, 1960.]