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# Oxidative Degradation of Monosaccharides by Iron(III) Chlorides with a Near-UV to Visible Light under Aerobic Atmosphere

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Monosaccharides were oxidatively degraded by $FeCl_3$ with irradiation of a near-UV to visible light under aerobic atmosphere. D-Fructose and D-arabinose were degraded to D-erythrose in a yield of more than 80 mol%. D-Glucose and D-mannose were at first degraded to D-arabinose, which was subsequently degraded to D-erythrose. While, D-ribose was directly degraded to D-erythrose and D-glyceraldehyde. The degradation processes were selective, and these reactions were shown to proceed *via* formation of an Fe(III)-monosaccharide complex. The kinetic data and other features of these reactions were also discussed.

Carbohydrate is one of the main components of living organisms bearing variety of functions, and is the most abundant organic resources in nature.[1] Many metal ions are known to form complexes with carbohydrates and other polyhydroxy compounds, and these complexes are the subject of intense studies because of their physiological and clinical importances.[2-8] Among them, an Fe(III)-carbohydrate complex has been studied by several workers in relation to its potential use for the treatment of iron-deficient anemia.[5-8] However, only a little has been known as to the photochemical properties of these complexes.[9]

Photooxidation of organic substrates by an aqueous Fe(III) ion has been studied for long time,[10] and alcohols are known to be oxidized to give the corresponding aldehydes or ketones in high yields.[11,12] The photoreaction was suggested to proceed by radical processes,[13] and, therefore, the reaction was inhibited by the presence of oxygen.[11,12]

In the preceding letter, we reported that photooxidation of D-fructose by $FeCl_3$ gave D-erythrose in a high yield and that the reaction proceeded even under aerobic conditions *via* formation of an Fe(III)-D-fructose complex.[14] Since this finding might imply physiological importance, we further extended this study, and we now wish to report the more detailed studies of the photooxidation of D-fructose and several other monosaccharides by $FeCl_3$ under aerobic conditions.

## Experimental

*Materials and Photoreactions.* D-Erythrose was purchased from Aldrich Chem. Co., and other monosaccharides were obtained from Wako Pure Chem. Ind. Ltd. Other chemicals were also commercial products, and some of them were purified by conventional methods before use.

Sample solutions were prepared freshly with deionized water, and 70 or 500 ml of the solution was irradiated internally under aerobic conditions. For the irradiation under anaerobic conditions, the solution was degassed by three times of freeze-thaw cycles. Light-source was a 100 W high-pressure mercury lamp (Type UM-102, Ushio Electric Inc.) fitted in a Pyrex-made double jacket. The jacket and the reaction vessel were kept at 20 °C by circulating water during irradiation.

For the measurement of quantum yield, a CRM-FA spectroirradiator with a 2 kW Xenon lamp (JASCO) was used. Sample solutions in quartz cells were irradiated by the light of known wavelength and energy at 20 °C.

*Analyses.* Decrease of pH of a solution during photoirradiation was monitored by a HM-20B pH meter (Toa Electronics Ltd.). The amount of $H^+$ formed was determined by titration of the irradiated solution with a 0.2 M† NaOH solution. Absorption spectra were recorded by a UVIDEC 505 spectrophotometer (JASCO) at 20 °C, and Fe(III) concentration of a sample solution was determined from the absorbance at 330 nm after 500 times of dilution with a 0.2 M HCl solution.

The irradiated solution was deionized by Amberlite IR-120 ($H^+$ form) and IRA-410 ($HCO_3^-$ form) (Rohm & Haas Co.), and then water was evaporated to give a colorless syrup. The syrup was analyzed by the following three chromatographic methods; 1) high-performance liquid chromatography (HPLC) (TSK-GEL LS-450$NH_2$, 300×4 (ID) mm; $CH_3CN$ 85%-$H_2O$ 15%) with a RI-8 refractometer (Toyo Soda Manufacturing Co., Ltd.); 2) gas-liquid chromatography (GLC) after acetylation of the syrup with *N*-methylimidazole-acetic anhydride according to the method of Wachowiak and Connors[15] (Type G-2800 gas chromatograph, Yanaco; Silicone OV-17, 2000×3 (ID) mm); and 3) thin-layer chromatography (TLC) after treating the syrup with 2,4-dinitrophenylhydrazine hydrochloride (DNPH)-1,2-dimethoxyethane (DME) according to the method of Honda *et al.*[16] (Silica Gel 60$F_{254}$, E. Merck A G.; $CHCl_3$ 80%-$CH_3OH$ 20%). The mass spectrum of the pre-acetylated sample after gas chromatographic separation was recorded by a JMS-DX300 mass spectrometer (JEOL).

Gases evolved from the irradiated solution were analyzed both by gas-solid chromatography (GC-4B gas chromatograph, Shimadzu; Molecular Sieve 5A or Unibeads 1S, 2000×3 (ID) mm) and mass spectrometry (RMU-7M high-resolution mass spectrometer, Hitachi, Ltd.).

## Results

*Oxidation of D-Fructose.* An $FeCl_3$ (0.25 M)-D-fructose (0.5 M) solution (70 ml), pH of which was 1.38, was irradiated for 3 h. The initial brown solution became colorless with considerable pH decrease after irradiation. Absence of Fe(III) and formation of Fe(II) were confirmed by color reactions with potassium thiocyanate and 1,10-phenanthroline, respectively.[17] A colorless syrup obtained from the irradiated solution (yield 95—98 wt% to the initial D-fructose) was subjected to further analyses. HPLC showed the consumption of D-fructose during photoirradiation. Gas chromatogram of the pre-acetylated sample indicated the existence of a single oxidation product, and the retention time of the peak of this product coincided with that of pre-acetylated D-erythrose. Structural information of this product was further derived from

† 1 M=1 mol $dm^{-3}$.

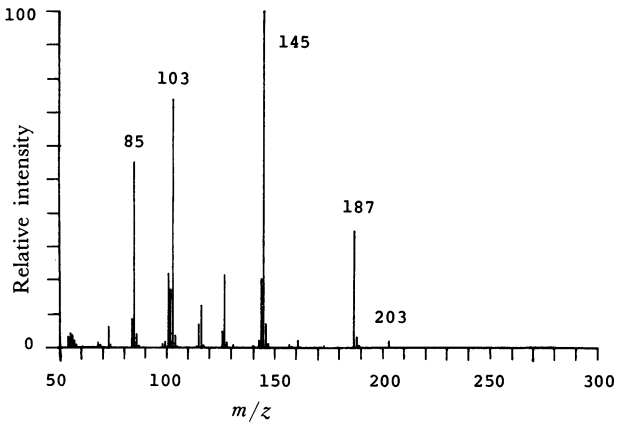


Fig. 1. The mass spectrum of the pre-acetylated oxidation product after gas chromatographic separation (23 eV E. I.).

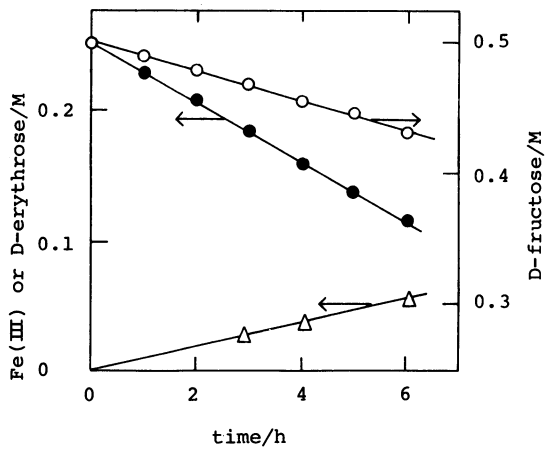


Fig. 2. Photoreaction of the $FeCl_3$ (0.25 M)–D-fructose (0.5 M) solution (500 ml) at 20°C. D-Fructose (○), Fe(III) (●), and D-erythrose (△) concentrations as a function of the irradiation time.

the GC-mass spectrometric analysis. The mass spectrum of the compound shown in Fig. 1 was found to be indistinguishable from that of D-erythrose triacetate (MW 246). Though no molecular ion peak was observed in the spectrum ($m/z_{max}$=203 at 23 eV E. I.), peracetyl derivatives of monosaccharides have been reported not to exhibit their molecular ion peaks.[18] In addition, the fragmentation pattern of the spectrum could reasonably be interpreted for D-erythrose triacetate based on the fragmentation pattern of other peracetylated monosaccharides.[18,19] Thus, the product was concluded to be D-erythrose. Quantitation of D-erythrose by GLC using dihydroxyacetone and/or caffeine as an internal standard revealed that D-erythrose comprised nearly 90 mol% of D-fructose oxidized, confirming that D-erythrose is the main product of the photooxidation of D-fructose.

Analysis of the syrup after treating with DNPH-DME showed several spots ($R_f$ valuses: 0.39 (major), 0.41 (minor), 0.54 (minor), and 0.81 (minor)) in addition to those corresponding to D-fructose (0.22) and unreacted DNPH (0.62). They were assigned to be due to D-erythrose (0.39 (major) and 0.41 (minor)), D-glyceraldehyde (0.53), and formaldehyde and/or glyoxal (0.80).

A small amount of gas evolution was also observed during photoirradiation. Gases evolved under anaerobic conditions were analyzed only qualitatively by gas chromatography and mass spectrometry, which indicated the formation of CO, $CO_2$, and $H_2$.

Based on these results, we concluded that the irradiation of a Pyrex-filtered light to an acidic $FeCl_3$–D-fructose solution induces mainly the oxidative degradation of D-fructose to D-erythrose.

Figure 2 shows the time course of the reaction for a 500 ml of an $FeCl_3$ (0.25 M)–D-fructose (0.5 M) solution irradiated under aerobic atmosphere. The amount of D-fructose and Fe(III) decreased linearly as a function of time with a concomitant linear increase in the formation of D-erythrose. Even when 70 ml of this solution was irradiated under the same conditions, Fe(III) decreased linearly with the same decreasing rate. Therefore, the reaction is dependent on the light intensity under our experimental conditions. No reaction proceeded without irradiation or in the absence of any one of the substrates.

Table 1 summarizes the results of irradiation under different conditions. In all cases, 2 mol of Fe(III) oxidatively degraded 1 mol of D-fructose to give 2 mol of $H^+$

TABLE 1. CHANGES IN THE SOLUTION COMPOSITION OF THE Fe(III)-D-FRUCTOSE SOLUTION AFTER IRRADIATION[a]

| Initial conditions | | | | Irradiation time/h | Changes after irradiation | | | |
|---|---|---|---|---|---|---|---|---|
| Fructose/M | Fe(III)/M | | Atmosphere | | Fructose/M | Fe(III)/M | $H^+$/M | Erythrose/M[b] |
| 0.5 | $FeCl_3$ | 0.25 | Anaerobic | 2 | −0.099 | −0.198 | +0.196 | +0.080 (81%) |
| 0.5 | $FeCl_3$ | 0.25 | Aerobic | 2 | −0.099 | −0.199 | +0.192 | +0.084 (85%) |
| 0.5[c] | $FeCl_3$ | 0.25 | Anaerobic | 2.5 | −0.112 | −0.224 | +0.220 | +0.092 (82%) |
| 0.5[c] | $FeCl_3$ | 0.25 | Aerobic | 2.5 | −0.112 | −0.226 | +0.222 | +0.097 (87%) |
| 0.5 | $Fe(NO_3)_3$ | 0.25 | Aerobic | 2.5 | −0.108 | −0.222 | +0.219 | +0.092 (85%) |
| 0.1 | $FeCl_3$ | 0.1 | Aerobic | 0.5 | −0.016 | −0.034 | +0.034 | +0.014 (88%) |
| 0.2 | $FeCl_3$ | 0.1 | Aerobic | 0.5 | −0.019 | −0.040 | +0.040 | +0.016 (84%) |
| 0.2 | $FeCl_3$ | 0.2 | Aerobic | 0.5 | −0.014 | −0.030 | +0.030 | +0.012 (86%) |
| 0.3 | $FeCl_3$ | 0.1 | Aerobic | 0.5 | −0.030 | −0.062 | +0.062 | +0.026 (87%) |
| 0.5 | $FeCl_3$ | 0.1 | Aerobic | 0.5 | −0.038 | −0.078 | +0.078 | +0.033 (87%) |
| 0.5 | $FeCl_3$ | 0.25 | Aerobic | 0.5 | −0.027 | −0.055 | +0.053 | +0.023 (85%) |

a) Sample solutions (70 ml) were irradiated internally at 20 °C. b) Conversion based on the D-fructose oxidized (mol%). c) Ref. 14.

according to the Eq. 1, and more than 80 mol% of D-fructose oxidized was converted to D-erythrose. Little

$$\text{D-fructose} + 2\text{Fe(III)} \xrightarrow{h\nu} \text{D-erythrose} + 2\text{Fe(II)} + 2\text{H}^+ \quad (1)$$

difference was observed for the reactions under aerobic and anaerobic atmosphere. These results are in good accordance with the earlier findings.[14] Use of $Fe(NO_3)_3$ instead of $FeCl_3$ did not practically alter the result, excluding the possible participation of counter anions in the reaction. Changes in the initial concentrations of the substrates did not affect the reaction scheme either. However, the reaction rate was sensitive to the initial substrate concentrations, and a higher D-fructose concentration increased the rate, while a higher Fe(III) concentration decreased the rate.

*Oxidation of* D-Glucose. Addition of D-glucose to an aqueous $FeCl_3$ solution caused the similar changes in color and pH of those observed when D-fructose was added. A brown $FeCl_3$ solution became reddish with a slight decrease in pH, suggesting the formation of an Fe(III)–D-glucose complex. Fig. 3 shows the difference spectrum between before and after addition of D-glucose to the Fe(III) solution, which is thought to represent the absorption due to the complex.

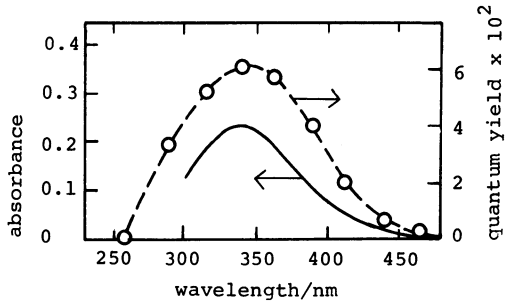


Fig. 3. The difference spectrum between before and after addition of D-glucose (——), and quantum yields of the reduction of Fe(III) (--O--) for the $FeCl_3$ ($2\times10^{-3}$ M)–D-glucose ($5\times10^{-1}$ M) solution at 20 °C.

Irradiation of a Pyrex-filtered light to an $FeCl_3$–D-glucose solution caused the reduction of Fe(III) with the concomitant consumption of D-glucose under aerobic atmosphere. Quantum yields of the reduction of Fe(III) at different wavelengths were also shown in Fig. 3, and this action spectrum coincided well with the difference spectrum, confirming that the Fe(III)–D-glucose complex is the photoreactive species. These photochemical properties of an $FeCl_3$–D-glucose solution were little different from those of an $FeCl_3$–D-fructose solution.

Colorless syrup was obtained from the irradiated solution (yield 96—100 wt% to the initial D-glucose). Analysis by HPLC and GLC indicated the formation of two products, D-arabinose and D-erythrose, as the main oxidation products. TLC after treating with DNPH also confirmed that these two compounds were the main products ($R_f$ for D-arabinose is 0.30) along with minor spots corresponding to those for D-glyceraldehyde and for formaldehyde and/or glyoxal. Thus, more than 80 mol% of D-glucose oxidized by $FeCl_3$ was found to be degraded to D-arabinose and D-erythrose.

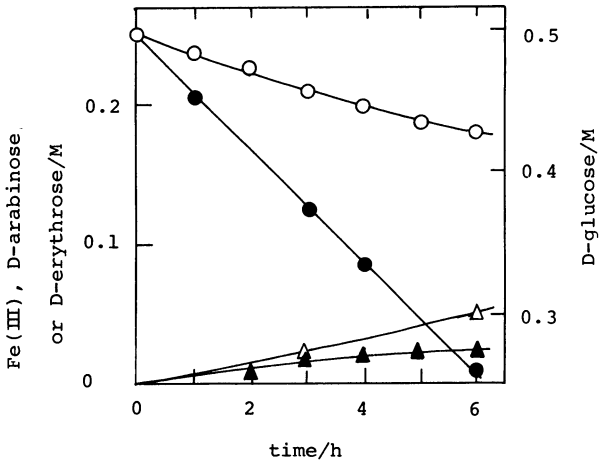


Fig. 4. Photoreaction of the $FeCl_3$ (0.25 M)–D-glucose (0.5 M) solution (500 ml) at 20 °C. D-Glucose (○), Fe(III) (●), D-arabinose (▲), and D-erythrose (△) concentrations as a function of the irradiation time.

The time course of the reaction is shown in Fig. 4, which is somewhat more complex compared to that for the oxidation of D-fructose. Fe(III) concentration decreased linearly as a function of time, indicating that the reaction is light intensity dependent. However, decrease in D-glucose concentration and increase in D-arabinose and D-erythrose concentrations were not linear, suggesting that more than one step may be

Table 2. Changes in the solution composition of D-glucose–$FeCl_3$ solution after irradiation[a]

| Initial conditions | | Irradiation time/h | Changes after irradiation | | | | |
|---|---|---|---|---|---|---|---|
| Glucose/M | Fe(III)/M | | Glucose/M | Fe(III)/M | $H^+$/M | Arabinose/M[b] | Erythrose/M[b] |
| 0.5 | 0.25 | 3 | −0.072 | −0.25 | +0.248 | +0.020(28%) | +0.043(62%) |
| 0.1 | 0.1 | 0.5 | −0.008 | −0.034 | +0.034 | +0.004(50%) | +0.004(50%) |
| 0.2 | 0.1 | 0.5 | −0.013 | −0.046 | +0.046 | +0.005(38%) | +0.007(54%) |
| 0.2 | 0.2 | 0.5 | −0.008 | −0.036 | +0.036 | +0.004(50%) | +0.004(50%) |
| 0.2 | 0.4 | 0.5 | Trace[c] | −0.016 | +0.016 | Trace[c] | Trace[c] |
| 0.3 | 0.1 | 0.5 | −0.016 | −0.062 | +0.062 | +0.005(31%) | +0.010(63%) |
| 0.5 | 0.1 | 0.5 | −0.025 | −0.083 | +0.082 | +0.007(28%) | +0.017(68%) |
| 0.5 | 0.25 | 0.5 | −0.018 | −0.054 | +0.052 | +0.006(33%) | +0.009(50%) |

a) Sample solutions (70 ml) were irradiated internally at 20 °C under aerobic atmosphere. b) Conversion based on the D-glucose oxidized was given in parenthesis (mol%). c) Changes were too small to be quantitized.

Table 3. Changes of the solution composition of D-arabinose-, D-mannose-, and D-ribose-$FeCl_3$ solutions after irradiation[a)]

| Substrate | | $FeCl_3$/M | Product | | | |
|---|---|---|---|---|---|---|
| Monosaccharide/M | | | $H^+$/M | Arabinose/M[b)] | Erythrose/M[b)] | Glyceraldehyde/M[b)] |
| D-Arabinose | −0.124 | −0.25 | +0.248 | — | +0.111(89%) | — |
| D-Mannose | −0.088 | −0.25 | +0.246 | +0.025(28%) | +0.040(45%) | — |
| D-Ribose | −0.123 | −0.25 | +0.248 | — | +0.064(52%) | +0.028(23%) |

a) Monosaccharide (0.5 M)-$FeCl_3$ (0.25 M) solutions (70 ml) were irradiated internally for 3 h at 20 °C.
b) Conversion based on the substrate oxidized was given in parenthesis (mol%).

involved in the reaction. The results of the irradiation under different conditions are summerized in Table 2. The reaction rate was affected by the initial substrate concentrations, and higher concentration of D-glucose increased the rate, while higher concentration of $FeCl_3$ decreased the rate.

*Oxidation of D-Arabinose, D-Mannose, and D-Ribose.* Photooxidations of D-arabinose, D-mannose, and D-ribose by $FeCl_3$ were also studied under aerobic atmosphere, and the results are shown in Table 3. All of these monosaccharides were susceptible to the photooxidation. The oxidation product from D-arabinose was identified to be D-erythrose with nearly 90 mol% of yield. D-Mannose yielded D-arabinose and D-erythrose, quite similar to D-glucose. In the case of D-ribose, however, formation of a considerable amount of D-glyceraldehyde in addition to D-erythrose was observed by HPLC and GLC.

## Discussion

D-Fructose was oxidatively degraded by $FeCl_3$ with a Pyrex-filtered light according to the Eq. 1, and more than 80 mol% of D-fructose oxidized was converted to D-erythrose, demonstrating that the oxidation process has high specificity. The reaction was shown in the preceding letter to proceed *via* formation of the Fe(III)-D-fructose complex.[14] This conclusion was deduced from the results that little difference was observed for the reactions under aerobic and anaerobic conditions and that the action spectrum of the quantum yield for the reduction of Fe(III) coincided with the absorption band of the complex. The formation of D-erythrose can best be explained by the oxidative cleavage of the bond between C-2 and C-3 of D-fructose. Therefore, it is quite probable that both or at least one of hydroxyl groups at C-2 and C-3 are involved in coordination with Fe(III). Though Charley *et al.* presented the possible structure of the Fe(III)-D-fructose complex precipitated from a weakly basic solution, no experimental evidences as to the position of iron chelation were shown,[5] and the structure of the complex in an acidic solution is not yet clear now. It is worth to note that lead tetraacetate also cleaves the bond between C-2 and C-3 of D-fructose to yield 3-*O*-glycoloyl-D-erythrose.[20] This reaction was reported to proceed from β-D-fructofuranose where hydroxyl groups at C-2 and C-3 are in *cis* configuration feasible for metal coordination. In our photoreaction, D-erythrose instead of its glycolic ester was directly formed. As formations of formaldehyde, CO, $CO_2$, and $H_2$ were observed, glycolic ester unit may be further degraded into these compounds.

The reaction was linearly dependent on the light intensity. Therefore, higher initial D-fructose concentrations increased the rate because of the increase in the concentration of the complex. However, higher initial Fe(III) concentrations decreased the rate. As the free Fe(III) ion itself has the absorption at the region where the complex shows its absorption band (300—400 nm), the result is explained by assuming that light absorption of the complex was comparatively decreased because of the light absorption by the free Fe(III) ion. To clarify more detailes of the reaction, however, the structure and other properties of the complex have still to be studied.

Photooxidation of D-glucose was also shown to proceed *via* formation of the Fe(III)-D-glucose complex, and photochemical properties of the complex were substantially similar to those of the Fe(III)-D-fructose complex. However, more than two moles of Fe(III) with respect to the D-glucose oxidized was reduced during photoirradiation, and the time course of the reaction was more complex compared to that of D-fructose (Fig. 4). Though Fe(III) decreased almost linearly, consumption of D-glucose became slower as the reaction proceeded, suggesting that the primary oxidation product was further oxidized by Fe(III). As shown in Table 3, D-arabinose was oxidized to D-erythrose in a high yield under similar conditions. Therefore, it is likely that D-glucose is oxidatively degraded to the primary product, D-arabinose, which is subsequently oxidized to D-erythrose according to the Eq. 2. This

$$\begin{aligned} \text{D-glucose} + 2\text{Fe(III)} &\xrightarrow{h\nu} \text{D-arabinose} + 2\text{Fe(II)} + 2\text{H}^+ \\ \text{D-arabinose} + 2\text{Fe(III)} &\xrightarrow{h\nu} \text{D-erythrose} + 2\text{Fe(II)} + 2\text{H}^+ \end{aligned} \quad (2)$$

view is further supported by the following fact. The sum of the amount of D-arabinose and D-erythrose is almost the same as the amount of D-glucose decreased, and the total amount of monosaccharides oxidized by $FeCl_3$ is approximately the half of the Fe(III) reduced if we assume the Eq. 2 (Table 2). Lead tetraacetate is also known to cause the stepwise degradation of α-D-glucose into 3-*O*-formyl-D-arabinose, which is further degraded to 2,3-di-*O*-formyl-D-erythrose.[21]

The first and second steps of the reaction in the Eq. 2 are the oxidative cleavage of the bond between C-1 and C-2 of monosaccharides. Since the photooxidation of D-fructose cleaved the bond between C-2 and C-3, it seems that the photooxidation by Fe(III) causes the

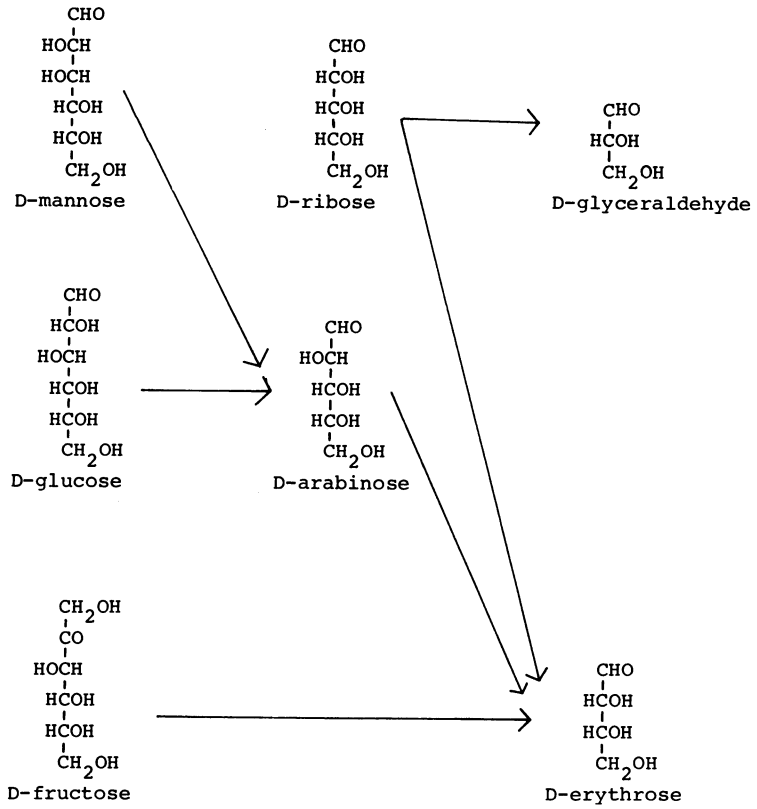


Fig. 5. Oxidative degradation of monosaccharides by $FeCl_3$ with irradiation of a Pyrex-filtered light.

cleavage of the bond between the anomeric and its adjacent carbons. In order to test whether this is the general feature of the oxidation of monosaccharides by $FeCl_3$, we studied the oxidation of D-mannose and D-ribose. Reaction of D-mannose was quite similar to that of D-glucose, suggesting that D-mannose is also oxidized stepwise *via* D-arabinose to D-erythrose. These are also the bond cleavage at the anomeric carbon. While in the case of D-ribose, approximately two moles of Fe(III) with respect to the D-ribose oxidized was reduced, suggesting that both D-erythrose and D-glyceraldehyde are directly formed from D-ribose. Though the formation of D-erythrose is due to the cleavage of the bond between C-1 and C-2, the formation of D-glyceraldehyde may be the result of the cleavage of the bond between C-2 and C-3. The latter process does not involve the anomeric carbon at C-1, and is different from other results observed here. Unlike D-arabinose, hydroxyl groups of D-ribose at C-2 and C-3 are *cis*-diol. This may enable the participation of the C-3 hydroxyl group in coordination with Fe(III), and can be the possible reason for the formation of D-glyceraldehyde. Indeed, $Ca^{2+}$ and $La^{3+}$ are reported to bind preferentially with $\alpha$-furanose and $\alpha$-pyranose forms of D-ribose which have three consecutive *cis*-hydroxyl groups from C-1 to C-3.[22]

The results presented in this paper demonstrated that many of monosaccharides are oxidatively degraded by $FeCl_3$ with irradiation of a near-UV to visible light under aerobic conditions. Except for D-ribose, the degradation processes are selective. These degradation pattern of monosaccharides are summarized in Fig. 5.

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