the yield of oxalic acid from *d*-fructose reaches a maximum, a minimum, and a second maximum, successively, while the yield of carbon dioxide shows correspondingly opposite changes. These variations in the value of the yields of oxalic acid and carbon dioxide are due to the reactions which arise from the shifting of the equilibrium between the three enediols of *d*-fructose, and their subsequent splitting and oxidation. At 50° and 75° a similar tendency towards a minimum was observed.

5. The splitting products obtained from the enediols of the hexoses may also form enediols and subsequently split, a process which results in adding more components to the general equilibrium condition in these carbohydrate systems. Formaldehyde, glycolic aldehyde and glyceric aldehyde, products arising from the splitting of the hexose-1,2-, 2,3-, and 3,4-enediols, respectively, are thought to be the compounds producing the final oxidation products. Formaldehyde is oxidized to carbon dioxide, and glycolic aldehyde and glyceric aldehyde are oxidized to oxalic acid and carbon dioxide with potassium permanganate in the presence of alkali.

6. The tendency of the yield of oxalic acid from *d*-fructose to approach a second maximum at 100° is thought to be due to the formation of lactic acid under the influence of increasing concentrations of alkali and also of increased temperature, both of which factors tend to produce a greater formation of glyceric-aldehyde-methylenenol. Lactic acid is formed by the action of alkalies on glyceric aldehyde through the intermediate formation of pyruvic aldehyde.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE MECHANISM OF CARBOHYDRATE OXIDATION. II. THE OXIDATION OF *d*-GALACTOSE

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The differences which may theoretically exist in alkaline solutions of *d*-galactose and *d*-glucose after these well-known aldohexoses have formed 1,2-, 2,3-, and 3,4-enediols, and then these enediols reacted in the presence of oxidizing agents by undergoing a splitting at the double bonds, pointed to a possible difference in the behavior of these two compounds when they were oxidized under the same experimental conditions. Before oxidation takes place, however, *d*-galactose in undergoing the enediol formation and subsequent splitting at the double bonds should give rise to the methylenenols of *d*-lyxose, *l*-threose, glyceric aldehyde, glycolic aldehyde, and formaldehyde, while *d*-glucose, as pointed out

[1] Du Pont Fellow, 1922.

in the preceding paper, gives rise to the methylenenols of *d*-arabinose, *d*-erythrose, glyceric aldehyde, glycolic aldehyde, and formaldehyde. To learn whether these differences would produce differences in the oxidation phenomena was one of the main objects of our experiments.

Furthermore, if the products derived from this decomposition of the several enediols of *d*-galactose form an equilibrium, then one should be able to influence the character of the oxidation phenomena by means of such agencies as a change in the concentration of the alkali used and also a change in the temperature of the reaction. To ascertain whether this was possible was another objective we had in mind.

The general behavior of *d*-galactose under the same conditions as *d*-glucose was also of much interest since we wanted to make a study of the behavior of lactose towards oxidizing agents under carefully controlled experimental conditions. Less work has been done on the oxidation of *d*-galactose than on that of *d*-glucose. The oxidizing agents that have been used most frequently are cupric hydroxide,[2] copper acetate,[3] and hydrogen peroxide.[4]

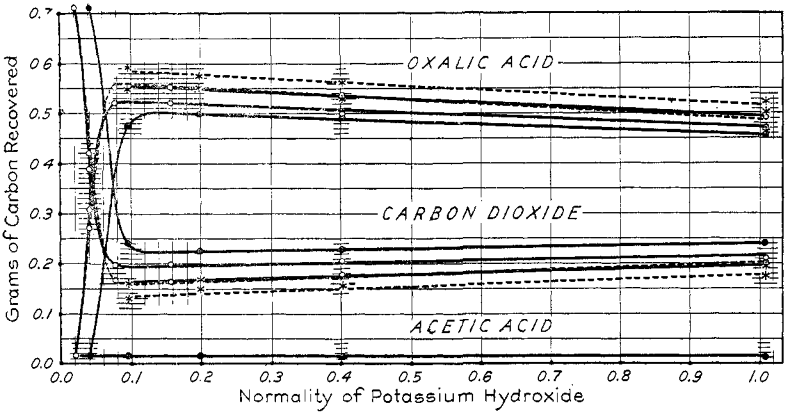

Fig. 1.—Comparison of amounts of products from *d*-galactose (▬▬▬▬) and *d*-glucose (— — — —) 25° C. (*) – 50° (O) – 75° (●).

Manipulation and Experimental Results.—The general experimental procedure followed in this work was exactly the same in every detail as that described in the preceding paper. Our experimental results with *d*-galactose are shown in Fig. 1. In order to make a graphic comparison of the work with *d*-glucose, the oxidation data of the latter carbohydrate are shown in dotted lines.

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[2] Habermann and Hönig, *Monatsh.*, **3**, 651 (1883). Nef, *Ann.*, **357**, 289 (1914). Anderson, *Am. Chem. J.*, **42**, 401 (1909).

[3] McLeod, *Am. Chem. J.*, **37**, 20 (1907).

[4] (a) Morrell and Crofts, *J. Chem. Soc.*, **75**, 787 (1899). (b) Spoehr, *Am. Chem. J.*, **43**, 227 (1910).

In conclusion, we wish to thank E. I. du Pont de Nemours and Company whose kindly interest and good will have made certain parts of this work possible.

Theoretical Discussion and Summary

1. Our results show that *d*-galactose and *d*-glucose when oxidized with alkaline potassium permanganate solutions at 25° and 50° do not give the same oxalic acid-carbon dioxide ratio at all alkalinities. This fact fulfils our expectation, because at the lower alkalinities the three enediols of *d*-galactose and those of *d*-glucose give rise to two different pentose derivatives (*l*-lyxose and *d*-arabinose, respectively) and two different tetrose derivatives (*l*-threose and *d*-erythrose, respectively). Under such conditions it is clear that the active portion of the system undergoing oxidation would be composed of different materials in each case and hence one would expect that the oxalic acid-carbon dioxide ratio would be different in the two cases.

2. When the concentration of the alkali becomes sufficiently great, the equilibrium existing between the three respective enediols of both *d*-galactose and *d*-glucose ought to shift more towards the 3,4-enediol formation, thus giving rise by splitting to a greater concentration of glyceric-aldehyde-methylenenol in the alkaline solution of both carbohydrates. Under these conditions, the composition of the respective active portions of the carbohydrate solutions would then tend to become more nearly the same. Our experimental results actually do show that the oxalic acid-carbon dioxide ratios tend to become identical. Obviously, this must be true for the allose as well as the gulose series of sugars. From these statements, therefore, it follows that there must be some concentration of alkali corresponding to which the curves for the oxidation products for all aldohexoses and ketohexoses should be exactly superimposed. In this connection, it is worthy of note that in the methods used for the determination of sugars by means of alkalies and permanganate[5] a high concentration of the base is always used. As pointed out above, this procedure results in the common formation of glyceric-aldehyde-methylenenol in all of the hexoses.

3. Lobry de Bruyn and Alberda van Ekenstein have shown that an alkaline solution of *d*-galactose as well as that of *d*-glucose is also made up of an equilibrated system which, in the case of *d*-galactose, we may represent by the following reaction.

d-galactose ⇄ *d*-talose ⇄ *d*-tagatose ⇄ pseudo-tagatose ⇄ *d*-α-galtose ⇄ *d*-β-galtose.

From the facts presented in the preceeding paper with reference to the common oxidation mechanism in the glucose (mannose and fructose) series, it is highly probable that the active portion of the alkaline solutions

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[5] Greifenhagen, König and Scholl, *Biochem. Z.*, 35, 169 (1910).

of the hexoses in the galactose series (*d*-talose, *d*-tagatose, etc.) is the same in each case and hence the oxalic acid-carbon dioxide ratio obtained under the conditions of these experiments is probably the same for each one of these sugars. It is hoped that this point may be tested experimentally in this Laboratory in the near future. In view of these relationships it is to be expected that the aldopentoses in dilute alkaline solutions would establish an equilibrium of the same general nature as that formed by the hexose under similar conditions.[6] This would mean that the results obtained in the oxidation of *d*- and *l*-arabinose by neutral and alkaline potassium permanganate (see the preceding paper) are in all probability the same as those which ought to be obtained from *d*- and *l*-ribose and its corresponding 2-ketopentose. Obviously the same general relationship would also hold true in the xylose series, save in this case, however, the 1–2 enediol forms would be optical antipodes.[7] The results obtained in the oxidation of the arabinose-ribose series and in the xylose-lyxose series would probably be related to each other as are the results of oxidation obtained in the *d*-glucose and *d*-galactose series, respectively.[4b]

4. **Effect of Temperature.**—As the temperature of these reactions is increased, the equilibrium between the several enediol forms of the aldohexoses will shift in the direction of the 3,4 form, thus yielding the glyceric aldehyde. The effect of this would be that both *d*-galactose and *d*-glucose should give approximately the same oxalic acid-carbon dioxide ratio. Our experiments at 75° show that this is true at this temperature, our lines being identical (Fig. 1). At 25° and 50°, it is seen that the differences in the amounts of oxidation products are more marked at 25° than they are at 50°.

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[6] Nef, *Ann.*, **403**, 214 (1914).

[7] Compare Armstrong, "The Simple Carbohydrates and Glucosides," Longmans, Green and Co., **1919**, p. 80. Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Veit and Co., **1913**, vol. I, part 2, p. 950.