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BROMINE OXIDATION AND MUTAROTATION MEASUREMENTS OF THE ALPHA- AND BETA-ALDOSES *

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ABSTRACT

Rates of oxidation by bromine water, specific rotations, mutarotation coefficients, heats of activation, and other data are reported for α-*d*-glucose, β-*d*-glucose, α-*d*-galactose, β-*d*-galactose, α-*d*-talose, α-*d*-mannose, β-*d*-mannose, mannose $CaCl_2.4H_2O$, α-*d*-gulose $CaCl_2.H_2O$, α-*d*-xylose, α-*d*-lyxose, β-*d*-lyxose, α-*l*-arabinose, β-*l*-arabinose $CaCl_2.4H_2O$, *d*-ribose, *l*-ribose, α-*l*-rhamnose, α-lactose, β-lactose, and β-maltose. The bromine oxidation measurements reveal that the equilibrium solutions are composed for the most part of the normal alpha and beta isomers. Small quantities of other modifications appear to be present in the solutions of arabinose, galactose, talose, and ribose. Fundamental characteristics of the alpha and beta sugars which furnish the basis for the changes in nomenclature previously suggested by Isbell are discussed. It is shown that the sugars which appear as beta modifications under the proposed classification are oxidized by bromine more rapidly than the alpha.

CONTENTS

I. REACTIONS OF THE ALPHA AND BETA SUGARS WITH BROMINE WATER AND A SYSTEM FOR THEIR CLASSIFICATION

An examination of the reaction rates of all the members of a stereomeric series brings out important information relative to the mechanism of the reactions and the structures of the reactive substances which cannot be obtained by other methods. The determination of

*This paper, with the exception of part of the experimental work, is also published in the Journal of Organic Chemistry. A résumé of the general method and the results obtained by the oxidation of the various modifications of glucose, mannose, galactose, lactose, maltose, xylose, arabinose, and rhamnose, was given before the Division of Sugar Chemistry of the American Chemical Society in March 1932 at New Orleans.

the relative reactivity of the various modifications of the sugars is of value in order to understand their reactions in biological systems and in aqueous solutions in general. Previously Isbell and Hudson [1] [1] found that the aldose sugars on oxidation with bromine water in slightly acid solution are converted into delta lactones, while Isbell [2] showed qualitatively that the beta sugars are oxidized more rapidly than the alpha sugars, and that the pyranose modifications give delta lactones without the intermediate formation of the free acid. Lippich [3] found that the alpha sugars react with hydrogen cyanide in neutral or alkaline solution slightly more rapidly than the beta sugars. Since the relative rates of reaction for the alpha and beta isomers with bromine and with hydrogen cyanide are different, the reactions do not take place in the same manner. Supposedly the aldehyde modification reacts rapidly with hydrogen cyanide, so that the reaction rate is determined by the rate at which the free aldehyde is formed. On the other hand, the cyclic forms of the sugars are oxidized by bromine water without the intermediate formation of the free aldehyde, so that the reaction rate is not dependent on the rate of aldehyde formation. Our studies [4] with *d*-glucose show that the rate of oxidation of the sugar by bromine water in the presence of barium carbonate is determined by the concentration of the oxidant (free bromine) and by the concentrations and proportions of the alpha and beta modifications of the sugar. The bromine oxidation is particularly suitable for investigation because it gives nearly quantitative yields of the free aldonic acids or their lactones and takes place under conditions such that the change of one sugar to another is slow.

Although there is considerable variation in the reactivity of the separate sugars, the most striking difference is found for the alpha and beta modifications of the same sugar. The existence of the alpha and beta modifications requires the presence of a ring structure and the difference in the reactivity indicates an important structural difference in the two modifications. If the sugars had a uniplanar ring, the oxygen of the ring would lie in the plane of the carbon chain and the alpha and beta positions would be symmetrical with respect to the carbon-oxygen skeleton of the sugar. But if the oxygen and the carbon atoms forming the ring did not lie in one plane [5, 6, and 7] the alpha and beta positions would not be symmetrical with respect to the carbon oxygen skeleton. That is, the alpha and beta positions would be inclined at different angles to the ring and would be influenced to different degrees by the neighboring groups, especially the oxygen. It was pointed out by Isbell [8] that if the sugars are divided into two groups, alpha when the hydroxyl of the first carbon lies in the same direction as the oxygen of the ring, and beta when it lies in the opposite direction, in reactions involving the first carbon atom there is marked similarity in the behavior of all alpha sugars (and derivatives) on the one hand, and of the beta on the other.

The alpha-beta nomenclature most generally used at the present time was originated by Hudson [9]. It has been recognized for a long time that this nomenclature results in classifying as beta those derivatives of *l*-arabinose which exhibit chemical and physical properties similar to the properties of the alpha derivatives of *d*-galactose.

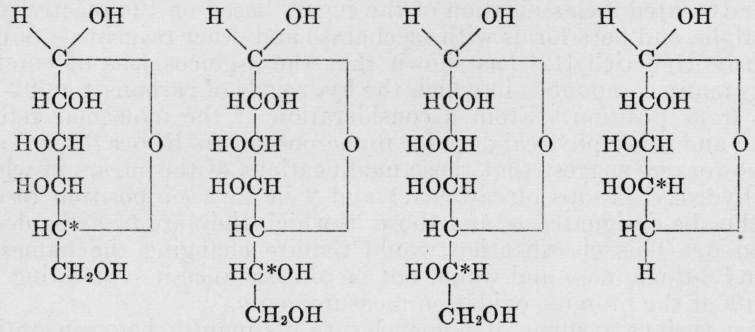
[1] Figures in brackets here and elsewhere in the text correspond to the numbered literature references at the end of this paper.

Several attempts to avoid this confusion have been made and other systems of nomenclature advanced. In 1924 Svanberg and Josephson [11] advocated a classification of the sugars based on the reactivity of the alpha and beta forms with saccharase and other reagents. Subsequently Helferich [12] has shown that the β-glucosidase of emulsin splits many compounds in which the hydroxyls of carbons 1 and 2 are in a *trans* position. From a consideration of the molecular refractivity and other physical data for numerous sugars Riiber [13, 14] and his coworkers suggest that those modifications of the sugars in which the hydroxyl groups of carbons 1 and 2 lie in a *cis* position to one another be designated α, and those in which they are *trans* be designated β. This classification would require changing the names of α- and β-*d*-mannose and would not be of assistance in correlating the results of the bromine oxidation measurements.

The various systems of nomenclature distinguish between optical antipodes by the prefixes *d* and *l*. The substances are allocated to the *d* and *l* series according to the system originated by Rosanoff [10]. Substances in which the hydroxyl on the terminal asymmetric carbon lies to the right are designated *d*, and those in which it lies to the left are called *l*. Thus the antipode of α-*d*-glucose is α-*l*-glucose. This *d* and *l* classification is satisfactory and no changes seem desirable. The change which is advocated is merely the nomenclature of the alpha and beta isomers. Hudson's nomenclature of alpha and beta compounds is based on two factors, the *d* and *l* configuration, and the optical rotation. But there is no relation between the *d* and *l* configuration on the one hand and the structure of the reducing carbon on the other. In the heptose series particularly his nomenclature results in naming the analogs of certain alpha sugars as beta, and vice versa. Isbell overcomes this fundamental defect by taking into consideration another structural characteristic, namely, the configuration of the oxygen ring for differentiating between alpha and beta compounds. Moreover, the oxygen of the ring is united directly with the first carbon and plays an important part in determining the properties of the alpha and beta sugars. By using Hudson's comparison of optical rotations in conjunction with the position of the oxygen of the ring, a system of nomenclature is obtained which is based on the relative positions of all the groups united with the first carbon. The resulting nomenclature can be applied as readily as that in current use and has the distinct advantage that it results in the classification of substances of *like structure and similar properties.*

According to the nomenclature of Hudson the names for the alpha and beta sugars are so selected that "in the *d* series of sugars the more dextrorotatory substance of an α, β pair is designated the α-form, in the *l*-series the more levorotatory one is so named." This nomenclature is not satisfactory because the characterization as α or β depends on whether the sugar belongs in the *d* or *l* series, which in turn depends on the configuration of the terminal asymmetric carbon atom. This key carbon is frequently situated outside of the pyranose ring remote from the group being named. It can be observed from the following formulas that the terminal asymmetric carbon atom (the carbon marked with an asterisk) determines the position of the oxygen ring in the hexoses, as for example in α-*d*-galactose, but in the

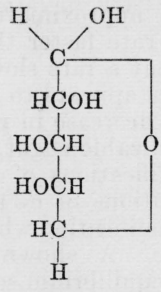
heptoses it lies outside of the pyranose ring and does not have anything to do with the configuration of the first carbon:

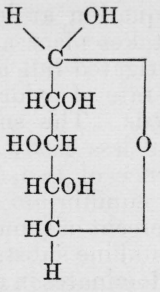


α-*d*-Galactose α-*d*-α-Mannoheptose α-*l*-β-Guloheptose α-*l*-Arabinose

In the pentose pyranoses, the terminal asymmetric carbon is not involved in the formation of the oxygen ring and hence it does not have any direct bearing on the configuration of the first carbon. The four sugars illustrated above have the same structure for the pyranose ring and exhibit similar properties, yet according to Hudson's nomenclature two of these are designated alpha and two beta. According to the nomenclature suggested by Isbell [8] all four of these sugars would be designated alpha. *The names of the members of the alpha and beta pair of sugars or sugar derivatives are so selected that when the oxygen ring lies to the right, as in d-glucose, the more dextrorotatory member of the α-β pair shall be designated α, and the less dextrorotatory member β; when the oxygen ring lies to the left, as in l-glucose (or in d-gala-heptose), the less levorotatory member is called β.* This results in names for which the subtraction of the rotation of the beta form from that of the alpha gives a positive difference whenever the oxygen ring lies to the right, and a negative difference when the oxygen ring lies to the left. If the carbon atom united with the hydroxyl forming the oxygen ring is asymmetric, the oxygen of the resulting ring is considered to lie in the direction of the parent hydroxyl. This direction is ascertained by inspection of the Fischer projectional formulas. In the case of the pentoses the direction of the ring is allocated empirically after comparison of their properties with those of sugars with similar configurations. The studies of Hibbert [15], Cox [16], and others show that the oxygen of the ring in the pentose series is not in the plane of the carbon atoms. Therefore, the molecule as a whole is dissymmetric so that it is permissible to postulate structural differences in the alpha and beta pentoses similar to those of the hexoses. In this respect it may be noted that the alpha and beta pentoses reveal differences in the chemical reactions of the first carbon which are analogous to those found for the alpha and beta hexoses.

A comparison of the structures of the pentoses with the hexoses reveals certain similarities which aid in their classification. According to the Fischer projectional method the formulas are represented in the following manner:


α-*l*-arabinose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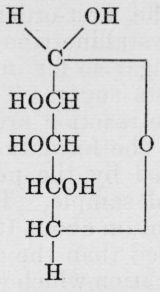
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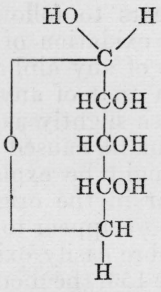
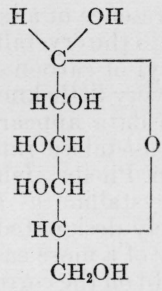

d-ribose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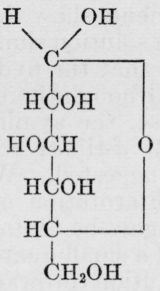
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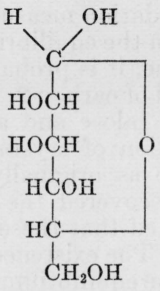
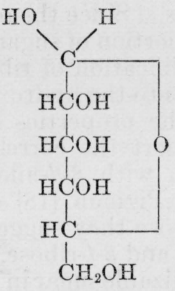
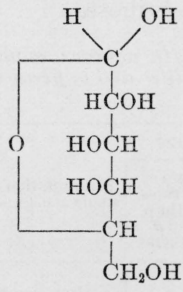

α-*d*-mannose


β-*d*-allose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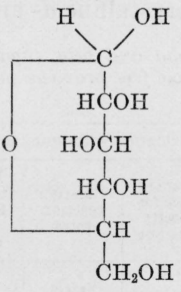
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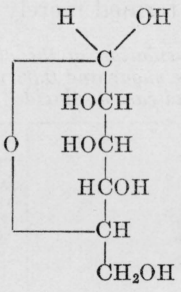
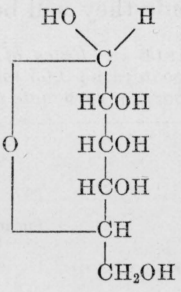

β-*l*-gulose


α-*l*-talose

It may be observed from these formulas that crystalline *l*-arabinose could be structurally related to either α-*d*-galactose or to β-*l*-altrose. The marked similarity of crystalline *l*-arabinose (+191) to α-*d*-galactose has been stressed by Hudson [17], Riiber [13], and others. The rates of oxidation reported in this paper substantiate the correlation of crystalline *l*-arabinose with α-*d*-galactose and indicate that it should be classified with the alpha sugars. Crystalline *d*-xylose (+94) could be related to either α-*d*-glucose or to β-*l*-idose. It resembles α-*d*-glucose in that it is oxidized slowly and hence it is properly classified as α-*d*-xylose. Crystalline α- and β-*d*-lyxose resemble *d*-mannose rather than *l*-gulose. Since α-*d*-lyxose is oxidized more slowly than β-*d*-lyxose they are properly classified. Classification of crystalline *d*- and *l*-ribose, however, is more perplexing. The *d*-sugar could be structurally related to *l*-talose or to *d*-allose. Ribose [18] gives a rapid and complex mutarotation but the total change is small. The compound character of its mutarotation shows that the equilibrium solution contains at least three modifications. The mutarotation of α-*d*-talose is also complex [19], while the mutarotation of β-*d*-allose [20]

appears to follow the first-order equation at least approximately. The oxidation of crystalline ribose takes place at a rate faster than that of any alpha sugar so far investigated but also at a rate slower than that of any beta sugar. The rate of oxidation appears to decrease slightly as the reaction proceeds. This small decrease in rate might be caused by the formation of less easily oxidizable sugar, or it might be explained by the presence of two modifications of the sugar in the original sample. The equilibrium solutions of *d*- and *l*-ribose appear to contain about 10 percent of some modification which is more easily oxidized than the crystalline substance. As shown on page 153, the modification which predominates in the equilibrium solution is the isomer for which the hydroxyls of carbons 1 and 2 are *trans*. Since the oxidation measurements show the presence of a large proportion of sugar in the equilibrium solution similar to the crystalline modification of ribose, it is probable that the hydroxyl of carbon 1 is *trans* to the hydroxyl of carbon 2. Although there is very little known of the properties of talose and allose, the available data appear to support the correlation of crystalline *d*-ribose with *α-l*-talose rather than with *β-d*-allose as originally suggested. When Phelps, Isbell, and Pigman [18] discovered the mutarotation of crystalline *d*- and *l*-ribose they suggested that these sugars be tentatively designated as *β-d*- and *β-l*-ribose. The existence of a small quantity of a more easily oxidizable sugar in the equilibrium solution throws doubt on the correctness of this classification, and until a more thorough study has been made they will be termed merely crystalline *d*- and *l*-ribose.

TABLE 1.—*Rates of oxidation of the alpha and beta sugars in aqueous solutions containing 0.05 mole sugar and 0.08 mole free bromine per liter and buffered with barium carbonate and carbon dioxide*

Sugar	Oxidation with bromine water			Mutarotation constants at 0.2 ±0.2° C	
	Average value for velocity constant	Relative reaction rates	Ratio of the rates for the α and β isomers		
	$k \times 10^3$	$\frac{k_{sugar}}{k_{\alpha\text{-}d\text{-glucose}}}$	k_β/k_α	$m_1 \times 10^3$	$m_2 \times 10^3$
α-*d*-Glucose	32	1	39.2	0.741	
β-*d*-Glucose	1,255	39		.738	
α-*d*-Mannose	51	1.6	15.3	2.16	
β-*d*-Mannose	781	24		2.14	
α-*d*-Galactose	42	1.3	37.9	0.93	11.9
β-*d*-Galactose	1,590	50		.90	16.7
α-*d*-Talose	78	2.4	10.8	3.62	25.5
β-*d*-Talose (from equilibrium solution)	844	26			
α-*d*-Gulose $CaCl_2.H_2O$	71	2.2	5.9	1.88	
β-*d*-Gulose (from equilibrium solution)	418	13			
α-*l*-Arabinose	95	3.0	17.5	3.62	21.7
β-*l*-Arabinose $CaCl_2.4H_2O$	1,658	52		3.84	36.9
α-*d*-Xylose	90	2.8	18.6	2.45	
β-*d*-Xylose (from equilibrium solution)	1,673	52			
α-*d*-Lyxose	156	4.9	2.9	8.44	
β-*d*-Lyxose	449	14		8.40	
d-Ribose (crystalline)	196	6.1	5.2		
β-*d*-Ribose (from equilibrium solution)	1,010	32			
l-Ribose (crystalline)	195	6.1	7.5	6.87	54.0
β-*l*-Ribose (from equilibrium solution)	1,456	45.5			
α-*l*-Rhamnose, hydrate	90	2.8	8.6	5.68	
β-*l*-Rhamnose (from equilibrium solution)	770	24			
α-Lactose, hydrate	29	0.9	32.8	0.54	
β-Lactose	952	30		.52	
α-Maltose (from equilibrium solution)	24	0.8	64		
β-Maltose, hydrate	1,528	48		.58	

It may be seen from the results given in table 1 that if the sugars are classified as suggested, the beta isomers are oxidized by bromine more rapidly than the alpha isomers. This generalization is based on all the sugars so far investigated, which include the alpha and beta modifications of five of the eight pyranose types. Measurements on the idose, allose, and altrose types are necessary, however, before it is certain that the generalization applies to all pyranose sugars.

The study of the mechanisms of the reactions is complicated by the interconversion of the various modifications which exist in the aqueous solutions. The mutarotation reaction which occurs when the sugar is dissolved in water results in the formation of either more or less easily oxidizable modifications. The production of a less readily oxidizable substance retards the rate of oxidation, while the formation of more readily oxidizable substance accelerates the rate. Thus the reaction of the alpha sugars with bromine water can be considered to consist in two simultaneous reactions. One of these is the oxidation of the alpha sugar directly, and the other the conversion of the alpha sugar to beta or other easily oxidizable substance and the subsequent oxidation thereof. In the oxidation of α-*d*-glucose it was shown [4] that if the concentration of the oxidant (free bromine) is held constant, and if it is assumed that the beta sugar is oxidized as fast as it is formed, the usual formula for two simultaneous reactions gives the equation

$$k_1+ak_\alpha=\frac{1}{t}\ln\frac{A}{A-X}.$$

In this equation k_1 is the velocity constant for the conversion of α-glucose to easily oxidizable sugar, a is the concentration of free bromine, k_α the velocity constant for the oxidation of the alpha isomer, and A and $A-X$ are the quantities of sugar present at the beginning and end of the time interval, t. There is no reliable method for determining k_1. In our previous paper on the oxidation of *d*-glucose its value was assumed to be the same as that obtained from the mutarotation coefficient, k_1+k_2 (expressed in natural logarithms). This represents an approximation which permits an evaluation of the relative importance of the mutarotation and direct oxidation reactions. Since the mutarotations of many sugars are complex, the value of k_1 cannot be determined even approximately, and consequently a correction for the mutarotation reaction is not feasible. In certain cases the oxidation of the beta isomers is less rapid than that of glucose, and hence the assumption that the beta isomer is oxidized as rapidly as it is formed is not justified. For these reasons the reaction rates for the alpha and the beta sugars were calculated, using common logarithms, by the simple formula

$$ak=\frac{1}{t}\log\frac{A}{A-X}$$

without attempting to make a correction for the mutarotation reaction.

It can be seen from the data of table 1 that the pentoses, with the exception of β-*d*-lyxose, are oxidized more readily than the corresponding hexoses. The more rapid oxidation of the alpha pentoses is probably caused by the more rapid mutarotation reaction with the accompanying production of easily oxidizable modifications; the less rapid oxidation of β-*d*-lyxose may result from a similar cause, the formation

of the less readily oxidizable alpha modification. The values for the mutarotation constants, m_1 and m_2, are given in table 1 so that the reader can judge for himself the importance of these reactions in the interpretation of the oxidations. The constants, m_1 and m_2, were obtained as described on page 156. m_1 is the same as the mutarotation coefficient, k_1+k_2, calculated for the later part of the mutarotation; m_2 also represents the sum of several constants which individually cannot be satisfactorily evaluated.

It will be noted that the velocity constants given for β-*d*- and *l*-ribose do not agree closely. These constants were obtained from a very rapid reaction involving only 10 percent of the sugar in the equilibrium solution and consequently the experimental error is large and the values are only approximate.

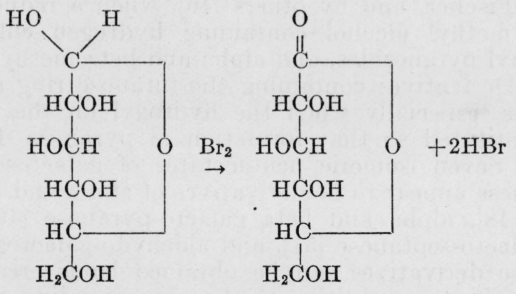
It can be seen from the data in table 1 that α-*d*-galactose is oxidized slightly more rapidly than α-*d*-glucose but less rapidly than β-*d*-glucose, while β-*d*-galactose is oxidized more rapidly than either α- or β-*d*-glucose. The properties of the alpha and beta modifications of *d*-galactose and *d*-glucose in the equilibrium solutions are such that the oxidation of the equilibrium solution of *d*-galactose is more rapid than that of *d*-glucose. Hence our results confirm and extend the observation [21] that *d*-galactose is oxidized by bromine water more rapidly than *d*-glucose. It may be noted also that α-*d*-talose, α-*d*-mannose, and α-*d*-gulose $CaCl_2.H_2O$ are oxidized more rapidly than α-*d*-glucose. On the other hand, the corresponding equilibrium solutions are initially oxidized more slowly than the equilibrium solution of glucose, while in the latter stages they are oxidized more rapidly. Therefore it is evident that a comparison of the reaction rates should not be made in general terms. Although several relationships between the configurations and the rates of reaction are apparent, such comparisons will be held in abeyance until sugars containing the allose, altrose, and idose structures have been investigated.

II. COMPOSITION OF EQUILIBRIUM SUGAR SOLUTIONS

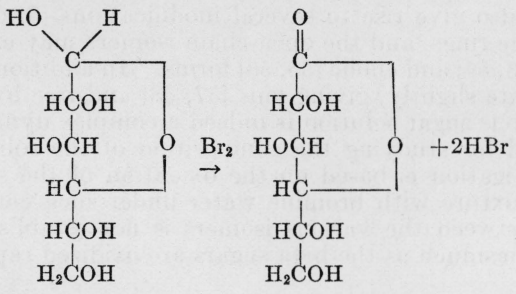
In 1846, Dubrunfaut [22] discovered that when glucose is dissolved in water the optical rotatory power of the solution decreases on standing until finally it reaches a constant value. Subsequently Pasteur [23, 24], Erdmann [25], Urech [26], and others [27] found that the optical rotations of freshly prepared solutions of the reducing sugars in general change on standing, a phenomenon which came to be known as mutarotation. In the beginning Dubrunfaut suggested that the change in optical rotation is caused by a change in molecular structure, but at that time the structures of even simple organic compounds were not known. The aldehyde structure for glucose was suggested by Von Baeyer in 1870 [28], but it did not satisfactorily represent the experimental facts because the sugar did not give the characteristic aldehyde reactions. In order to explain the absence of these reactions Colley [29] postulated an ethylene oxide structure and Tollens [30] a butylene oxide structure. It was pointed out by Von Lippman [31] that the first carbon in the cyclic sugar is asymmetric and that two stereomeric isomers are possible. Erdmann [25] had previously prepared two forms of lactose, one having a higher rotation than the stable solution and the other a lower rotation. Modifications of similar character were found for numerous sugars by Tanret [32] and others. A ring structure is necessary to account for these isomeric forms, and for the two methyl glucosides prepared by Fischer [33].

These glucosides did not give the aldehyde reactions and apparently contained ring structures. Because they resembled the gamma lactones they were assigned a 1,4 ring structure and erroneously considered as such, until later work by Haworth [34] and others established that they contain the 1,5 or pyranose ring. In the meantime other glycosides had been prepared which do contain the 1,4 or furanose ring [35] so that there are two series of glycosides containing different ring structures. Supposedly, the 1,4 ring modifications of the sugars also exist but little is known about the proportions of these in aqueous solutions or of their part in the mutarotation reaction. Because products corresponding to both ring types are obtained by methylation of the sugars [36], other methods must be used to ascertain their structure.

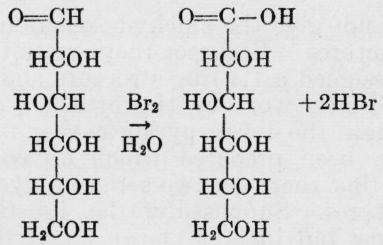
The methods for determining the ring structure of the sugars are (1) a comparison of the optical rotations of the sugars with the optical rotations of the corresponding methyl glycosides whose structures are known [37, 38, 39, 40]; (2) a correlation of the methyl glycosides with the alpha and beta sugars by enzymatic hydrolysis [41]; (3) a measurement of the direction of the optical rotation of a solution containing equivalent quantities of the alpha and beta isomers [42]; (4) a comparison of the X-ray diffraction patterns of crystalline sugars and crystalline glycosides of known structure [43]; and (5) a study of various chemical reactions under conditions such that the rate of change from one form of the sugar to another is slow, as in the oxidation of the sugars with bromine water in the presence of a suitable buffer. According to the last method [1, 2] delta lactones are obtained by the oxidation of pyranoses, gamma lactones from furanoses, and supposedly free acids from aldehyde sugars. The reactions are represented by the following equations:



β-*d*-Gluco-pyranose Gluconic-δ-lactone



β-*d*-Gluco-furanose Gluconic-γ-lactone



Aldehydo-glucose Gluconic acid

The results obtained by one of us [2] with α- and β-*d*-glucose, α- and β-*d*-mannose, α- and β-*l*-rhamnose, α- and β-lactose, β-cellobiose, and β-maltose show that on oxidation with bromine these sugars give delta lactones. Mannose $CaCl_2.4H_2O$, however, gives mannonic gamma lactone and presumably has the furanose structure [44]. The information thus derived shows that the crystalline sugars which have been investigated, with the exception of mannose $CaCl_2.H_2O$, have the pyranose structure. The results obtained by the other methods also lead to this conclusion, but since *d*-talose, *d*-ribose, and *l*-ribose have not been extensively studied the allocation of the pyranose structure to these is entirely arbitrary.

The spontaneous crystallization of the alpha and beta pyranoses, the course of the mutarotation reactions, the solubility measurements with the crystalline sugars [45], and the bromine oxidation method indicate that the pyranose modifications comprise by far the largest part of the sugar in solution. Nevertheless, the complex character of the solutions is plainly apparent from the numerous products which can be derived from reaction with various reagents. As shown by Fischer, and by others [46], when a reducing sugar is treated with methyl alcohol containing hydrogen chloride, alpha and beta methyl pyranosides, and alpha and beta methyl furanosides are formed. Derivatives containing the furanose ring are given by other reactions, especially when the hydroxyl on the first or fifth carbon is substituted so that formation of pyranose derivatives is not possible. Seven isomeric pentacetates of galactose are known products. These appear to be derivatives of alpha and beta galactofuranose [47, 48], alpha and beta galacto-pyranose [49, 50], alpha and beta *d*-galacto-septanose [51], and aldehydo-galactose [52]. The fact that these derivatives can be obtained lends credence to the concept that minute quantities of the corresponding modifications of the sugars are present in aqueous solutions. The various ring isomers may also give rise to several modifications [5, 6] containing strainless Sache rings, and the open-chain isomers may exist partially in hydrated [53, 54] and enolic [55, 56] forms. In addition to these the sugars dissociate slightly, giving ions [57, 58] and free hydrogen [59]. Thus an aqueous sugar solution is indeed a complex dynamic system.

The method for studying the composition of the solutions in the present investigation is based on the oxidation of the sugars in the equilibrium mixture with bromine water under such conditions that equilibrium between the various isomers is not established prior to oxidation. Inasmuch as the beta sugars are oxidized rapidly and the

alpha sugars slowly, the proportion of the beta isomer in the original solution cannot exceed the proportion of the easily oxidizable substance, and the proportion of the alpha cannot exceed the proportion of the slowly oxidizable material. It was shown previously [4] that about 64 percent of the sugar present in the equilibrium solution of glucose is oxidized rapidly at a rate comparable to the oxidation of β-*d*-glucose, and 36 percent is oxidized slowly at a rate comparable to the oxidation of the alpha isomer. Since these proportions agree with the amounts of α- and β-*d*-glucose estimated from the rotation of the solution, and calculated on the assumption that the solution contains only two isomers, it appears that the equilibrium solution of glucose contains, at least largely, the alpha and beta normal forms.

Application of this method to numerous equilibrium solutions of sugars has shown that a portion of the sugar in each case is oxidized

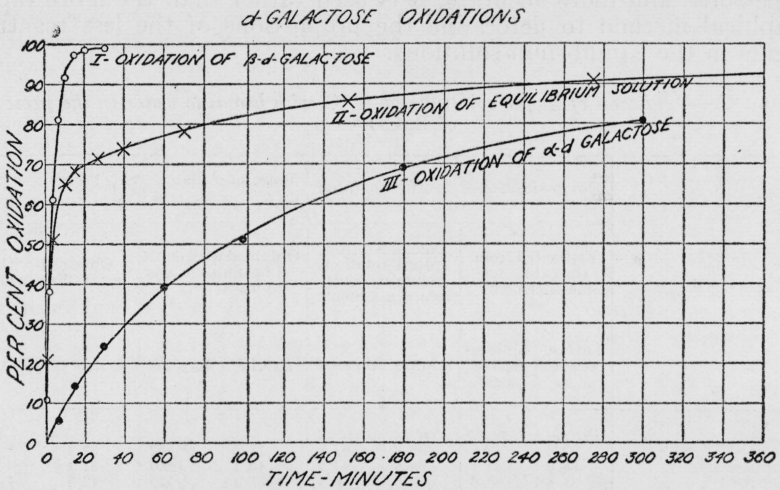


FIGURE 1.—*d-Galactose oxidations.*

rapidly at a rate comparable to the oxidation of the corresponding beta sugar, while the remainder is oxidized slowly at a rate corresponding to that of the alpha sugar. This can be seen by the results illustrated for *d*-galactose in figure 1. The oxidation of β-*d*-galactose is rapid and virtually complete in 20 minutes, while α-*d*-galactose requires 5 hours for approximately 80 percent of oxidation. The equilibrium solution supposedly containing these constituents is oxidized rapidly for about 20 minutes and then more slowly. When the percentage of oxidation is expressed on a logarithmic scale, the oxidation curve should be linear for a first-order reaction, or for a second-order reaction in which the concentration of the oxidant is maintained constant. In figures 2 and 3 the oxidations of lactose and *d*-mannose are given on such a scale. It will be noted that the curves representing α- and β-lactose and α- and β-*d*-mannose are approximately linear. The small curvature is largely due to a decrease in the concentration of the oxidant, free bromine, as the reaction progressed. This explanation may be verified by an inspection of the velocity constants for these sugars given in table 7. Thus the value of k obtained after correction for the variation in the free bromine concentration is more nearly constant than the uncorrected constant, ak. For α-*d*-gulose,

α-*d*-galactose, and α-*d*-xylose the drifts in the velocity constants (see table 7) appear to be slightly larger than the experimental error. This may be due to an accumulation of unknown, less readily oxidizable modifications of the sugars in the solution, or to the production of other products which interfere with the analytical method.

The latter portion of the curves for the oxidation of the equilibrium solutions of lactose and *d*-mannose parallel those for the corresponding alpha isomers when the semilog scale is used as in figures 2 and 3. The equal slopes indicate that the reactions proceed at equal rates. Extrapolation of the portion of the curve representing the oxidation of the less reactive sugar as represented by the dotted line to zero time, gives the logarithm of the less reactive sugar at zero time. The extrapolation can be conducted graphically, or mathematically as described on page 177. Because the mathematical extrapolation is impersonal and more accurate, it is used rather than the more rapid graphical method to determine the proportions of the less reactive sugars in the equilibrium solutions.

TABLE 2.—*Oxidation of sugar solutions at* 0° C *with bromine water in the presence of* $BaCO_3$[a]

Sugar	Composition of equilibrium solution				Rates of oxidation with bromine water at 0° C			
	Estimated from the oxidation measurements		Calculated from optical rotations assuming only two constituents		Obtained with equilibrium solutions at 0.3° C		Obtained with crystalline sugars	
	Less reactive sugar	More reactive sugar	α-Sugar	β-Sugar	$k_A \times 10^3$	$k_B \times 10^3$	$k_\alpha \times 10^3$	$k_\beta \times 10^3$
	Percent	*Percent*	*Percent*	*Percent*				
d-Glucose	37.4	62.6	36.2	63.8	27.5	1,362	32.4	1,255
d-Mannose	68.9	31.1	68.8	31.2	45.2	860	51.1	781
d-Galactose	31.4	68.6	29.6	70.4	37.9	1,720	42.3	1,590
d-Talose	55.9	44.1	----	----	84.8	844	78.5	----
(*d*-Gulose)$_2$ $CaCl_2.H_2O$	18.5	81.5	----	----	52.6	418	54.8	328
l-Arabinose	32.4	67.6	26.5	73.5	84.2	1,608	95.3	1,658
d-Xylose	32.1	67.9	[b] 34.8	[b] 65.2	80.3	1,673	89.9	----
d-Lyxose	79.7	20.3	76.0	24.0	189	717	156	449
d-Ribose	89.3	10.7	----	----	180	1,010	196	----
l-Ribose	89.0	11.0	----	----	170	1,456	195	----
l-Rhamnose	69.0	31.0	[b] 73.1	[b] 26.9	83.4	770	89.7	----
Lactose	37.5	62.5	36.8	63.2	20.9	1,475	29.3	952
Maltose	37.7	62.3	[b] 36.0	[b] 64.0	23.7	1,388	----	1,528

[a] The experimental details for the oxidation measurements are given on page 173 and for the optical rotations on page 158.

[b] Percentage calculated from Hudson's optical rotations derived from measurements of the initial and final solubilities at 20° C (BS Sci. Pap. 21, 267 (1926) S533.

It may be observed from the data given in table 2 that the proportions of the less reactive and more reactive sugars do not differ widely from the hypothetical proportions of the alpha and beta sugars, which were calculated from the optical rotations by assuming that the equilibrium solutions contain only normal alpha and beta isomers. Inasmuch as all of the less reactive sugar is not necessarily alpha, nor all of the more reactive, beta, the proportions of the less reactive and of the more reactive sugar represent limiting values for the alpha and beta normal sugars rather than absolute values. The striking agree-

ment of the proportions obtained from the oxidation studies with those obtained from the optical measurements, however, makes it seem probable that the equilibrium solution consists, at least largely, of the normal alpha and beta isomers.

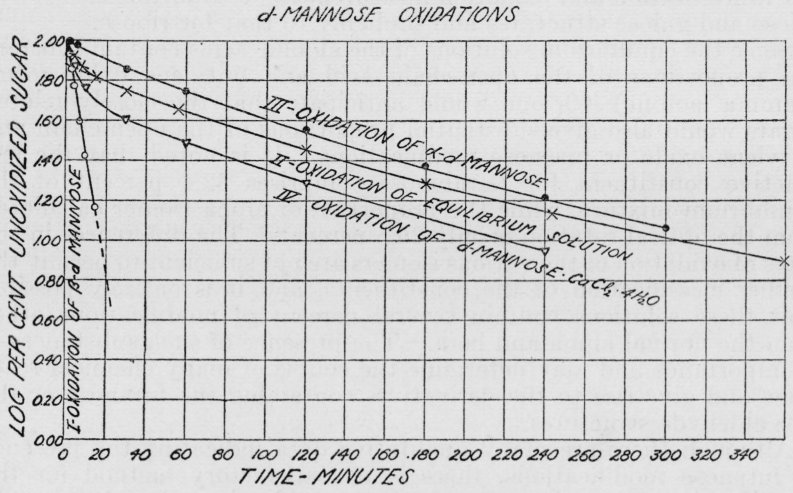


FIGURE 2.—*d-Mannose oxidations.*

It may be observed from the data of table 2 that the equilibrium solutions of sugars of similar structure frequently have approximately the same proportions of less reactive and more reactive substances. Thus the proportions of the two fractions for glucose, lactose, and

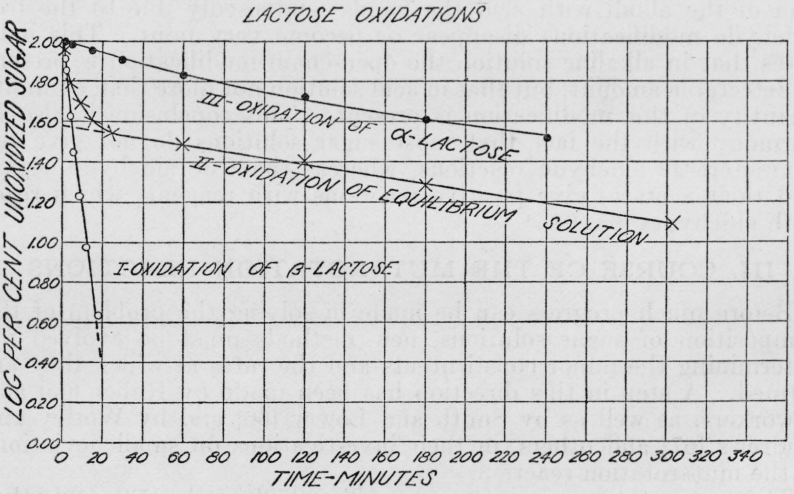


FIGURE 3.—*Lactose oxidations.*

maltose are nearly the same. Also the proportions for galactose and arabinose and for mannose and rhamnose are alike, while the proportions for xylose, lyxose, and ribose differ slightly from those for glucose, mannose, and talose, respectively. For every sugar so far investigated, the less reactive modification (the alpha form according to the suggested nomenclature) predominates in the equilibrium solution

whenever the hydroxyl of carbon 2 is directed away from the ring. This generalization is in agreement with the statement of Haworth and Hirst [108] "that in the equilibrium mixture of the two isomerides the tendency is for the *trans* form to predominate." The results of our mutarotation and oxidation measurements extend this rule to the talose and gulose structures and probably to that for ribose.

Since the equilibrium solutions of the aldonic acids contain substantial proportions of the open-chain acid and butylene oxide forms (gamma lactone) [60] one would anticipate that the closely related sugars would also give substantial proportions of the open-chain and butylene oxide or furanose modifications. It is noted that the less reactive constituent for *l*-arabinose comprises 32.4 percent of the equilibrium mixture, while the proportion of alpha isomer calculated from the optical rotation is only 26.5 percent. The differences in the rates of oxidation of the various isomers are not sufficient to permit the further classification of the constituents, and it is entirely possible that these solutions contain several percent of modifications other than the normal alpha and beta. The presence of such substances is of importance and may determine the course of many chemical reactions and give rise to the derivatives containing the furanose or the free aldehyde structures.

Although there are many qualitative data indicating the presence of furanose modifications, there is no satisfactory method for the identification and estimation of these modifications, but fortunately the presence or absence of even a small quantity of the aldehyde modification can be ascertained with certainty. Thus it has been shown by Gabryelski and Marchlewski [61] and others [62] that glucose, galactose, maltose, arabinose, and rhamnose in alkaline solution give strong absorption bands in the ultraviolet, but after neutralization of the alkali with acid the bands (supposedly due to the free aldehyde modification) disappear or become very faint. This indicates that in alkaline solution the open-chain modification is present in detectable amount, but that in acid solution not more than a minute quantity of this modification is present. This conclusion is also in harmony with the fact that most sugar solutions do not give the characteristic aldehyde reactions, whereas the true aldehyde sugars and their acetates give positive reactions with reagents which react with aldehydes [63, 64].

III. COURSE OF THE MUTAROTATION REACTIONS

Before much progress can be made in solving the problem of the composition of sugar solutions, new methods must be evolved for determining the minor constitutents and the rates at which they are formed. A step in this direction has been made by Riiber [65] and coworkers, as well as by Smith and Lowry [66] and by Worley and Andrews [67] and others, in their investigations on small deviations in the mutarotation reaction.

The mutarotation measurements of Trey [72], Osaka [73], and other early investigators appeared to follow the first-order or unimolecular law. According to this law, the optical rotation at any time after dissolving the sugar in water can be expressed by the equation

$$[\alpha]_D = Ae^{-kt} + C, \tag{1}$$

in which $[\alpha]_D$ is the specific rotation at the time t, e the logarithmic base, A the difference between the initial and final specific rotations,

C the final or equilibrium specific rotation, and k the velocity constant for the change in rotation. In 1899 Lowry [69] (see also Hudson [68]) suggested that the mutarotation reaction was a reversible one, and in 1903 Hudson [70] showed that the two forms of lactose have equal velocity constants for their mutarotations, and that the maximum rate of solution is in accord with the hypothesis that the changes in rotation are not due to different reactions but to opposite parts of one balanced reaction. By applying the mass action law to the reversible reaction represented as $\alpha \underset{k_2}{\overset{k_1}{\rightleftarrows}} \beta$ Hudson [71] developed the following equation:

$$k_1+k_2=\frac{1}{t}\log\frac{r_o-r_\infty}{r_t-r_\infty}, \qquad (2)$$

in which t equals the time after dissolution, r_0 the optical rotation at zero time, r_t the rotation at the time t, and r_∞ the final or equilibrium rotation. The mutarotation coefficient, k_1+k_2, was shown to be the sum of the constants for the two opposing reactions. The mutarotation coefficient is usually expressed in common logarithms, but if the values of k_1 and k_2 are to be applied in kinetic problems they must be reduced to a natural logarithmic base by multiplication by 2.3026. This equation is merely the logarithmic form of equation 1 expressed in terms of the observed rotations and the separate velocity constants.

Until relatively recently it was believed that the monomolecular equation adequately represents the mutarotation of the reducing sugars. In 1926 Riiber and Minsaas published a paper [65] on the existence of a third modification of galactose in which they showed that during the mutarotation of alpha and beta galactose the changes in refractive index and molecular volume give evidence for at least three modifications of the sugar. Shortly afterwards Smith and Lowry [66] as well as Worley and Andrews [67] reported deviations in the mutarotation of α- and β-d-galactose which had been neglected by earlier workers. By assuming that three substances are involved Riiber and Minsaas developed an equation which satisfactorily expresses their experimental results. By a somewhat similar process Smith and Lowry applied equations previously developed by Lowry and John [74] to their measurements and calculated the optical rotations and proportions of the constituents in the equilibrium solutions. The calculations were based on different hypothetical three-component systems, on the measurement of different physical properties, and on deviations only slightly larger than the experimental error. Consequently it is not surprising that there was considerable difference in the results from the two laboratories. As pointed out by Riiber, Minsaas, and Lyche [75] the proportions estimated by Riiber and Minsaas, as well as those calculated by Smith and Lowry, are based on the assumption that only three isomers are present; if more substances are present the proportions will be incorrect. The prevalence of equilibrium systems containing three or more constituents is shown by recent work. Thus Dale [76] reported a calcium chloride compound of mannose which exhibits a complex mutarotation, while Phelps, Isbell, and Pigman [18] and Isbell [77] showed that d- and l-ribose and d-β-glucoheptose give similar mutarotations. The compound character of these mutarotations clearly shows that the reactions are more complex than the simple interconversion of two isomers,

and that it is necessary to adopt a method for expressing the mutarotation which takes account of these characteristic properties.

Smith and Lowry's fundamental equation for expressing the complex mutarotations is difficult to apply because it involves numerous constants which must be determined by laborious mathematical calculations. The evaluation of these constants requires the postulation of a definite number of reactions taking place in a certain manner so that values thus obtained are highly speculative. The fundamental equation was simplified by them to the following form:

$$[\alpha]_D = Ae^{-m_1't} + Be^{-m_2't} + C. \tag{3}$$

This equation satisfactorily represents two consecutive reactions as $x \rightleftarrows y \rightleftarrows z$. As applied to the sugar series the equation is more or less empirical, but it appears to fit the data for the simple and complex mutarotations as completely as the monomolecular equation fits the simple alpha-beta interconversions. Term C in equation 3 represents the equilibrium rotation, A the total change in optical rotation due to the slow or principal mutarotation reaction, and B the deviation between the initial rotation and that obtained by extrapolation of the slow mutarotation to zero time.

The exponents m'_1 and m'_2 are functions of the velocity constants for the separate reactions which occur during the mutarotation and represent the rate at which the optical rotation changes. The equation can be conveniently expressed to the base 10 rather than e, in which case m_1 and m_2 are in common logarithms rather than in natural logarithms.

In order to develop equations of this type from the experimental data by the method of Lowry and Smith [78] the mutarotation is divided into two periods, a short period, beginning at zero time during which a rapid change occurs, and a long period, beginning when the rapid change is substantially complete. By applying the formula

$$m_1 = \frac{1}{t_2 - t_1} \log \frac{r_1 - r_\infty}{r_2 - r_\infty} \tag{4}$$

to the data representing the long period (that is, the last part of the mutarotation) values of m_1 are obtained. It will be observed that m_1 is the ordinary mutarotation coefficient measured for the latter part of the mutarotation, and that a mutarotation which follows the unimolecular law gives rise to only one exponential term. The constant, m_2, for the initial rapid change is calculated from the following equation:

$$m_2 = \frac{1}{t_2' - t_1'} \log \frac{d_1'}{d_2'}, \tag{5}$$

in which d_1 and d_2 represent the differences between the observed rotations and those obtained by extrapolation of the long period back to the corresponding times. The extrapolation is accomplished mathematically by substitution of the calculated value of m_1, the observed equilibrium rotation, r_∞, and the observed rotation, r_2, at the time, t_2, selected after the rapid period is over, in equation 4, and solving for the rotation, r_1, at the desired time, t_1.

The following example based on the data for the mutarotation of α-*l*-arabinose at 0° C, reported in table 11, page 184, is given to clarify this description. Column 2 gives the observed rotations at the indicated times. The calculation of m_1 is begun at 60.4 minutes, since calculations started at earlier times give a drift in the constant. The values of m_1 given in column 4 are obtained by application of equation 4 using $r_1=75.01$, $t_1=60.4$, and for r_2, readings taken at later times. The slow reaction is carried back to times earlier than 60.4 minutes by substituting the average value of m_1 (3.62×10^{-3}) in equation 4 and solving for r_1 at each of the times, t_1, earlier than 60.4 minutes (including zero time), using $r_2=75.01$, $r_\infty=52.20$, and $t_2=60.4$. (The equilibrium rotation, subtracted from the calculated value at zero time, gives A in equation 6.) These values, subtracted from the observed rotations at the corresponding times, give the deviations shown in column 5 of the table. The constant, m_2, for the rapid change is then obtained by substituting the deviations in equation 5, using $d_1=2.28$, $t'_1=4.3$, and for d_2 successively each of the values recorded at the later times, t'_2, and solving for m_2. By placing the average value of m_2 (21.7×10^{-3}) in equation 5, and using $d_2=2.28$ and $t_2=4.3$, the value of d_1 at zero time, t_1, may be obtained by solution of the equation. The value so obtained (2.83) is that to be used for B in the following equation:

$$°S=A\times10^{-m_1t}+B\times10^{-m_2t}+C. \qquad (6)$$

The equilibrium rotation (52.20) is C, while A, as already explained, is 37.74. Substitution of these values in equation 6 gives

$$°S=37.74\times10^{-0.00362t}+2.83\times10^{-0.0217t}+52.20. \qquad (7)$$

If it is desired to use the natural logarithmic base, equation 7 would be changed only by replacement of the base "10" by "*e*" and by multiplying each of the exponents by 2.3026. This equation is converted to a specific rotation basis by multiplying by the ratio of the equilibrium specific rotation to the observed equilibrium rotation in sugar degrees (°S).

In this paper the mutarotations of sugars which follow the unimolecular course within the experimental error are expressed by the equation containing only one exponential term, while those which deviate considerably from the unimolecular course are expressed by equations containing two exponential terms. A summary of the results is given in table 3. The experimental procedure and the data are reported in more detail on page 178.

TABLE 3.—*Summary of optical-rotation measurements made in this investigation*

1	2	3	4	5	6	7	8	9
Sugar	Concentration	Temperature	Initial	Equilibrium	Molecular rotation	Hudson's 2A	$[\alpha]_D$ at t minutes after dissolving crystals	References to related data
	g/100 ml	°C	$[\alpha]_D$	$[\alpha]_D$	$[M]$	$[M]_\alpha - [M]_\beta$		
-*d*-Glucose	3.9	20.0	+112.2	+52.7	+20,210	+16,840	$+59.5\times10^{-.00632t}+52.7$	[100, 101]
α-*d*-Glucose	3.9	0.2	+111.5	+52.1	+20,080	+16,770	$+59.4\times10^{-.00074t}+52.1$	[81, 90]
β-*d*-Glucose	3.9	20.0	+18.7	+52.7	+3,370		$-34.0\times10^{-.00625t}+52.7$	[102, 103]
β-*d*-Glucose	3.9	0.2	+18.4	+52.1	+3,310		$-33.7\times10^{-.000738t}+52.1$	[81, 67]
α-*d*-Galactose	5.0	20.0	+150.7	+80.2	+27,150	+17,640	$+64.9\times10^{-.00803t}+5.6\times10^{-.0790t}+80.2$	[65, 78]
α-*d*-Galactose	4.1	0.0	+152.9	+84.0	+27,540	+17,630	$+66.3\times10^{-.000930t}+2.7\times10^{-.0119t}+84.0$	[66, 67]
β-*d*-Galactose	4.0	20.0	+52.8	+80.2	+9,510		$-32.3\times10^{-.00812t}+4.9\times10^{-.0883t}+80.2$	[78, 75]
β-*d*-Galactose	4.1	0.0	+55.0	+84.0	+9,910		$-31.5\times10^{-.000897t}+2.5\times10^{-.0167t}+84.0$	[66]
α-*d*-Mannose	4.0	20.0	+29.3	+14.2	+5,280	+8,340	$+15.1\times10^{-.0173t}+14.2$	[104, 105]
α-*d*-Mannose	4.0	0.2	+28.8	+14.6	+5,190	+8,200	$+14.2\times10^{-.00216t}+14.6$	[104]
β-*d*-Mannose	4.0	20.0	−17.0	+14.2	−3,060		$-31.2\times10^{-.0178t}+14.2$	[89, 45]
β-*d*-Mannose	4.0	0.3	−16.7	+14.6	−3,010		$-31.3\times10^{-.00214t}+14.6$	[89, 104]
Mannose $CaCl_2.4H_2O$	9.1	20.0	−31.3	+6.0	−11,370		$+4.0\times10^{-.0245t}-41.1\times10^{-.311t}+6.0$	[76]
Mannose $CaCl_2.4H_2O$	8.4	0.0	−29.7	+6.2	−10,790		$+4.5\times10^{-.00267t}-40.3\times10^{-.0608t}+6.2$	[76]
α-*d*-Talose	3.8	20.0	+68.0	+20.8	+12,250		$+9.3\times10^{-.0263t}+37.9\times10^{-.126t}+20.8$	[106, 19]
α-*d*-Talose	4.0	0.1	+62.5	+25.2	+11,260	+9,870	$+9.8\times10^{-.00632t}+27.5\times10^{-.0255t}+25.2$	[19]
β-*d*-Talose[b]	4.0	20.0	+13.2	+21.0	+2,380		$-17.5\times10^{-.0262t}+9.7\times10^{-.101t}+21.0$	
α-*d*-Gulose $CaCl_2.H_2O$	6.807	20.0	+37.1	−10.0	+11,470		$+47.1\times10^{-.0191t}-10.0$	[82]
α-*d*-Gulose $CaCl_2.H_2O$	6.468	0.2	+40.5	−9.4	+12,520		$+49.9\times10^{-.00188t}-9.4$	
(*d*-Gulose)$_2$ $CaCl_2.H_2O$	4.281	20.1	+29.4	−16.5	[a]+7,190		$+45.9\times10^{-.0197t}-16.5$	[83]
(*d*-Gulose)$_2$ $CaCl_2.H_2O$	4.215	0.2	+34.6	−16.9	[a]+8,460		$+51.5\times10^{-.00202t}-16.9$	
α-*l*-Arabinose	4.3	20.0	+190.6	+104.5	+28,610	+17,050	$+77.3\times10^{-.0300t}+8.8\times10^{-.138t}+104.5$	[14, 93]
α-*l*-Arabinose	4.1	0.0	+194.0	+109.2	+29,120	+17,330	$+78.9\times10^{-.00362t}+5.9\times10^{-.0217t}+109.2$	[19]
β-*l*-Arabinose $CaCl_2.4H_2O$	8.9	20.0	+34.7	+48.0	+11,560		$-16.8\times10^{-.0300t}+3.5\times10^{-.169t}+48.0$	[92, 93]
β-*l*-Arabinose $CaCl_2.4H_2O$	9.3	0.0	+35.4	+50.1	+11,790		$-16.8\times10^{-.00384t}+2.1\times10^{-.0369t}+50.1$	[19]
α-*d*-Xylose	4.4	20.0	+93.6	+18.8	+14,050		$+74.8\times10^{-.0203t}+18.8$	[45]
α-*d*-Xylose	4.2	0.0	+95.2	+17.3	+14,310		$+77.9\times10^{-.00245t}+17.3$	[45]
α-*d*-Lyxose	4.0	20.0	+5.6	−13.8	+860	+11,790	$+19.4\times10^{-.0568t}-13.8$	[45]
α-*d*-Lyxose	3.9	0.2	+4.7	−13.4	+710	+11,340	$+18.1\times10^{-.00944t}-13.4$	

β-*d*-Lyxose	4.0	20.0	−72.6	−13.8	−10,930		$-58.8\times10-.^{0591t}-13.8$	[108]
β-*d*-Lyxose	4.0	0.2	−70.8	−13.4	−10,630		$-57.4\times10-.^{00840t}-13.4$	
l-Ribose	4.0	20.0	+20.3	+20.7	+3,050		$-7.6\times10-.^{0492t}+7.2\times10-.^{331t}+20.7$	[109]
l-Ribose	4.1	0.2	+23.4	+23.2	+3,510		$-7.9\times10-.^{00687t}+8.1\times10-.^{054t}+23.2$	[18]
α-*l*-Rhamnose.H_2O	4.0	20.2	−8.6	+8.2	−1,570		$-16.8\times10-.^{0430t}+8.2$	[45, 110]
α-*l*-Rhamnose.H_2O	4.5	0.0	−7.4	+8.7	−1,370		$-16.1\times10-.^{00568t}+8.7$	
α-Lactose.H_2O	7.6	20.0	+85.0	+52.6	+30,620	+18,680	$+32.4\times10-.^{00471t}+52.6$	[105, 45, 111]
α-Lactose.H_2O	4.9	0.2	+86.4	+53.6	+31,130	+18,710	$+32.8\times10-.^{000544t}+53.6$	[71]
β-Lactose	4.0	20.0	+34.9	+55.4	+11,940		$-20.5\times10-.^{00466t}+55.4$	[111, 72]
β-Lactose	3.9	0.2	+36.3	+56.4	+12,420		$-20.1\times10-.^{000524t}+56.4$	[71]
β-Maltose.H_2O	4.2	20.0	+111.7	+130.4	+40,240		$-18.7\times10-.^{00527t}+130.4$	[45]
β-Maltose.H_2O	4.5	0.0	+114.8	+131.5	+41,360		$-16.7\times10-.^{000580t}+131.5$	

[a] [*M*] for 1 molecule of *d*-gulose.

[b] We have prepared this new sugar recently and have included it in order to make this table more complete. Oxidation data are also given in table 7. Additional data concerning this sugar, as well as some of the derivatives of *d*-talose, are now being prepared for publication.

By inspection of table 3 it may be seen that the values of m_1 (the constant representing the principal mutarotation reaction) obtained from the alpha sugars agree within reasonable experimental error with those obtained from the corresponding beta-sugars. The values of m_2 (the constant representing the rapid change) vary over a wider range, but since the experimental error is large the differences are not significant.

The molecular rotations and the differences in the molecular rotations ($2A$) for the alpha and beta isomers are given for convenience in comparing the optical rotations, and to show that the differences in the molecular rotations of the alpha and beta sugars at 0° C are practically the same as those obtained at 20° C.

The initial specific rotation for α-*d*-talose was calculated by Isbell, [39] in 1929 to be +60. This is in approximate agreement with that found (+68). The predicted rotation was based on values for the optical rotations of the various asymmetric carbon atoms, which were calculated by application of the van't Hoff [79, 80] theory of optical superposition. According to the accepted formulas, α-*d*-talose differs from α-*d*-galactose in the configuration of the second carbon, and this difference is analogous to the difference in the structures of α-*d*-mannose and α-*d*-glucose. Sugars which differ in the stereomeric configuration of the second carbon have been designated "epimers" and the difference in their optical rotation is called epimeric difference [38]. According to our measurements at 20° C the difference in the molecular rotations of α-*d*-glucose and α-*d*-mannose is 14,930, and of α-*d*-galactose and α-*d*-talose is 14,900. The approximate agreement might have been anticipated because the two calculations are made on substances which differ only in the configuration of the fourth carbon, and this carbon is removed from the asymmetric center involved in the calculation. The agreement of the optical rotation of talose with the calculated value is probably due in large measure to the similarity of the structures. The new measurements extend the field for such comparison and should aid in the correlation of optical rotation and structure.

The mutarotations of α- and β-*d*-glucose were studied very closely in order to detect any deviations. Reference to table 10, page 179, shows that within experimental error neither alpha nor beta glucose mutarotations deviate from the first-order equation. This is in opposition to the deviations reported by Worley and Andrews. A total of 14 measurements with α- and β-glucose and with α-glucose hydrate were made at 0 and 20° C, and no deviations from the monomolecular equation beyond the experimental error were found. Although the equilibrium specific rotation of *d*-glucose is reported to be independent of the temperature [81] our measurements at 20° C and at 0° C give values of 52.7 and 52.1, respectively. Even though the difference is not large it is sufficient to require revision of the concept that the equilibrium rotation of this sugar is independent of temperature.

The equilibrium rotations of *d*-mannose $CaCl_2.4H_2O$ and *l*-arabinose $CaCl_2.4H_2O$ differ slightly from the equilibrium rotations of the sugars in the absence of calcium chloride. This is due, at least in part, to an alteration in the equilibrium between the various modifications of the sugars by the calcium chloride which is similar to that found by

Isbell for *d*-gulose [82]. By changing the concentration of calcium chloride in aqueous solutions of galactose, arabinose, and mannose, sufficient equilibrium displacements occur to give rise to mutarotation.

As may be seen from the equations in table 3 and the data given on page 180, the mutarotations of both α-*d*-gulose $CaCl_2.H_2O$ and (*d*-gulose)$_2$ $CaCl_2.H_2O$ take place in the same direction and at like rates, but the initial rotations (calculated on the same basis) have widely different values. Although the two compounds are crystalline and apparently homogeneous, since the mutarotations follow the monomolecular equation, it seems probable that the compound with lower optical rotation contains some of the heretofore unknown beta modification. The bromine oxidation of α-*d*-gulose $CaCl_2.H_2O$ (page 170) proceeds at a fairly uniform rate but that of (*d*-gulose)$_2$ $CaCl_2.H_2O$, table 9, proceeds rapidly until a part of the sugar is used up, and then more slowly as the remaining sugar continues to be oxidized. The rates of reaction indicate that (*d*-gulose)$_2$ $CaCl_2.H_2O$ contains about 32 percent of easily oxidizable sugar. When (*d*-gulose)$_2$ $CaCl_2.H_2O$ was first reported it was thought to represent another ring modification [83] because its optical rotation changed in the same direction as the gulose $CaCl_2.H_2O$, first obtained, while the rate of mutarotation appeared to increase after the first few minutes. Unfortunately the optical rotation was measured in a polariscope tube made of nickel-plated brass. Subsequent investigation has revealed that such tubes give erratic mutarotation measurements. The metal or oxide film appears to dissolve and catalyze the mutarotation reaction. Sugar solutions taken from brass tubes give positive tests for heavy metals with hydrogen sulphide. Although it is recorded in the literature [84] that traces of metals accelerate the rate of mutarotation, this has not been emphasized sufficiently and is not generally appreciated. According to our experience contact of the sugar solutions with nickel, monel metal, brass, and copper causes a drift in the mutarotation constants of the sugars. On the other hand, silver tubes give mutarotation constants which agree with those obtained with glass tubes. The small deviation in the mutarotation of xylose, previously reported by Isbell [85] also appears to be due to experimental error.

The only mutarotations in the group (summarized in table 3) which require two exponential terms for expression are α- and β-*d*-galactose, α- and β-*l*-arabinose, α-*d*-talose, *d*- and *l*-ribose, and mannose $CaCl_2.4H_2O$. It is possible that there are very small deviations in the mutarotations of some of the others, but careful investigation at 0° C has failed to establish any larger than the experimental error.

In the following table the values of m_1 and m_2 as determined by the various investigators are compared for α- and β-*d*-galactose and α-*l*-arabinose. Where no references are given the values are taken from table 3.

The mutarotations of α- and β-*d*-galactose are given in figure 4, in which the observed optical rotations are represented by the solid lines; the dotted lines represent the course of a first-order reaction calculated from the constant obtained for the last part of the mutarotation. The distances between the solid and dotted lines represent the deviations. For galactose and arabinose (fig. 4 and 5) the deviations are small; larger differences are found for α-*d*-talose (fig. 6) and *l*-ribose (fig. 7).

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TABLE 4.—*Comparison of mutarotation constants obtained by different investigators*

Sugar	Temperature	Concentration	m_1	m_2	References
	°C	*Percent*			
α-*d*-Galactose	20.0	5.0	0.00799	0.079	
	20.0	7	.00803	.078	Lowry and Smith [1] [78].
β-*d*-Galactose	20.0	4.0	.00812	.0883	
	20.0	7.7	.00834	.113	Lowry and Smith [78].
	20.0		.0083	.060	Riiber, Minsaas, and Lyche [75].
α-*d*-Galactose	.0	4.1	.00093	.0119	
	.8	10	.00094	.0161	Lowry and Smith [78].
β-*d*-Galactose	.0	4.1	.00090	.0167	
	.8	10	.00094	.0161	Lowry and Smith [78].
α-*l*-Arabinose	20.0	4.3	.030	.138	
	20.0		.029	.108	Riiber and Sørenson [14].

[1] The constants reported by Lowry and Smith were calculated for the natural logarithmic base, but in the above table they have been made comparable to the other values by conversion to the base 10 by use of the factor 0.4343. Since the paper of Lowry and Smith (J. Phys. Chem. **33**, 9 (1929)) is of unusual importance to those applying their method of analysis, it seems desirable to correct a number of obvious typographical errors which might prove confusing. Comparison of the values given in table 4 with those in table 1 (both of their paper) shows that m_1 for the latter table should be 0.00216 instead of 0.000216. In tables 3 and 4 and on page 13, the first terms of the equations representing the mutarotations of the beta forms should be negative. Similarly the values of k_4 at 20° on page 13 should be 0.0788 instead of 0.788; and at 0.8° should be 0.02163 rather than 0.2163.

The reality of the deviations in the mutarotation of *d*-galactose is demonstrated by measuring the optical rotation of a freshly prepared solution containing α- and β-*d*-galactose in the proportions required to give a solution whose optical rotatory power equals the equilibrium rotation. As may be seen by inspection of curve 3 in figure 8 and the data given in table 5, the optical rotation decreases to a minimum at a rate comparable to that of the rapid mutarotation reaction, and thereafter increases at a rate comparable to the slow mutarotation until it reaches the initial value. This complex mutarotation is in marked contrast to the total absence of mutarotation in the case of a similar solution of *d*-glucose [86]. The presence of any mutarotation proves that the equilibrium mixture does not consist solely of the normal alpha and beta isomers.

TABLE 5.—*Mutarotation at 0.3° C of an aqueous solution of α- and β-d-galactose in proportions corresponding to the equilibrium rotation* [1]

$[°S = 37.91 - 1.15 \times 10^{-.00106t} + 1.22 \times 10^{-.0168t}]$

Time	Observed reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$	Time	Observed reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^2$
Minutes	°S				*Minutes*	°S			
3.09	37.84	----------	1.08	----------	61.38	37.05	----------	.13	15.8
4.71	37.78	----------	1.01	18.0	88.4	36.98	----------	----------	----------
9.19	37.62	----------	0.84	17.9	138.8	37.09	1.08	----------	----------
12.85	37.55	----------	.76	15.6	180.6	37.16	1.01	----------	----------
15.49	37.51	----------	.71	14.7	244.8	37.27	1.04	----------	----------
21.02	37.35	----------	.54	16.8	376.2	37.46	1.10	----------	----------
25.88	37.27	----------	.44	17.1	∞	37.91	----------	----------	----------
31.62	37.20	----------	.36	16.7					
43.38	37.07	----------	.20	18.2	Average	----------	1.06	----------	16.8
51.26	37.05	----------	.16	17.2					

[1] The experiment was conducted in a manner analogous to the usual mutarotation measurement, except that a mixture of β-*d*-galactose (2.1334 g) and α-*d*-galactose (0.8975 g) was used. The solution, made by adding approximately 75 ml of water to this mixture, was read in a 4-dm tube.

Another method for the study of the complex mutarotation reactions was outlined in a previous publication [19] in which we called attention to the surprisingly large differences in the equilibrium rotations of gal-

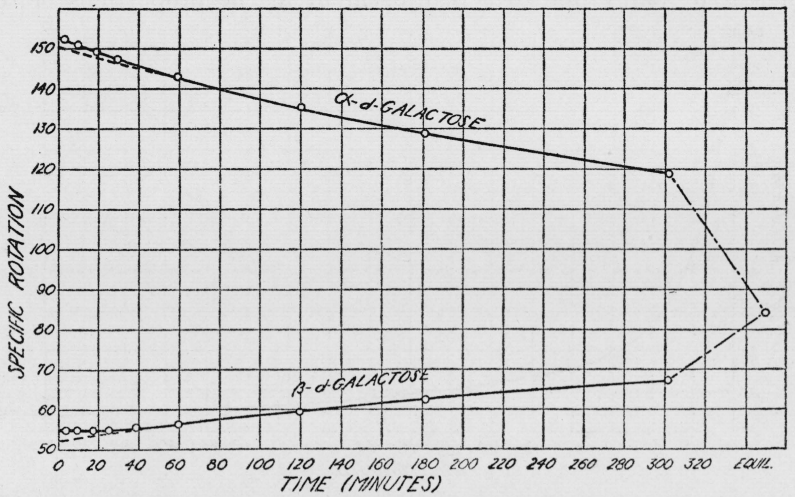

FIGURE 4.—*Mutarotation of α- and β-d-galactose in water at* 0° C.

actose, arabinose, and talose at various temperatures and showed that after changing the temperature complex "thermal mutarotations" occur. As may be seen from curve *II* in figure 8, the optical rotation of an aqueous solution of *d*-galactose after lowering the temperature

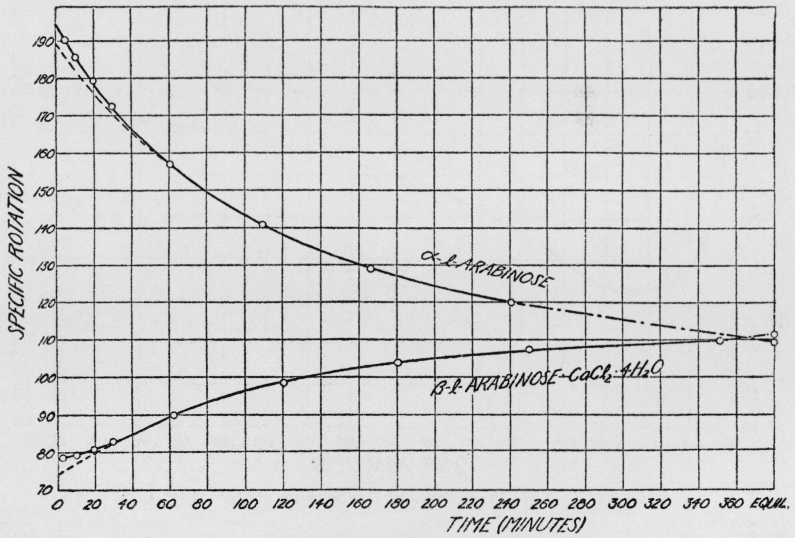

FIGURE 5.—*Mutarotations of α-l-arabinose and β-l-arabinose* $CaCl_2.4H_2O$ *in water at* 0° C.

from 25 to 0° C rises to a maximum and then decreases. Analysis of the data and the development of equations similar to those used for the mutarotations of the crystalline sugars show that the thermal mutarotation consists in two reactions. The first is rapid and appears

to take place at the same rate as the rapid reaction found in the mutarotations of α- and β-*d*-galactose. A large part of the thermal mutarotation is due to this rapid reaction; the subsequent slow reaction, which is probably due to a readjustment in the proportions of the

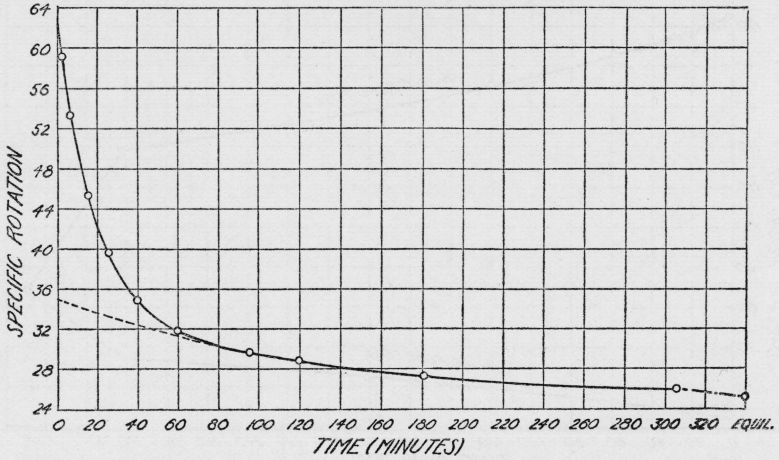

FIGURE 6.—*Mutarotation of α-d-talose in water at* 0° C.

normal alpha and beta isomers, causes only a small change in optical rotation. As might be expected, the thermal mutarotation of arabinose (curve *I*) is similar to that of galactose. The thermal mutarotation of talose consists in a rapid change which is followed by a small but

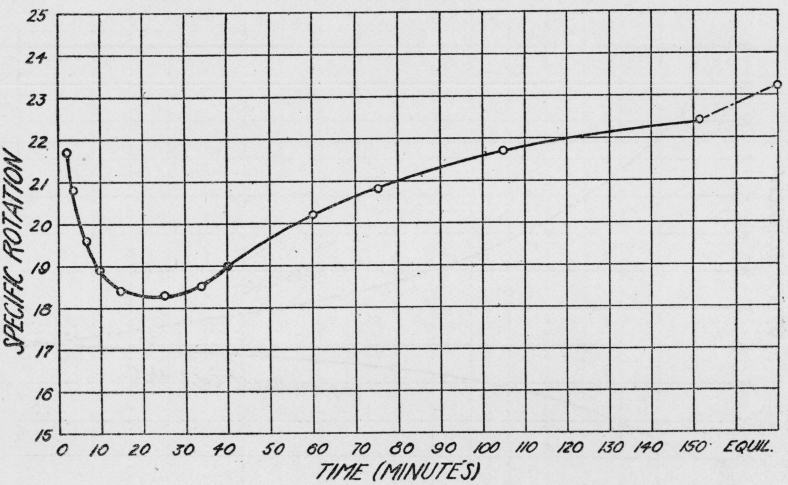

FIGURE 7.—*Mutarotation of l-ribose in water at* 0° C.

real slow change. The data on the thermal mutarotations are given in detail in table 12.

The variation of the equilibrium proportions of the labile constituents with temperature, as revealed by the thermal mutarotations, indicates that the heat of the rapid reaction is considerable and probably larger than the heat of reaction for the slow change. Information

with respect to the heat of activation, Q, can be derived from a comparison of the velocity constants at different temperatures. The results of such comparison are given in table 6.

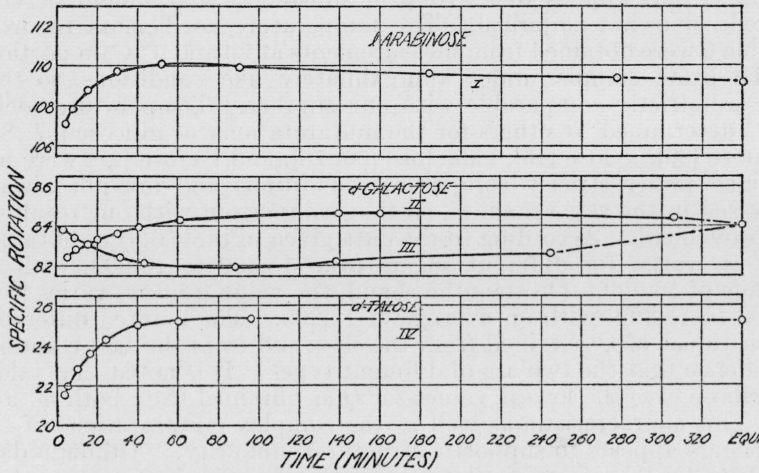

FIGURE 8.—*New methods for demonstrating complex character of equilibrium solutions*

Curve *I.* Thermal mutarotation of *l*-arabinose at 0° C.

Curve *II.* Thermal mutarotation of *d*- galactose at 0° C.

Curve *III.* Mutarotation at 0.3° C of an aqueous solution of α- and β-*d*-galactose in proportions corresponding to the equilibrium rotation.

Curve *IV.* Thermal mutarotation of *d*-talose at 0° C.

TABLE 6.—*Effect of temperature on rates of mutarotation*

Sugar	Slow change						Rapid change			
	t_1°C	$m_1 \times 10^3$ at t_1° C	t_2°C	$m_2 \times 10^3$ at t_2°C	Q	Temperature coefficient [1]	$m_2 \times 10^3$ at t_1°C	$m_2 \times 10^3$ at t_2°C	Q	Temperature coefficient [1]
α-*d*-Glucose	20.0	6.32	0.2	0.741	17,200	2.6				
β-*d*-Glucose	20.0	6.25	.2	.738	17,200	2.6				
α-*d*-Mannose	20.0	17.3	.2	2.16	16,700	2.5				
β-*d*-Mannose	20.0	17.8	.3	2.14	17,100	2.5				
Mannose $CaCl_2.4H_2O$	20.0	24.5	.0	2.67	17,600	2.6	311	60.8	13,000	2.0
α-*d*-Galactose	20.0	8.03	.0	.93	17,100	2.5	79.0	11.9	15,000	2.3
β-*d*-Galactose	20.0	8.12	.0	.90	17,500	2.6	88.3	16.7	13,200	2.1
α-*d*-Talose	20.0	26.3	.1	3.62	15,900	2.4	126	25.5	12,800	2.0
α-*d*-Gulose $CaCl_2.H_2O$	20.0	19.1	.2	1.88	18,600	2.8				
(*d*-Gulose)$_2$ $CaCl_2.H_2O$	20.1	19.7	.2	2.02	18,200	2.7				
α-*l*-Arabinose	20.0	30.0	.0	3.62	16,800	2.5	138	21.7	14,700	2.2
β-*l*-Arabinose $CaCl_2.4H_2O$	20.0	30.0	.0	3.84	16,300	2.4	169	36.9	12,100	1.9
α-*d*-Lyxose	20.0	56.8	.2	8.44	15,300	2.3				
β-*d*-Lyxose	20.0	59.1	.2	8.40	15,700	2.4				
α-*d*-Xylose	20.0	20.3	.0	2.45	16,800	2.5				
l-Ribose	20.0	49.2	.2	6.87	15,800	2.4	231	54	11,700	1.9
α-*l*-Rhamnose.H_2O	20.2	43.0	.0	5.68	15,900	2.4				
α-Lactose.H_2O	20.0	4.71	.2	.544	17,300	2.6				
β-Lactose	20.0	4.66	.2	.524	17,600	2.6				
β-Maltose.H_2O	20.0	5.27	.0	.580	17,500	2.6				
Average					16,900	2.52			13,200	2.06

[1] $\frac{m \text{ at } 35° \text{ C}}{m \text{ at } 25° \text{ C}}$ as calculated from the value of Q by use of the equation $\log \frac{m \text{ at } 35°}{m \text{ at } 25°} = \frac{Q}{42{,}111}$.

Inasmuch as m_1 and m_2 are not necessarily true velocity constants but probably represent complex changes, Q as obtained by the Arrhenius equation does not correspond to the activation of any one substance but applies to a group of substances and should be considered somewhat empirical. The temperature coefficients reported in table 6 were obtained from measurements at 20 and 0° C on portions of the same sample under approximately like conditions, so that they are strictly comparable with one another. Temperature coefficients determined by others for the mutarotations of glucose [67, 88], mannose [89], xylose [45], galactose [66, 78], and lactose [27] were not obtained under strictly comparable conditions and are not always expressed in the same manner, so that comparison with our results is not convenient. According to the data given in table 6, Q as obtained from m_1 varies for different sugars from 15,300 to 18,600, with an average of 16,900. On the other hand, the value from m_2 varies from 11,700 to 15,000, with an average of 13,200. The marked difference in the values of Q obtained from the slow and from the fast reactions is evidence that the two are of different types. It is noted that talose and ribose give the lowest values for Q as obtained from both m_1 and m_2. This characteristic as well as the complex mutarotations of the two sugars appears to support a structural similarity. Although data are given for 20 sugars, similar measurements are being conducted on the remaining sugars because a complete study may reveal important differences and correlations which are not apparent from the study of only a few individuals.

IV. EXPERIMENTAL PROCEDURE

1. PREPARATION AND PURIFICATION OF THE SUGARS

The numerous errors in the optical rotations recorded in the literature attest to the need of great care in the preparation and purification of the sugars used for physical measurements. The tendency of two or more forms of the same sugar to crystallize simultaneously always leaves some uncertainty as to the homogeneity of the product, and it is only after many crystallizations under widely different conditions that it may be assumed that the product is pure. Because pure products are obtained only by slow crystallizations, whenever possible the sugars used in this investigation were crystallized very slowly in the following manner: A slightly supersaturated solution of the sugar was prepared, seeded with the desired modification and placed in a flask, which was rotated slowly for at least 1 week while crystallization took place. The crystals were then separated, washed thoroughly with aqueous alcohol, and dried at 50° C in vacuo. The samples of *α-d*-glucose, mannose $CaCl_2.4H_2O$, *α-d*-galactose, *α-d*-talose, *α-d*-gulose $CaCl_2.H_2O$, *α-l*-arabinose, *α-d*-xylose, *α-l*-rhamnose hydrate, lactose hydrate, and maltose hydrate were crystallized in this manner from aqueous solution; *α-* and *β-d*-lyxose, *α-d*-mannose, and *d-* and *l*-ribose were crystallized slowly from aqueous methyl or ethyl alcohol, while *β-d*-mannose was crystallized in like manner from acetic acid. The crystallizations of *β-d*-glucose and *β-d*-galactose were carried out rapidly from aqueous acetic acid according to the method of Hudson and Dale [90]. Although two forms of *l*-arabinose are known, only

one exists as the free crystalline sugar. The other modification is available as a calcium chloride compound which was prepared by Dale [91] and also, independently at about the same time, by Austin and Walsh [92], who kindly supplied us with some of their product for use in the present investigation. As explained on page 145, the crystalline form of *l*-arabinose (+191) is called *α-l*-arabinose, and the calcium chloride modification is designated *β-l*-arabinose $CaCl_2.4H_2O$, in contradiction to the nomenclature of Austin and Walsh as well as of Montgomery and Hudson [93]. Inasmuch as the initial specific rotation of *β-l*-arabinose $CaCl_2.4H_2O$ was reported by Austin and Walsh to correspond to +75 for the arabinose constituent, while Montgomery and Hudson gave +89.4, we prepared a new sample and determined the specific rotation. It gives $[\alpha]_D^{20}=+34.7$, which corresponds to a specific rotation of +77 for the arabinose constituent. In our experience *β-l*-arabinose $CaCl_2.4H_2O$ on recrystallization loses calcium chloride very readily and gives a mixture containing $(\alpha\text{-}l\text{-arabinose})_2CaCl_2.2H_2O$. This can be avoided by conducting the crystallization at a low temperature in the presence of an excess of calcium chloride.

The sample of $(d\text{-gulose})_2\ CaCl_2.H_2O$ used in this investigation was obtained by adding hot ethyl alcohol to a concentrated aqueous solution of $\alpha\text{-}d\text{-gulose}\ CaCl_2.H_2O$. By crystallization in this manner the original double compound gives up half of its calcium chloride.[3] The resulting crude product was recrystallized by dissolving it in a small quantity of water, adding several volumes of ethyl alcohol, and allowing crystallization to proceed slowly over the course of about 1 week.

The sample of *α-d*-talose was prepared from *d*-galactose by the method of Levene and Tipson [94]. The crude sugar was recrystallized from aqueous alcohol until further recrystallization did not lower the equilibrium rotation. It was then recrystallized very slowly from water.

The samples of *α*- and *β-d*-lyxose were prepared from calcium galactonate by the method of Ruff and Ollendorf [95] as modified by Hockett and Hudson [96]. The crystalline sugars were separated originally from aqueous alcoholic solutions without the use of seed crystals. Particular care must be used in the crystallization of the alpha form to avoid accidental seeding with the beta form. The recrystallizations were conducted slowly from aqueous methyl alcohol in the usual manner.

2. BROMINE OXIDATION MEASUREMENTS

In conducting the oxidation measurements the crystalline sugar (0.025 mole) or the equilibrium solution (0.025 mole of sugar in 100 ml of water) was added to a cold mixture consisting of 10 ml of bromine, 30 g of barium carbonate, and either 500 ml or 400 ml of aqueous barium bromide solution containing 30 g of $BaBr_2.2H_2O$ and saturated with carbon dioxide. The oxidation mixture was contained in a 1-liter 3-neck flask which was surrounded with a cooling bath and equipped with a mechanical stirrer and a thermocouple for measuring the temperature. A slow stream of carbon dioxide saturated with bro-

[3] According to a private communication from J. K. Dale, *d*-glucose $CaCl_2$ also loses $CaCl_2$ by crystallization from ethyl alcohol and gives a product which appears to be similar to $(d\text{-gulose})_2\ CaCl_2.H_2O$.

mine vapor was bubbled through the flask during the reaction. The concentration of bromine was determined at various times by sodium thiosulphate titration of the iodine liberated from potassium iodide by a weighed sample of the mixture. The concentration of the sugar was measured at intervals on samples in which the oxidation had been stopped by the removal of the bromine with linseed oil solution (1 part of raw oil dissolved in 2 parts of benzene). Sugar was determined in the filtered solutions by Scales' method [97], slightly modified by increasing the time of boiling to 6 minutes and increasing the time required to produce boiling to 4 minutes. The procedure was standardized by determinations on known quantities of the sugar in the presence of various concentrations of barium bromide. In calculating the results, allowance was made for the increase in volume caused by reaction of the barium carbonate with hydrobromic acid to produce barium bromide. This was determined by measuring the change in volume caused by adding known quantities of barium bromide to glucose solutions. The initial increase of volume resulting from the addition of the crystalline sugar was also measured and taken into account.

It was shown previously [4] that the oxidant is free bromine and that the oxidation can be represented by the equation in which a is the

$$ak=\frac{1}{t}\log\frac{A}{A-X}, \tag{7}$$

concentration of free bromine, while A and $A-X$ are the quantities of the unoxidized sugar at the beginning and end of the time interval, t. The concentrations of free bromine were read from a chart based on results obtained from the following equation, which was developed in a previous article [4]:

$$Br^3{}_2+(0.482+2B-C)Br^2{}_2+[0.0246+0.482(B-C)]Br_2-0.0246C=0, \tag{8}$$

in which Br_2 is the concentration of free bromine, B is the average bromide, and C is the average bromine concentration. The average bromide content for each oxidation period is calculated from the mean amounts of bromide present by multiplying each mean by the time interval for which it is the average and dividing the sum of the products by the total time covered. The average bromine content and the temperature were averaged in like manner. The oxidations of the various crystalline sugars are outlined in table 7, while a summary of the results is given in table 1, page 146. In general, the values of k were as uniform as could be expected for measurements of this type. In a few cases, notably for α-*d*-galactose, α-*d*-xylose, α-*d*-mannose, and *d*-gulose $CaCl_2.H_2O$ the value of k appears to decrease as the reaction proceeds. This may be caused by the accumulation of less readily oxidizable material in solution or by the production of by-products which are capable of reducing the alkaline copper reagent used in determining the unoxidized sugar.

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{t}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine a	$ak\times10^3$	$k\times10^3$
				α-*d*-GLUCOSE				
Minutes	g	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
1.4	4.59	0						
5.1	4.47	2.6	+0.3	0.360	0.368	0.089	3.11	34.9
30.0	3.83	16.6	+.2	.367	.372	.088	2.75	31.3
60.1	3.27	28.8	+.2	.374	.374	.086	2.51	29.2
120.0	2.335	49.1	+.4	.386	.375	.084	2.47	29.4
180.2	1.640	64.3	+.3	.396	.374	.081	2.50	30.9
240.0	1.190	74.1	+.5	.403	.373	.078	2.46	31.5
300.2	.565	87.7	+.5	.411	.375	.077	3.04	39.5
Average			+.3	.385	.373	.083	2.69	32.4
				β-*d*-GLUCOSE				
0	(4.756)	0						
1.3	3.495	26.5	+0.5	0.369	0.358	0.082		
3.3	2.330	51.0		.384	.355	.078	88.0	1,128
5.1	1.655	65.2	+.3	.394	.352	.074	85.4	1,154
8.3	.837	82.4		.408	.346	.069	88.7	1,286
11.1	.483	89.8	.0	.417	.341	.065	87.7	1,349
15.5	.204	95.7		.426	.340	.064	86.9	1,358
25.3	.080	98.3	−.2	.437	.340	.062	(68.3)	(1,102)
Average			+.2	.405	.347	.071	87.3	1,255
				α-*d*-GALACTOSE				
2.8	4.570	0	(+0.47)					
6.8	4.355	4.7	+.51	0.360	0.384	0.095	5.19	54.6
16.2	4.020	11.9	+.64	.365	.383	.091	4.16	45.7
29.9	3.590	21.3	+.57	.371	.381	.090	3.87	43.0
59.8	2.883	36.9	+.44	.375	.379	.088	3.51	39.9
90.4	2.380	47.9	+.41	.387	.377	.084	3.23	38.5
119.8	1.985	56.6	+.38	.396	.376	.081	3.10	38.3
179.6	1.440	68.5	+.34	.405	.374	.078	2.84	36.4
Average			+.47	.376	.379	.087	3.70	42.3
				β-*d*-GALACTOSE				
0	(4.895)	0	(+0.12)					
0.7	4.008	18.1	+.30	0.363	0.350	0.078		
2.1	2.790	43.0	+.54	.376	.347	.076	112.4	1,479
4.0	1.748	64.3	+.72	.391	.344	.072	109.2	1,517
6.9	.848	82.7	+.80	.407	.342	.068	108.9	1,600
10.1	.379	92.3	+.79	.419	.340	.065	109.0	1,677
15.0	.116	97.6	+.70	.430	.338	.063	107.6	1,708
20.1	.057	98.8	+.60	.435	.337	.061	95.2	1,561
30.2	.041	99.2					(67.4)	
Average			+.64	.403	.343	.069	107.0	1,590
				α-*d*-MANNOSE				
1.5	4.473	0	(+0.14)					
5.0	4.300	3.9	+.15	0.360	0.366	0.088	4.89	55.6
30.1	3.258	27.2	+.14	.373	.364	.083	4.81	58.0
59.9	2.491	44.3	+.14	.384	.364	.080	4.35	54.4
120.0	1.591	64.4	+.15	.398	.362	.076	3.79	49.9
179.8	1.063	76.2	+.14	.409	.361	.073	3.50	47.9
240.0	.737	83.5	+.14	.416	.361	.072	3.28	45.6
300.2	.519	88.4	+.15	.422	.361	.068	3.13	46.0
Average			+.14	.395	.363	.077	3.96	51.1

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*—Continued

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{t}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine a	$ak\times10^3$	$k\times10^3$
				β-*d*-MANNOSE				
Minutes	g	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
0	(4.625)	0	(+0.20)					
1.2	3.850	16.8	+.46	0.366	0.363	0.085		
2.4	3.257	29.6	+.59	.373	.362	.083	60.5	729
3.8	2.680	42.1	+.65	.380	.360	.080	60.5	756
6.8	1.777	61.6	+.66	.392	.356	.076	60.0	789
9.9	1.206	73.9	+.63	.402	.353	.072	57.9	804
14.9	.656	85.8	+.45	.414	.349	.068	56.1	825
29.9	.218	95.3	+.36	.431	.344	.064	(43.4)	(678)
Average			+.54	.394	.355	.075	59.0	781
				α-*d*-TALOSE				
0.9	4.650	0	(+0.19)					
4.2	4.440	4.5	+.22	0.361	0.388	0.096	(6.08)	(63.3)
15.0	3.777	18.8	+.23	.368	.385	.092	6.46	70.2
29.9	2.891	37.8	+.23	.378	.383	.089	7.12	80.0
60.2	1.822	60.8	+.21	.393	.384	.084	6.86	81.7
90.0	1.172	74.8	+.20	.404	.384	.082	6.72	82.0
150.2	.535	88.5	+.19	.418	.389	.080	6.29	78.6
210.7	.295	93.7	+.18	.428	.399	.081	5.71	(70.5)
Average			+.21	.393	.387	.085	6.69	78.5
				β-*d*-TALOSE				
0	0.180	0	(+0.5)					
1.1	.1585	11.9		0.364	0.362	0.083	50.3	607
10.0	.0517	71.3		.393	.333	.068	54.2	797
Average			(+.5)	.378	.348	.076	52.3	702
				α-*d*-GULOSE $CaCl_2$. H_2O				
0.8	4.313	0						
5.1	3.987	7.6	+0.32	0.365	0.394	0.097	7.94	81.9
15.2	3.560	17.5	+.32	.375	.371	.086	5.79	67.3
30.0	2.861	33.7	+.30	.384	.346	.077	6.10	79.2
60.7	2.047	52.5	+.30	.394	.348	.073	5.40	74.0
123.4	1.133	73.7	+.28	.409	.350	.068	4.74	69.7
180.1	0.730	83.1	+.26	.418	.346	.064	4.30	67.2
305.8	.359	91.7		.429	.350	.063	3.54	56.2
Average			.30	.396	.358	.075	5.43	70.8
				α-LACTOSE				
4.9	8.800	0	(+0.15)					
30.3	7.540	14.3	+.17	0.372	0.364	0.084	2.64	31.4
61.6	6.280	28.6	+.17	.380	.361	.080	2.58	32.3
119.9	4.820	45.2	+.17	.390	.358	.077	2.27	29.5
180.1	3.780	57.0	+.16	.398	.354	.074	2.09	28.2
239.9	3.055	62.3	+.15	.404	.351	.071	1.96	27.6
300.0	2.480	71.8	+.14	.409	.348	.069	1.86	27.0
Average			+0.16	0.392	0.356	0.076	2.23	29.3

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*—Continued

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{t}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine *a*	$ak\times10^3$	$k\times10^3$
β-LACTOSE								
Minutes	g	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
0	(9.978)	0						
1.2	7.833	21.5	+0.19	0.363	0.379	0.092		
2.3	6.503	34.8	+.34	.368	.376	.089	73.5	826
4.1	4.216	57.7	+.47	.380	.372	.084	92.8	1,105
7.0	2.928	70.7	+.52	.396	.369	.079	73.7	933
10.0	1.811	81.9	+.51	.406	.366	.075	72.3	964
13.1	1.109	88.9	+.45	.414	.364	.073	71.3	977
20.0	0.502	95.0	+.37	.426	.362	.070	63.5	907
30.2	.330	96.7	(+.27)	(.435)	(.361)	(.068)	(47.4)	(697)
Average			+.46	.404	.367	.076	74.6	952
β-MALTOSE								
0	(10.488)	0						
1.2	7.060	32.7	+0.44	0.369	0.359	0.083		
3.3	4.493	57.2	+.69	.385	.356	.077	(178.4)	(2,317)
5.6	2.717	74.1	+.82	.399	.352	.073	94.3	1,292
8.8	1.358	87.1	+.82	.412	.349	.071	94.2	1,327
14.7	.469	95.5	+.68	.427	.345	.067	131.6	1,964
30.0	.231	97.8	+.48	.441	.342	.059	(168.5)	(2,856)
Average			+0.65	0.405	0.350	0.072	106.7	1,528
α-*l*-RHAMNOSE								
1.0	4.625	0	(+0.10)					
5.1	4.270	7.7	+.14	0.362	0.365	0.086	8.45	98.3
31.3	2.705	41.5	+.16	.381	.365	.081	7.69	94.9
65.3	1.625	64.9	+.16	.397	.350	.075	7.06	94.1
120.1	.838	81.9	+.16	.413	.344	.067	6.23	93.0
183.8	.437	90.6	+.16	.424	.341	.064	5.61	87.7
240.2	.265	94.3	+.16	.430	.340	.063	5.19	82.4
300.2	.179	96.1	+.16	.435	.338	.061	4.72	77.4
Average			+.16	.406	.349	.071	6.42	89.7
α-*l*-ARABINOSE								
1.0	3.862	0	(+0.09)					
2.0	3.792	1.8	+.11	0.359	0.363	0.087	7.94	91.3
4.2	3.648	5.5	+.16	.361	.362	.086	7.74	90.0
8.1	3.397	12.0	+.23	.364	.361	.085	7.85	92.4
12.2	3.127	19.0	+.25	.368	.361	.083	8.19	98.7
19.9	2.740	29.1	+.31	.374	.359	.081	7.89	97.4
50.1	1.660	57.0	+.26	.390	.356	.076	7.47	98.3
80.0	1.064	72.4	+.26	.403	.354	.072	7.09	98.5
119.9	0.610	84.2	+.27	.414	.351	.069	6.74	97.7
180.0	.295	92.4	+.27	.425	.349	.067	6.24	93.1
Average			+.23	.384	.357	.078	7.46	95.3
β-*l*-ARABINOSE $CaCl_2.4H_2O$								
0	(3.956)	0						
0.8	3.070	22.4	+0.31	0.367	0.359	0.083		
2.1	2.166	45.2	+.51	.380	.356	.078	116.5	1,494
3.9	1.298	67.2	+.62	.395	.354	.074	120.6	1,630
6.8	.586	85.2	+.66	.411	.352	.070	119.9	1,713
12.9	.119	97.0	+.57	.429	.347	.065	116.7	1,795
Average			+.53	.396	.354	.074	118.4	1,658

TABLE 7.—*Bromine oxidation of freshly dissolved crystalline sugars*—Continued

Time after beginning oxidation	Unoxidized sugar	Oxidation	Averages for oxidation period				Velocity constants $ak=\frac{1}{t}\log\frac{A}{A-X}$	
			Temperature	Bromide Br^-	Bromine Br_2	Free bromine a	$ak\times10^3$	$k\times10^3$
α-*d*-XYLOSE								
Minutes	g	*Percent*	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*		
1.2	3.740	0	(+0.20)					
5.0	3.480	7.0	+.26	0.360	0.357	0.084	8.23	98.0
30.1	2.140	42.8	+.30	.374	.353	.078	8.39	107.6
60.0	1.410	62.3	+.30	.395	.350	.073	7.20	98.6
120.3	.704	81.2	+.28	.412	.346	.067	6.09	90.9
182.3	.391	89.5	+.26	.423	.344	.065	5.42	83.4
240.3	.258	93.1	+.25	.430	.343	.064	4.86	75.9
300.0	.144	96.1	+.24	.434	.343	.063	4.73	75.1
Average			+.27	.404	.348	.071	6.42	89.9
CRYSTALLINE *d*-RIBOSE								
0.9	3.641	0	(+0.17)					
1.8	3.357	7.8	+.22	0.363	0.373	0.089	(39.2)	
7.3	2.742	24.7	+.31	.368	.368	.086	19.2	223
29.8	1.245	65.8	+.29	.397	.359	.075	16.1	215
60.3	.554	84.8	+.27	.416	.353	.069	13.8	200
120.2	.139	96.2	+.25	.431	.347	.065	11.9	183
209.4	.033	99.1	+.24	.441	.345	.062	9.8	158
Average			+.26	.403	.358	.074	14.2	196
CRYSTALLINE *l*-RIBOSE								
0.8	3.760	0	(+0.16)					
2.9	3.420	9.0	+.22	0.362	0.390	0.097	19.6	202
6.9	2.830	24.7	+.26	.369	.386	.092	20.2	220
14.8	2.090	44.4	+.27	.382	.383	.087	18.2	209
30.0	1.226	67.4	+.24	.398	.378	.081	16.7	206
45.2	.785	79.1	+.21	.409	.375	.077	15.2	197
60.0	.522	86.1	+.20	.417	.374	.075	14.5	193
180.2	.054	98.6	+.15	.439	.371	.070	10.3	147
Average			+.22	.397	.380	.083	16.4	195
α-*d*-LYXOSE								
1.1	3.734	0	(+0.20)					
5.0	3.317	11.2	+.26	0.363	0.390	(0.096)	(13.2)	(138)
15.2	2.376	26.4	+.28	.377	.386	.090	13.9	154
30.1	1.520	59.3	+.26	.391	.382	.084	13.5	161
60.2	.699	81.3	+.20	.410	.377	.078	12.3	158
90.2	.348	90.7	+.18	.421	.375	.075	11.6	155
120.2	.175	95.3	+.17	.429	.375	.073	11.2	153
180.4	.061	98.4	+.16	.438	.376	(.072)	10.0	(139)
Average			+.22	.404	.380	.080	12.3	156
β-*d*-LYXOSE								
0	(3.808)	0						
0.8	3.543	7.0	+0.20			0.087		
3.1	2.882	24.3	+.30	0.373	0.376	.087	39.0	448
5.7	2.320	39.1	+.37	.381	.373	.084	37.5	446
9.0	1.782	53.2	+.45	.390	.364	.079	36.4	461
13.1	1.345	64.7	+.45	.399	.358	.075	34.2	456
20.0	.893	76.5	+.44	.409	.354	.072	31.2	433
30.4	.594	84.4	+.44	.419	.349	(.067)	(26.2)	(391)
Average			+.38	.395	.362	.079	35.7	449

In order to measure the rates for the oxidation of the equilibrium solutions the required quantity of sugar was dissolved in 100 ml of water and allowed to stand at 0° C until equilibrium was established, after which the solution was added to the oxidation mixture in place of the crystalline sugar. Samples of the reacting mixture were taken and analyzed, as previously described.

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (*a*)	Total	More reactive fraction	Less reactive fraction		More reactive fraction		Less reactive faction	
									$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
					d-GLUCOSE							
Minutes	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*	g	g	g	*Percent*				
0	+0.6				(4.727)	2.960	1.767	0.0				
1.3	+.6	0.365	0.346	0.079	3.900	2.145	1.755	17.5				
4.8	+.6	.379	.344	.075	2.740	1.013	1.727	43.0	93.1	1,241		
9.7	+.5	.393	.342	.071	1.990	.299	1.691	57.1	101.9	1,435		
15.0	+.4	.402	.340	.068	1.760	.104	1.656	62.8	95.9	1,410		
30.2	+.4	.412	.338	.065	1.560		1.560	66.0				
122.4	+.4	.425	.334	.062	1.055		1.055	77.7			1.84	29.7
239.9	+.4	.432	.330	.060	.710		.710	85.0			1.63	27.2
329.9	+.4	.436	.326	.058	.560		.560	88.2			1.48	25.5
Average	+.48	.406	.337	.067						1,362		27.5
					d-MANNOSE							
0	(+0.10)				(4.634)	1.440	3.194	0.0				
0.9	+.24	0.360	0.372	0.090	4.395	1.227	3.168	5.1				
3.9	+.29	.366	.372	.087	3.806	.722	3.084	17.9	76.8	883		
7.9	+.30	.372	.372	.085	3.352	.373	2.979	27.7	73.9	869		
15.0	+.30	.380	.372	.082	2.946	.136	2.810	36.4	67.8	827		
30.2	+.27	.389	.372	.078	2.499		2.499	46.1				
55.9	+.19	.398	.372	.075	2.017		2.017	56.5			3.62	48.3
119.9	+.17	.410	.372	.071	1.274		1.274	72.5			3.26	45.9
179.9	+.16	.418		.069	.876		.876	81.1			3.04	44.1
243.4	+.18	.425		.068	.609		.609	86.9			2.88	42.4
359.7	+.19	.432		.067	.355		.355	92.3			(2.57)	(38.4)
Average	+.23	.395	.372	.077						860		45.2
					d-GALACTOSE IN EQUILIBRIUM AT 0° C							
0	(+0.19)				(4.782)	3.280	1.502	0.0				
1.4	+.49	0.368	0.359	0.083	3.557	2.070	1.487	25.6				
4.8	+.83	.387	.357	.077	2.210	.755	1.455	53.8	128.8	1,673		
10.1	+.55	.399	.354	.073	1.561	.152	1.409	67.4	130.4	1,786		
15.1	+.36	.408	.352	.071	1.414	.046	1.368	70.4	120.7	1,700		
26.7	+.21	.417	.349	.068	1.282		1.282	73.2				
40.0	+.22	.422	.348	.067	1.178		1.178	75.4			2.76	41.2
70.2	+.22	.427	.346	.065	.990		.990	79.3			2.58	39.7
152.2	+.20	.433	.347	.062	.650		.650	86.4			2.35	37.9
275.0	+.18	.440	.348	.062	.405		.405	91.5			2.02	32.6
400.0	+.20	.443	.349	.062	.330		.330	93.1			1.58	(25.5)
Average	+.35	.414	.351	.069						1,720		37.9

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*—Continued

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		More reactive fraction		Less reactive faction	
									$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
d-GALACTOSE IN EQUILIBRIUM AT 20° C												
0	(−1.09)				(4.521)	3.069	1.452	0.0				
1.1	+.85	0.368	0.350	0.079	3.590	2.148	1.442	20.6				
4.9	+.12	.388	.349	.074	2.169	.760	1.409	52.0	118.7	1,604		
15.0	+.24	.409	.345	.068	1.366	.030	1.336	69.8	133.4	1,962		
25.7	+.15	.417	.343	.066	1.264		1.264	72.0				
40.1	+.14	.422	.341	.065	1.558		1.158	74.4			2.64	40.6
80.4	+.14	.429	.343	.064	.924		.924	79.6			2.49	38.9
127.7	+.15	.433	.345	.064	.736		.736	83.7			2.30	35.9
193.1	+.17	.437	.352	.065	.557		.557	87.7			2.13	32.8
240.2	+.15	.439	.359	.069	.466		.466	89.7			2.02	29.3
360.2	+.11	.442	.374	.070	.346		.346	92.3			(1.68)	(24.0)
Average	+.22	.418	.350	.068						1,783		35.5
(d-GULOSE)$_2$ $CaCl_2.H_2O$												
0	(+0.12)				(4.732)	3.855	0.877					
0.8	+.34	0.358	0.368	0.089	4.470	3.600	.870	5.5				
4.9	+.53	.368	.365	.085	3.440	2.606	.834	27.3	34.2	402		
14.8	+.43	.387	.360	.078	2.015	1.252	.763	57.4	32.8	421		
29.9	+.37	.405	.354	.072	1.126	.450	.676	76.2	31.0	431		
59.8	+.30	.423	.348	.066	.544		.544	88.5				
119.7	+.23	.436	.352	.065	.318		.318	93.3			3.89	59.8
179.9	+.19	.441	.357	.066	.238		.238	95.0			2.99	45.3
302.6	+.19	.446	.362	.066	.183		.183	96.1			(1.95)	
Average	+.32	.415	.357	.071						418		52.6
d-TALOSE												
0					(4.903)	2.164	2.739	0.0				
0.9	+0.27	0.362	0.386	0.094	4.530	1.836	2.694	7.6				
4.8	+.45	.373	.383	.090	3.470	.953	2.517	29.2	73.0	811		
10.0	+.46	.384	.379	.086	2.720	.405	2.315	44.5	72.1	838		
20.0	+.38	.396	.381	.083	2.052	.072	1.980	58.1	73.6	887		
30.7	+.31	.404	.381	.081	1.685		1.685	65.6				
45.2	+.26	.411	.377	.077	1.330		1.330	72.9			7.09	92.1
75.3	+.22	.421	.378	.076	.871		.871	82.2			6.43	84.6
121.8	+.21	.430	.387	.077	.480		.480	90.2			5.99	77.8
Average	+.32	.398	.382	.083						844		84.8
l-ARABINOSE												
0	(+0.12)				(3.930)	2.655	1.275	0.0				
1.0	+.62	0.364	0.360	0.084	3.200	1.946	1.254	18.6				
2.9	+.80	.376	.358	.080	2.367	1.148	1.219	39.8	120.5	1,506		
6.9	+.84	.393	.355	.073	1.526	.370	1.156	61.2	122.2	1,674		
15.0	+.34	.409	.354	.071	1.082	.045	1.037	72.5	116.8	1,645		
30.0	+.19	.421	.351	.068	.858		.858	78.2				
60.0	+.20	.430	.351	.066	.578		.578	85.3			5.72	86.7
107.2	+.14	.437	.350	.065	.327		.327	91.7			5.43	83.5
150.0	+.14	.441	.350	.064	.200		.200	94.9			5.27	82.3
209.7	+.14	.444	.351	.064	.125		.125	96.8			(4.66)	(72.8)
269.9	+.11	.447	.351	.063	.087		.087	97.8			(4.14)	(65.7)
Average	+.35	.416	.353	.070						1,608		84.2

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*—Continued

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
									More reactive fraction		Less reactive faction	
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
					d-XYLOSE							
0	(+0.19)				(3.938)	2.675	1.263	0.0				
0.9	+.41	0.365	0.351	0.081	3.267	2.020	1.247	17.0				
4.7	+.64	.385	.348	.075	1.809	.625	1.184	54.1	134.1	1,788		
9.8	+.57	.402	.346	.070	1.301	.188	1.113	67.0	115.9	1,656		
14.9	+.50	.410	.345	.068	1.112	.064	1.048	71.8	107.1	1,575		
29.9	+.35	.421	.343	.065	.882		.882	77.6				
60.1	+.28	.430	.342	.063	.607		.607	84.6			5.37	85.2
120.1	+.23	.438	.343	.062	.310		.310	92.1			5.03	81.1
180.0	+.21	.443	.343	.061	.183		.183	95.4			4.55	74.6
240.0	+.20	.445	.344	.061	.124		.124	96.9			(4.06)	(66.6)
353.4	+.20	.449	.346	.061	.074		.074	98.1			(3.33)	(54.6)
Average	+.36	.419	.345	.067						1,673		80.3
					d-LYXOSE							
0					(3.740)	0.758	2.982	0.0				
0.9	+0.27	0.361	0.386	0.095	3.530	.658	2.872	5.6				
5.0	+.41	.372	.383	.090	2.800	.348	2.452	25.1	67.5	750		
9.9	+.42	.381	.379	.086	2.250	.194	2.056	39.8	58.9	685		
20.1	+.39	.395	.363	.077	1.517		1.517	59.4				
29.9	+.36	.404	.369	.077	1.111		1.111	70.3			13.8	179
44.9	+.32	.414	.365	.073	.686		.686	81.7			13.9	190
59.8	+.28	.421	.362	.071	.423		.423	88.7			14.0	197
90.7	+.24	.432	.359	.068	.111		.111	97.0			(16.1)	(237)
Average	+.34	.398	.372	.080						717		189
					d-RIBOSE							
0	(+0.07)				(3.716)	0.396	3.320	0.0				
0.7	+.35	0.358	0.378	0.093	3.572	.340	3.232	3.9				
2.7	+.38	.362	.377	.091	3.220	.222	2.998	13.3	92.6	1,018		
6.6	+.40	.370	.373	.087	2.720	.104	2.616	26.8	87.2	1,002		
14.7	+.28	.382	.366	.082	2.012		2.012	45.9				
29.8	+.23	.398	.360	.075	1.210		1.210	67.4			14.6	195
61.4	+.14	.416	.357	.070	.522		.522	86.0			12.5	179
119.9	+.14	.432	.363	.069	.127		.127	96.6			11.4	165
179.9	+.14	.440	.363	.068	.039		.039	99.0			(10.4)	(153)
Average	+.26	.395	.367	.079						1,010		180
					l-RIBOSE							
0	(+0.20)				(4.096)	0.452	3.644	0.0				
0.9	+.35	0.358	0.387	0.096	3.861	.338	3.523	5.7				
2.4	+.45	.361	.386	.095	3.515	.186	3.329	14.2	172.9	1,820		
7.1	+.47	.370	.382	.090	2.920	.083	2.837	28.7	98.4	1,093		
14.9	+.48	.382	.379	.086	2.208		2.208	46.1				
29.9	+.48	.397	.374	.080	1.371		1.371	66.5			13.8	173
45.0	+.40	.408	.372	.077	.902		.902	78.0			12.9	168
60.1	+.35	.416	.371	.075	.586		.586	85.7			12.7	169
180.0	+.30	.440	.369	.069	.050		.050	98.8			(10.0)	(145)
Average	+.41	.392	.378	.083						1,456		170

TABLE 8.—*Bromine oxidations of aqueous sugar solutions in equilibrium at the beginning of the oxidation*—Continued

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
									More reactive fraction		Less reactive fraction	
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (a)	Total	More reactive fraction	Less reactive fraction		$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
					l-RHAMNOSE							
0	(+0.17)	-------	-------	-------	(4.260)	1.321	2.939	0.0	-------	-------	-------	-------
1.0	+.33	0.359	0.374	0.091	4.012	1.124	2.888	5.8	-------	-------	-------	-------
3.9	+.36	.365	.370	.088	3.478	.727	2.751	18.4	65.3	742	-------	-------
8.0	+.49	.372	.367	.084	2.970	.387	2.583	30.3	66.2	788	-------	-------
15.1	+.46	.381	.364	.081	2.468	.145	2.323	42.1	63.1	779	-------	-------
30.0	+.39	.393	.361	.077	1.886	-------	1.886	55.7	-------	-------	-------	-------
61.4	+.31	.408	.356	.072	1.211	-------	1.211	71.6	-------	-------	6.13	85.1
120.0	+.25	.421	.350	.067	.573	-------	.573	86.6	-------	-------	5.75	85.8
185.1	+.23	.430	.349	.066	.290	-------	.290	93.2	-------	-------	5.24	79.4
240.2	+.22	.435	.349	.065	.184	-------	.184	95.7	-------	-------	(4.81)	(74.0)
300.2	+.21	.439	.349	.064	.135	-------	.135	96.8	-------	-------	(4.24)	(66.3)
Average	+.33	.400	.359	.075	-------	-------	-------	------	-------	770	-------	83.4
					LACTOSE							
0	-------	-------	-------	-------	(9.399)	5.876	3.523	0.0	-------	-------	-------	-------
0.7	+0.29	0.361	0.369	0.089	8.150	4.639	3.511	13.3	-------	-------	-------	-------
3.0	+.65	.377	.364	.082	5.160	1.699	3.461	45.1	114.8	1,435	-------	-------
10.0	+.70	.402	.358	.074	3.470	.128	3.342	63.1	110.6	1,515	-------	-------
29.5	+.43	.419	.353	.069	3.190	-------	3.190	66.1	-------	-------	-------	-------
60.3	+.30	.425	.353	.067	2.870	-------	2.870	69.5	-------	-------	1.53	22.5
120.1	+.22	.430	.352	.066	2.358	-------	2.358	74.9	-------	-------	1.46	21.8
183.7	+.20	.435	.351	.065	1.959	-------	1.959	79.2	-------	-------	1.41	21.0
240.2	+.19	.439	.351	.064	1.661	-------	1.661	82.3	-------	-------	1.35	20.1
364.3	+.18	.443	.351	.064	1.421	-------	1.421	84.9	-------	-------	1.29	19.0
Average	+.35	.415	.356	.071	-------	-------	-------	------	-------	1,475	-------	20.9
					MALTOSE							
0	(+0.21)	-------	-------	-------	(9.421)	5.871	3.550	0.0	-------	-------	-------	-------
0.8	+.42	0.362	0.375	0.090	8.200	4.664	3.536	13.0	-------	-------	-------	-------
3.8	+.66	.377	.373	.085	5.640	2.152	3.488	40.1	112.0	1,318	-------	-------
7.9	+.70	.390	.371	.081	4.160	.732	3.428	55.8	113.3	1,399	-------	-------
14.9	+.60	.402	.367	.077	3.460	.125	3.335	63.3	111.5	1,448	-------	-------
30.0	+.43	.412	.362	.073	3.150	-------	3.150	66.6	-------	-------	-------	-------
60.0	+.32	.419	.360	.071	2.760	-------	2.760	70.7	-------	-------	1.91	26.9
100.1	+.27	.423	.359	.070	2.371	-------	2.371	74.8	-------	-------	1.76	25.1
162.1	+.24	.428	.360	.069	1.908	-------	1.908	79.7	-------	-------	1.65	23.9
207.0	+.23	.430	.360	.069	1.675	-------	1.675	82.2	-------	-------	1.55	22.5
360.0	+.20	.435	.365	.069	1.092	-------	1.092	88.4	-------	-------	1.39	20.1
Average	+.41	.408	.365	.075	-------	-------	-------	------	-------	1,388	-------	23.7

A comparison of the results obtained with the freshly dissolved crystalline sugars (table 7) with those for the equilibrium solutions (table 8) shows that in each case a part of the sugar is oxidized rapidly while the rest is oxidized slowly. In order to calculate the velocity constants and the proportions of the more reactive and of the less reactive sugar the oxidation is divided into two periods, a short period beginning at zero time, during which a rapid oxidation occurs, and a long period beginning when the rapid change is substantially complete. The time selected for the beginning of the calculations for each of the sugars is that given in the table for the sample immediately preceding the first recorded value of ak_A. By applying equation 7 to the data representing the long period (that is, the data representing the latter part of the oxidation) values of ak_A are obtained. The values of k_A are then obtained by dividing by a, the concentration of the free bromine given in column 5. Using the average value of k_A, values of ak_A are calculated for each of the samples taken during the initial period, using the corresponding value of a. The slow oxidation is then extrapolated to times corresponding to the taking of the earlier samples by means of equation 7, thereby obtaining values for the less reactive unoxidized sugar. The difference between the total sugar (obtained by analysis) and the less reactive sugar gives the amount of the more reactive sugar, which amount is reported in column 7. Application of equation 7 to these data gives the values of ak_B reported in column 10. The values of k_B are arrived at by dividing by a. Since the slowly oxidizable substance appears to be largely the normal alpha isomer, and the rapidly oxidizable material the beta form, the constants k_A and k_B are analogous to the constants k_α and k_β obtained by the oxidation of the crystalline sugars. To ascertain the quantity of more reactive sugar in the original solution the rapid reaction is extrapolated to zero time by means of equation 7 in a manner analogous to that used for obtaining the quantities of less reactive sugar. These calculations provide the velocity constants and the proportions of the less reactive and more reactive sugars in the equilibrium solutions.

In order to determine if there were any detectable difference in the behavior of solutions of galactose in equilibrium at different temperatures, solutions of this sugar were prepared at 20° C and at 0° C and oxidized. The oxidation of the sugar solution in equilibrium at 0° C was conducted as usual; the oxidation of the sugar solution in equilibrium at 20° C was conducted in like manner except that compensation was made for the difference in temperature by cooling the oxidant (before adding the sugar solution) below 0° C. The amount of cooling was adjusted so that on mixing the sugar solution at 20° C with the cold oxidant the temperature of the solution rose to approximately 0° C. No difference in the results obtained in the two experiments could be detected.

The oxidation of freshly dissolved (*d*-gulose)$_2$ $CaCl_2.H_2O$ shows the presence of two modifications of the sugar and consequently it was handled like an equilibrium solution. The results, which were discussed on page 161, are given in table 9.

TABLE 9.—*Bromine oxidation of freshly dissolved* (*d-gulose*)$_2$ $CaCl_2.H_2O$

Time	Temperature	Averages for the oxidation period			Unoxidized sugar			Oxidized sugar	Velocity constants			
		Bromide (Br^-)	Bromine (Br_2)	Free bromine (*a*)	Total	More reactive fraction	Less reactive fraction		More reactive fraction		Less reactive fraction	
									$ak_B \times 10^3$	$k_B \times 10^3$	$ak_A \times 10^3$	$k_A \times 10^3$
1	2	3	4	5	6	7	8	9	10	11	12	13
Minutes	°C	*Moles/liter*	*Moles/liter*	*Moles/liter*	g	g	g	*Percent*				
0	+0.17	0.358	-------	-------	(4.635)	1.485	3.150	0	-------	-------	-------	-------
0.8	+.29	.368	0.375	0.088	4.530	1.408	3.122	2.3	-------	-------	-------	-------
4.9	+.43	.401	.370	.088	4.060	1.077	2.983	12.4	28.4	323	-------	-------
30.0	+.28	.418	.362	.080	2.562	.235	2.327	44.7	26.6	333	-------	-------
60.0	+.21	.436	.357	.075	1.785	-------	1.785	61.5	-------	-------	-------	-------
124.7	+.22	.443	.350	.069	.990	-------	.990	78.6	-------	-------	3.96	57.4
179.9	+.17	.450	.348	.067	.682	-------	.682	85.3	-------	-------	3.49	52.1
300.2	+.14	-------	.350	.066	.381	-------	.381	91.8	-------	-------	(2.79)	(42.3)
Average	-------	-------	-------	-------	-------	-------	-------	-------	-------	328	-------	54.8

3. MUTAROTATION MEASUREMENTS

The optical rotations, with the exception of the thermal mutarotations, were measured in a 4-dm Schmidt and Haensch water-jacketed glass tube on a Bates saccharimeter. For reducing saccharimeter readings to angular degrees, Bates and Jackson [98, 99] obtained the conversion factor 0.34620 for sucrose. The carefully purified sugars were dried at 50° C, powdered in an agate mortar, and passed through a fine sieve. The weighed sample (usually 2 g) was placed in a dry 100-ml glass-stoppered flask and about 50 ml of pure distilled water at the correct temperature (either 20 or 0° C) was added quickly with agitation, from a pipette which had the tip cut off so that it drained in about 10 seconds. Time was measured with a stop watch, starting with the addition of the water. About 10 seconds were required to dissolve the sugar. The measurements at 20° C were conducted in a room held at about 19.5° C, while those at 0° C were conducted in essentially the same manner except that the flasks and the solutions were cooled in ice water. The readings were made by one observer while another measured the time and recorded the results. The separate readings given in tables 10 and 11 represent the average of five or more consecutive observations. The method used for the calculations of the velocity constants and the initial rotations is given on page 156.

TABLE 10.—*First-order mutarotations*

α-*d*-GLUCOSE					
3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S = 23.74 + 27.05 \times 10^{-.000741t}$ $[\alpha]_D^{0.2} = 2.1946 \times °S$			3.9 g per 100 ml at 20° C read in a 4-dm tube $°S = 23.94 + 27.01 \times 10^{-.00632t}$ $[\alpha]_D^{20} = 2.2013 \times °S$		
Time	Observed reading	$(k_1+k_2)\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$
Minutes	°S		*Minutes*	°S	
2.70	+50.67	----------	1.59	+50.33	----------
3.89	+50.60	(0.950)	2.56	+49.98	(5.98)
6.84	+50.46	(.821)	4.76	+49.15	6.27
10.58	+50.31	.742	7.44	+48.13	6.46
15.44	+50.08	.755	9.93	+47.29	6.37
24.91	+49.61	.785	16.36	+45.19	6.37
41.48	+48.90	.761	20.63	+43.92	6.35
60.08	+48.14	.747	25.51	+42.53	6.36
90.80	+46.93	.737	30.03	+41.39	6.32
120.34	+45.84	.730	39.94	+39.07	6.30
182.52	+43.63	.732	49.83	+37.01	6.33
240.68	+41.81	.728	59.95	+35.27	6.29
299.05	+40.10	.730	75.01	+33.08	6.27
409.4	+37.34	.730	89.84	+31.28	6.30
556.0	+34.34	.732	120.94	+28.62	6.29
747.4	+31.44	.730	169.19	+26.31	6.25
1,352.1	+26.50	.733	∞	+23.94	----------
∞	+23.74	----------	----------	----------	----------
Average	----------	.741	Average	----------	6.32

β-*d*-GLUCOSE					
3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S = 23.66 - 15.29 \times 10^{-.000738t}$ $[\alpha]_D^{0.2} = 2.2020 \times °S$			3.9 g per 100 ml at 20° C read in a 4-dm tube $°S = 23.98 - 15.45 \times 10^{-.00625t}$ $[\alpha]_D^{20} = 2.1927 \times °S$		
3.02	+8.45	----------	1.48	+8.86	----------
4.59	+8.48	(.548)	2.46	+9.06	(5.90)
10.01	+8.68	(.947	4.96	+9.57	6.00
21.83	+8.92	.725	9.91	+10.57	6.18
39.84	+9.39	.753	14.96	+11.52	6.23
59.90	+9.85	.737	19.96	+12.39	6.25
90.00	+10.56	.746	29.95	+13.96	6.28
120.17	+11.19	.736	45.32	+15.95	6.27
181.9	+12.45	.741	60.04	+17.53	6.32
246.8	+13.61	.738	90.07	+19.81	6.31
302.6	+14.56	.745	120.20	+21.30	6.33
390.4	+15.80	.740	183.95	+22.93	6.35
544.6	+17.60	.738	∞	+23.98	----------
1,366.3	+22.09	.723	----------	----------	----------
∞	+23.66	----------	----------	----------	----------
Average	----------	.738	Average	----------	6.25

TABLE 10.—*First-order mutarotations*—Continued

Time	Observed reading	$(k_1+k_2)\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$
α-*d*-MANNOSE					
4.0 g per 100 ml at 0.1° C read in a 4-dm tube; °S = 6.63 + 6.47 × 10^−.00216t; [α]^0.1_D = 2.2021 × °S			4.0 g per 100 ml at 20° C read in a 4-dm tube; °S = 6.63 + 7.07 × 10^−.0173t; [α]^20_D = 2.1418 × °S		
Minutes	° S		*Minutes*	° S	
3.80	+12.98	----------	1.74	+13.23	----------
7.63	+12.84	(2.53)	3.10	+12.86	(18.4)
10.10	+12.78	2.20	4.60	+12.51	17.5
14.98	+12.66	2.01	7.25	+11.93	17.3
29.98	+12.24	2.06	9.96	+11.39	17.3
45.13	+11.77	2.22	15.66	+10.43	17.2
59.95	+11.44	2.15	20.80	+9.71	17.4
89.99	+10.76	2.17	30.25	+8.75	17.3
121.17	+10.16	2.17	39.90	+8.06	17.4
240.67	+8.53	2.21	50.18	+7.59	17.3
300.33	+8.02	2.22	62.29	+7.24	17.1
421.96	+7.40	2.19	90.10	+6.87	(16.3)
∞	+6.63	----------	∞	+6.63	----------
Average	----------	2.16	Average	----------	17.3
β-*d*-MANNOSE					
4.0 g per 100 ml at 0.3° C read in a 4-dm tube; °S = 6.66 − 14.28 × 10^−.00214t; [α]^0.3_D = 2.1922 × °S			4.0 g per 100 ml at 20.1° C read in a 4-dm tube; °S = 6.38 − 14.01 × 10^−.0178t; [α]^20.1_D = 2.2257 × °S		
2.64	−7.44	----------	2.20	−6.42	----------
5.53	−7.27	(1.82)	3.59	−5.72	17.6
20.19	−6.28	2.12	6.64	−4.29	17.9
44.88	−4.79	2.14	10.13	−2.85	17.9
59.93	−3.99	2.13	15.48	−1.12	17.5
90.03	−2.46	2.17	20.05	+.16	17.6
120.31	−1.21	2.15	29.90	+2.21	17.6
180.00	+.79	2.15	39.94	+3.62	17.7
240.10	+2.29	2.14	49.99	+4.56	17.7
299.90	+3.39	2.14	60.01	+5.20	17.9
363.30	+4.27	2.14	78.45	+5.87	18.4
420.30	+4.81	2.11	99.76	+6.21	(19.2)
∞	+6.66	----------	∞	+6.38	----------
Average	----------	2.14	Average	----------	17.8
α-*d*-GULOSE $CaCl_2.H_2O$					
6.468 g per 100 ml at 0.2° C read in a 4-dm tube; °S = −6.79 + 36.08 × 10^−.00188t; [α]^0.2_D = 1.3844 × °S			6.807 g per 100 ml at 20° C read in a 4-dm tube; °S = −7.85 + 37.00 × 10^−.0191t; [α]^20_D = 1.2739 × °S		
2.85	+28.85	----------	3.17	+24.33	----------
6.44	+28.30	1.88	4.63	+22.28	19.6
14.88	+27.08	1.84	7.46	+18.71	19.4
29.84	+24.85	1.92	10.38	+15.57	19.1
60.06	+20.88	1.92	16.30	+10.23	19.1
119.94	+14.59	1.90	21.04	+6.85	19.0
183.42	+9.48	1.89	25.86	+4.10	19.0
239.9	+5.97	1.88	29.93	+2.16	19.0
299.7	+3.11	1.87	39.63	−1.30	19.0
397.5	−.25	1.87	49.92	−3.67	19.0
567.5	−3.62	1.86	60.09	−5.16	18.9
739.5	−5.33	1.88	76.31	−6.56	19.1
∞	−6.79	----------	∞	−7.85	----------
Average	----------	1.88	Average	----------	19.1

TABLE 10.—*First-order mutarotations*—Continued

(*d*-GULOSE)$_2$ $CaCl_2.H_2O$					
4.215 g per 100 ml at 0.2° C read in a 4-dm tube $°S = -8.01 + 24.40 \times 10^{-.00202t}$ $[\alpha]^{0.2}_D = 2.1099 \times °S$			4.281 g per 100 ml at 20.1° C read in a 4-dm tube $°S = -7.88 + 21.94 \times 10^{-.0197t}$ $[\alpha]^{20.1}_D = 2.0939 \times °S$		
Time	Observed reading	$(k_1+k_2)\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$
Minutes	°S		*Minutes*	°S	
2.68	+16.09		2.13	+13.85	
5.86	+15.74	2.00	3.46	+12.64	18.7
14.90	+14.73	2.06	5.77	+10.50	20.0
29.88	+13.16	2.07	11.31	+6.41	19.8
44.99	+11.76	2.03	15.26	+4.02	19.9
60.00	+10.46	2.02	19.84	+1.82	19.8
91.36	+7.91	2.03	25.76	−.07	18.8
139.76	+4.72	2.02	30.07	−1.77	19.7
181.61	+2.52	2.01	40.62	−4.11	19.8
244.20	−.15	2.01	49.92	−5.41	19.8
300.78	−1.94	2.01	61.30	−6.45	20.0
361.76	−3.42	2.01	75.30	−7.15	20.1
∞	−8.01		∞	−7.88	
Average		2.02	Average		19.7
α-*d*-XYLOSE					
4.2 g per 100 ml at 0° C read in a 4-dm tube $°S = 8.46 + 38.09 \times 10^{-.00245t}$ $[\alpha]^{0.0}_D = 2.0449 \times °S$			4.4 g per 100 ml at 20° C read in a 4-dm tube $°S = 9.58 + 38.10 \times 10^{-.0203t}$ $[\alpha]^{20}_D = 1.9624 \times °S$		
3.0	+45.91		1.6	+44.93	
5.9	+45.30	2.46	2.5	+43.53	(19.5)
15.0	+43.49	2.42	4.2	+40.96	19.9
20.0	+42.45	2.48	6.5	+37.71	20.2
29.9	+40.60	2.47	10.6	+32.77	20.3
49.8	+37.20	2.46	15.0	+28.39	20.4
76.1	+33.25	2.45	25.0	+21.34	20.4
104.7	+29.50	2.46	34.9	+16.99	20.4
156.6	+24.21	2.45	40.1	+15.43	20.3
210.1	+20.08	2.45	49.8	+13.27	20.4
270.2	+16.77	2.45	60.0	+11.89	20.3
374.4	+13.94	2.44	98.0	+10.00	(20.0)
∞	+8.46		∞	+9.58	
Average		2.45	Average		20.3
α-*d*-LYXOSE					
3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S = -6.09 + 8.20 \times 10^{-.00844t}$ $[\alpha]^{0.2}_D = 2.2003 \times °S$			4.0 g per 100 ml at 20° C read in a 4-dm tube $°S = -6.46 + 9.10 \times 10^{-.0368t}$ $[\alpha]^{20}_D = 2.1362 \times °S$		
2.92	+1.66		1.71	+0.82	
5.77	+1.24	8.49	1.92	+.63	54.7
9.99	+.66	8.49	2.25	+.36	52.5
15.01	+.10	8.07	3.45	−.59	53.7
20.20	−.49	8.17	4.74	−1.52	55.6
26.11	−1.11	8.28	5.86	−2.27	57.8
30.12	−1.54	8.50	7.80	−3.26	58.6
40.05	−2.32	8.43	10.10	−4.13	59.0
50.11	−3.00	8.46	12.99	−4.91	59.6
59.90	−3.63	8.75	17.64	−5.64	59.5
89.79	−4.67	8.48	27.10	−6.21	57.7
120.01	−5.35	8.71	30.26	−6.28	56.3
∞	−6.09		∞	−6.46	
Average		8.44	Average		56.8

TABLE 10.—*First-order mutarotations*—Continued

Time	Observed reading	$(k_1+k_2)\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$
β-*d*-LYXOSE					
4.0 g per 100 ml at 0° C read in a 4-dm tube $°S=-6.12-26.20\times10^{-.00840t}$ $[\alpha]^0_D=2.1895\times°S$			4.0 g per 100 ml at 20° C read in a 4-dm tube $°S=-6.43-27.39\times10^{-.0591t}$ $[\alpha]^{20}_D=2.1462\times°S$		
Minutes	°S		*Minutes*	°S	
2.02	−31.31		1.56	−28.58	
4.91	−29.89	8.71	2.33	−26.40	58.4
10.01	−27.64	8.56	3.18	−24.26	58.2
15.02	−25.71	8.40	3.69	−23.04	58.7
19.96	−23.94	8.38	4.40	−21.55	58.4
24.84	−22.34	8.38	5.57	−19.30	58.8
29.97	−20.85	8.34	6.65	−17.50	59.2
40.72	−18.08	8.36	7.58	−16.17	59.3
50.88	−15.99	8.33	9.73	−13.67	59.4
60.10	−14.43	8.29	12.14	−11.64	59.4
90.59	−10.73	8.33	20.04	−8.14	60.2
119.70	−8.74	8.35	29.90	−6.87	60.1
∞	−6.12		∞	−6.43	
Average		8.40	Average		59.1
α-*l*-RHAMNOSE. H_2O					
4.5 g per 100 ml at 0° C read in a 4-dm tube $°S=4.56-8.46\times10^{-.00568t}$ $[\alpha]^0_D=1.9079\times°S$			4.0 g per 100 ml at 20.2° C read in a 4-dm tube $°S=3.81-7.81\times10^{-.0430t}$ $[\alpha]^{20.2}_D=2.1522\times°S$		
3.1	−3.56		1.43	−2.97	
10.1	−2.83	5.85	1.84	−2.71	41.4
15.2	−2.37	5.69	2.37	−2.39	41.3
30.3	−1.05	5.90	3.65	−1.66	42.0
42.1	−.35	5.60	5.08	−.95	42.1
60.2	+.65	5.56	7.68	+.21	44.0
75.4	+1.40	5.67	9.93	+.91	43.4
91.5	+1.98	5.63	15.31	+2.16	44.2
119.7	+2.77	5.63	20.24	+2.82	44.4
149.9	+3.36	5.66	24.92	+3.15	43.1
180.2	+3.77	5.71	29.96	+3.43	43.9
241.2	+4.19	5.63	40.89	+3.72	
∞	+4.56		∞	+3.81	
Average		5.68	Average		43.0
α-LACTOSE . H_2O					
4.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S=30.43+18.60\times10^{-.000544t}$ $[\alpha]^{0.2}_D=1.7614\times°S$			7.2 g per 100 ml at 20° C read in a 4-dm tube $°S=46.15+28.40\times10^{-.00471t}$ $[\alpha]^{20}_D=1.1398\times°S$		
5.19	+48.91		1.98	+73.95	
10.06	+48.80	0.532	2.95	+73.61	4.67
20.76	+48.54	.564	4.83	+73.09	4.79
59.90	+47.69	.542	10.42	+71.52	4.71
120.26	+46.48	.532	20.05	+69.04	4.67
181.2	+45.28	.540	30.04	+66.67	4.70
241.5	+44.18	.543	60.12	+60.98	4.69
401.5	+41.66	.546	91.00	+56.76	4.70
590.9	+39.30	.544	119.93	+53.91	4.70
832.4	+37.00	.543	180.50	+50.17	4.70
1,347.3	+33.84	.547	239.80	+48.19	4.77
1,834.4	+32.28	.546	∞	+46.15	
∞	+30.43				
Average		0.544	Average		4.71

TABLE 10.—*First-order mutarotations*—Continued

β-LACTOSE

3.9 g per 100 ml at 0.2° C read in a 4-dm tube $°S=25.56-9.09\times10^{-.000524t}$ $[\alpha]^{0.2}_D=2.2066\times°S$			4.0 g per 100 ml at 20° C read in a 4-dm tube $°S=25.34-9.38\times10^{-.00466t}$ $[\alpha]^{20}_D=2.1863\times°S$		
Time	Observed reading	$(k_1+k_2)\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$
Minutes	°S		*Minutes*	°S	
4.85	+16.52	----	1.97	+16.16	----
10.22	+16.59	(0.629)	3.16	+16.27	(4.39)
30.28	+16.80	.538	5.04	+16.42	(4.07)
59.96	+17.08	.504	10.06	+16.91	4.57
120.51	+17.71	.530	19.91	+17.76	4.64
240.4	+18.78	.531	30.10	+18.54	4.63
384.8	+19.82	.519	60.03	+20.46	4.73
549.3	+20.89	.527	89.71	+21.78	4.69
801.8	+22.13	.528	120.24	+22.77	4.67
1,340.6	+23.79	.530	149.50	+23.48	4.70
1,892.7	+24.57	.509	182.80	+24.02	4.66
2,842.8	+25.26	.521	244.10	+24.66	4.67
∞	+25.56	----	∞	+25.34	----
Average	----	0.524	Average	----	4.66

β-MALTOSE. H_2O

4.5 g per 100 ml at 0° C read in a 4-dm tube $°S=68.80-8.75\times10^{-.000580t}$ $[\alpha]^0_D=1.9113\times°S$			4.2 g per 100 ml at 20° C read in a 4-dm tube $°S=62.81-9.00\times10^{-.00527t}$ $[\alpha]^0_D=2.0761\times°S$		
4.9	+60.11	----	2.33	+54.06	----
22.8	+60.34	0.583	3.46	+54.18	5.31
31.1	+60.45	.593	5.38	+54.39	5.48
62.2	+60.83	.585	10.13	+54.85	5.27
120.2	+61.46	.565	19.92	+55.74	5.26
182.1	+62.09	.560	29.93	+56.53	5.22
241.8	+62.72	.576	59.95	+58.44	5.23
300.1	+63.28	.583	103.96	+60.22	5.20
353.3	+63.70	.577	137.43	+61.09	5.23
487.2	+64.71	.580	180.11	+61.78	5.23
686.8	+65.93	.584	240.00	+62.32	5.27
1406.	+68.35	.589	300.90	+62.61	(5.50)
∞	+68.80	----	∞	+62.81	----
Average	----	0.580	Average	----	5.27

TABLE 11.—*Complex mutarotations of sugars in water*

α-*l*-ARABINOSE

4.1 g per 100 ml at 0° C read in a 4-dm tube $°S = 37.74 \times 10^{-.00362t} + 2.83 \times 10^{-.0217t} + 52.20$ $[\alpha]^0_D = °S \times 2.0920$						5.0 g per 100 ml at 20° C read in a 2-dm tube $°S = 22.13 \times 10^{-.030t} + 2.53 \times 10^{-.138t} + 29.92$ $[\alpha]^{20}_D = °S \times 3.4926$					
Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$
1	2	3	4	5	6	1	2	3	4	5	6
Minutes	° S			° S		*Minutes*	° S			° S	
4.3	+90.89			+2.28		2.1	+50.36			+1.30	
6.6	+89.94	4.70		+2.02	22.9	3.1	+48.70	36.8		+.91	155
9.9	+88.70	4.52		+1.75	20.5	5.1	+46.00	34.7		+.52	133
15.3	+86.75	4.47		+1.33	21.3	7.1	+43.70	34.2		+.23	150
19.9	+85.16	4.46		+.99	23.2	10.1	+41.10	32.8		+.16	114
25.0	+83.66	4.34		+.82	21.5	15.0	+37.78	32.2		(+.01)	
29.8	+82.29	4.28		+.65	21.4	20.0	+35.48	31.6			
40.3	+79.59	4.17		+.42	20.4	30.0	+32.70	31.1	30.1		
60.4	+75.01	4.09				40.0	+31.36	30.4	29.3		
90.0	+69.94	3.95	3.69			60.0	+30.29	30.1	29.4		
109.8	+67.26	3.88	3.65			75.0	+30.03	31.1	31.0		
135.5	+64.33	3.84	3.65			90.00	+29.94				
166.2	+61.57	3.80	3.65			∞	+29.92				
197.0	+59.49	3.76	3.63								
240.3	+57.33	3.72	3.60								
300.0	+55.38	3.67	3.57								
448.4	+53.16	3.61	3.55								
∞	+52.20										
Average			3.62		21.7	Average			30.0		138

9.3 g per 100 ml at 0° C read in a 4-dm tube $°S = -18.01\times10^{-.0038t}+2.23\times10^{-.0369t}+53.63$ $[\alpha]_D^0 = °S\times0.9342$						8.9 g per 100 ml at 20.0° C read in a 4-dm tube $°S = -17.29\times10^{-.0301t}+3.58\times10^{-.169t}+49.33$ $[\alpha]_D^{20} = °S\times0.9730$					
3.0	+37.82			+1.73		1.40	+36.13			+2.50	
6.0	+37.85			+1.30	41.4	2.32	+36.32	6.8		+1.72	177
10.3	+38.11	1.10		+.92	37.6	2.90	+36.58	10.0		+1.40	168
12.7	+38.30	1.38		+.76	36.8	3.58	+36.92	12.3		+1.09	165
15.0	+38.51	1.61		+.65	35.4	4.86	+37.61	14.9		+.64	171
19.9	+38.98	1.96		+.45	34.6	6.09	+38.40	17.5		+.42	165
24.8	+39.41	2.11		+.24	39.4	10.46	+40.96	21.8		+.02	
29.8	+40.01	2.42		+.22	33.4	19.91	+44.96	25.9			
42.6	+41.42	2.83		+.15	(26.8)	25.03	+46.28	26.9	30.5		
62.3	+43.25	3.08				29.94	+47.15	27.4	30.1		
90.1	+45.54	3.34	3.89			40.17	+48.23	27.8	29.6		
120.8	+47.41	3.44	3.80			50.13	+48.79	28.5	30.0		
180.5	+50.00	3.60	3.87			60.28	+49.02	27.7	(28.5)		
212.1	+50.81	3.58	3.78			∞	+49.33				
250.0	+51.68	3.68	3.87								
307.6	+52.46	3.71	3.86								
351.2	+52.80	3.68	3.80								
∞	+53.63										
Average			3.84		36.9	Average			30.0		169

TABLE 11.—*Complex mutarotations of sugars in water*—Continued

α-*d*-GALACTOSE

4.1 g per 100 ml at 0° C read in a 4-dm tube $°S=31.70\times10^{-.00093t}+1.31\times10^{-.0119t}+40.19$ $[\alpha]_D^0=°S\times2.0901$						5.0 g per 100 ml at 20.0° C read in a 4-dm tube $°S=37.51\times10^{-.00803t}+3.25\times10^{-.079t}+46.34$ $[\alpha]_D^{20}=°S\times1.7307$					
Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$
1	2	3	4	5	6	1	2	3	4	5	6
Minutes	° S			° S		*Minutes*	° S			° S	
3.3	+72.87			+1.20		1.9	+84.85			+2.30	
10.1	+72.24	1.24		+1.03	9.6	3.0	+83.67	12.3		+1.84	88.1
15.2	+71.75	1.27		+.86	12.1	4.4	+82.44	11.3		+1.52	72.0
19.7	+71.40	1.22		+.81	10.4	6.6	+80.54	11.0		+1.00	77.0
29.9	+70.51	1.22		+.58	11.9	8.6	+79.03	10.6		+.69	78.0
39.9	+69.72	1.20		+.43	12.2	10.2	+77.95	10.3		+.55	74.9
49.8	+68.93	1.20		+.25	14.6	12.0	+76.73	10.2		+.34	83.9
59.6	+68.34	1.15		+.24	12.4	14.8	+75.09	9.8		+.22	79.0
90.7	+66.36	1.10				29.7	+68.00	9.0			
120.4	+64.69	1.07				45.0	+62.66	8.7	8.04		
181.2	+61.65	1.03	0.947			59.8	+58.75	8.5	8.04		
240.2	+59.11	1.00	.937			80.0	+54.92	8.4	8.00		
302.4	+56.80	.98	.927			100.7	+52.18	8.3	8.02		
391.3	+53.94	.97	.926			119.5	+50.47	8.2	8.01		
542.8	+50.15	.96	.925			149.9	+48.66	8.2	8.07		
670.7	+47.79	.95	.924			∞	+46.34				
766.0	+46.37	.95	.927								
∞	+40.19										
Average			.930		11.9	Average			8.03		79.0

β-d-GALACTOSE

4.1 g per 100 ml at 0° C read in a 4-dm tube $°S = -14.83 \times 10^{-.00090t} + 1.16 \times 10^{-.0167t} + 39.56$ $[\alpha]_D^0 = °S \times 2.1234$						4.0 g per 100 ml at 20° C read in a 4-dm tube $°S = -14.86 \times 10^{-.00812t} + 2.25 \times 10^{-.0883t} + 36.86$ $[\alpha]_D^{20} = 2.1758 \times °S$					
3.9	+25.81			+0.97		2.00	+24.05			+1.50	
9.3	+25.84	0.000		+.84	11.6	3.41	+24.05	0.00		+1.13	87.2
17.4	+25.82	.000		+.57	17.1	4.66	+24.14	1.15		+.90	83.4
25.3	+25.87	.089		+.39	18.4	7.51	+24.43	2.37		+.48	89.8
39.2	+26.15	.308		+.27	15.7	10.02	+24.81	3.31		+.27	92.9
50.3	+26.33	.361		+.13	18.8	20.27	+26.68	5.46		(+.10)	
59.9	+26.54	.423		+.09	18.4	30.25	+28.42	6.41			
91.4	+27.25	.549				40.18	+29.85	6.86	8.12		
119.6	+27.98	.645				49.98	+31.00	7.08	8.03		
181.6	+29.36	.730	(0.889)			59.86	+32.01	7.29	8.12		
242.4	+30.58	.776	.899			76.40	+33.30	7.47	8.12		
302.1	+31.61	.761	.895			89.83	+34.11	7.61	8.17		
369.3	+32.64	.816	.895			119.33	+35.23	7.63	8.02		
519.5	+34.50	.842	.899			149.98	+36.00	7.93	8.28		
618.3	+35.40	.845	.892			181.2	+36.40	8.06	(8.37)		
755.7	+36.47	.862	.902			∞	+36.86				
1370	+38.63	.856	(.876)								
∞	+39.56										
Average			.897		16.7	Average			8.12		88.3

TABLE 11.—*Complex mutarotations of sugars in water*—Continued

MANNOSE $CaCl_2.4H_2O$

8.4 g per 100 ml at 0° C read in a 4-dm tube $°S=4.34\times10^{-.00267t}-39.28\times10^{-.0608t}+6.04$ $[\alpha]_D^0=°S\times1.0265$						9.1 g per 100 ml at 20° C read in a 2-dm tube $°S=2.16\times10^{-.0245t}-22.13\times10^{-.311t}+3.23$ $[\alpha]_D^{20}=°S\times1.8576$					
Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$	Time	Observed reading	$(k_1+k_2)\times10^3$	$m_1\times10^3$	Deviation	$m_2\times10^3$
1	2	3	4	5	6	1	2	3	4	5	6
Minutes	°S			°S		*Minutes*	°S			°S	
1.3	−22.40			−32.75		1.2	−4.12			−9.37	
3.6	−13.05			−23.33	64.0	1.8	−1.07			−6.25	293
8.2	−2.16			−12.33	61.5	2.0	−.27			−5.43	296
11.8	+2.48			−7.57	60.6	2.3	+.81			−4.32	306
20.9	+7.61			−2.25	59.3	2.6	+1.63			−3.46	309
25.3	+8.50			−1.25	59.1	2.8	+2.33			−2.74	334
29.9	+9.02			−.63	60.0	3.1	+2.73			−2.31	320
39.8	+9.29			−.15	60.8	3.4	+3.08			−1.93	312
44.7	+9.22			−.12		4.3	+3.88			−1.04	308
60.4	+8.99			−.04		4.7	+4.18			−.71	320
75.4	+8.77					7.8	+4.62				
150.5	+7.74		2.74			9.9	+4.44		(28.7)		
179.7	+7.49		2.63			13.8	+4.22		24.5		
208.5	+7.24		2.68			19.5	+3.96		23.9		
240.2	+7.06		2.59			31.2	+3.59		25.1		
300.0	+6.71		2.72			45.6	+3.33		(30.2)		
∞	+6.04					∞	+3.23				
Average			2.67		60.8	Average			24.5		311

α-d-TALOSE

4.0 g per 100 ml at 0.1° C read in a 4-dm tube
$°S = 4.49\times10^{-.00362t} + 12.60\times10^{-.0255t} + 11.56$
$[\alpha]_D^{0.1} = °S \times 2.1799$

2.13	+27.09			+11.12	
6.52	+24.46	18.36		+8.65	24.9
15.27	+20.76	17.30		+5.25	24.8
25.18	+18.15	16.15		+2.95	25.0
30.14	+17.28	15.49		+2.23	24.9
40.01	+15.98	14.41		+1.20	25.5
50.13	+15.15	13.25		+0.63	26.0
59.89	+14.59	12.29		+.30	27.2
95.27	+13.59	9.49			
119.83	+13.22	8.25	3.56		
180.79	+12.53	6.74	3.75		
240.86	+12.16	5.92	3.64		
305.45	+11.93	5.35	3.52		
∞	+11.56				
Average			3.62		25.5

4.0 g per 100 ml at 20° C read in a 4-dm tube
$°S = 4.25\times10^{-.0263t} + 17.35\times10^{-.126t} + 9.51$
$[\alpha]_D^{20} = °S \times 2.1872$

2.86	+20.65			+7.57	
4.42	+17.71	85.3		+4.95	118.3
6.57	+15.05	81.8		+2.68	121.6
8.92	+13.34	76.5		+1.35	123.6
11.85	+12.09	70.7		+.51	130.3
14.82	+11.42	64.0		+.18	135.8
17.41	+11.03	59.5		+.04	(156.5)
20.08	+10.77	55.0			
25.13	+10.43	48.6	27.0		
30.08	+10.21	44.2	25.5		
∞	+9.51				
Average			26.3		125.9

l-RIBOSE

4.1 g per 100 ml at 0.2° C read in a 4-dm tube
$°S = -3.72\times10^{-.0069t} + 3.83\times10^{-.054t} + 10.98$
$[\alpha]_D^{0.2} = °S \times 2.1129$

2.23	+10.28			+2.90	
3.73	+9.83			+2.36	59.7
6.82	+9.23			+1.64	53.9
9.87	+8.95			+1.15	52.6
14.91	+8.71			+.67	50.2
19.89	+8.67			+.40	48.7
25.11	+8.64			+.16	55.0
30.37	+8.76			+.08	55.4
40.08	+9.01				
60.07	+9.58		7.42		
75.51	+9.85		6.81		
89.77	+10.08		6.85		
104.99	+10.28		6.92		
120.19	+10.46		7.22		
151.45	+10.61		6.52		
181.15	+10.73		6.36		
∞	+10.98				
Average			6.87		53.6

4.0 g per 100 ml at 20° C read in a 4-dm tube
$°S = -3.64\times10^{-.049t} + 3.46\times10^{-.231t} + 9.90$
$[\alpha]_D^{20} = °S \times 2.0909$

1.59	+9.27			+2.41	
2.22	+8.83			+1.76	217
2.77	+8.58			+1.34	216
3.33	+8.36			+.96	230
4.44	+8.18			+.48	246
5.78	+8.22			+.21	248
7.38	+8.39			+.07	
8.76	+8.59			+.04	
9.90	+8.71				
13.68	+9.10		45.6		
17.33	+9.39		49.5		
20.48	+9.55		50.2		
25.08	+9.70		51.0		
29.88	+9.78		49.9		
∞	+9.90				
Average			49.2		231

The thermal mutarotations were conducted in the following manner: The sugar solution in a 4-dm water-jacketed silver tube was allowed to reach equilibrium at 25° C, and its optical rotation read. The water (at 25° C) was drained from the water jacket and a stream of aqueous alcohol cooled to 0° C was pumped through the jacket. Time was measured from the moment when the cold aqueous alcohol was turned on. The temperature dropped in about 3 minutes to approximately 0° C, at which time saccharimeter readings were made. The calculation of the results is described on page 156.

TABLE 12.—*Thermal mutarotations*

Time[a]	Saccharimeter reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Thermal mutarotation of a 10-percent aqueous solution of *d*-galactose after cooling from 25 to 0.3° C. $°S = 1.10 \times 10^{-.00107t} - 3.49 \times 10^{-.0132t} + 97.87$.				
Minutes	°S		°S	
5.74	+96.02	----------	−2.93	----------
6.95	+96.13	----------	−2.82	13.8
10.00	+96.49	----------	−2.45	18.2
15.13	+96.74	----------	−2.19	13.5
20.09	+97.04	----------	−1.88	13.4
26.15	+97.32	----------	−1.58	13.1
30.20	+97.46	----------	−1.43	12.7
40.27	+97.76	----------	−1.10	12.3
50.11	+98.02	----------	−0.82	12.5
60.96	+98.23	----------	−.59	12.6
75.23	+98.41	----------	−.37	12.9
89.97	+98.48	----------	−.27	12.3
126.54	+98.53	----------	−.14	10.9
139.88	+98.60	----------	−.05	13.2
160.18	+98.61	----------	----------	----------
244.19	+98.45	1.26	----------	----------
306.1	+98.39	1.05	----------	----------
365.2	+98.30	1.15	----------	----------
502.1	+98.24	0.88	----------	----------
738.7	+98.06	1.02	----------	----------
∞	+97.87	----------	----------	----------
Average	----------	1.07	----------	13.2
Thermal mutarotation of an 8-per cent aqueous solution of *l*-arabinose after cooling from 25.2 to 0.2° C. $°S = 1.52 \times 10^{-.00364t} - 4.56 \times 10^{-.0271t} + 101.71$				
4.57	+99.74	----------	−3.43	----------
5.94	+100.01	----------	−3.15	27.0
8.29	+100.38	----------	−2.75	25.8
10.64	+100.75	----------	−2.35	27.1
15.16	+101.30	----------	−1.75	27.6
20.21	+101.71	----------	−1.28	27.4
25.58	+102.01	----------	−.93	27.0
30.06	+102.20	----------	−.69	27.3
40.10	+102.45	----------	−.35	27.9
51.15	+102.55	----------	−.12	(31.3)
75.14	+102.52	----------	----------	----------
90.19	+102.41	4.21	----------	----------
121.06	+102.26	3.66	----------	----------
154.66	+102.11	3.85	----------	----------
184.1	+102.06	3.34	----------	----------
214.6	+101.98	3.42	----------	----------
277.9	+101.87	3.47	----------	----------
330.6	+101.81	3.56	----------	----------
389.9	+101.77	3.59	----------	----------
∞	+101.71	----------	----------	----------
Average	----------	3.64	----------	27.1

[a] Time is measured from the beginning of the cooling process.

TABLE 12.—*Thermal mutarotations*—Continued

Thermal mutarotation of an 8-percent aqueous solution of *d*-talose after cooling from 25.8 to 0.1°C. $°S = 0.14 \times 10^{-.0036t} - 4.69 \times 10^{-.0289t} + 23.62$

Time	Saccharimeter reading	$m_1 \times 10^3$	Deviation	$m_2 \times 10^3$
Minutes	°S		°S	
3.94	+20.14	----------	−3.61	----------
5.41	+20.57	----------	−3.18	(37.5)
7.42	+20.93	----------	−2.82	30.8
10.24	+21.35	----------	−2.39	28.4
13.55	+21.84	----------	−1.90	29.0
16.85	+22.15	----------	−1.59	27.6
19.97	+22.40	----------	−1.33	27.0
24.98	+22.76	----------	−.97	27.1
29.92	+23.10	----------	−.63	29.2
39.98	+23.45	----------	−.27	31.2
50.07	+23.56	----------	−.15	29.9
60.09	+23.61	----------	−.09	28.6
96.3	+23.68	[b](3.8)	----------	----------
∞	+23.62	----------	----------	----------
Average	----------	----------	----------	28.9

[b] The mutarotation due to the slow reaction is scarcely more than the experimental error and, therefore, the value of m_1 (.0036) obtained from the mutarotation of *α-d*-talose was used for extrapolating the slow reaction back to zero time. The existence of the maximum was shown by comparing the average of a large number of readings at about 90 minutes with the average of similar readings after equilibrium was established. Several duplicate experiments revealed a difference of about 0.08° S, which corresponds to a total change of 0.14° S.

Because of the general applicability to experiments requiring a continuous flow of cold water at a constant temperature, the apparatus used for the low-temperature measurements will be described, although the general methods involved are not new. A copper tank of 40 gallons capacity was placed inside a standard electric refrigerator (10 ft.^{3} capacity) in such a manner that the cooling coils dipped about 10 inches into the tank. An outlet at the bottom of the tank allowed liquid to flow into a standard centrifugal pump (operated by a ¼ hp motor) which circulated the cooling medium. Instead of passing the liquid through the jacket of the polariscope tube, the major portion was bypassed so as to allow the pump to operate at full capacity. The return flow was led through the back of the refrigerator and split into two streams which were discharged over the upper shelves of the two cooling coils. The temperature was held constant by use of a mercury thermoregulator. The most satisfactory cooling medium was found to be 95-percent ethyl alcohol. The advantages of the alcohol over aqueous solutions containing but little alcohol are (1) the lower specific heat of the alcohol allows more rapid cooling of the liquid to the desired temperature, a quicker establishment of a constant temperature in the circulating water after the pump is started, and a lower operating temperature; and (2) the alcohol reduces corrosion. The apparatus described was found quite satisfactory for the mutarotation measurement at 0° C. Polariscope tubes were kept at a constant temperature of 0 ± 0.03° C for a week at a time.

V. SUMMARY

Fundamental characteristics of the alpha and beta sugars which furnish the basis for the changes in nomenclature previously suggested by Isbell are discussed, and it is shown that the sugars which appear

as beta modifications under the proposed classification are oxidized by bromine more rapidly than the alpha isomers.

The oxidation of the equilibrium solutions of the sugars proceeds rapidly until a part of the sugar is used up and then more slowly as the remaining sugar continues to be oxidized. The oxidation of the more reactive fractions takes place at rates comparable to those found for the beta sugars, while the rates for the less reactive fractions agree within reasonable experimental error with the rates for the oxidation of the alpha sugars. The proportions of the more rapidly and the less rapidly oxidizable sugars were determined and compared with the proportions of the alpha and beta isomers calculated from the optical rotations on the assumption that the equilibrium solutions contain only the alpha and beta normal isomers. The results of these comparisons indicate that the equilibrium solutions are principally of the normal alpha and beta sugars, but the presence of small quantities of other modifications is not excluded, especially for the solutions of galactose, arabinose, talose, and ribose. The oxidation of equilibrium solutions of *l*-ribose has revealed that they contain a small quantity of some modification which is more easily oxidizable than the crystalline sugar which was previously classified as *β-l*-ribose. The existence of this easily oxidizable modification throws doubt on the correctness of the classification of the known sugar as the beta form. The oxidation of (*d*-gulose)$_2$ $CaCl_2$. H_2O shows that the crystalline sugar contains about 32 percent of an easily oxidizable modification which is presumably the heretofore unknown beta isomer.

Mutarotation measurements at 20° C and at 0° C reveal that the mutarotations of *α*- and *β-d*-glucose, *α*- and *β-d*-mannose, *α-d*-gulose $CaCl_2.H_2O$, (*d*-gulose)$_2$ $CaCl_2.H_2O$, *α*- and *β-d*-lyxose, *α-d*-xylose, *α-l*-rhamnose (hydrate), *α*- and *β*-lactose, and *β*-maltose follow the first-order equation, while the mutarotations of *α*- and *β-d*-galactose, *α-l*-arabinose, *β-l*-arabinose $CaCl_2.4H_2O$, *d*-mannose $CaCl_2.4H_2O$, *α-d*-talose, and *l*-ribose are complex. The initial and equilibrium specific rotations of these sugars were determined at 0 and 20° C, and values for the rotation of the first carbon (Hudson's *A*) were calculated at both temperatures. The effect of traces of heavy metals on the rates of mutarotation is pointed out and attention is directed to errors caused by the use of nickel-plated brass tubes in mutarotation measurements. The optical rotations of mannose $CaCl_2.4H_2O$ and arabinose $CaCl_2.4H_2O$ are reduced to equations containing two exponential terms, and attention is directed to the fact that the addition of calcium chloride produces a change in the equilibrium between the various modifications of these sugars in solution. Detailed data for the optical rotations of *α-d*-talose at 20° C and at 0° C are reported for the first time.

Temperature coefficients were determined for the mutarotations of 20 sugars. The principal mutarotation reactions (supposedly the reversible interconversion of the normal alpha and beta isomers) are on the average 8.34 times as fast at 20° C as at 0° C, while the rapid reactions are on the average only 5.32 times as fast at 20° C as at 0° C. The higher temperature coefficient for the principal mutarotation reaction shows that the heat of activation is greater for the interconversion of the normal isomers than for the rapid reaction. The mutarotations which occur after a sudden change in temperature prove that the compositions of equilibrium solutions of galactose, arabinose, and talose are altered markedly by a change in temperature. The pro-

portions of the labile constituents vary with temperature more than the proportions of the normal alpha and beta isomers. In this respect it is shown that the bromine oxidation of solutions of *d*-galactose in equilibrium at 20° C does not differ widely from the oxidation of solutions in equilibrium at 0° C.

The optical rotation of a freshly prepared solution containing α- and β-*d*-galactose in proportions corresponding to the equilibrium rotation decreases to a minimum and then increases to the original value. This is conclusive proof that the deviations in the mutarotations of α- and β-*d*-galactose are real.

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