

needles melting at 43-5° to an oil. The substance contained sulfur and bromine and a nitrogen determination agreed with the calculated value for 2-ethylmercapto-5-bromopyrimidine.

Calc. for  $C_6H_7N_2SBr$ : N, 12.78. Found: N, 12.90.

When the carbon tetrachloride was evaporated more of this same base was obtained and melted at 43-45°.

NEW HAVEN, CONN.

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY,  
UNITED STATES DEPARTMENT OF AGRICULTURE.]

## SOME NUMERICAL RELATIONS AMONG THE ROTATORY POWERS OF THE COMPOUND SUGARS.

By C. S. HUDSON.

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The general group of polysaccharides includes many pure crystalline substances of definite chemical individuality, such as the di-, tri-, and tetrasaccharides, together with a series of amorphous products, such as starch, glycogen, inulin, cellulose, pentosans, mannans, galactans, etc. To distinguish the pure crystalline polysaccharides from their less definitely characterized relatives, it is suggested that they be classed under the group name of *compound sugars*, a designation which separates them very well also from the simple sugars, or monosaccharides, into which they may be decomposed by hydrolysis. In the present article, it is sought to extend to several of the compound sugars the numerical relationships that have been found to hold among the rotatory powers of the alpha and beta forms of the monosaccharides and their glucosidic derivatives.<sup>1</sup>

### Sugars of the Sucrose Group.

**Known Members of the Group.**—The trisaccharide raffinose may be split by complete hydrolysis into its three component simple sugars, galactose, glucose and fructose; by partial hydrolysis, best through the agency of enzyme action, it may be split either into fructose and melibiose (= galactose < glucose <<sup>2</sup>) by the use of invertase or weak acids, or into galactose and sucrose (= glucose < > fructose) by the aid of emulsin. Raffinose may accordingly be regarded as galactose < glucose < > fructose, a derivative of sucrose, a combination between that sugar and galactose. Other sugars which are now regarded as derivatives of sucrose are<sup>3</sup> gentianose (= glucose < glucose < > fructose) and stachyose (= galactose <

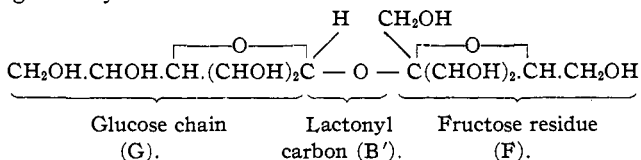
<sup>1</sup> THIS JOURNAL, 31, 66 (1909).

<sup>2</sup> The symbol < denotes the carbonyl or lactonyl group. See THIS JOURNAL, 31, 661 (1909). The term lactonyl, which has been suggested by S. F. Acree (*Science*, 42, 101 (1915)) to indicate an aldehyde or ketone group that has formed a lactone-like ring, as in the sugars, seems very appropriate.

<sup>3</sup> Bourquelot and Bridel, *Compt. rend.*, 152, 1060 (1911).

*galactose* < *glucose* > *fructose*). It will be convenient to designate sucrose and its three derived compound sugars as members of the sucrose group. The evidence that gentianose and stachyose belong in the group is not direct and conclusive as in the case of raffinose, though it appears convincing, as will be seen. The action of invertase upon either sucrose or raffinose causes specific hydrolysis of the union between glucose and fructose, which may be designated the *sucrose union*. Invertase may be regarded therefore, as a specific hydrolyst of the "sucrose union," and the action of this enzyme upon a compound sugar may be taken as evidence that the sugar contains the "sucrose union" and is a derivative of sucrose. Bourquelot and Hérissé<sup>1</sup> have shown that invertase splits gentianose into fructose and gentiobiose (= *glucose* < *glucose* <) and C. Tanret<sup>2</sup> has shown that it splits stachyose into fructose and mannitriose (= *galactose* < *galactose* < *glucose* <), hence these sugars are considered to be derivatives of sucrose. Recently Bourquelot and Bridel<sup>3</sup> have isolated a new crystalline compound sugar, verbascose, which is hydrolyzed by invertase to fructose and another sugar, not yet isolated; probably verbascose belongs in the sucrose group.

**Rotatory Relationships in the Sucrose Group.**—The fact that sucrose is not a reducing sugar indicates that the lactonyl hydroxyl groups of its two constituents are bound in glucosidic union, and the further fact that only one molecule of water per molecule of sucrose becomes combined during hydrolysis shows that the groups in question are joined with each other, because if the union were otherwise, two molecules of water per molecule of sugar would be used up. The same conclusion may be drawn from the fact that sucrose yields an octacetate and contains, therefore, eight hydroxyl groups per molecule. The structure of sucrose is accordingly generally considered to be



In this formula it is assumed that the lactonyl ring is upon the gamma carbon in both hexoses, which appears likely, but the following argument would not be affected if these rings should prove to be in other positions:<sup>4</sup> Let G represent the rotation due to the glucose chain, not including,

<sup>1</sup> *J. pharm. chim.*, [6] 13, 305 (1901).

<sup>2</sup> *Bull. soc. chim.*, 27, 955 (1902). See also Vintilesco, *J. pharm. chim.*, 30, 167 (1909).

<sup>3</sup> *Compt. rend.*, 151, 760 (1910).

<sup>4</sup> What really is assumed, as will be understood from the continuation, is that the glucose lactonyl ring in sucrose is upon the same carbon atom as in the case of the alpha and beta forms of glucose.

however, the asymmetric lactonyl carbon of rotation  $B'$ , and let  $F$  be the rotation of the fructose residue. Summing these values the molecular rotation of sucrose may be written  $[M]_S = G + B' + F$ . According to this plan the molecular rotations of the members of the sucrose group may be formulated as follows, when  $(Mb)$ ,  $(Gb)$  and  $(Mn)$  indicate the rotations of the melibiose, gentiobiose and manninotriose chains, respectively:

Parent sugar.	Hydrolytic products with invertase.	Molecular rotation of the parent sugar.
Sucrose (M.W. 342)	Glucose (180) + Fructose (180)	$G + B' + F$ (1)
Raffinose (504)	Melibiose (342) + Fructose	$(Mb) + B' + F$ (2)
Gentianose (504)	Gentiobiose (342) + Fructose	$(Gb) + B' + F$ (3)
Stachyose (666)	Manninotriose (504) + Fructose	$(Mn) + B' + F$ (4)

Subtracting the molecular rotation of sucrose from that of raffinose,  $[M]_R$ , gives

$$[M]_R - [M]_S = (Mb) - G. \quad (5)$$

The specific rotation of sucrose is  $+66.5$ , and its molecular rotation  $(66.5)(342) = +22700 = [M]_S$ . In the article first cited it was shown that  $G$  may be obtained as half the *sum* of the molecular rotations of the alpha and beta forms of glucose, which gives the value  $+11900$  if the specific rotations of the two forms of glucose are taken as  $113^1$  and  $19.2$ . Introducing these values in Equation 5 and transposing gives

$$(Mb) = [M]_R - 10800. \quad (6)$$

To pass now from  $(Mb)$  to the rotation of either the alpha or beta form of melibiose it is necessary to add the rotation of the end asymmetric lactonyl carbon atom of melibiose. It has been shown in the former article that the rotation of this carbon is equal to half the *difference* of the molecular rotations of the alpha and beta forms of glucose, or  $8460$ , hence the molecular rotations of the forms of melibiose are written:

$$\text{Molecular rotation of } \alpha\text{-melibiose} = (Mb) + 8460 = [M]_R - 2340$$

$$\text{Molecular rotation of } \beta\text{-melibiose} = (Mb) - 8460 = [M]_R - 19300$$

Similar equations with the same numerical terms express the same relation between the molecular rotations of gentiobiose and gentianose, and of manninotriose and stachyose. *For the sugars of the sucrose group that are hydrolyzed by invertase to yield fructose and an aldose, the molecular rotation of the aldose is less than that of its parent sugar by 2340 for its alpha form and 19300 for its beta modification.* The rotatory powers of melibiose, gentiobiose, and manninotriose may be calculated by this relation.

**The Rotation of Melibiose.**—Since the specific rotation of raffinose is  $+123$ , its molecular rotation is  $+62000$ , and the molecular rotations of the alpha and beta forms of melibiose are calculated from the foregoing relation to have the values  $+59700$  and  $+42700$ , respectively, and from

<sup>1</sup> Hudson and Yanovsky, forthcoming publication.

<sup>2</sup> Hudson and Dale, forthcoming publication.

these the specific rotations are found to be  $+175^\circ$  and  $+125^\circ$ . The latter value agrees almost exactly with Loiseau's<sup>1</sup> measurement of the initial specific rotation of  $\beta$ -melibiose (124), and recently E. Yanovsky and the writer,<sup>2</sup> in repeating the measurement, have obtained the same value as Loiseau. The alpha form of melibiose has never been prepared in a pure state and the only experimental value known for its specific rotation is that which Yanovsky and the author have found indirectly through a measurement of the increase in solubility of  $\beta$ -melibiose during its mutarotation. Our value is  $+179^\circ$ .<sup>2</sup> The agreement is very good in view of the indirectness of the experimental measurement.

**The Rotation of Gentiobiose.**—The specific rotation of gentianose is  $+31$ ,<sup>3</sup> hence its molecular rotation is  $+15600$  and the specific rotations of the alpha and beta forms of gentiobiose may be calculated by the method which has just been followed to be  $+39$  and  $-11$ , respectively. Bourquelot and Hérissé<sup>4</sup> record  $+9.8$  as the final specific rotation of gentiobiose, a value which refers to the equilibrium in solution between the alpha and beta forms of the sugar. By crystallizing gentiobiose from methyl alcohol they obtained a crystalline derivative of it containing two molecules of methyl alcohol of crystallization. This substance had an initial specific rotation in water of about  $+18$ , decreasing to  $+9.8$  (both numbers are referred to the solvent-free sugar, m. w. 342) on standing. By crystallizing gentiobiose from ethyl alcohol solution they prepared the crystalline sugar itself, which had a specific rotation of  $-6$  six minutes after dissolving, changing likewise to  $+9.8$  on standing. If one extrapolates as well as possible the value  $-6$  back through the first six minutes according to the rate of mutarotation that Bourquelot and Hérissé observed a value near the calculated  $-11$  is obtained. It would seem that the alpha form of melibiose which they evidently had in hand in the form of a compound with methyl alcohol of crystallization contained some of the beta modification.

**The Rotation of Manninotriose.**—The specific rotation of stachyose being  $+148$ ,<sup>5</sup> its molecular rotation is  $+98600$ , and hence the specific rotations of the alpha and beta forms of manninotriose are calculated to be  $+191$ , and  $+157$ , respectively. These rotations do not appear to have ever been measured but C. Tanret<sup>6</sup> records  $+167$  as the final specific rotation of manninotriose. This value lies between the calculated numbers, as should be the case, and is also at approximately the same position between them as in the case of glucose, melibiose and gentiobiose. The

<sup>1</sup> *Z. Ver. Zuckerind.*, **52**, 1050-9 (1903).

<sup>2</sup> Forthcoming publication.

<sup>3</sup> Bourquelot and Nardin, *Compt. rend.*, **126**, 280 (1898).

<sup>4</sup> *J. pharm. chim.*, [6] **16**, 418 (1902).

<sup>5</sup> Schulze and Planta, *Ber.*, **24**, 2705 (1890).

<sup>6</sup> *Bull. soc. chim.*, [3] **29**, 891 (1903).

ratio of the concentrations of the beta and alpha forms which are present at equilibrium is for glucose  $(113 - 52^8)/(52 - 19) = 1.8$ , for melibiose  $(175 - 143^8)/(143 - 124) = 1.6$ , for gentiobiose  $(39 - 10^8)/(10 + 11) = 1.3$ , and for mannanotriose  $(191 - 167^1)/(167 - 157) = 2.4$ . If the final rotation of mannanotriose were 169 rather than 167 the ratio would be the same as for glucose, and if it were 172 the ratio would be the same as for gentiobiose.

**Other Possible Members of the Sucrose Group.**—Since lactose, cellose, and maltose have structures in which the free lactonyl hydroxyl is a part of the glucose group, it is conceivable that these disaccharides might be united with fructose through a sucrose union to yield derivatives of sucrose. The expected specific rotations of these compounds can be calculated according to the preceding considerations. For example, since the specific rotation of  $\beta$ -lactose (m. w. 342) is +35, its molecular rotation is +12000, and the specific rotation of the hypothetical  $\alpha$ -lactose <  $\alpha$ -fructose (m. w. 504) is calculated to be  $(12000 + 19300)/504 = +62$ .

**The Acetylated Sugars of the Sucrose Group.**—Referring back to the structural formula for sucrose, consider the rotation of sucrose octacetate. Its molecular rotation is the sum of a new quantity  $G'$ , which is the rotation of an acetylated glucose chain, plus  $B''$ , which may possibly be different in value from  $B'$ , plus  $F'$ , the rotation of an acetylated fructose residue. In the same way that  $G$  was obtained from the specific rotations of the alpha and beta forms of glucose  $G'$  may be found from those of the corresponding glucose pentacetates (m. w. 390), which have the values +102 and +4, respectively, in chloroform solution.<sup>2</sup> Half of the sum of their molecular rotations is +20700 =  $G'$ , and half the difference is +19100, the latter being the rotation of the end asymmetric carbon in glucose pentacetate. The specific rotation of sucrose octacetate (m. w. 678) in chloroform is +59.6,<sup>3</sup> and hence its molecular rotation is +40400. The molecular rotation of the glucose pentacetate chain is therefore 19700 less than that of sucrose octacetate or the molecular rotation of  $\alpha$ -glucose pentacetate is  $(19700 - 19100) = 600$  less than that of sucrose octacetate, while that of the  $\beta$ -pentacetate is  $(19700 + 19100) = 38800$  less. These numerical differences apply also to the molecular rotations of the corresponding acetylated derivatives of the pairs raffinose and melibiose, gentianose and gentiobiose, stachyose and mannanotriose. The beta octacetates (m. w. 678) of melibiose and gentiobiose have the specific rotations +102<sup>4</sup> and -5,<sup>5</sup> respectively, in chloroform solution. From

<sup>1</sup> Final specific rotations of the sugars.

<sup>2</sup> Hudson and Dale, *THIS JOURNAL*, **37**, 1265 (1915).

<sup>3</sup> Hudson and Johnson, *Ibid.*, **37**, 2753 (1915).

<sup>4</sup> Hudson and Johnson, *Ibid.*, **37**, 2752 (1915).

<sup>5</sup> Zemplén, *Z. physiol. Chem.*, **85**, 402 (1913).

these data the specific rotations of the hendecacetates (m. w. 966 and formula  $C_{28}H_{21}(C_2H_3O)_{11}O_{10}$ ) of raffinose and gentianose in chloroform are calculated to be +112 and +43, respectively. Scheibler and Mittelmeier<sup>1</sup> have found +92 for crystalline raffinose hendecacetate in alcohol, but the value in chloroform is not known. It is probably higher than +92, because the specific rotation of sucrose octacetate in chloroform is +60 (see preceding) and in alcohol, +38.<sup>2</sup> Gentianose hendecacetate does not appear to have ever been prepared.

### Sugars of the Trehalose Group.

**Trehalose and Isotrehalose.**—Since trehalose is not a reducing sugar, combines with only one molecule of water per molecule of sugar during hydrolysis, and also forms an octacetate, its structure may be considered to be *glucose* < > *glucose*, the lactonyl hydroxyls being united with the elimination of water. The three possible combinations which fit this structure, assuming gamma-lactonyl rings, are  $\alpha$ -*glucose* < >  $\alpha$ -*glucose*, the  $\alpha,\beta$  form, or the  $\beta,\beta$  form. If G represents the rotation of the glucose chain, as before, and A' that of the asymmetric lactonyl carbon (+A' for the  $\alpha$ -glucoside form and -A' for the  $\beta$ ) the molecular rotations of the three combinations may be formulated:

$$\begin{aligned} \alpha,\alpha\text{-Trehalose} & \dots\dots\dots G + A' + A' + G = 2G + 2A' \\ \alpha,\beta\text{-Trehalose} & \dots\dots\dots G + A' - A' + G = 2G \\ \beta,\beta\text{-Trehalose} & \dots\dots\dots G - A' - A' + G = 2G - 2A' \end{aligned}$$

The value of 2G has already been found from the sum of the molecular rotations of the alpha and beta forms of glucose to be +23800, and hence the specific rotation of  $\alpha,\beta$ -trehalose (m. w. 342) is calculated to be +70. This value is entirely different from the observed specific rotation of trehalose, +197, hence the natural sugar is not the  $\alpha,\beta$  combination. Neither can it be the  $\beta,\beta$  form because it should then be less dextrorotatory than +70 since the value of -A' for the known  $\beta$ -glucosides is a quantity of considerable magnitude. On the other hand, the high dextrorotation of trehalose agrees well with what would be expected for  $\alpha$ -*glucose* < >  $\alpha$ -*glucose*. Assuming this to be the structure of the natural sugar, its molecular rotation ( $197 \times 342 = +67400$ ) is  $2G + 2A'$ , and since 2G is +23800, 2A' is +43600, and the molecular rotation of  $\beta,\beta$ -trehalose ( $2G - 2A'$ ) may be calculated to be -19800, and the specific rotation -58. Under the name *isotrehalose*, Fischer and Delbrück<sup>3</sup> have recently described a sugar of the trehalose type which they prepared by the saponification of crystalline *isotrehalose octacetate*, a substance which in its turn was made by the condensation of bromo-acetyl glucose. Isotrehalose was not obtained in a crystalline state and the amorphous sub-

<sup>1</sup> *Ber.*, 23, 1443 (1890).

<sup>2</sup> Herzfeld, *Ibid.*, 13, 267 (1880).

<sup>3</sup> *Ber.*, 42, 2776 (1909).

stance was not free from ash. Under such conditions the specific rotation of the impure material can only be considered as an approximate value of the rotation of the pure sugar. Fischer and Delbrück found  $-39$ , a value which strongly suggests that isotrehalose is  $\beta,\beta$ -trehalose. This view is supported by the fact that all other derivatives that have been prepared from bromo-acetyl glucose belong to the  $\beta$  series. It is also supported by the result of the following considerations, which indicate that the parent substance, *isotrehalose octacetate*, is a  $\beta,\beta$  form.

**Octacetates of the Trehalose Sugars.**—The relations which have just been derived among the rotations of the three trehaloses and the alpha and beta forms of glucose apply likewise to the fully acetylated derivatives of these five substances. Thus the molecular rotation of  $\alpha,\beta$ -trehalose octacetate may be regarded equal to the sum of the molecular rotations of the alpha and beta glucose pentacetates, which is known to be  $+41400$ , and its specific rotation (m. w. 678) in chloroform is calculated to be  $+61$ . The observed specific rotation of pure trehalose octacetate in chloroform is  $+162$ ,<sup>1</sup> which indicates again that trehalose is the  $\alpha,\alpha$  form. The specific rotation of the  $\beta,\beta$  form, or isotrehalose octacetate, is calculated from these two rotations, by the same method that was used with the sugars, to be  $-40$  in chloroform. Fischer and Delbrück found  $-17$  in benzene, a difference which may be due to the change of solvent, because trehalose octacetate rotates  $-162$  in chloroform and  $+171$  in benzene.<sup>2</sup>

**Other Compound Sugars of the Trehalose Type.**—It may be useful to indicate that the rotation of nearly all the possible sugars of this type may be calculated from existing data. As an illustration consider the tetrasaccharide *lactose*  $\langle \rangle$  *lactose*, a combination which E. Fischer and H. Fischer<sup>3</sup> have sought to prepare through the condensation of bromo-acetyl lactose. Since the alpha and beta forms of lactose (m. w. 342) rotate  $+86$  and  $+35$ , respectively, twice the molecular rotation of the lactose chain is  $+41400$ . Since the molecular weight of the tetrasaccharide is 666, the specific rotation of its  $\alpha,\beta$  form is calculated to be  $41400/666 = +62$ . Assuming that the asymmetric lactonyl carbons uniting the glucose residues have the same rotations that were found for them in trehalose,  $2A' = +44000$ , and hence the specific rotation of the  $\alpha,\alpha$  form of the tetrasaccharide is calculated to be  $(41400 + 44000)/666 = +128$ , and that of the  $\beta,\beta$  form  $(41400 - 44000)/666 = -4$ .

From the specific rotations of the alpha and beta lactose octacetates (m. w. 678),  $+54$  and  $-4$  in chloroform,<sup>4</sup> and the value  $+68500$  for the

<sup>1</sup> Hudson and Johnson, *THIS JOURNAL*, 37, 2752 (1915).

<sup>2</sup> Measured recently in this laboratory by Dr. J. M. Johnson.

<sup>3</sup> *Ber.*, 43, 2532 (1910).

<sup>4</sup> Hudson and Johnson, *THIS JOURNAL*, 37, 1273 (1915).

two lactonyl carbons (calculated as in the case of the trehalose octacetates), the specific rotation of the fully acetylated derivatives (m. w. 1255) of *lactose*  $\langle \rangle$  *lactose* may be calculated to be, for the  $\alpha, \beta$  form  $+33900/1255 = +27$ , for the  $\alpha, \alpha$  form  $(33900 + 68500)/1255 = +82$ , for the  $\beta, \beta$  form  $-28$ . The similar derivatives of maltose and cellose can be treated in the same way. The calculations are here indicated because the work of E. Fischer with H. Fischer, and Zemplen<sup>2</sup> appear to open a way for synthesizing these compounds of lactose, maltose and cellose, respectively, when sufficient material is available.

Lastly, the expected specific rotation of  $\beta, l$ -*arabinose*  $\langle \rangle$   $\beta, l$ -*arabinose* (m. w. 282) may be calculated from the specific rotations of the alpha and beta forms of the sugar,  $+76$  and  $+184$ , respectively, to be  $((76 + 184) 150 + 44000^3)/282 = +294^\circ$ . This rotation is of interest because it appears to be the largest specific rotation that can be expected among the sugars from present data.

### The Related Rotations of Lactose and Cellose.

There are three disaccharides which have the general structure *glucose*  $\langle$  *glucose*  $\langle$ , namely, maltose, cellose and gentiobiose, and two of the composition *galactose*  $\langle$  *glucose*  $\langle$ , namely, melibiose and lactose. In these structures the place of attachment of the left hand glucose or galactose molecule is evidently its lactonyl carbon, but several points of union for the right hand glucose molecule are possible. Without more knowledge of this point of attachment for each of the compound sugars, it does not seem possible in general to obtain relations among their rotatory powers. However, there is one special case which can be adequately treated at present and it leads to an interesting relation between the rotations of lactose and cellose. The structures shown above indicate that for each point of attachment in the right hand glucoside residue, there can be four related sugars according as the left hand member is  $\alpha$ - or  $\beta$ -glucose, or  $\alpha$ - or  $\beta$ -galactose. To formulate the rotations of these forms let G and Ga, respectively, be the rotations of the left hand glucose and galactose chains, L that of their bound lactonyl carbons, and R that of the common right hand glucose residue. Since the free lactonyl group of this residue permits  $\alpha$  and  $\beta$  forms, let R refer throughout to the same one of these. The molecular rotations of the four structures are thus:

$$\begin{array}{ll}
 \alpha\text{-galactose} \langle \text{glucose} \langle & = \text{Ga} + \text{L} + \text{R} & \beta\text{-galactose} \langle \text{glucose} \langle & = \text{Ga} - \text{L} + \text{R} \\
 \alpha\text{-glucose} \langle \text{glucose} \langle & = \text{G} + \text{L} + \text{R} & \beta\text{-glucose} \langle \text{glucose} \langle & = \text{G} - \text{L} + \text{R}
 \end{array}$$


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$$\begin{array}{ll}
 \text{Difference Ga} - \text{G} & & & \text{Ga} - \text{G}
 \end{array}$$

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ber.*, 43, 2536 (1910).

<sup>3</sup> The assigning of a positive rather than negative sign to 44,000 (= 2A), although the compound is a  $\beta$ -derivative, is made because the arabinose is the levo form. See *THIS JOURNAL*, 31, 72 (1909).



The differences are equal to each other, and as will be seen readily are also equal to the difference of the molecular rotations of the corresponding  $\alpha$  and  $\beta$  forms of galactose and glucose, or of methyl galactoside and methyl glucoside. We reach the conclusion, therefore, that if either of the *galactose* < *glucose* < sugars (melibiose or lactose) has a structure in which the right hand glucose residue is identical with the similar component of one of the *glucose* < *glucose* < sugars (maltose, cellose or gentiobiose) the pair of sugars, in case both are  $\alpha$ -glucosidic compounds or both beta, should differ in molecular rotation by the difference between the molecular rotations of the galactose and glucose chains. The difference in specific rotation of  $\beta$ -methyl galactoside ( $0^\circ$ ) and  $\beta$ -methyl glucoside ( $-32^\circ$ ) (of m. w. 194) is  $+32^\circ$ , which amounts to  $(32)(194)/342 = +18^\circ$  in the specific rotation of the disaccharides (m. w. 342). If  $+18$  be added to the specific rotation of the beta forms of maltose ( $+118$ )<sup>1</sup> and of gentiobiose ( $-11$ ) the sums,  $+136$  and  $+7$  do not agree with the rotations of either  $\beta$ -melibiose ( $+124$ ) or  $\beta$ -lactose ( $+35$ ). On the other hand, the rotation of  $\beta$ -cellose ( $+16$ )<sup>1</sup> plus  $18$  is equal to that of  $\beta$ -lactose ( $35$ ) almost exactly.

**The Rotations of the Octacetates of These Sugars.**—It is highly desirable to test in independent ways this conclusion, that lactose and cellose have the same structure for their common glucose residue, and that the galactose residue of one belongs to the same series (probably the  $\beta$ , judging from the low rotation of lactose) as the glucosidic glucose residue of the other. If the similarity does exist, it would be expected to extend to many derivatives of these sugars, and it should be possible to decide from a comparison of the rotations of each pair of derivatives whether the agreement that has been found to hold for the parent sugars is a general one and really has for its basis the assigned reason, or is an accidental agreement in the one case tested. The rotations in chloroform solution of the pure octacetates of the disaccharides in question are known, and a comparison of them appears to be of special value because in them the rotations of the individual asymmetric carbon atoms in the glucose residue are doubtless quite different from the values for the sugars themselves. The difference between the specific rotations of tetra-acetyl  $\beta$ -methyl galactoside ( $-13$ )<sup>1</sup> of m. w. 362, and the corresponding acetylated  $\beta$ -methyl glucoside ( $-18$ )<sup>2</sup> is  $+5$ , which corresponds to  $(5)(362)/678 = 3^\circ$  for the disaccharide octacetates. The addition of this value to the specific rotation of  $\beta$ -maltose octacetate ( $+63$ ) gives a sum entirely different from the rotation of the  $\beta$ -octacetate of either melibiose ( $+102$ ) or lactose ( $-4$ ). On the other hand, the rotations of the  $\beta$ -octacetates of both cellose ( $-15$ ) and gentiobiose ( $-5$ ) yields sums ( $-12$  and  $-2$ )

<sup>1</sup> Hudson and Yanovsky, forthcoming publication.

<sup>2</sup> Hudson and Dale, THIS JOURNAL, 37, 1265 (1915).

which are near the rotation of  $\beta$ -lactose octacetate ( $-4$ ). The combination of this result with that obtained from the rotations of the sugars themselves, in which gentiobiose was clearly ruled out, gives strong evidence that the common glucose residues of lactose and cellose have identical structure.

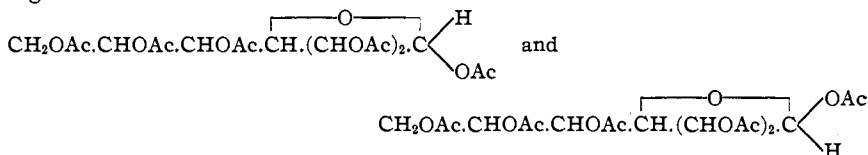
WASHINGTON, D. C.

## THE ISOMERIC ALPHA AND BETA HEXACETATES OF $\alpha$ -GLUCOHEPTOSE.

By C. S. HUDSON AND E. YANOVSKY.<sup>1</sup>

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E. Fischer<sup>2</sup> has shown that two isomeric fully acetylated derivatives of  $\alpha$ -glucoheptose could be prepared by the action of acetic anhydride on the sugar. When sodium acetate was used to catalyze the reaction, the crystalline product was a hexacetate which melted at  $132^\circ$ , but the use of zinc chloride gave an isomeric hexacetate of m. p.  $156^\circ$ . Fischer has mentioned that these isomeric hexacetates of  $\alpha$ -glucoheptose are produced by the same reactions which yield the alpha and beta pentacetates of glucose. Since the isomerism of the glucose pentacetates can be explained, according to Fischer,<sup>3</sup> as due to the existence of the structures that are now generally named the alpha and beta forms, it appears probable that the similarly produced hexacetates of  $\alpha$ -glucoheptose have the corresponding structures:



in which the asymmetry of the right-hand terminal carbon atom permits the two configurations. If this view is correct, the molecular rotatory power of the alpha form may be written  $+A + B'$ , and that of the beta form  $-A + B'$ , where  $A$  is the rotation of the terminal asymmetric carbon and  $B'$  is that due to the remainder of the structure.<sup>4</sup> It follows then that the difference of the molecular rotations of the two forms is  $2A$ , which is the same as the *difference* in the molecular rotations of the alpha and beta pentacetates of glucose, of rotations  $+A + B$  and  $-A + B$ , respectively. The rotations of the  $\alpha$ -glucoheptose hexacetates are not recorded in Fischer's article, and we have consequently prepared the sub-

<sup>1</sup> Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

<sup>2</sup> *Ann.*, **270**, 64 (1892); *Ber.*, **26**, 2400 (1893).

<sup>3</sup> *Ber.*, *loc. cit.*

<sup>4</sup> Hudson, *THIS JOURNAL*, **31**, 66 (1909).