

THE RING STRUCTURE OF MANNOSE. THE OPTICAL ROTATION OF 4-GLUCOSIDO- α -MANNOSE

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ABSTRACT

A comparison of the rotation of two pairs of sugars, which can not form a 1, 4 ring, shows that one pair gives an epimeric difference in rotation, which agrees with the value obtained from α -*d*-mannose (+30) and the normal form of glucose, while the other pair gives a value which agrees with that obtained from β -*d*-mannose (-17) and the normal form of glucose. These results may be interpreted as indicating that 4-glucosido- α -mannose and 4-galactosido- β -mannose have structures similar to α - and β -mannose, respectively. However, regardless of the particular interpretation, the different values show that a decision between the rival ring classifications can not be reached from a comparison of the rotations of cellobiose and glucosido-mannose.

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I. INTRODUCTION

The development of experimental carbohydrate chemistry in recent years has resulted in the evolution of new ideas which in turn has led to conflicting views. Particularly the assignment of ring structures has been the source of considerable controversy. The apparent ring structures may be determined experimentally by the methylation method first used by Purdie and Irvine.¹ In 1926 Hudson² advanced a new system of ring structures in which he attributed to the methyl glucosides a 1, 4 oxidic ring, and to α -methyl-*d*-mannoside a 1, 5 oxidic ring. This classification was based upon the assumption that the normal methyl xylosides, galactosides, and arabinosides possess a 1, 5 ring as shown by methylation studies. In a recent publication Hudson³ states that the methylation data upon which his previous assignments were based are invalid. He now assigns the 1, 5 ring to the methyl glucosides and the 1, 4 ring to α -methyl-*d*-mannoside. It is claimed that the whole system of ring structures, as developed

¹ Purdie and Irvine, J. Chem. Soc., 83, p. 1021; 1903.

² Hudson, J. Am. Chem. Soc., 48, p. 1434; 1926.

³ Hudson, J. Am. Chem. Soc., 52, p. 1680; 1930.

by numerous investigators from the methylation method, is not sound and that the ring structures of the sugars, both simple and compound, must be redetermined. The importance of this conclusion and its far-reaching consequences demand that the evidence must be conclusive.

The criterion by which Hudson sought to reach a decision between the rival classifications of rings depends upon the comparison of the rotations of a pair of substances, having configurations that could be epimeric, but in which only one of the two rings 1, 4 and 1, 5 could be assumed to exist. He pointed out that cellobiose and 4-glucosido-mannose are a pair of substances which fulfill these requirements and that the same is true for lactose and 4-galactosido-mannose. It was found from a comparison of the rotations⁴ of the acetoalogen derivatives of cellobiose and 4-glucosido-mannose that the "epimeric difference"⁵ in rotation, $2R_2$, for the acetylated compounds was 11,800. This value agrees with the value of $2R_2$ (11,300) which he had previously obtained from certain substances in the glucose and mannose series, while it does not agree with the value of $2R_2$ (29,500) obtained from the molecular rotations of the tetra-acetates of α -methyl *d*-glucoside and α -methyl *d*-mannoside. The test which has just been outlined was followed by the statement⁶ "that Haworth's assignment of the same ring to normal methyl glucoside and mannoside must be invalid." The final decision was drawn from a comparison of the rotations of the acetylated derivatives. If a shift in the ring occurs during methylation, a ring shift might also occur during the acetylation of a methyl glycoside.⁷ Probably a ring shift does not occur, but in any case it is more desirable to compare the rotations of the sugars or methyl glycosides than the rotations of the acetylated derivatives.

II. COMPARISON OF THE ROTATIONS OF 4-GLUCOSIDO- α -MANNANOSE AND CELLOBIOSE

Only roughly approximate data are available in the literature for the rotations of 4-glucosido- α -mannose⁸ and 4-galactosido- β -mannose.⁹ A comparison of such approximate data, however, indicates that the epimeric difference obtained from β -cellobiose and 4-glucosido- α -mannose, differs widely from the value obtained from β -lactose and 4-galactosido- β -mannose.

In the light of this conflicting evidence it was deemed necessary to obtain accurate data upon the rotations of 4-glucosido- α -mannose and 4-galactosido- β -mannose. 4-glucosido- α -mannose was prepared by the hydrogen-fluoride method of D. H. Brauns.¹⁰ The initial specific rotation of 4-glucosido- α -mannose monohydrate was found to be +14.6, and the equilibrium specific rotation was found to be +5.88, which agrees with the value +5.8 previously reported by Brauns.

⁴ Brauns, J. Am. Chem. Soc., 48, p. 2776; 1926.

⁵ The "epimeric difference" in rotation, $2R_1$, is supposedly twice the rotation of the second carbon atom.

⁶ Hudson, J. Am. Chem. Soc., 52, p. 1683; 1930.

⁷ The word glycoside is used in the generic sense; the term glucoside is limited to the glycosides of glucose.

⁸ The rotation of 4-glucosido-mannose was determined by Bergmann and Schotte (Ber. 64, p. 1564; 1921) who give the following data: $[\alpha]_D^{16} = +15.07$, 7 minutes after solution; $[\alpha]_D^{16} = +10.65$, constant. The same substance was also prepared by D. H. Brauns who gives the following data for the monohydrate: $[\alpha]_D^{16} = +7.3$,

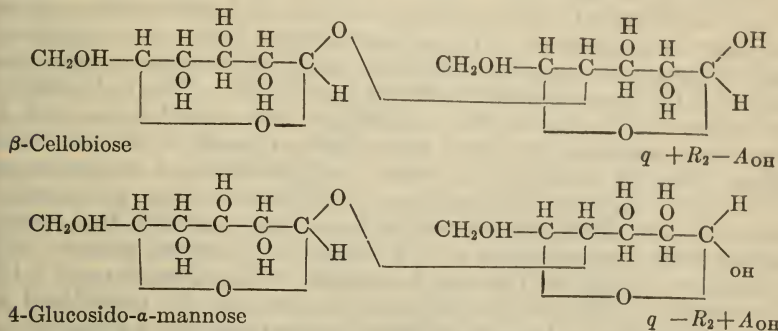
15 minutes after solution; $[\alpha]_D^{16} = +6.5$, after 35 minutes; $[\alpha]_D^{16} = +5.8$ constant. These values indicate that the initial rotation of 4-glucosido-mannose is about +15.

⁹ See p. 1182.

¹⁰ D. H. Brauns, J. Am. Chem. Soc., 48, p. 2781; 1926.

The sugar mutarotates from a positive to less positive rotation; hence it is the alpha form.

The epimeric difference in rotation between β -cellobiose and 4-glucosido- α -mannose is obtained from the following computation, which is based upon the fundamental assumption that, as Hudson claims, cellobiose and 4-glucosido-mannose are a pair of truly epimeric substances.



Let the rotation of β -cellobiose be separated into the components: $-A_{OH}$ (the rotation of the pseudo aldehydic carbon); R_2 (the rotation of the epimeric carbon; that is, the carbon adjacent to the pseudo aldehydic carbon), and q (the rotation of the rest of the molecule). Then the molecular rotation of β -cellobiose is $q + R_2 - A_{OH}$. According to the same system the rotation of the alpha form of the epimeric substance, 4-glucosido-mannose, becomes $q - R_2 + A_{OH}$. The difference in the molecular rotations of β -cellobiose (+5,470)¹¹ and 4-glucosido- α -mannose (+5,270) equals $2R_2 - 2A_{OH}$. The value for the epimeric difference, $2R_2$, is obtained by adding the value of $2A_{OH}$ (16,700) to value of $2R_2 - 2A_{OH}$, which gives 16,900. This agrees approximately with the value (14,900) obtained from α -*d*-glucose (+113) and α -*d*-mannose (+30) and also with the value (15,300) obtained from α -methyl-*d*-glucoside (+157.9) and α -methyl-*d*-mannoside (+79). Since analogous rotational relations exist between the pairs the same structural relations probably exist, which indicates that α -*d*-mannose (+30) and α -methyl-*d*-mannoside (+79) have structures similar to 4-glucosido- α -mannose. According to the structure generally accepted, 4-glucosido- α -mannose can not form a 1, 4 primary ring. Thus α -*d*-mannose (+30) and α -methyl-*d*-mannoside seemingly do not have the 1, 4 ring as recently assigned by Hudson.

This interpretation is in harmony with the recent work of Haworth and Porter¹² who have prepared a new crystalline methyl mannoside which Haworth, Hirst, and Webb¹³ have shown has a 1, 4 ring. In consequence the whole system of ring structures which Hudson has built upon his conclusion that α -methyl-*d*-mannoside has a 1, 4 ring is rendered uncertain.¹⁴

¹¹ Hudson, B. S., Sci. Paper No. 533.

¹² Haworth and Porter, J. Chem. Soc., p. 649; 1930.

¹³ Haworth, Hirst, and Webb, J. Chem. Soc., p. 651; 1930.

¹⁴ The methyl glycosides of 4-glucosido-mannose are being prepared with the object of extending the comparison to those compounds.

III. CORRELATION OF 4-GLUCOSIDO- α -MANNOSE AND 4-GALACTOSIDO- β -MANNOSE WITH α -*D*-MANNOSE AND β -*D*-MANNOSE

As pointed out by Hudson the epimeric difference in rotation may be obtained also from lactose and 4-galactosido-mannose. From data given by Bergmann¹⁵ ($[\alpha]_D^{20} = +23.5$, 5 minutes after solution; $[\alpha]_D^{20} = +30$, constant), the specific rotation of 4-galactosido- α -mannose may be estimated to be approximately +20. A comparison of this approximate rotation (20×342) with the rotation of β -lactose ($+35 \times 342$) gives an epimeric difference of 5,130. This value differs widely from the value (16,900) calculated from β -cellobiose and 4-glucosido- α -mannose, but does not differ so much from the value (6,480) obtained from β -*D*-glucose ($+19 \times 180$) and β -*D*-mannose (-17×180). Apparently the epimeric differences from 4-glucosido- α -mannose and from 4-galactosido- β -mannose parallel the results obtained from a comparison of the rotations of normal glucose with α -*D*-mannose (+30) on the one hand and with β -*D*-mannose (-17) on the other. Hence 4-glucosido- α -mannose may be considered at least provisionally to be a substituted α -mannose and 4-galactosido- β -mannose a substituted β -mannose.

The correlations of the rotations of 4-glucosido- α -mannose and 4-galactosido- β -mannose with the rotations of α - and β -mannose are based upon the assumption that the members of each pair of sugars differ only in the reducing hexose molecule. The substances were suggested by Hudson who had used the acetohalogen derivatives of one pair in an attempt to disprove Haworth's¹⁶ assignment of the same ring structure (1, 5), to α -methyl glucoside and α -methyl mannoside. Hudson neglected to consider a possible difference in the secondary hexose structures of these disaccharides. By various combinations of secondary ring structures it is possible to interpret all of the results obtained from these disaccharides as favorable to either one of the two rival classifications.

Such calculations have been made, but are not presented here because they are based upon the assumption that the substances have different secondary ring structures, which is not in agreement with the experimental evidence from chemical studies.

The final decision between the various interpretations must await the accumulation of more experimental evidence. However, in any case Hudson's proof for the invalidity of the results from the methylation of α -methyl glucoside and α -methyl mannoside appears not to be sound because of the following reasons: (1) The numerical values for the epimeric difference in rotation for the two pairs of sugars which he suggested as suitable to decide the issue are conflicting, (2) the substances he selected may differ in secondary ring structures, and (3) his conclusion as to the structure of the methyl glycosides was drawn from a comparison of the rotations of the acetohalogen derivatives; if a ring shift occurs on methylation it may likewise occur upon acetylation; therefore, any conclusions drawn from the rotations of the acetylated derivatives may be erroneous.

¹⁵ Bergmann, Ann., 434, p. 94; 1923.

¹⁶ Charlton, Haworth, and Peat, J. Chem. Soc., p. 89; 1926.

IV. NOTE ON OPTICAL ROTATION AND RING STRUCTURE

Recently the writer¹⁷ determined the optical rotation of *a-d*-gulose which, in conjunction with the rotations of glucose, mannose, and galactose, completed the data necessary for calculating the optical rotatory powers of the individual asymmetric carbon atoms in the aldohexose sugars. As explained in a previous publication¹⁸ the values, which were calculated by means of the van't Hoff¹⁹ principle of optical superposition, are based upon the fundamental assumption that the compared substances have similar structures. As a working hypothesis the structures of the methyl glycosides as determined by methylation studies were assumed to be valid. This assignment, which is the outgrowth of the work of a considerable number of investigators, but which has been avocated particularly by Haworth,²⁰ is not in agreement with the conclusions reached by Hudson.²¹ It is shown in this paper that the rotations of one pair of substances, which Hudson had previously suggested as suitable to decide between the rival ring classifications, give an epimeric difference in rotation of 16,900; while the rotations of another pair of similar substances give an epimeric difference of 5,130. One of these values agrees with the values previously reported by the writer which were declared erroneous by Hudson,²² while the other agrees with the value which Hudson believes to be correct. The cause²³ of this discrepancy must await future developments, but since the evidence for the assignment of ring structures is conflicting it is desirable to approach the subject from different angles.

One of the angles of approach is to assume that the ring structures as determined by methylation of the normal methyl glycosides are correct. This viewpoint was adopted in the writer's previous publication and upon that basis the optical rotations of the hexose and pentose sugars and methyl glycosides were compared.

It was pointed out that the optical rotatory values which were thus obtained from the methyl glycosides were of like sign and of the same order of magnitude as the values obtained from the sugars. Although the values from the methyl glycosides were of the same order they were numerically greater than the values from the sugars, which it was stated explains the deviation from a constant in the value of Hudson's $A_{Me} - A_{Oh}$. Hudson²⁴ objected to this explanation, stating that it was an "obvious algebraic misstatement" because the values of $A_{Me} - A_{Oh}$ are obtained from the same equations from which the values for the optical rotations of the individual carbon atoms are derived. The writer's explanation was not given as a proof for the correctness of the values, but rather as a comparison of the data. For this reason it was placed in the portion of the paper devoted to

¹⁷ Isbell, B. S. Jour. Research, 5 (RP226), p. 741; 1930.

¹⁸ Isbell, B. S. Jour. Research, 3, p. 1041; 1929.

¹⁹ van't Hoff, The Arrangement of Atoms in Space, p. 160, Longmans, Green & Co.; 1898.

²⁰ Haworth Constitution of Sugars, London; 1929.

²¹ Hudson, J. Am. Chem. Soc., 52, p. 1683; 1930.

²² Hudson, J. Am. Chem. Soc., 52, p. 1698; 1930.

²³ Recently Haworth, Hirst, and Miller (J. Chem. Soc., p. 2469; 1929) have shown that the three forms of the acetylated methyl rhamnosides which were previously believed to be ring isomers upon methylation give results which indicate all three substances have a 1, 5 ring. To explain the anomaly of three isomers of the same ring, they postulate a new type of isomerism.

The correlations in optical rotations which Hudson has found in the mannose, rhamnose, and lysoc series and which have been interpreted as different ring types might represent correlations between isomeric substances of the type just mentioned. In other words, the system to which Hudson allocates the 1, B ring might contain the same ring as the 1, A but have a different structure.

²⁴ See footnote 3, p. 1179.

the "Discussion of results" under the subheading "Comparison of the Rotations of the Methyl Glycosides with the Rotations of the Sugars." Further evidence that the writer did not intend the interpretation which Doctor Hudson has made may be seen from the following quotation.

Van't Hoff's idea may be put in the form of four simultaneous equations which contain only three variables, and if the experimental values of A , B , and C , determined from any three of the equations check the fourth equation, his theory as applied in the given case is definitely proved. * * * The investigation, which is still in progress, has been successful, in that the optical rotations of α - D -gulose and α - and β -methyl D -gulosides have been determined. These values complete the data necessary for the computation of the optical rotation of each of the several asymmetric carbon atoms in the hexose sugars and in the methyl glycosides.

It was pointed out that the preparation of other substances was in progress in order to check the values, and for that purpose the rotations of the unknown hexose sugars and methyl glycosides were predicted.

The pertinent point in the writer's explanation of the deviations in the value of Hudson's $A_{Me} - A_{OH}$ was that in order for this value to be constant the rotations of the individual asymmetric carbon atoms in the sugars must be equal to the rotations of the corresponding carbon atoms in the methyl glycosides; if there be any difference in the values, deviations will occur. That there is a difference in the values obtained from the sugars and methyl glycosides was indicated by the computations from the methyl glycosides giving larger numerical values than were obtained for the sugars. Probably this difference is real since so many calculations give slightly larger values for the methyl glycosides. Moreover, there are other cases in the carbohydrate field where there is similar evidence that a change in the first carbon atom may alter the rotation of the rest of the molecules. For example, Purves²⁵ has found that irregularities occur in the rotations of the acetylated thiophenol glycosides which indicate that "different substituents occasion varying small but definite changes in the rotation of the rest of the molecule."

It is regretted that it was not more clearly pointed out in the previous publication that the value of $1/2 (2A_{Me} - 2A_{OH})$ was the average of the results obtained by solving separately the equations which were subsequently combined to give the values of $A_{Me} - A_{OH}$. The determination of the values of $A_{Me} - A_{OH}$ from the latter equations does not constitute a proof for the values and, as stated above, it was not intended as such.

The writer's new compounds of D -gulose are new links in the chain of experimental carbohydrate chemistry which are necessary for the calculation of the rotations of the individual asymmetric carbon atoms in the hexose sugars and methyl glycosides. The rotations of the substances may be compared in various ways giving different values. At this time we can not say which values are correct; nevertheless it is only by approaching the subject from different angles that we can hope to arrive at the true interpretation.

²⁵ Purves, J. Am. Chem. Soc., 51, p. 3621; 1929.

V. EXPERIMENTAL

1. FLUORO-HEXA-ACETYL 4-GLUCOSIDO-MANNOSE

This compound was prepared from cellobiose octa-acetate by the action of anhydrous hydrogen fluoride according to the method of Brauns.²⁶ Two hundred grams of cellobiose octa-acetate after standing five hours with 560 g of hydrogen fluoride (prepared from 2,000 g of NaHF_2) gave a yield of 23 g of crystalline fluoro-hexa-acetyl glucosido mannose and 70 g of noncrystalline material. The crystalline product after recrystallization melted at 153° and gave in chloroform solution $[\alpha]_D^{20} = +21$. Brauns gave the melting point as 145° (not sharp) and $[\alpha]_D^{20} = +20.75$.

2. OCTA-ACETYL 4-GLUCOSIDO-MANNOSE

Thirty grams of fluoro-hexa-acetyl 4-glucosido mannose, after acetylation with 150 ml of acetic anhydride containing 2 g of zinc chloride according to the method previously used by Brauns, gave 24 g of octa-acetyl 4-glucosido mannose melting at 203° C. After recrystallization the specific rotation was found to be $+36.3^\circ$ (1.7390 g dissolved in 25 ml (HCCl_3) gave a rotation of 14.55° S.). The melting point and rotation agree with the values previously found by Brauns.

The same substance may be prepared as pointed out by Brauns from the mother liquor from the preparation of fluoro-hexa-acetyl glucosido-mannose. The writer found it very difficult to separate the product thus obtained from a small amount of unchanged cellobiose octa-acetate with which it was mixed. A separation was finally obtained by means of crystallization from glacial acetic acid.²⁷

3. DEACETYLATION OF OCTA-ACETYL 4-GLUCOSIDO-MANNOSE

4-glucosido- α -mannose was first obtained in good yield by saponification of the above-described octa-acetate according to the method described by Brauns using the theoretical quantity of barium methylate. Subsequent preparations were deacetylated by a modified method which the writer believes is a very satisfactory method for the deacetylation of similar substances. Zemplen^{28,29} and Pacsu have found that a small amount of sodium methylate will deacetylate a large quantity of acetylated product. The reaction results in the formation of methyl acetate and the regeneration of sodium methylate. The use of a small amount of the reagent is advisable because of rearrangements which occur in strongly alkaline solutions. Since barium methylate may be completely removed after a reaction, it seemed desirable to substitute barium methylate for sodium methylate in the method of Zemplen and Pacsu.

Six grams of octa-acetyl 4-glucosido mannose were suspended in 150 ml of absolute methyl alcohol and cooled in an ice-salt mixture.

²⁶ See footnote 10, p. 1180.

²⁷ In addition to the compounds mentioned above a small quantity of another acetate of cellobiose was separated. The new substance melted at 185° C. and gave $[\alpha]_D^{20} = +31$, approximately. After deacetylation by the barium methylate method given in the next paragraph, a crystalline product was obtained. This unique substance contains one acetyl group combined in some manner with cellobiose. It does not exhibit mutarotation: $[\alpha]_D^{20} = +63$, approximately. With the new method for acetylation by means of a small quantity of barium methylate it may be possible to prepare other similar compounds from certain acetyl sugars and glycosides. The reaction and the properties of the substances are being further investigated.

²⁸ Zemplen, Ber., 59, p. 1258; 1926.

²⁹ Zemplen and Pacsu, Ber., 62, p. 1613; 1929.

After 5 ml of a 0.5 *N* barium methylate solution³⁰ were added the solution was allowed to stand in the ice box with occasional shaking. After about 20 hours the barium methylate in the solution was decomposed by the addition of an equivalent quantity of 0.5 *N*. sulphuric acid; the exact amount of sulphuric acid was determined by the titration (phenolphthalein) of a second portion of the barium methylate solution. The barium sulphate was separated by filtration. The filtrate was evaporated in vacuo to a thick sirup. After the addition of ethyl alcohol to saturation this sirup was allowed to stand overnight. The following day 2.4 g of crystalline product was separated. A total of 2.6 g of pure 4-glucosido- α -mannose monohydrate was obtained. This is 81 per cent of the theoretical. It melted at 137° C., in agreement with results reported by the previous investigators. The equilibrium rotation $[\alpha]_D^{20} = 5.88$ agrees with the value reported by Brauns, $[\alpha]_D^{20} = 5.8$.

4. OPTICAL ROTATION OF 4-GLUCOSIDO- α -MANNOSE

The samples of 4-glucosido- α -mannose monohydrate from the two deacetylations given above were combined; after one recrystallization from 60 per cent ethyl alcohol, $[\alpha]_D^{20} = +14.7$, initial; +5.7, final. This product was recrystallized and the measurements given below were made.

For the rotation measurements 1.355 g of 4-glucosido- α -mannose monohydrate was dissolved in 24.927 g of water (20° C.) which was delivered from a pipette. Time was measured from the moment the water was released from the pipette. The sugar was completely dissolved in 15 seconds. A portion of the solution was transferred to a 2 dm water-jacketed polariscope tube and the optical rotations given in Table 1 were measured with a Bates saccharimeter. The density of the solution was found to be 1.0165. (A picnometer of 10.686 ml capacity held 10.8628 g of solution at 20° C.)

TABLE 1.—Mutarotation of 4-glucosido- α -mannose monohydrate

Time (in minutes)	Saccharimeter reading	$[\alpha]_D^{20}$	$\frac{k_1+k_2}{t} \log_{10} \frac{r_0-r_\infty}{r-r_\infty}$
0	° S.	14.64	
3.6	4.10	13.55	
4.18	4.05	13.38	0.017
5.97	3.92	12.95	.015
11	3.60	11.89	.014
13	3.40	11.23	.017
15	3.32	10.97	.016
20	3.08	10.18	.015
25	2.85	9.42	.016
35	2.43	8.04	.017
45	2.25	7.43	.017
60	2.00	6.61	.017
75	1.93	6.33	.017
	1.78	5.88	
Average			.0162

¹ This value (*r*) is extrapolated from the first reading by the following equation:

$$0.016 = \frac{1}{3.6} \log_{10} \frac{r-5.88}{13.55-5.88}$$

³⁰ The barium methylate was prepared by refluxing 100 g of barium oxide with 200 ml of absolute methyl alcohol. After filtering the solution to remove the insoluble barium hydroxide it was diluted to one liter with absolute methyl alcohol.

VI. SUMMARY

A comparison of the rotations of the two pairs of sugars which were previously suggested by Hudson as suitable to decide between the rival classifications of ring structures shows that the epimeric difference obtained from the molecular rotations of 4-glucosido- α -mannose and β -cellobiose is 16,900, while the value from 4-galactosido- β -mannose and lactose is approximately 5,130. These conflicting values clearly show that a decision between the rival classifications of ring structures can not be derived from the rotations of these substances.

The optical rotation of 4-glucosido- α -mannose monohydrate was determined. The sugar exhibits mutarotation, following approximately the course of a monomolecular reaction; the value of $k_1 + k_2$ being 0.016 at 20° C.; the initial rotation $[\alpha]_D^{20} = +14.64$; the equilibrium rotation $[\alpha]_D^{20} = +5.88$ agrees with the value previously reported by Brauns.

An improved method for the deacetylation of acetyl sugars and glycosides by means of only a small amount of barium methylate in absolute methyl alcohol is given.

VII. ACKNOWLEDGMENT

The writer expresses his appreciation to Dr. D. H. Brauns, to F. P. Phelps, and to other members of the polarimetry section who have aided in the course of the investigation.

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