RP396

THE PREPARATION OF CRYSTALLINE METHYL-*d*-GULOSIDES BY MEANS OF COORDINATION COMPOUNDS WITH CALCIUM CHLORIDE[1]

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ABSTRACT

The reaction between reducing sugars and methyl alcohol in the presence of hydrogen chloride gives a mixture of isomeric methyl glycosides. Frequently amorphous products are obtained which can not be brought to crystallization by the usual methods. The separation of two isomeric methyl gulosides from such a mixture was accomplished by means of crystalline coordination compounds with calcium chloride. So far as known these compounds are the first of this type to be prepared from the methyl glycosides. The calcium chloride was removed by means of silver oxalate, and crystalline α-methyl-*d*-guloside (monohydrate) and β-methyl-*d*-guloside were obtained for the first time.

The new α-and β-methyl-*d*-gulosides were acetylated and the crystalline tetra-acetyl-α-and β-methyl-*d*-gulosides were obtained for the first time. The optical rotations of these compounds are compared with the rotations of the corresponding derivatives of glucose, galactose, and mannose.

CONTENTS

I. INTRODUCTION

In 1893 Emil Fischer[2] discovered that two isomeric methyl glucosides are formed from glucose by the action of methyl alcohol in the presence of hydrochloric acid. Subsequently Fischer's method has been applied to other sugars giving many similar compounds. The reaction yields a mixture of glycosides from which crystalline products can not always be obtained. These mixtures are very complex, probably containing many substances, the separation of which is very desirable. Since in the aldohexose series only methyl glycosides of glucose, galactose,[3] and mannose[4] were known in the crystalline state, the preparation of additional methyl glycosides was undertaken.

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[1] An abstract of this paper was read before the National Academy of Sciences in September, 1930 (Proc. Nat. Acad. Sci., vol. 16, p. 699).

[2] Fischer, Ber., vol. 26, p. 2400; 1893.

[3] Fischer and Beensch, Ber., vol. 27, p. 2480; 1894.

[4] Fischer, Ber., vol. 26, p. 2401; 1893; Haworth and Porter, J. Chem. Soc., p. 649; 1930.

Recently the writer [5] found a new calcium chloride compound of *d*-gulose which makes available a crystalline derivative of that sugar. The new compound may be used as a raw material for the preparation of other derivatives. The synthesis of the methyl gulosides was first attempted by Blanksma and Van Ekenstein [6] who obtained a sirup which they were unable to bring to crystallization. The writer has repeated their work, starting with pure gulose which was prepared by removing the calcium chloride from α-*d*-gulose $CaCl_2.H_2O$ with silver oxalate. A relatively pure product was obtained, but it could not be brought to crystallization and, after a through trial, it was evident that a new method was necessary to reach the desired substance. Although crystalline calcium chloride compounds of the glycosides were unknown, the encouraging results obtained by the application of the calcium chloride compounds in the preparation of *d*-gulose, a sugar which had not been previously crystallized, led the writer to apply the same principle in the separation of the methyl gulosides. This resulted in the preparation of crystalline calcium chloride compounds of α- and β-methyl-*d*-gulosides. These compounds served for the separation of the α- and β-isomers from the complex reaction product and ultimately gave the pure methyl gulosides in the crystalline state.

II. THE PREPARATION AND PROPERTIES OF CALCIUM CHLORIDE METHYL GULOSIDES

The calcium chloride methyl gulosides were first prepared by the addition of calcium chloride to the gulose sirup obtained by the method of Blanksma and Van Ekenstein. Subsequently, the method was simplified by preparing the calcium chloride gulosides direct from *d*-gulose calcium chloride in the following manner: The calcium chloride compound was refluxed with methyl alcohol containing about 1 per cent hydrogen chloride. After several hours an excess of powdered calcium carbonate was added; the hydrochloric acid was neutralized, forming calcium chloride. This additional salt did not interfere appreciably with the crystallization of the calcium chloride methyl gulosides which were easily obtained upon evaporation of the solution. The first crystals separated in slender needle-like prisms which gave a specific rotation of about +60°. The analysis corresponds to the formula: α-methyl-*d*-guloside.$CaCl_2.2H_2O$. In the preliminary work the calcium chloride was removed from this crude product by means of silver oxalate. After considerable difficulty a crystalline product was obtained from the resulting solution which, after drying in vacuo over P_2O_5, gave the correct analysis for a methyl guloside. Its specific rotation, +106°, was commensurate with the value derived from the calcium chloride compound from which it was prepared, and the molecular rotation (20,600) differed normally from the molecular rotation (−16,100) of β-methyl-*d*-guloside.

Previously [7] these observations were considered as evidence that the substance was pure and that the molecular rotation of α-methyl-*d*-guloside was +20,600. Subsequent work, however, has shown that the product first obtained was not strictly pure and the value is somewhat low. The pure guloside is best prepared from a second calcium

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[5] Isbell, B. S. Jour. Research, vol. 5, (RP226), p. 741; 1930.

[6] Blanksma and Van Ekenstein, Chemisch Weekblad, vol. 5, p. 777; 1908.

[7] Isbell, B. S. Jour. Research, vol. 3, (RP128), p. 1041; 1929.

chloride compound (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$, which is obtained by the addition of ethyl alcohol to a hot aqueous solution of the calcium chloride compound mentioned above. After several crystallizations from aqueous ethyl alcohol, it gave $[\alpha]_D^{20} = +83$, which corresponds to a somewhat higher molecular rotation than that obtained from the parent substance. The pure guloside is readily obtained from this product by removing the calcium chloride with silver oxalate. It crystallizes from aqueous solution with 1 molecule of water of crystallization. The specific rotation of the monohydrate (+109) is in accord with the value obtained from (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$. The molecular rotation (23,100) differs from the molecular rotation of β-methyl-*d*-guloside (−16,100) by 39,200 which is slightly more than the value reported by Hudson for the methyl glucosides (37,460) and galactosides (37,900). The question remained whether the first calcium chloride compound constituted a different form of the guloside or whether it contained some impurity which lowered its rotation. This was answered by the preparation of both calcium chloride compounds from pure α-methyl-*d*-guloside (monohydrate). The first compound was obtained by adding an excess of calcium chloride, while the second compound was obtained by using the calculated amount of the salt. The specific rotation of the first compound (α-methyl-*d*-guloside $CaCl_2.2H_2O$) when prepared from the pure guloside is +67°. This is equivalent to a molecular rotation of 22,900 which is in accord with the values 23,100 and 23,000 obtained from α-methyl-*d*-guloside monohydrate and (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$, respectively.

The mother liquor from the preparation of the calcium compounds just described gave, on standing, a third calcium chloride methyl guloside. The substance separates in rectangular prisms which are moderately soluble in ethyl alcohol. The analysis corresponds to the formula β-methyl-*d*-guloside $CaCl_2.2H_2O$. It melts at 155° and gives a specific rotation of −46°. Upon recrystallization from hot absolute ethyl alcohol this compound changes into a fourth calcium chloride methyl guloside which separates in small, poorly defined crystals. It is easily obtained pure because it is very insoluble in absolute ethyl alcohol. It gives a specific rotation of −65° and the analysis corresponds to the formula (β-methyl-*d*-guloside)$_2$ $CaCl_2$. After removing the calcium chloride with silver oxalate β-methyl-*d*-guloside is easily obtained in the crystalline state. It separates in well-defined truncated prisms which melt at 176° (uncorrected) and give a specific rotation of −83°. This value is equivalent to a molecular rotation of −16,100 which is in agreement with the equivalent rotation −16,200 of the parent calcium chloride compound.

The calcium chloride gulosides are particularly well suited for the study of the equilibria which exist in calcium chloride solutions. In a previous publication [8] it was shown that calcium chloride alters the composition of a solution of *d*-gulose by combining selectively with the alpha form of the sugar. The behavior of the methyl gulosides further illustrates the difference in the stability of the calcium chloride compounds of isomeric substances. Thus α-methyl-*d*-guloside $CaCl_2$ $2H_2O$ on crystallization from aqueous alcohol is converted into (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$, which may be recrystallized from water without decomposition. β-Methyl-*d*-guloside $CaCl_2.2H_2O$

Isbell, B. S. Jour. Research, vol. 5, (RP226), p. 748; 1930.

on crystallization from alcohol is converted into (β-methyl-*d*-guloside)$_2$ $CaCl_2$. In contrast to the alpha isomer this compound is dissociated in water and pure β-methyl-*d*-guloside may be crystallized from the aqueous solution. The solvent and the concentration of calcium chloride are important factors in determining the solubility and stability of such compounds.

The method for the separation of the methyl gulosides which has been described may be applicable for the separation of other glycosides as yet unknown in the crystalline state. It is not to be expected that glycosides of all sugars will form crystalline compounds with calcium chloride or other salts. However, a number of compounds of this type have already been prepared and undoubtedly many more will be found in the future.

III. TETRA-ACETYL-METHYL-*d*-GULOSIDES

As pointed out in a previous publication [9] the optical rotations of the methyl gulosides are of particular importance in regard to the relation between optical rotation and stereomeric configuration. In this respect the rotations of acetyl derivatives are only slightly less important; consequently the alpha and beta methyl gulosides were acetylated and the corresponding acetyl derivatives were prepared.

The new compounds are crystalline substances which resemble the acetylated methyl glucosides. Tetra-acetyl-α-methyl-*d*-guloside gives $[\alpha]^{20}_{D} = 97.3$ which is equivalent to a molecular rotation of 35,200, while tetra-acetyl-β-methyl-*d*-guloside gives $[\alpha]^{20}_{D} = -32.1$ which is equivalent to a molecular rotation of $-11,600$. The difference in the molecular rotations of these alpha and beta isomers is 46,800. This value is considerably less than the "normal" value, obtained by Dale and Hudson [10] from the corresponding derivatives of glucose (53,900) and galactose (53,460); nevertheless it is considerably greater than the values obtained from the corresponding derivatives of mannose [11] (34,600) and 4-glucosido-mannose [12] (34,130). In a previous publication [12] it was clearly shown that certain derivatives of 4-glucosido-mannose give abnormal rotations, and since 4-glucosido-mannose can not form a 1, 4 ring, these exceptional rotations are not caused by that structure. The existence of numerous instances, wherein it may be shown that combination occurs between sugar derivatives and the solvent or added substances, such as calcium chloride, shows that sugar solutions are extremely complex. The stability of many of the coordination compounds, such as the calcium chloride compounds of *d*-gulose depends largely on the stereomeric structure of the substance and the solvent employed. Likewise one would expect that intermolecular combination with possible distortion and change in optical rotation would be influenced by the stereomeric configuration and the solvent. The effect of these factors on the comparative optical rotations of the sugar derivatives is largely a matter of speculation; but, regardless of the interpretation, the data at hand appear to indicate that only substances of closely related structure invariably give like constants, whereas substances of widely different configuration frequently give exceptional values.

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[9] Isbell, B. S. Jour. Research, vol. 3, (RP128), p. 1041; 1929.

[10] Dale and Hudson, J. Am. Chem. Soc., vol. 52, p. 2534; 1930.

[11] Dale, J. Am. Chem. Soc., vol. 46, p. 1046; 1924.

[12] Isbell, B. S. Jour. Research, vol. 7, (RP392), p. 1115; 1931.

IV. EXPERIMENTAL DETAILS

1. α-METHYL-*d*-GULOSIDE $CaCl_2.2H_2O$

Forty grams of α-*d*-gulose $CaCl_2.H_2O$ was refluxed six hours with 300 ml of absolute methyl alcohol containing 4.5 g of anhydrous hydrogen chloride. The warm solution was cautiously neutralized with finely powdered calcium carbonate using a slight excess. After the addition of about 1 g of decolorizing charcoal the solution was filtered. The filtrate was concentrated in vacuo to a thick sirup which was transferred to a beaker using about 50 ml of absolute ethyl alcohol. In the course of several hours long slender needlelike crystals began to form. After 24 hours the crystals were collected upon a filter and washed with a mixture of equal parts of absolute ethyl alcohol and ethyl acetate. The mother liquor was evaporated in vacuo to a thick sirup which was then saturated with ethyl acetate, and a second crop of crystals was obtained. By evaporating the mother liquor more crystalline material was obtained. The first crop weighed 15 g, $[\alpha]^{20}_D = +60.8$; the second, 3.72 g, $[\alpha]^{20}_D = +37.5$; the third, 6.0 g, $[\alpha]^{20}_D = +17.3$; the fourth, 3.5 g, $[\alpha]^{20}_D = -36.0$. The second and third fractions were recrystallized, giving 5 g of product, $[\alpha]^{20}_D = +59.7$, which was added to the first fraction. The combined product which gave a specific rotation of about +60 was dried at 40° C. and subsequently analyzed. The analysis (Ca, 11.67; Cl, 20.67) corresponded to the formula $C_7H_{14}O_6\ CaCl_2.2H_2O$, but the molecular rotation $(60 \times 341 = 20{,}460)$ is less than that obtained from the product prepared by the addition of calcium chloride to pure α-methyl-*d*-guloside (monohydrate). The specific rotation (+67) of the synthetic product indicates that the first preparation contained some impurity (probably β-methyl-*d*-guloside $CaCl_2.2H_2O$) which lowered its rotation.

Three grams of α-methyl-*d*-guloside.H_2O were dissolved in a few milliliters of water and 3 g of $CaCl_2$ were added. After standing several days in a desiccator a crystalline product was obtained which was collected upon a filter and thoroughly washed with 95 per cent ethyl alcohol. The crystals are like those of the calcium chloride derivative first obtained. They are very faintly double refracting and appear as slender pointed prisms which melt at 185° to 190°. *Analysis calculated for* $C_7H_{14}O_6\ CaCl_2.2H_2O$: Ca, 11.75; Cl, 20.79. *Found*: Ca, 11.54; Cl, 20.77. $[\alpha]^{20}_D = +66.8$ in water (0.7474 g α-methyl-*d*-guloside $CaCl_2.2H_2O$ dissolved in 20 ml read 14.42° S. in a 2 dm tube). The substance is very soluble in water and methyl alcohol, less soluble in ethyl alcohol, and nearly insoluble in ether. It changes on crystallization from ethyl alcohol into a second derivative which is described in the next paragraph.

2. (α-METHYL-*d*-GULOSIDE)$_2$ $CaCl_2 . 3H_2O$

This substance was obtained from α-methyl-*d*-guloside $CaCl_2.2H_2O$ by crystallization from ethyl alcohol and water. About 15 g of α-methyl-*d*-guloside $CaCl_2.2H_2O$ was dissolved in a small amount of hot water (10 ml) and about 200 ml of absolute ethyl alcohol were added. After a few minutes, strongly double-refracting, short prismatic crystals began to separate and soon thereafter some needlelike faintly double-refracting crystals also began to form. The crystals were then separated and recrystallized. After a number of crystallizations a homogenous product was obtained, which was not changed by recrystallization from water or alcohol. The new substance is very soluble in water, and methyl alcohol, but difficultly soluble in ethyl alcohol. For analysis the product, which contains three molecules of water of crystallization, was air-dried at 40° C. It gives up its water of crystallization at 100° in vacuo; the anhydrous material absorbs moisture very rapidly but the hydrate is not hygroscopic. The anhydrous material melts with decomposition at about 215° C. The melting point of the hydrate depends upon the rate of heating; when heated slowly it melts with decomposition at about 205°, but when placed in a hot bath it melts at as low as 170° C. *Analysis calculated for* $(C_7H_{14}O_6)_2\ CaCl_2.3H_2O$: C, 30.37; H, 6.19; Ca, 7.24; Cl, 12.82. *Found*: C, 30.46; H, 6.35; Ca, 7.23; Cl, 12.83. *Loss on drying three hours at 100° C. in vacuo*: Subs., 0.7889; loss, 0.0755. *Calculated for 3 molecules of water*: 0.0771. $[\alpha]^{20}_{D} = +82.8$ in water (0.8671 g in 25 ml read 16.58° S. in a 2 dm tube, $[\alpha]^{20}_{D} = +82.75$; 0.1980 g in 25 ml read 7.58° S. in a 4 dm tube, $[\alpha]^{20}_{D} = +82.83$).

3. α-METHYL-*d*-GULOSIDE H_2O

About 10 g of (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$ was shaken with about 15 g of freshly prepared silver oxalate. The insoluble calcium and silver salts were separated, leaving a relatively pure solution of α-methyl-*d*-guloside. This was evaporated in vacuo to a thick sirup which was diluted somewhat with ethyl alcohol and saturated with ether. The solution was allowed to stand in the ice box. After several days a crystalline product separated. The new substance crystallizes in thin plates which frequently appear hexagonal. It is very soluble in water and ethyl alcohol but difficultly soluble in ether. It melts at 77° C. losing its water of crystallization. The hydrate is not hygroscopic, but the anhydrous material readily absorbs water. It has a sweet taste. For analysis the substance was dried at 35° to 40° C. in air. After one crystallization the specific rotation in water was +108.8; after a second crystallization $[\alpha]^{20}_{D} = +109.4$ (0.5166 g of α-methyl-*d*-guloside.H_2O dissolved in 25 ml read 13.06° S. in a 2 dm tube). *Analysis calculated for* $C_7H_{14}O_6.H_2O$: C, 39.60; H, 7.60. *Found:* C, 39.62; H, 7.75. *Loss on drying three hours at 100° C. in vacuo:* Subs., 1.8208; loss, 0.1545. Calculated for one molecule of water, 0.1546.

4. β-METHYL-*d*-GULOSIDE $CaCl_2.2H_2O$

This substance is obtained from the residue which remains after separating the positively rotating calcium chloride methyl gulosides. The fraction which gave a specific rotation of −36 was recrystallized from aqueous alcohol. β-methyl-*d*-guloside $CaCl_2.2H_2O$ separates in needlelike crystals which on further growth appear as slender rectangular prisms. It melts at 155° C. The new substance is very soluble in water and methyl alcohol, less soluble in ethyl alcohol, and insoluble in ether. *Analysis calculated for* $C_7H_{14}O_6.CaCl_2.2H_2O$: Ca, 11.75; Cl, 20.79. *Found:* Ca, 11.87; Cl, 20.85.C $[\alpha]^{20}_{D} = -45.7$ in water (0.3695 g dissolved in 25 ml read −3.9° S. in a 2 dm tube.)

On recrystallization from absolute alcohol it loses calcium chloride, forming (β-methyl-*d*-guloside)$_2$ $CaCl_2$. However, it may be crystallized without decomposition from alcohol containing a small quantity of calcium chloride.

5. (β-METHYL-*d*-GULOSIDE)$_2$ CaCl$_2$

A solution of β-methyl-*d*-guloside $CaCl_2.2H_2O$ in absolute ethyl alcohol decomposes on warming, giving (β-methyl-*d*-guloside)$_2$ $CaCl_2$. This substance separates as a fine crystalline precipitate which is almost insoluble in absolute ethyl alcohol. It melts with decomposition at 238° C. (uncorrected) and gives the following analysis: *Analysis calculated for* $(C_7H_{14}O_6)_2$ $CaCl_2$: Ca, 8.03; Cl, 14.21. *Found:* Ca, 8.01, Cl, 14.14. $[\alpha]_D^{20} = -64.9$ in water (0.6669 g (β-methyl-*d*-guloside)$_2$ $CaCl_2$ dissolved in 25 ml read $-10.0°$ S. in a 2 dm tube).

The new substance is very soluble in water, less soluble in methyl alcohol, and nearly insoluble in absolute ethyl alcohol and ether. As shown in the next paragraph, methyl alcoholic and aqueous solutions give on evaporaton β-methyl-*d*-guloside rather than the original material.

6. β-METHYL-*d*-GULOSIDE

β-Methyl-*d*-guloside is obtained from (β-methyl-*d*-guloside)$_2$ $CaCl_2$ by crystallization from water or methyl alcohol. The salt is dissolved in a small quantity of hot water; on cooling, β-methyl-*d*-guloside separates in beautiful prismatic crystals. A portion of the β-methyl-*d*-guloside, however, remains in solution, probably combined with the calcium chloride which results from the dissociation of the original compound. This residual methyl guloside is easily crystallized after the calcium chloride is removed by silver oxalate and a nearly quantitative yield of β-methyl-*d*-guloside is thus obtained. This new glycoside melts at 176° (uncorrected). It tastes slightly sweet. It is fairly soluble in water and methyl alcohol, less soluble in ethyl alcohol, and nearly insoluble in ether. For analysis it was recrystallized from ethyl alcohol and dried at 60° C. in vacuo. *Analysis calculated for* $C_7H_{14}O_6$: C, 43.27; H, 7.27. *Found:* C, 42.92; H, 7.27.$[\alpha]_D^{20} = -83.32$ in water (0.7297 g of β-methyl-*d*-guloside dissolved in 25 ml read $-28.1°$ S. in a 4 dm tube).

7. TETRA-ACETYL-α-METHYL-*d*-GULOSIDE

One gram of α-methyl-*d*-guloside monohydrate was dissolved in a mixture of 7 ml of acetic anhydride and 4 ml of pyridine. After standing 24 hours the solution was poured in ice water and the product was extracted with chloroform. The chloroform solution was washed successively with cold dilute sulphuric acid, sodium bicarbonate, and water. On evaporation it gave 1.6 g of crude crystalline tetra-acetyl-α-methyl-*d*-guloside. The substance separates in irregular clusters of slender crystals which frequently become wider and more prismatic. It is somewhat soluble in water, easily soluble in alcohol, ether, and chloroform. It melts at 98° and tastes slightly bitter. After one crystallization from hot water, $[\alpha]_D^{20}$ (in chloroform) = $+96.8$; after two crystallizations, $[\alpha]_D^{20} = +97.3$; after three crystallizations, $[\alpha]_D^{20} = +97.3$ (0.8054 g of substance dissolved in 25 ml read $+18.1°$ S. in a 2 dm tube). *Analysis calculated for* $C_{15}H_{22}O_{10}$: C, 49.70; H, 6.12. *Found:* C, 49.76; H, 6.17.

8. TETRA-ACETYL-β-METHYL-*d*-GULOSIDE

One gram of β-methyl-*d*-guloside was dissolved in a mixture of 7 ml of acetic anhydride and 4 ml of pyridine. After standing 24 hours the solution was poured in ice water and the product was extracted with chloroform. The chloroform solution was washed successively with cold dilute sulphuric acid, sodium bicarbonate, and water. On evaporation, a colorless sirup was obtained which readily crystallized after the addition of a few drops of ether. The new substance, tetra-acetyl-β-methyl-*d*-guloside weighed 1.55 g, melted at 66° to 67° and in chloroform solution $[\alpha]_D^{20} = -32.0$. After one crystallization from hot water it melted at 67° and in chloroform solution $[\alpha]_D^{20} = -32.1$ (0.7259 g dissolved in 25 ml read −5.39° S. in a 2 dm tube). *Analysis calculated for* $C_{15}H_{22}O_{10}$: C, 49.70; H, 6.12. *Found:* C, 49.81; H, 6.10.

V. SUMMARY[13]

The separation of two crystalline methyl-*d*-gulosides has been accomplished by means of crystalline coordination compounds with calcium chloride. The following new compounds are reported:

α-Methyl-*d*-guloside $CaCl_2.2H_2O$,	$[\alpha]_D^{20} = +66.8$.
(α-Methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$,	$[\alpha]_D^{20} = +82.8$.
α-Methyl-*d*-guloside $.H_2O$,	$[\alpha]_D^{20} = +109.4$.
α-Methyl-*d*-guloside tetra-acetate,	$[\alpha]_D^{20} = +97.3$.
β-Methyl-*d*-guloside $CaCl_2.2H_2O$,	$[\alpha]_D^{20} = -45.7$.
(β-Methyl-*d*-guloside)$_2$ $CaCl_2$,	$[\alpha]_D^{20} = -64.9$.
β-Methyl-*d*-guloside,	$[\alpha]_D^{20} = -83.3$.
β-Methyl-*d*-guloside tetra-acetate,	$[\alpha]_D^{20} = -32.1$.

VI. ACKNOWLEDGMENT

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[13] In addition to the compounds reported in this paper, a new crystalline penta-acetate of *d*-gulose has been prepared by acetylation of α-*d*-gulose $CaCl_2.H_2O$ with acetic anhydride and zinc chloride. The specific rotation of the substance is about 85°. By treating this compound with hydrogen bromide a bromo-acetyl derivative is obtained from which crystalline tetra-acetyl-β-methyl guloside may be prepared by the Königs and Knorr reaction. These products will be the subject of a future publication.