glucoside, distilling at 89–92° (glass wool in flask) at 0.4 mm., were obtained; $[\alpha]^{27}_{D}$ +150.1°, $c$ = 4.32 in $H_2O$. Moelwyn-Hughes[8] found +151.1° at 25°; $n^{20}_{D}$ 1.4460. Purdie and Irvine found 1.4464 and Haworth 1.4454.

Twenty-seven grams of tetramethyl-α-methylglucoside obtained above was steam hydrolyzed in 2 *N* hydrochloric acid for three hours and worked up in the usual way; twenty grams of tetramethylglucose, $[\alpha]^{28}_{D}$ +80.0°, $c$ = 4.26 in $H_2O$, was obtained. After one crystallization from petroleum ether–ether $[\alpha]_D$ 80.6°, which remained unchanged after five crystallizations from petroleum ether–ether. The chloroform solution of tetramethyl-α-methylglucoside may be used for hydrolysis without isolating the compound.

**Products Formed during First Stage of the Direct Methylation of Glucose.**—Nearly all of this material consisted of tri- and tetramethylmethylglucosides, as indicated by the methoxyl content of 55.67%.

**Properties of Tetramethylglucose Prepared in Different Ways.**—I. Prepared by hydrolysis of tetramethyl-α,β-methylglucoside with 2 *N* hydrochloric acid for two and one-half hours at 61°, followed by three hours at 90°. The product was crystallized five times and gave the following rotations (temp. 23–26°) and melting points (in parentheses), respectively: crude, $[\alpha]_D$ 77.80°; 78.76° (90–91°); 80.84° (93–94°); 80.56° (95–96°); 80.44° (96°); 80.48° (96°).

II. As in I except hydrolyzed in 2 *N* hydrochloric acid by steam distillation. Crude, 79.44°; 80.51° (90–93°); 80.64° (97°); 80.40° (98°); 80.48° (98°); 80.41° (98°).

III. Tetramethyl-α-methylglucoside was hydrolyzed in 8% hydrochloric acid according to Purdie and Irvine:[3] crude, 79.88°; 79.79° (80–85°); 79.76° (83–86°); 80.06° (84–87°); 80.55° (87°); 80.46°.

IV. As in III except hydrolyzed by steam distillation: crude, 80.53°; 80.40° (94–96°); 80.41° (98°); 80.54° (98°); 80.52° (99°); 80.44° (99°).

It will be noted that steam hydrolysis gave a purer product than the procedure of Purdie and Irvine and the crude product from steam hydrolysis of tetramethylmethylglucoside was apparently pure without recrystallization.

**Effect of Temperature upon the Rotation of Tetramethylglucose.**—The rotation of pure tetramethylglucose was found to be 84.29° ($c$ = 4.28) at 5°, 80.41° ($c$ = 4.08) at 24°, and 78.22° ($c$ = 4.28) at 37°, the solutions being equilibrated for two weeks at each temperature without the addition of a catalyst. The equation $[\alpha]_D = 85 - 0.1846\ t$, expresses the relation between specific rotation and temperature between 5 and 37°.

**Effect of Solvent upon the Rotation of Tetramethylglucose.**—Solutions of the pure compound in benzene, ethyl alcohol, methyl alcohol and chloroform were equilibrated for ten days and their rotations observed. The results were: benzene, 86.57° ($t$ 24°, $c$ = 4.86); ethyl alcohol, 81.3° ($t$ 24°, $c$ = 4.35); methyl alcohol, 82.91° ($t$ 25°, $c$ = 4.87); chloroform, 85.42 ($t$ 24°, $c$ = 3.98).

## Summary

A simplified method for the preparation of tetramethylmethylglucoside and tetramethylglucose is presented. The method should be of general application to the simple sugars. Evidence is presented that the generally accepted specific rotation of pure tetramethylglucose is in error. Various data relative to the properties of tetramethylmethylglucoside and tetramethylglucose are given.

St. Louis, Mo. Received December 11, 1933

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[8] Moelwyn-Hughes, *Trans. Faraday Soc.*, **25**, 81 (1929).

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# Crystalline Compounds of *d*-Xylose and of *l*-Arabinose with Calcium Chloride

By J. K. Dale

In an earlier work[1] the author reported the preparation and properties of two isomeric crystalline compounds of *d*-mannose with calcium chloride. One of these compounds, exhibiting a very unusual course of mutarotation, was believed to be a compound of calcium chloride with a new form of mannose. The preparation of calcium chloride compounds with other sugars has been undertaken with a view to comparing their mutarotation curves and specific rotations with that of the sugar component. In the meantime other investigators have reported crystalline double compounds of sugars with calcium chloride. Isbell[2] has described a gulose-calcium chloride compound, Hann and Hudson[3] one of galactose and calcium chloride, while Austin and Walsh[4] have prepared a crystalline compound, α-*l*-arabinose·$CaCl_2 \cdot 4H_2O$. The rotational data on only one of these compounds can be compared with that of the crystalline sugar component since gulose and α-arabinose have not been crystallized; the galactose-calcium chloride gives a mutarotation curve similar to that of α-*d*-galactose.

The xylose calcium chloride compound and

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[1] Dale, This Journal, **51**, 2788 (1929).

[2] Isbell, *Bureau Standards J. Res.*, **5**, 741 (1930).

[3] Paper presented before the Division of Organic Chemistry at the Chicago meeting of the American Chemical Society, September, 1933.

[4] The author has independently prepared the compound α-*l*-arabinose. $CaCl_2 \cdot 4H_2O$ described in the succeeding paper by Austin and Walsh. In general, the original observations of these authors on this compound are confirmed.

the two arabinose calcium chloride compounds described in this article show normal courses of mutarotation, hence are undoubtedly derivatives of the normal forms of these sugars. The mutarotation curves indicate an initial specific rotation for the xylose and arabinose components, respectively, of 98.5 and 186. These values are higher than those obtained by Hudson and Yanovsky,[5] namely, 92 and 175, from solubility measurements.

## Experimental Part

**Preparation of α-*d*-Xylose·Calcium Chloride·$3H_2O$.**—Twenty grams of xylose and 32 g. of calcium chloride dihydrate were partially dissolved in 28 cc. of water, then brought to boiling and complete solution on a hot-plate. The solution did not crystallize on standing, but when an equal volume of absolute alcohol was added and the solution evaporated on a bath, it soon crystallized to a rather solid mass. This was thinned with a small amount of absolute alcohol and the crystals drained by filtration with suction and then washed with absolute alcohol. Air dried, there was obtained 18 g. It melted at 126°. The mother liquor on further evaporation yielded 16 g., melting at 125°.

**Recrystallization.**—Ten grams of the first fraction was dissolved in 15 cc. of absolute alcohol and 2.5 cc. of water and filtered through a mat of asbestos. The solution was evaporated to one-half the original volume and 10 cc. of absolute alcohol was added. On further evaporation the solution crystallized. After standing for a short time at room temperature the crystals were drained by filtration with suction. The air dried crystals weighed 6 g. The melting point was 126°.

*Anal.* Calcd. for $(C_5H_{10}O_5)\cdot CaCl_2\cdot 3H_2O$: Ca, 12.71; Cl, 22.50. Found: Ca, 12.59; Cl, 22.48.

The initial and final specific rotations in water obtained from a mutarotation curve were found to be 46.8 and 9.33°, respectively. On the basis of the formula $(C_5H_{10}O_5)\cdot CaCl_2\cdot 3H_2O$ this would be 98.5° as the initial and 19.6° as the final specific rotation of the xylose component. The mutarotation constant, $k_1 + k_2$, was 0.022 at 20°.

**Preparation of β-*l*-Arabinose·Calcium Chloride·$H_2O$.**—Twenty grams of *l*-arabinose and 32 g. of calcium chloride dihydrate were partially dissolved in 28 cc. of water on a water-bath and then brought to boiling and complete solution on a hot-plate. The solution was replaced on the water-bath where in a few minutes a crust of crystals formed on the surface and sides of the beaker. The crystallizing solution was removed from the bath, stood one day at room temperature, then another day in an ice chest. The resulting rather thick mass was thinned with absolute alcohol and the crystals drained by filtration with suction, then washed on the funnel with absolute alcohol. The yield of the air dried material was 11.0 g. Three additional fractions of 15.0, 3.8 and 5.1 g., respectively, were obtained by further evaporations on the bath with the addition of absolute alcohol to each mother liquor. The decomposition point of the first fraction was 212°. Calcium and chlorine determinations indicated this product to have the formula $(C_5H_{10}O_5)\cdot CaCl_2\cdot H_2O$. The initial specific rotations of the four fractions ranged from 98.8 to 103° and the final specific rotations from 55.9 to 57.5°, which on the basis of the formula above would be 182.8 to 191.6° as the initial and 104 to 107° as the final specific rotations for the arabinose component.

**Recrystallization.**—The four fractions were united and 20 g. was dissolved in 20 cc. of water then diluted with 100 cc. of absolute alcohol. The solution was filtered then evaporated on a water-bath, adding more absolute alcohol from time to time until crystallization started. The crystallizing solution stood one day at room temperature, then one day in an ice chest after which the crystals were drained by filtration with suction and washed on the funnel with alcohol. The yield of the air dried material was only 3.0 g. It decomposed sharply at 212°.

*Anal.* Calcd. for $(C_5H_{10}O_5)\cdot CaCl_2\cdot H_2O$: Ca, 14.36; Cl, 25.41. Found: Ca, 14.66; Cl, 25.34.

The initial and final specific rotations in water were 99.59 and 56.6°. On the basis of the formula $(C_5H_{10}O_5)\cdot CaCl_2\cdot H_2O$ these figures give 184.3 and 105.3° as the initial and final specific rotations of the arabinose component; found, $k_1 + k_2 = 0.036$ at 20°.

**Preparations of (β-*l*-Arabinose)$_2\cdot CaCl_2\cdot 2H_2O$.**—In the recrystallization of the first arabinose calcium chloride compound described above, from 20 g. taken only 3 g. was recovered as the original compound. The mother liquor was evaporated on a water-bath to a thin sirup, then placed in a desiccator over sulfuric acid. After a few days this sirup had crystallized to a rather solid mass. This was triturated with alcohol and the crystals drained on a funnel with suction and well washed with alcohol. Air dried, there was obtained 7.5 g. This product instead of being merely a second fraction of the original, was a second arabinose·calcium chloride compound. Analysis indicated its formula to be $(C_5H_{10}O_5)_2\cdot CaCl_2\cdot 2H_2O$. Its initial and final specific rotations were 124.9 and 69.6°, respectively, corresponding to 186.2 and 103.8° for the arabinose component. This compound was more readily prepared by a simple recrystallization of the original arabinose·$CaCl_2\cdot H_2O$ from 95% alcohol. Nine grams was treated with 200 cc. of boiling alcohol, then filtered from a trace of undissolved material. Crystallization did not take place immediately, but on scratching the wall of the beaker crystallization was induced and proceeded slowly. After standing at room temperature for several days, the crystals were separated by filtration with suction and washed with 95% alcohol. Air dried, there was obtained 3.4 g. It gradually darkened in a melting point tube from 160° up, but showed no melting point or point of sudden decomposition.

*Anal.* Calcd. for $(C_5H_{10}O_5)_2\cdot CaCl_2\cdot 2H_2O$: Ca, 8.96; Cl, 15.86. Found: Ca, 8.91; Cl, 15.58.

The initial and final specific rotations were found to be 124.6 and 69.94°, respectively, which on the basis of the formula $(C_5H_{10}O_5)_2\cdot CaCl_2\cdot 2H_2O$ would be 185.6 and 104.2° for the arabinose component; found, $k_1 + k_2 = 0.034$ at 20°.

**Recrystallization of (β-*l*-Arabinose)$_2\cdot CaCl_2\cdot 2H_2O$.**—Four and six-tenths g. was dissolved in 5 cc. of water and 5 cc. of alcohol. The solution was filtered through a small

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(5) Hudson and Yanovsky, THIS JOURNAL, **39**, 320 (1917).

asbestos mat and then placed in a desiccator over sulfuric acid. After some days a few well-formed crystals had separated. On stirring, the sirup quickly crystallized to a thick magma. This was thinned with alcohol, filtered and the crystals washed with alcohol. Air dried, there was obtained 3.3 g. The analysis of this product together with its initial and final specific rotations was not essentially different from the corresponding data given above for the unrecrystallized material.

**Acknowledgment.**—The author is pleased to acknowledge his indebtedness to the Polarimetric Section of the U. S. Bureau of Standards and to the National Institute of Health for laboratory facilities furnished during this work. He also thanks the National Research Council for the fellowship under which this work was commenced. The interest of Dr. C. S. Hudson in the course of this work has been greatly appreciated.

## Summary

1. A crystalline double compound of *d*-xylose with calcium chloride and two crystalline compounds of *l*-arabinose with this salt have been prepared.

2. The mutarotation curves of these compounds are similar to those of their sugar components.

3. The initial specific rotations calculated for the xylose and arabinose components are higher than have been found previously.

DECATUR, ILL. RECEIVED DECEMBER 13, 1933

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[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, LOYOLA UNIVERSITY SCHOOL OF MEDICINE]

# A New Crystalline Compound of $\alpha$-*l*-Arabinose with Calcium Chloride and Water[1]

BY W. C. AUSTIN AND J. P. WALSH

Many of the simple sugars have been shown to form with calcium chloride crystalline compounds, capable of mutarotation. After reviewing the literature of the previously known compounds Dale[2] described a new crystalline compound of calcium chloride with $\beta$-*l*-arabinose, $(\beta\text{-}l\text{-arabinose})_2\cdot CaCl_2\cdot 2H_2O$. The authors have independently confirmed the published findings of Dale on this substance and add herewith their studies of an analogous compound, $\alpha\text{-}l\text{-arabinose}\cdot CaCl_2\cdot 4H_2O$.

This second new compound of *l*-arabinose with calcium chloride also exhibited mutarotation, and gave the value $[\alpha]^{20}_{\mathrm{D}}$ +47.65°, at equilibrium, in aqueous solution. The conclusion has been drawn by Riiber,[3] in studies of highly purified *l*-arabinose, that the mutarotation conformed best to a bimolecular equation expressing the rate of change between at least three modifications of this sugar. His conclusions would indicate a surprisingly large and spontaneous change, during mutarotation, between two or more types of rings in the structure of this sugar. The authors have preferred to interpret their observations by the unimolecular equation, $k_1 + k_2 = 1/t \log (r_0 - r_\infty)/(r - r_\infty)$, which has been more generally applied to the changes in rotation between alpha and beta forms of one common structural ring. The value of $k_1 + k_2$, 0.029, so obtained is very near the value of 0.031 calculated by Osaka[4] from the observations on *l*-arabinose by Parcus and Tollens.[5] The rotation of the substance at zero time after solution was then calculated by the same unimolecular equation, which gave $[\alpha]^{20}_{\mathrm{D}}$ +33.86°, initial, in water.

A consideration of the mutarotation of the substance identified the *l*-arabinose constituent as $\alpha$-*l*-arabinose, in accordance with the nomenclature of Hudson.[6] The initial and final rotations of the compound were found to correspond to $[\alpha]^{20}_{\mathrm{D}}$ +75.18°, the calculated initial value for the $\alpha$-*l*-arabinose constituent; and to $[\alpha]^{20}_{\mathrm{D}}$ +105.8°, the calculated equilibrium value for the *l*-arabinose constituent. This last value is within 1° of the previously accepted value of the rotation of this sugar at equilibrium.[7]

The value calculated for $\alpha$-*l*-arabinose, $[\alpha]^{20}_{\mathrm{D}}$ +75.18°, is new, being derived from observations on the first-known crystalline compound contain-

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(1) These studies, a portion of which were reported on the program of the meeting of the American Chemical Society in Chicago, Sept. 12, 1933, were abstracted from a dissertation submitted by Mr. Walsh to the Graduate School of Loyola University in partial fulfilment of the requirements for the degree of Master of Science.

(2) Dale, THIS JOURNAL, **56**, 932 (1934).

(3) Riiber, *Det kongelige norske Videnskabers Selskabs forhandlinger*, Vol. III, No. 17 (1930).

(4) Osaka, *Z. physik. Chem.*, **35**, 671 (1900).

(5) Parcus and Tollens, *Ann.*, **257**, 160 (1890).

(6) Hudson, THIS JOURNAL, **31**, 66 (1909).

(7) (a) Ruff, *Ber.*, **32**, 554 (1899); (b) v. Faber, *Z. angew. Chem.*, **12**, 962 (1899); (c) Hudson and Yanovsky, THIS JOURNAL, **39**, 1013 (1917).