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.

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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

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

A New Crystalline Compound of α-*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 β-*l*-arabinose, (β-*l*-arabinose)$_2$·$CaCl_2$·$2H_2O$. The authors have independently confirmed the published findings of Dale on this substance and add herewith their studies of an analogous compound, α-*l*-arabinose·$CaCl_2$·$4H_2O$.

This second new compound of *l*-arabinose with calcium chloride also exhibited mutarotation, and gave the value $[\alpha]^{20}_{D}$ +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 $[\alpha]^{20}_{D}$ +33.86°, initial, in water.

A consideration of the mutarotation of the substance identified the *l*-arabinose constituent as α-*l*-arabinose, in accordance with the nomenclature of Hudson.[6] The initial and final rotations of the compound were found to correspond to $[\alpha]^{20}_{D}$ +75.18°, the calculated initial value for the α-*l*-arabinose constituent; and to $[\alpha]^{20}_{D}$ +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 α-*l*-arabinose, $[\alpha]^{20}_{D}$ +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).

ing α-*l*-arabinose, although Simon[8] reported a value of $[\alpha]^{20}_{D} < +76.0°$ for a modification of this sugar, which he termed "gamma." The studies of Hudson and Yanovsky[7c] supplied a separate calculation of the rotation of α-*l*-arabinose, $[\alpha]_D$ +54.0°, which is 21° lower than that given above by the authors. The reasons for this large divergence are not yet clear, for the presence of the calcium chloride in a solution of the compound described here has not greatly influenced either the velocity of the mutarotation or the rotation at equilibrium of the carbohydrate constituent.

Experimental

A mixture of 16.7 g. of *l*-arabinose, 32 g. of $CaCl_2 \cdot 2H_2O$, and 28 cc. of water was heated on the steam-bath in a gentle stream of air until crystals of hexagonal tablets began to form. The reaction product was refrigerated overnight, the crystals filtered out, washed quickly with alcohol, and dried at 50° *in vacuo* to 16.7 g. (37% of the calcd. for a substance of the formula later determined). The substance was recrystallized to constant properties by concentration of a solution of 9.5 g. in 7.5 cc. of water *in vacuo* over calcium chloride at 25°. The purified substance softened at 106–108°, slowly liquefied at 112–115°, and decomposed at 214–215°. A freshly prepared 4% aqueous solution of the substance was observed to give, at 20°, the following values of $[\alpha]^{20}_{D}$: +36.41°, 3 minutes after solution; +40.44°, 9.6 minutes after solution; +44.48°, 22.2 minutes after solution; and +47.65°, constant, 18 hours after solution. Samples of the substance, dried *in vacuo* at room temperature for twelve hours over calcium chloride, were found to contain 12.15% Ca; 21.20% Cl; and 21.45% H_2O (from loss in weight at 106° and 127° at 0.12 mm. Hg). For a substance of the accepted formula, $C_5H_{10}O_5 \cdot CaCl_2 \cdot 4H_2O$, the calculated values are 12.02% Ca; 21.28% Cl and 21.70% H_2O.

Summary

The preparation of a crystalline compound of calcium chloride and *l*-arabinose, α-*l*-arabinose·$CaCl_2 \cdot 4H_2O$, the first known substance containing α-*l*-arabinose as the carbohydrate constituent, has been described. The observations and calculations on the mutarotation of the substance have afforded a new determination of the rotation of α-*l*-arabinose.

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[8] Simon, *Compt. rend.*, **132**, 487 (1901).

[CONTRIBUTION FROM NORTHWESTERN UNIVERSITY MEDICAL SCHOOL]

Studies on Proteins in Liquid Ammonia. II. Reaction of Sodium in Liquid Ammonia with Amino Acids and Related Substances[1]

BY C. O. MILLER AND R. G. ROBERTS

In the previous article[2] of this series, it was shown that proteins are acidic in liquid ammonia and react readily with sodium to form hydrogen and ammonolytic products containing sodium. We have investigated quantitatively the amount of hydrogen which is liberated by given amounts of proteins, peptones, dipeptides, diketopiperazine, amino acids and related substances, and have correlated the amount of hydrogen evolved with the nitrogen content of the sample and the amount of sodium used. Preliminary reports have been given on investigations in which proteins and peptones were used.[3] Complete reports will be given on these later.

Experimental

The substances used in the analyses were dried in an oven at 80° for several days and kept over concentrated sulfuric acid in a vacuum desiccator. Approximately one gram samples were used. One hundred and fifty cc. of dried liquid ammonia was placed in the vacuum flask.[4] The apparatus was arranged so that small pieces of sodium could be dropped into the liquid ammonia, a piece at a time, without opening the flask. The hydrogen was collected in a gasometer over 10% sodium hydroxide. Rubber stoppers and a glass delivery tube were used. The air in the reaction flask was displaced by allowing the ammonia to boil for fifteen minutes. The vacuum flask was then connected to the gasometer and sodium was dropped into the liquid ammonia a piece at a time. The ammonia was allowed to boil until the gas bubbles were completely absorbed. From one-half to three hours were required for this, depending upon the substance being used. The sodium hydroxide solution in the gasometer was slowly replaced by distilled water and then by 2 *N* hydrochloric acid, which was sprayed into the gas until the solution remained acid. Portions of the gas were then mixed with oxygen and the hydrogen was determined in the Hempel apparatus. Tests for oxygen, carbon monoxide, carbon dioxide and hydrocarbons were negative.

A given weight of each substance was treated with varying quantities of sodium, and the amount of hydrogen

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[1] A part of the material in this paper was presented before the Organic Division of the meeting of the American Chemical Society, Indianapolis, March, 1931.

[2] McChesney and Miller, THIS JOURNAL, **53**, 3888 (1931).

[3] C. O. Miller and R. G. Roberts, *Proc. Soc. Exptl. Biol. Med.*, **29**, 533 (1932); R. G. Roberts and C. O. Miller, *ibid.*, **30**, 821 (1933).

[4] The liquid ammonia was dried by the method described by Fernelius and Johnson, *J. Chem. Ed.*, **6**, 20 (1929).