7. The catalytic method, when applicable, gives excellent yields and is superior to other methods.

8. A convenient method for reducing 0.01 to 0.0025 mole is described.

9. Benzoin is recommended as a standard for calibrating the apparatus for one mole of hydrogen and benzil for two moles.

10. The complete series of reduction products of anisoin may be prepared catalytically.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE PREPARATION OF ALLOMUCIC ACID AND CERTAIN OF ITS DERIVATIVES

BY C. L. BUTLER AND LEONARD H. CRETCHER

RECEIVED MARCH 1, 1929 PUBLISHED JULY 5, 1929

While engaged in the investigation of certain sugar acids, it was desired to prepare allomucic acid in comparatively large amounts. This is one of the less common dibasic acids in the sugar group and but few of its derivatives have been described. The only published method of preparation is that of Fischer,[1] who obtained the acid by epimerization of mucic acid with excess of pyridine at 140°. The yield was 14%.

The present authors have been able to prepare pure allomucic acid from mucic acid in yield of 33%. This was accomplished under the conditions of epimerization previously employed in this Laboratory for the preparation of *d*-talonic acid from *d*-galactonic acid.[2]

It was shown by Fischer[1] that allomucic acid is partially converted into a monolactone on boiling or evaporation of a water solution. Fischer did not isolate this lactone and we were not able to prepare it in crystalline form. A solution of the lactone was used in the present work for the preparation of the mono-amide.

Diethyl allomucate was prepared by the method employed by Malaguti[3] for the esterification of mucic acid, namely, the use of a comparatively large amount of concd. sulfuric acid and alcohol. The yield was 42% of the theoretical. It was found that it was also possible to esterify with alcohol containing 1% of hydrochloric acid. This method gives a better yield (58%) of ester and is somewhat simpler in manipulation. The ester was easily converted into the diamide by addition of concd. ammonia water.

It was shown by Kiliani[4] that *l*-mannosaccharic dilactone reduces

[1] Fischer, *Ber.*, **24**, 2136 (1891).

[2] Hedenburg and Cretcher, THIS JOURNAL, **49**, 478 (1927).

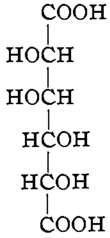
[3] Malaguti, *Ann. chim. phys.*, [2] **63**, 86 (1836).

[4] Kiliani, *Ber.*, **20**, 339, 2710 (1887).

Fehling's solution and that in alkaline solution it rapidly becomes yellow when heated. Very recently,[5] he again studied the properties of this lactone and made the surprising discovery that it adds hydrogen cyanide to give a compound which can be hydrolyzed to a tricarboxylic acid.

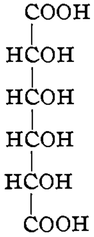
Fischer[6] has reported that *d*-mannosaccharic dilactone also reduces Fehling's solution. This fact has been confirmed in our laboratory.

Mannosaccharic acid, so far as the authors have been able to learn, is the only dibasic sugar acid possessing these properties. Inspection of the formulas of mannosaccharic and allomucic acids shows that they are similar in that the two hydroxyl groups adjacent to each of the carboxyl groups are in the *cis*position.



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HOCH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{COOH}\end{array}$$

Mannosaccharic acid



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{HCOH}\\ |\\ \mathrm{COOH}\end{array}$$

Allomucic acid

This is not true of any other of the dibasic sugar acids. If this configuration is responsible in any way for the properties of mannosaccharic acid, it might be expected that similar properties would be observed in the case of allomucic acid. However, tests failed to confirm this prediction. Allomucic acid was found to be non-reducing, both when tested with Fehling's reagent immediately after solution and when tested after boiling an aqueous solution for one-half hour to convert to lactone. It remained colorless when boiled with 10% sodium hydroxide. Moreover, while mannosaccharic acid readily forms the dilactone, allomucic acid apparently forms only a monolactone under ordinary conditions.

Experimental

Preparation of Allomucic Acid.—One hundred g. of mucic acid, 1000 cc. of water and 100 g. of pyridine were placed in a 2-liter round-bottomed flask and the mixture was heated to boiling. The flask was then tightly closed with a rubber stopper which was wired in position. The flask was wrapped with cloth and heated for 115 hours on a steam-bath. One hundred and fifty g. of crystallized barium hydroxide dissolved in hot water was then added. This precipitated the barium salts of mucic and allomucic acids. The mixture was vacuum distilled until practically all of the pyridine was removed. After cooling, the crude barium salt was filtered off, washed with water and dried. The yield was 160 g. The salt was suspended in 1500 cc. of hot water and the calculated amount of sulfuric acid (based on the amount of barium found by analysis) was added. The mixture was heated, with stirring, on a steam-bath for two hours.

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[5] Kiliani, *Ber.*, 61, 1155 (1928).

[6] Fischer, *ibid.*, 24, 539 (1891).

It was then filtered and the residue, which consisted of a mixture of barium sulfate and unchanged mucic acid, removed by filtration and washed with a little hot water. After treatment with decolorizing carbon, the filtrate was obtained as a pale yellow liquid. It was then concentrated under reduced pressure to 500 cc. and allowed to stand overnight in the ice box. The mucic acid which crystallized was removed by filtration. The filtrate was evaporated to half its volume under reduced pressure, at about 60°, and allowed to stand in the ice box overnight. The crystalline material, which still contained a small amount of mucic acid, was filtered off and treated with ten times its weight of boiling water. The mixture was filtered hot. Crude allomucic acid separated from the filtrate on cooling. The main bulk of mother liquor was again evaporated to half its volume and cooled. The crystalline acids were filtered off and treated with ten times their weight of boiling water as before. After filtration of the mixture, the filtrate deposited further crystals of crude allomucic acid. This process was repeated with the original mother liquor until only a small amount of dark colored sirup remained. The several fractions of crude allomucic acid were washed with a little 95% alcohol and recrystallized to constant melting point. The total yield was 33 g. which melted at 167–168° with effervescence. The melting point as determined by Fischer[1] was 166–171°. The higher melting point of 172–173° reported by Patterson and Fulton[7] was found on rapid heating.

Allomucic Mono-amide.—Twenty grams of allomucic acid was dissolved in 300 cc. of water and boiled for forty minutes. The solution was allowed to stand overnight and was then filtered from a small amount of allomucic acid. The filtrate was evaporated under reduced pressure until most of the acid had crystallized out. After filtering, the solution was again evaporated until about 25 g. of a sirupy mixture of acid and lactone was obtained. This was cooled in ice and treated with 30 cc. of concentrated ammonia water. After standing for about five hours, the solution was carefully neutralized with cold, concentrated hydrochloric acid, using Congo Red as indicator. On standing overnight a mixture of crystals of ammonium chloride and allomucic mono-amide was obtained. The former was removed by washing with water. The yield of practically pure amide melting at 175–175.5° was 2 g. Two additional crystallizations from water raised the melting point only 0.5°, An additional gram of amide was obtained on concentrating the mother liquor.

Anal. Calcd. for $C_6H_{11}O_7N$: N, 6.69; 4.78 cc. of 0.1 N NaOH. Found: N, 6.66; 0.1000 g. required 4.77 cc. of 0.1 N NaOH.

Diethyl Allomucate.—This ester was prepared according to the method employed by Malaguti[4] in preparing diethylmucate. The yield was 42%. It was also prepared as follows: 3.4 g. of allomucic acid was placed in a flask with 20 cc. of 1% hydrochloric acid in absolute ethyl alcohol. After refluxing for twenty minutes, a clear solution was obtained. Boiling was continued for three and one-half hours. The volume then was reduced about one-third by evaporation and the solution allowed to stand in the ice box overnight. The crystals of diethyl allomucate were filtered off and washed with absolute alcohol. The yield of crude product was 3.3 g. On recrystallization from alcohol 2.5 g. (58% of the theoretical) of pure ester was obtained, melting point 137–138°. On evaporation of the mother liquor and washing, an additional 0.6 g. of crude material melting at about 130° was obtained. The melting point of the second crop did not change after one recrystallization from alcohol.

Anal. Subs., 0.1000: CO_2, 0.1653; H_2O, 0.0624. Calcd. for $C_{10}H_{18}O_8$: C, 45.11; H, 6.76. Found: C, 45.08; H, 6.93.

Allomucic Diamide.—0.47 g. of diethyl allomucate was treated at room tempera-

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[7] Patterson and Fulton, *J. Chem. Soc.*, 50 (1927).

ture with 3 cc. of concd. ammonia water. The ester dissolved and the diamide separated out almost immediately. It was washed thoroughly with water and alcohol and dried. The yield was 0.27 g., 75% of the theoretical. The substance is practically insoluble in water, ethyl alcohol and ether. It commenced to discolor at 185° and gradually darkened as the temperature was raised. It melted at 209°, with effervescence.

Anal. Calcd. for $C_6H_{12}O_6N_2$: N, 13.46. Found: N, 13.50, 13.38 (Kjeldahl).

Summary

1. An improved method for the preparation of allomucic acid is described.
2. Methods for the preparation of several new derivatives of the acid are presented.
3. A comparison is made of some of the properties of allomucic and mannosaccharic acids.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

THE MOLECULAR WEIGHT OF EDESTIN

BY THE SVEDBERG AND ALFRED J. STAMM[1]

RECEIVED MARCH 6, 1929 PUBLISHED JULY 5, 1929

The proteins that have thus far been subjected to the ultracentrifuge analysis in this Laboratory in order to determine their molecular weights as well as other physical characteristics have been water soluble[2] with the exception of serum globulin.[2f] This protein required only relatively small salt concentrations to hold it in solution. There are a number of other proteins of the globulin class that are soluble only in strong salt solutions. It was thus the authors' desire to see if the previously developed methods of study were completely applicable to the study of proteins dissolved in strong salt solutions.

The protein edestin, belonging to the vegetable globulin class, was chosen for this work so as to add another type of protein to the list of those studied. Edestin seemed especially suitable because of the ease with which it can be isolated and because of its definite crystalline structure, which is a strong indication of its homogeneity.

Preparation of Material.—Coarsely ground hemp seed (600 g.) was directly subjected to digestion and extraction with a mixture of 2000 cc. of 10% sodium chloride solution and 400 cc. of 2.1% disodium phos-

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[1] Fellow of the International Education Board.

[2] (a) T. Svedberg and R. Fåhraeus, THIS JOURNAL, **48**, 430 (1926); (b) T. Svedberg and J. B. Nichols, *ibid.*, **48**, 3081 (1926); (c) T. Svedberg and J. B. Nichols, *ibid.*, **49**, 2920 (1927); (d) T. Svedberg and N. B. Lewis, *ibid.*, **50**, 525 (1928); (e) T. Svedberg and E. Chirnoaga, *ibid.*, **50**, 1399 (1928); (f) T. Svedberg and B. Sjögren, *ibid.*, **50**, 3318 (1928).