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45. Sulphur Derivatives of 5-Hydroxyuracil: Preparation of 5-Benzylmercaptouracil and 5-Benzylmercaptocytosine. By Treat B. Johnson and Herbert H. Guest. *Am. Chem. J.*, 42, 271.

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47. The Action of Methyl Iodide, and of Benzyl Chloride upon 2-Oxy-4-methyl-6-mercaptopyrimidine. By Henry L. Wheeler and David F. McFarland. *Am. Chem. J.*, 42, 431.

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NEW HAVEN, CONN.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 189.]

A TETRA-ACETYL AMINOGLUCOSIDE.

BY MARSTON LOVELL HAMLIN.

Received March 27, 1911.

A preliminary report of work on chitin begun independently last October, suggested in part by investigations of Offer[1] as to the structure of chitin,

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[1] *Biochem. Z.*, 7, 117.

was just ready for publication when Irvine, McNicoll and Hynd[1] published an article reporting nearly identical experiments covering the same field. This paper is therefore published as corroborative of their work, with which it agrees on all points that are common.

The triacetylbromoglucosamine hydrobromide described in the present paper is evidently identical with the compound prepared by these authors, but the acetylated glucoside now reported is, I believe, new.

The investigation consisted in preparing a bromoacetyl derivative of glucosamine and from this an acetylated aminoglucoside. This is apparently not a derivative of the aminoglucoside recently prepared by Fischer and Zach[2] in quite a different way, since the latter on hydrolysis gave the hydrochloride of an amino sugar different in behavior from glucosamine hydrochloride.

Experimental.

1-Bromo-3,5,6-triacetylglucosamine Hydrobromide. — This compound was prepared in a way analogous to that in which Koenig and Knorr[3] made bromoacetylglucose; the reaction, however, can be carried out at a higher temperature, and goes very quickly.

Five grams of finely powdered free glucosamine, prepared according to Breuer,[4] were placed in a small flask connected with a reflux condenser, and 25 cc. Kahlbaum's acetyl bromide added, the flask being cooled by ice and water. A lively effervescence set in at once, due to the evolution of hydrobromic acid gas. After about ten minutes most of the solid went into a brown solution, which in about five minutes more suddenly became solid. The excess of acetyl bromide was sucked off by a vacuum pump at room temperature for $^1/_2$–1 hour, the residue dissolved in boiling chloroform, the brown solution filtered and allowed to cool, dry ether added till no more precipitate formed and, after a little standing, the white precipitate, tinged slightly brown, was filtered off on a Büchner funnel. The substance is pure enough at this point to use in preparing the glucoside, if the chloroform solution was not allowed to stand over night. All the apparatus must be thoroughly dry, and during the experiment the reflux condenser must be protected with a calcium chloride tube.

For analysis this precipitate was crystallized twice more in the same way, the product being a fine, pure white powder. Bromine was determined by dissolving this in water, adding nitric acid and boiling, then adding silver nitrate and weighing the precipitate as usual.

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[1] *J. Chem. Soc.*, 99, 250 (1911).

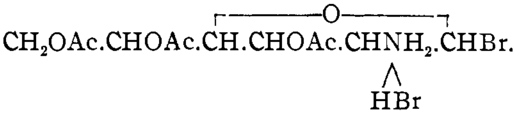
[2] *Ber.*, 44, 132 (1911).

[3] *Ibid.*, 34, 957 (1901).

[4] *Ibid.*, 31, 2193 (1898).

	Br.
Calculated for $C_6H_9O_4Ac_3BrN,HBr$:	35.63
Found: Sample I, *a.*	35.36
b.	35.43
Sample II, *a.*	35.55
b.	35.59

For this compound the following structure seems probable:



$$\mathrm{CH_2OAc.CHOAc.}\overbrace{\mathrm{CH.CHOAc.CH\underset{\wedge\atop HBr}{NH_2}.CH}}^{\mathrm{O}}\mathrm{Br.}$$

The compound is very easily soluble in water, alcohol, or chloroform, but not in ether. It has no distinct melting point, but turns brown at 138°, blackens at 148° and chars at 153° (uncor.). Irvine, McNicoll and Hynd[1] state that their product softens at 144°, and melts and decomposes at 149–150°.

Tetra-acetylglucosamine Methyl Glucoside.—Eight grams of the compound described above were shaken in a solution of about 175 cc. absolute methyl alcohol with 5.2 grams Kahlbaum's silver carbonate until the solution was halide-free; this required 6–18 hours according to the violence of the shaking. The solution was filtered by suction on a hardened filter, till as free as possible from the extremely fine precipitate of silver salts. About 20 cc. of acetic anhydride were added and the methyl alcohol and acetic anhydride evaporated off on the water bath *in vacuo*. The brown syrupy residue was boiled for half an hour with 20–30 cc. acetic anhydride which was gotten rid of as before. The residue, sometimes sirupy and sometimes crystallin, was taken up with absolute ethyl alcohol and boiled for 20 minutes with bone-black. On filtration the solution was a clear yellow or brown. 15–25 cc. amyl acetate were added and the solution evaporated on the water bath to a thick sirup, or until a heavy precipitate appeared. After standing over night, the sirup solidified and the amyl acetate was filtered off by suction. Occasionally the residue is sticky, of about the consistency of warm molasses candy, and in this case it can be dried on a porous plate, well mixed with 10–15 cc. dry ether and filtered.

If the precipitate is nearly white, it can be freed of the last traces of amyl acetate and acetic anhydride by boiling it a few minutes with ether, filtering and drying *in vacuo* over sulfuric acid and potassium hydroxide. Otherwise the precipitate must be recrystallized again and washed with dry ether.

The substance is a fine white crystallin powder and melts sharply at 150.5° (uncor.). It resolidifies without changing, and melts again at the same point.

Calculated for $C_{15}H_{23}O_9N$: C, 49.86; H, 6.36; N, 3.88.
Found: C, 50.11; H, 6.53; N, 4.20.

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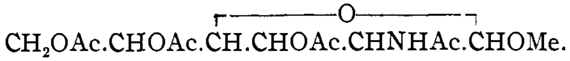
[1] *Loc. cit.*

This would indicate the structure:



$$\mathrm{CH_2OAc.CHOAc.}\overbrace{\mathrm{CH.CHOAc.CHNHAc.CH}}^{\mathrm{O}}\mathrm{OMe.}$$

The compound is easily soluble in water, alcohols (methyl, ethyl, isobutyl and isoamyl) and glacial acetic acid; it is difficultly soluble in acetone and warm ether, but practically insoluble in chloroform, the hydrocarbons, and ethyl and amyl acetates.

NEW BOOKS.

Introduction to General Chemistry. By JOHN TAPPAN STODDARD, PH.D. Published by The Macmillan Co., New York, 1910. xviii + 432 pages.

This small text-book of elementary chemistry is intended to be used in connection with lectures or recitation talks and discussions. It contains a concise account of some of the more important facts of descriptive chemistry and of those laws and theories that are usually considered in elementary courses. The order of arranging the elements is somewhat different from that usually followed, in that sulfur and sulfuric acid come immediately after oxygen and hydrogen, and precede the halogens. This is done, as the author states, for the purpose of "placing sulphuric acid in the position which it occupies in actual practice." The periodic law is not mentioned until the last chapter. Quantitative relations receive considerable attention and the student is referred for the details of these experiments to the author's "Quantitative Experiments." The appendix contains a number of useful tables.

Taken as a whole the book is carefully written and when used in connection with a course of lectures and discussions will undoubtedly aid the student in laying a good foundation upon which he can build in more advanced study. EDWARD H. KEISER.

Qualitative Chemical Analysis, Organic and Inorganic. By F. MOLLWO PERKIN, Late Head of the Chemistry Department, Borough Polytechnic Institute, London. Third edition, 337 pages. Published by Longmans, Green & Co.

In the preface the statement is made by the author that in the teaching of chemistry "the theoretical knowledge is generally kept rigidly apart from the facts practically gained, so that the student loses all the mutual help which the two branches of study afford each other," and, that, recognizing this difficulty, he has endeavored "to write a book in which theory and practice are more or less dovetailed." Nevertheless, in the opinion of the reviewer, the author has, in the inorganic part, kept the theory introduced fairly well separated from the practical work. The things which in reality are more or less dovetailed in the book (pp. 25–152) are dry tests, metathetical test-tube reactions, and descriptive chemistry. The theory, given for the most part in the form of dogmatic statements, is largely concentrated in the 13 pages of Chapter II. Mass action is