Mannitol was isolated from fermented cabbage to the extent of 2.0 to 2.5%.

Since no mannitol was obtained from the natural plant, that found in the fermented product must have had its origin in the bacterial decomposition of carbohydrates.

[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

METHYLTETRONIC ACID AND ITS AMIDE.

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Methyltetronic acid has been previously prepared by Ruff and Kohn[1] who obtained it in the form of its lactone through the oxidation of methyltetrose with bromine. Methyltetrose, however, is difficult to make. We have obtained this lactone very easily by a simple method recently described by Nef, Hedenburg and Glattfeld[2] for the oxidation of arabinose and xylose. By passing a current of air through dilute solutions of these pentoses, they obtained *l*-erythronic lactone from *l*-arabinose and *d*-threonic lactone from *d*-xylose. Applying this method to rhamnose one would expect that its oxidation should yield methyltetronic lactone, and this proves to be the fact. Our yield of lactone was 9.6% of the theoretical. This is considerably more than Ruff and Kohn obtained (2%), and as the method which we have followed is much more direct and simple than theirs, it is recommended for the preparation of this lactone.

The configuration of rhamnose has been established[3] to be that of a methylpentose,

$$\begin{array}{c} \text{OH OH H H} \\ \text{CH}_3\text{.C . C . C . C . CHO} \\ \text{H H OH OH} \end{array}$$

hence the configuration of methyltetronic lactone (considered to be a γ-lactone) is $\begin{array}{c} \text{O} \\ \text{OH H} \\ \text{CH}_3\text{.C . C . CO} \\ \text{H H OH} \end{array}$. By passing dry ammonia gas into a solution of this lactone in ether we have prepared the crystalline amide of methyltetronic acid, the structure of which must be $\begin{array}{c} \text{OH OH H} \\ \text{CH}_3\text{.C . C . C . CONH}_2 \\ \text{H H OH} \end{array}$. Since the hydroxyl group is on the right of the asymmetric α-carbon atom

[1] *Ber.*, **35**, 2365 (1902).

[2] THIS JOURNAL, **39**, 1638 (1917).

[3] Fischer and Morrell, *Ber.*, **27**, 382 (1894); Fischer and Zach, *Ibid.*, **45**, 3761 (1912); Hudson, THIS JOURNAL, **31**, 345 (1910).

of the amide it is to be expected[1] that the amide will be dextrorotary. This proves to be the case, its rotation in water being strongly to the right.

Experimental.

Methyltetronic Acid Lactone.—Fifty g. of crystalline rhamnose monohydrate was dissolved in 250 cc. of hot water and the solution was made up to 5250 cc. To this was added a solution of 93.5 g. of pure potassium hydroxide in 250 cc. of water. Air freed from carbon dioxide by passing over sodium hydroxide was then drawn through the mixture continuously for 3 days by the suction of a water pump. The diameter of the air inlet tube was 5 mm. The rate of flow was approximately 1.5 liters per minute. If the air is not admitted fast enough the solution will turn yellow, the color disappearing after several hours if the rate is increased. During daytime the solution was heated to 40–50°. At the end of the reaction the solution was colorless. Conc. hydrochloric acid was then added, the final addition being made with 10% acid using congo red paper as an indicator. The paper is pink in alkaline solution, takes on a light purple color when the organic sugar acids are liberated from their salts, and becomes dark blue fairly sharply when free hydrochloric acid is present. Acid was added just until the color became fairly blue, showing that the organic acids were entirely liberated from their salts but very little or no hydrochloric was present in the free state. The solution was then evaporated to dryness *in vacuo*. The distillate showed the presence of formic acid by reducing Fehling's solution. The white crystalline residue, somewhat gummy, was then boiled with absolute alcohol several times and filtered. The combined alcoholic solutions were then evaporated *in vacuo* to a thick red residue which was almost entirely soluble in ethyl acetate. This solution was filtered from the crystalline residue of potassium chloride. The ethyl acetate solution was evaporated on the steam bath, and the residue was triturated with warm ether until no more color dissolved. About 3 g. of a white crystalline substance was obtained from this ether extract by evaporating it almost to a sirup and letting stand several days. The residue that was insoluble in ether yielded about half a gram more of crystals of the same substance on standing in the open air several days.

The crystals melted at 121° and on recrystallization from absolute alcohol yielded 2 g. of needle-like crystals melting at 123°. A solution containing 0.3187 g. substance made up to 25 cc. with water rotated —1.14 circular degrees to the left in a 2 dcm. tube, hence $[\alpha]_D$ = —44.7°. Methyltetronic acid lactone that was obtained by Ruff and Kohn from the oxidation of methyltetrose with bromine melted at 121° and had a specific rotation of —47.5°.

The crystals of this lactone are easily soluble in cold absolute ether, contrary to the behavior of most lactones of the sugar group. Ruff and Kohn describe the crystals as rather difficultly soluble in benzene, ether or

[1] Hudson, THIS JOURNAL, 40, 813 (1918).

chloroform and very soluble in alcohol or ethyl acetate. We have verified these statements except with reference to ether, which dissolves the crystals readily.

Methyltetronic Acid Amide.—One g. of methyltetronic acid lactone was dissolved in 30 cc. of cold ether and dry ammonia gas was passed through the solution for 20 minutes. An amorphous white precipitate settled out on the bottom of the flask. By rubbing it under ether with a glass rod for several minutes it became crystalline and could easily be filtered by suction. The yield was nearly quantitative. The substance was recrystallized from absolute alcohol, in which it was very soluble. The crystals were large plates which melted with decomposition at 135°.

A solution of 0.5404 g. substance made up to 25 cc. with water, using a 4 dcm. tube, showed a dextrorotation of 4.74 circular degrees; hence $[\alpha]_D = +54.8°$. Nitrogen was determined by the Kjeldahl method.

Calc. for $C_6H_{11}O_4N$: N, 9.40. Found: 9.30.

Optical Data on the Crystals of the Lactone and Amide.

Dr. Edgar T. Wherry has kindly supplied the following data:

Methyltetronic lactone under the microscope has the form of rods suggesting the rhombic system. The refractive indices, by immersion in oils, in which the substance is but slowly soluble, were $\alpha = 1.500$, $\beta = 1.515$, $\gamma = 1.535$, all ± 0.005. Double refraction strong, 0.035. In polarized light brilliant interference colors are shown, mostly of the third or fourth order. Extinction is straight. Elongation may be positive or negative. In convergent polarized light partial interference figures are frequently shown. The axial angle is large, $2E = 120° \pm 10°$. Sign positive.

Methyltetronic amide under the microscope shows irregular plates, of which the crystal system could not be determined. The refractive indices by immersion in oils, in which it appears to be insoluble, were $\alpha = 1.510$, $\beta = 1.530$, $\gamma = 1.560$, all ± 0.005. Double refraction very strong, 0.050. In polarized light brilliant interference colors of mostly second order were observed. No edges could be found on which to base extinction or elongation data. In convergent polarized light partial interference figures were often found, the axial angle being very large, and the sign probably +.

WASHINGTON, D. C.

NEW BOOK.

Essentials of Volumetric Analysis. By HENRY W. SCHIMPF, Ph.G., M.D., Professor of Analytical Chemistry in the Brooklyn College of Pharmacy. Third Edition. 366 + xiv pages. 61 figures. John Wiley and Sons, Inc., New York, 1917. Price, cloth, $1.60 net.

In the present, as in the earlier editions of this work, the United States Pharmacopeia has been taken as a basis, and the essential points have been reduced within the limits of a small book. The subject matter is arranged under 5 headings: Neutralization, Precipitation, Oxidation, Indirect Oxidation, and Iodimetry. The author has made some changes, discarding some obsolete processes and substituting new and up-to-date methods of analysis for them. Nomenclature has been revised in accord with the new