LV. NOTE ON THE OXIDATION OF CARBOHYDRATES WITH NITRIC ACID.

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(Received June 16th, 1922.)

DURING the course of an examination of the carbohydrate constituent of *Chondrus crispus* we had occasion to oxidise the material with nitric acid, with a view to determining the amount of mucic acid produced. On examining the mother liquor from the mucic acid it was found to have a powerful reducing action upon Fehling's solution in the cold. On repeating the oxidation under rather more drastic conditions and evaporating the mixture to a syrup the same result was obtained. This seemed sufficiently remarkable to be worth investigating and samples of cane sugar, lactose, glucose and levulose were accordingly oxidised in the same way, and in every case it was found that the resulting product readily reduced Fehling's solution in the cold. Experiments were thereupon started upon pure glucose with the intention of isolating the material responsible for this strong reducing action. While these experiments were in progress a paper appeared by Kiliani [1922] in which he described the production of certain new reducing acids formed by carefully oxidising various carbohydrates at room temperature in the absence of air. As this author expressed the wish to reserve this field for himself we felt bound to discontinue our investigation, but thought it desirable to put on record our observations so far as they go in order to draw attention to the fact that powerful reducing substances are produced, not only under the rather peculiar conditions described by Kiliani, but even by oxidation of carbohydrates with hot nitric acid and without special precautions, although the yields obtained may possibly be smaller than those obtained by Kiliani. 25 g. of glucose were dissolved in 100 cc. of nitric acid (sp. gr. 1.15) and warmed over a boiling water-bath; after a short time a violent action set in which gradually subsided and the heating was continued until the solution had been reduced to one-third of its original volume. In order to avoid undue dilution the solution was neutralised by the addition of powdered crystallised sodium carbonate. The resulting liquid, which was of a light yellow colour, was found to darken slowly even when kept in a stoppered bottle protected from the light; it reduced Fehling's solution at once in the cold and likewise ammoniacal silver oxide.

The solution was treated with 20 % lead nitrate until no further precipitate was formed. This precipitate, *A*, was filtered off and when washed, suspended in water and decomposed with hydrogen sulphide yielded a solution which reduced ammoniacal silver nitrate but not Fehling's solution. The filtrate from precipitate *A*, though containing an excess of lead nitrate, gave no further precipitate on standing; the fact that the solution still reduced Fehling's

solution at once in the cold was taken to indicate that the reducing substance did not form an insoluble lead salt and was possibly not an acid, but on investigation it was found that the solution had acquired a markedly acid reaction, and on addition of a little alkali until the reaction was just on the acid side of neutrality a further heavy precipitate *B* was formed, which, after washing and decomposing with hydrogen sulphide, yielded an acid which reduced ammoniacal silver nitrate and Fehling's solution on heating but not in the cold. The filtrate from precipitate *B* which still reduced Fehling's solution in the cold was next treated with basic lead acetate, when it yielded a third precipitate *C*; the latter, when decomposed, gave the unknown acid *X* for whose isolation these experiments were undertaken; it was found to reduce both ammoniacal silver nitrate and Fehling's solution in the cold. The filtrate from precipitate *C* no longer had any reducing properties.

Subsequently it was found that the same acid *X* could be more rapidly obtained by replacing lead nitrate by lead acetate, since in using this reagent there was no change in the reaction of the solution; the addition of an excess of lead acetate caused the simultaneous precipitation of both the precipitates *A* and *B* of the previous experiment, leaving a filtrate containing only the acid *X* which could then be precipitated by the addition of basic lead acetate; after adding an excess of this reagent the precipitate was filtered and washed repeatedly with hot water until the washings were free from nitrate, an operation which resulted in considerable loss owing to the tendency of the precipitate to go through the filter paper. The washed precipitate decomposed with hydrogen sulphide yielded a powerfully reducing acid solution which, evaporated *in vacuo*, left a pale brown, viscous material which would not crystallise and which gradually darkened on keeping, especially if heated. This substance, dissolved in water and heated with concentrated hydrochloric acid, evolved a considerable quantity of furfural, thus showing it to contain at least five carbon atoms. The aqueous acid solution, treated with baryta solution, precipitated a small quantity of a sparingly soluble salt, the filtrate from which, however, still contained barium and reduced Fehling's solution in the cold. The neutral solution now also gave an immediate precipitate with lead acetate although this reagent would not precipitate it from the original oxidation mixture; this precipitate dissolved in caustic soda still reduced Fehling's solution in the cold.

Attempts to prepare a crystalline oxime, phenylhydrazone, *p*-bromophenylhydrazone and a cinchonine salt were unsuccessful. From the above facts it would appear that this substance, though in some respects similar to glycuronic acid, is not identical with it, but in view of the circumstances set forth above (with regard to the claim by Kiliani to reserve the field) and the possible identity of this substance with one of the compounds obtained by this author we have decided not to pursue the investigation any further.

REFERENCE.

Kiliani (1922). *Ber.* 55, B. 75.