THE PRESENCE OF MALTOSE IN ACID-HYDROLYZED STARCH PRODUCTS.

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REFERENCES have already been made, in a previous paper,[1] to the works of Salomon, Pellet, Johnson, and others which have led these investigators to conclude that maltose is not a product of the acid hydrolysis of starch. Lintner and Düll believed that "isomaltos" was produced. Morris and Rolfe and Defren have been among those who have maitained that maltose resulted from the hydrolysis. As has already been cited in a previous paper, Morris has stated that he has made crystals of undoubted maltosazone from the products of acid-hydrolyzed starch.

Having at hand a large quantity of commercial "glucose," of which we knew the circumstances of manufacture—it being the product of hydrochloric acid hydrolysis at a pressure of two atmospheres, and having a specific rotation of 126.5° D, and a cupric-reducing power of 0.575—we decided to make alcoholic fractions of this glucose with the object of separating maltose, if present, or some of its compounds, and, incidentally, of testing the law of relation of rotation to cupric reduction as applied to alcoholic fractions. The analytical figures of this sample showed that the hydrolysis had been carried only a little beyond the point for maximum maltose content as calculated from Rolfe and Defren's tables, and, in consequence, was specially suited for the investigation.

It can be easily calculated from the same tables that, were it possible to remove all the dextrin from a solution of this glucose leaving all of the maltose and dextrose, the resulting product would have a rotation of 105° and a reducing power of 0.76. If, however, the fractionation separated the glucose into a series of products more or less soluble in alcohol, but containing all three of the primary carbohydrates, it would be probable that they would conform to the law of relation, in which case, should a product be separated of the rotation 105°, its cupric-reducing power would be about 0.71 instead of 0.76.

In carrying out the fractioning, a 15 per cent. solution of glu-

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[1] Preceding paper.

[2] *Ber. d. chem. Ges.*, **28**, 1522.

cose was added, drop by drop, to about ten times its volume of 95 per cent. alcohol. After standing for a day or more, the precipitate was filtered off, washed thoroughly with alcohol, dried at a gentle heat till all traces of alcohol were expelled, and tested in the usual way. In the case of the alcoholic filtrates, the alcohol was removed by distillation, and the residues were concentrated to about 10 per cent. In order to economize time and alcohol, a little fuller's earth was mixed with the first precipitates to facilitate separation.

The following table gives the optical and reducing constants of those fractions which were investigated. It will be seen that, in general, they show a relationship between optical rotation and copper-reducing values which is in practical agreement with that found for homogenous acid-hydrolyzed products.

ALCOHOLIC FRACTIONS OF COMMERCIAL GLUCOSE SOLUTIONS.

		$[\alpha]_D$.	κ.
1st.	*Fractionation:*		
	1st. Precipitate	145.2°	0.489
	2nd. "	149.0°	0.423
	3rd. "	198.0°	0.047
	4th. "	197.6°	0.051
	1st. Filtrate	107.9°	0.765
	2nd. "	101.6°	0.717
	3rd. "	98.3°	....
	4th. "	96.8°	0.815
2nd.	*Fractionation:*		
	2nd. Precipitate	188.0°	0.117
	3rd. "	197.2°	0.093
	4th. "	196.0°	0.085
	2nd. Filtrate	88.8°	....
	4th. "	88.1°	0.811
3rd.	*Fractionation:*		
	1st. Precipitate	154.6°	....
	2nd. "	168.1°	....
	3rd. "	185.7°	0.163
	2nd. Filtrate	84.4°	....
4th.	*Fractionation:*		
	1st. Precipitate	137.5°	....
	2nd. "	152.3°	0.395
	3rd. "	165.9°	....
	4th. "	187.9°	0.127
	5th. "	189.1°	0.189
	6th. "	194.3°	0.075
	1st. Filtrate	96.0°	0.792

The values for the cupric-reducing powers of the filtrates of the first fractionation all show a wide departure from such relationship. These filtrates were peculiar in that they deposited, to some extent, granular precipitates quite different in appearance from the separated dextrins. It seemed probable that this precipitate was sugar in a free state. Moreover, it seems more than a coincidence accounted for by experimental error that the plots of these reducing values almost exactly fall on a straight line joining the 100 and 62.2 points which theoretically defines the reducing values of mixtures of pure maltose and dextrose. The apparently low reducing power of the second filtrate may be caused by an error in the rotation reading, as the aqueous solution in this case was turbid. This evidence seems to point to the possibility that under certain conditions, not clearly defined, alcoholic fractionation may break up the hydrolytic products, setting free one or more of the primary carbohydrates.

Some of the precipitates, especially those of high rotation, show unexpectedly high cupric-reducing powers. We are inclined to believe that this is caused by partial hydrolysis during drying. The precaution of drying in a vacuum at low temperature may not have prevented this entirely, as these low-converted dextrins seem very sensitive in this respect.

An aqueous solution made from the second filtrate of the third fractionation was heated on a water-bath with a small quantity of a solution of phenylhydrazine, in glacial acetic acid. Maltosazone was separated in the usual way by filtering off the dextrosazone in a hot funnel. On cooling the filtrate, characteristic crystals of maltosazone separated out. The dried crystals, tested by heating in a capillary tube, attached to a thermometer bulb, and immersed in a sulphuric acid bath, according to the usual method, began to decompose at about 195°, being entirely melted at 203°. The ordinary basic lead acetate solution of a density of 1.25, such as is commonly used in sugar analysis, proved very convenient for separating maltose. This solution was not precipitated when dropped into pure 95 per cent. alcohol, but formed a white, curdy precipitate when poured into the alcoholic filtrate from the glucose fractionation. After the lead was completely removed by hydrogen sulphide, the aqueous solution was heated with phenylhydrazine. No precipitate formed in the hot solution, but maltosazone separated out on cooling. As this seems a promising means of separating maltose, we intend to investigate it further.

We have made some photo-microscopic studies of the maltosazone and dextrosazone obtained from the alcoholic fractions and by means of the lead acetate separation, comparing them with corresponding osazones obtained from pure maltose and dextrose. When pure maltose is treated with phenylhydrazine acetate in the usual way, the osazone often separates out in crystal plates large enough to be seen without magnification. If examined under the microscope, it will be noticed that these plates tend to collect in spherical masses. Plate I shows such crystals of the osazone made from Kahlbaum's C. P. maltose. We have found it impossible to obtain these large crystals by recrystallization from hot water, the osazone being deposited in small balls[1] which show, on close examination, that they are aggregates of flat crystals. Plate II, while a poor photograph, is interesting because it represents these balls obtained from the crystals shown in the first plate by recrystallization from hot water. Plate III shows crystals of maltosazone obtained from the alcoholic filtrate previously mentioned. This shows the plates in loose aggregations and in balls. Plate IV is of osazone crystals from the lead acetate precipitate of the same filtrate. Plate V shows the same crystals after the aggregates have been broken up by gentle tapping of the cover-glass.

Dextrosazone has a quite different crystal habit. The crystals can be described as needles rather than plates. They form brush-like bundles resembling tufts of broom-corn, which, to some degree, suggest the maltosazone aggregations, but yet are quite different, showing none of the compact, spherical forms so characteristic of maltosazone. More highly magnified dextrosazone crystals closely resemble in shape those of stibnite, and apparently belong to the orthorhombic or hexagonal system. Plate VI shows these characteristics, especially the square basal angles. We have found these crystal forms so characteristic, when studied with the microscope, that we have felt warranted in presenting these photo-micrographs, and would have illustrated further the osazones of these two sugars had space permitted. The crystalline structure and the behavior of the two osazones with hot water

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[1] Grimbert: *J. Pharm. Chim.*, 7.17.5. aptly terms them "rosettes."

Plate I.

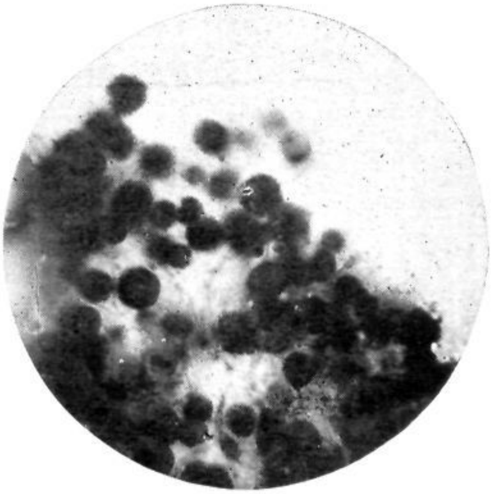

Plate II.

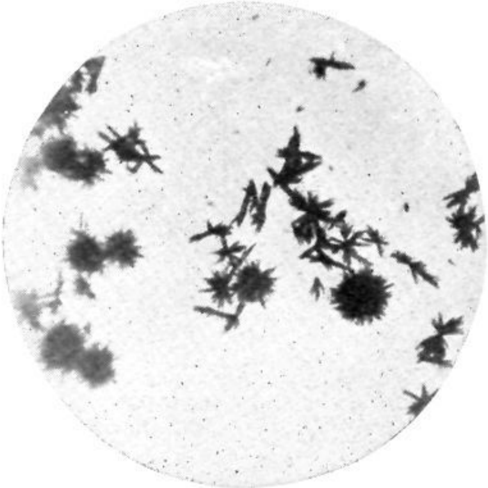

Plate III.

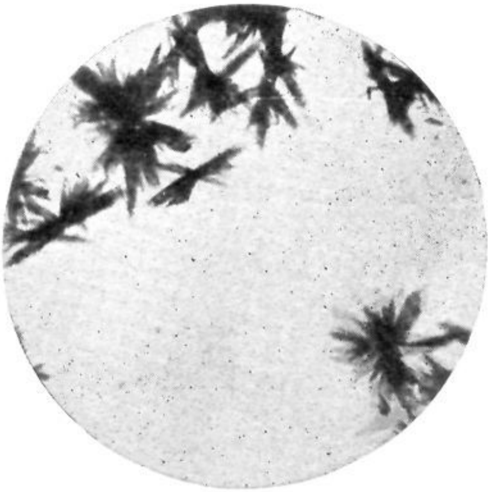

Plate IV.

Plate V.

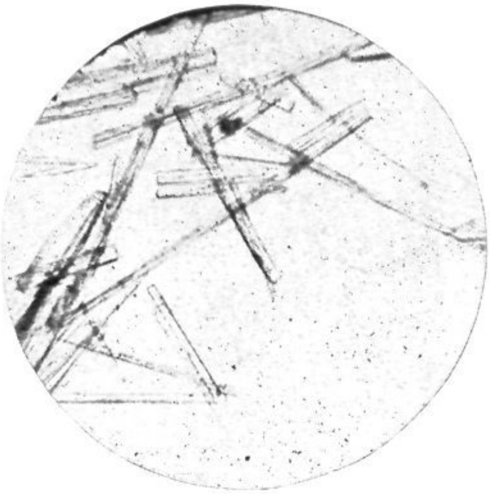

Plate VI.

are, in our opinion, their most easily recognized distinctions. The melting-point test by itself, as already pointed out by Brown, Morris and Miller,[1] is unreliable, and has led to serious errors of identification. This is due to the slight differences in the values in the case of many of the sugars, the difficulty in getting the exact melting-points owing to decomposition, and the great influence of very small amounts of impurities difficult to remove.

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A STUDY IN RAFFINOSE DETERMINATIONS.

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THE existence of several methods for the determination of raffinose in the presence of saccharose, together with variable results obtained in the application of the same to the analysis of the same product, have impelled me to investigate the matter more closely after the close of the "campaign." As the result of a study of the various methods, I have been led to combine the best features of some of them and believe that I have succeeded in applying a slight modification to the method of Clerget, which will secure for it accurate and satisfactory results with dark-colored products. The modification proposed is that of applying powdered zinc after inversion and at the temperature of inversion, with the production of an almost colorless solution with no change in the products of the hydrolysis of either sucrose or raffinose.

As the basis of these experiments a pure, doubly refined, white sugar, of undoubted cane origin, was employed and a commercial sample of raffinose from the house of Kahlbaum. The cane-sugar was perfectly free from invert-sugar and polarized 99.97 per cent. pure after being powdered and dried at a temperature of 60°-70° C.

The one sample of molasses was employed throughout the work.

Three samples of animal charcoal were purchased from a reliable Chicago firm and in original packages as bottled by the German firms of Merck and Dr. König. These chars were dried to constant weight before use at a temperature between 115° and

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[1] *J. Chem. Soc.* (London), **67**, 709: "The Isomaltose of C. J. Lintner."