STARCH AND THE TRANSFORMATIONS INDUCED BY ORGANIC AND OTHER ACIDS.

By F. SALOMON.

For the past five years the author has been investigating these changes, and the results obtained were frequently so contradictory and so at variance with all his expectations that he was often on the point of giving up the whole work, especially when Soxhlet showed that Fehling's test was still inaccurate, for this invalidated whole series of experiments.

The author, therefore, directed his entire attention to accurately establishing the prominent analytical characteristics. He then examined the starting point and end products, starch and dextrose; subsequently the intermediate products, such as soluble starch, dextrose, and maltose. The careful determination of the elementary composition of potato starch [$C_6H_{10}O_5$, or $X(C_6H_{10}O_5)_x$] and the quantity of sugar produced by its complete conversion with acids (namely, 111.11 per cent. of dextrose or starch sugar), as well as the elementary composition of rice starch and its quantitative estimation, have already been published in the *Chemiker Zeitung*, vi., 678 and 1,253. A general survey of the whole field and summary of the results are now given.

STARCH.

Allihn has shown (*J. Prac. Chem.*, xxii., 50), by very careful study of the process of saccharification, that under those conditions which generally prevail in starch analyses, only 95 per cent. of the starch is converted into sugar. Salomon also found that the conversion with sulphuric acid is totally useless for analytical purposes. But he gives another process of saccharification whereby all the starch can be converted into dextrose and the theoretical quantity obtained. The latter process was devised by Sachsé (*Chemisches Centralblatt*, 1877, 732). He makes use of hydrochloric acid in the following proportions: From $2\frac{1}{2}$ to 3 grammes of starch are dried at $120^\circ C$. (100° to 110° will not suffice) and placed in a flask with 200 c. c. of water and 20 c. c. of hydrochloric acid having a density of 1.125. It is heated for three hours with a return cooler (an upright tube 40 to 60 inches long will answer) on a water bath or in boiling water. At the close of this reaction a colorless liquid is obtained in which there are only a few white flocks, consisting chiefly of the remains of cell membranes. If this insoluble residue is to be determined, it is collected upon Soxhlet's asbestos filter, carefully washed, dried at $100^\circ C$, and weighed. The different filtrates are united and carefully neutralized with potassium hydrate.

The sugar is then estimated gravimetrically as follows: 60 c. c. of an alkaline copper solution (equal volumes of Rochelle salts and sulphate of copper solutions) are put in a beaker glass having a capacity of 800 c. c., diluted with 60 c. c. of water, and heated to boiling over an open flame or on a sand bath. From a pipette he runs 25 c. c. of sugar solution (with not more than 1 per cent. of sugar) into the boiling copper solution, boils again, and immediately filters out the suboxide of copper reduced. He uses for the purpose an asbestos filter made by drawing out a piece of combustion tubing 4 inches long to half its size, and filling the broader portion one-fourth with long fibers of freshly ignited asbestos. It is advisable to put a plug of glass wool (spun glass) below the asbestos to prevent any particles being carried through; the asbestos must not be packed in too firmly nor left too loosely. When filtering, a small funnel is placed on top and the apparatus connected with an aspirator. After decanting several times, the suboxide of copper is thrown on a filter and washed with water and then rinsed with alcohol and ether to hasten the operation of drying, which is done in an air bath. The oxide is reduced to metallic copper in the filtering tube by placing it in an inclined position over the point of a flame and passing dry hydrogen gas through it. The reduction is completed in a few minutes at a moderate heat. The operation is finished when the precipitate exhibits the characteristic color of copper and no little drops of water form in the cool end of the tube. It is cooled in the hydrogen current and then placed in a desiccator.

The following estimations are necessary for an accurate and complete analysis of starch, viz.:

Estimation of the moisture in it; of the non-combustible constituents (ash); the quantitative determination of the substances insoluble in dilute acids, such as cellulose, nitrogenized substances, etc.; also the conversion into sugar by acid and the estimation of the latter.

DEXTRINE.

Dextrose is also known as grape sugar and starch sugar (also glucose). The author ascertained by very carefully controlled experiments on the elementary composition of starch, that the mean specific gravity of a 10 per cent. solution of sugar (10 grains in 100 c. c.) at $17\frac{1}{2}^\circ C$. was 1.0381. From this he constructed a table for finding the number of grammes of anhydrous dextrose in 100 c. c. of any aqueous solution from its specific gravity at that temperature.

[We omit the table, which may be found in the *Chemiker Zeitung*, No. 74, p. 1194, as it can be easily constructed by any who need to consult it frequently.—TRANS.]

The table gives the number of grammes of sugar in 100 cubic centimeters of any solution; to find the number of grammes in 100 grammes of solution, the readings must be multiplied by the specific gravity of the solution.

In regard to the reducing power of dextrose for copper solutions, Soxhlet had already shown (*J. Prac. Chem.*, xxi., 227) that every kind of sugar examined, such as inverted sugar, grape and milk sugar, lactose and maltose, possessed a different reducing power, and that there was no constant reducing relation between copper and sugar, but that it varies with the concentration and is dependent upon the quantity of copper in the solution. The gravimetric method already so fully described in this article gives results that can be depended upon when no other substance is present except grape sugar. The method is absolutely accurate when the amount of sugar in solution is very near 1 per cent. If the dextrose is mixed with other substances, even if they are not of themselves reducing, they will sometimes increase the reducing power on long heating.

The optical action of aqueous solutions of dextrose has been very thoroughly investigated by Tollens, who found that the specific rotatory power of anhydrous grape sugar when in moderately concentrated solutions (5 to 14 per cent.) was 53.1° for the D line. Salomon found $D = 52.7^\circ$, and the rotatory power of aqueous solutions approaching 10 grammes in 100 c. c., in 20 mm. tube at $17\frac{1}{2}^\circ C$, was $j = 58.68^\circ$, while Brown and Heron found 58.65° , and Tollens 59.1° for the same.

The characteristics of dextrose may be stated to be that it dissolves readily in water and dilute alcohol; aqueous solution of iodine causes no perceptible change in solutions of this sugar; the specific gravity of a solution containing 10 grammes in 100 c. c. is 1.0381; the reducing power is esti-

mated by Allihn's process; the specific rotatory power for polarized light is α_j (alpha j) = 58.68° ; or 1 gramme of dextrose in a 200 mm. tube of the Soleil-Ventzke-Scheibler, or of the sensitive Jellet-Cornu half-shadow polariscope causes a deviation of $3.06 S$. V. S. or J. C.

MALTOSE.

This substance was first isolated by Saussure, in 1819, and was examined and named by Dubrunfaut, in 1847. It lay forgotten until O'Sullivan brought it to light again in 1872-6. Recently Brown and Heron (*Am. Chem. Pharm.*, xcix., 201) investigated it again, and then Soxhlet and Meissl (*J. Prac. Chem.*, xxv., 119) also took up its study.

Maltose is very soluble in cold water and in hot, acts like a real sugar, and when air dried has this composition: $C_{12}H_{22}O_{11} + H_2O$. Dried at $100^\circ C$, in *vacuo*, it becomes anhydrous and has the composition $C_{12}H_{22}O_{11}$. The aqueous solution of maltose gives no color with iodine solution, and no precipitate with strong alcohol. Brown and Heron state that the specific gravity of a solution containing 10 grammes of anhydrous maltose in 100 c. c. is 1.0393 at $15\frac{1}{2}^\circ C$. Salomon constructed a table based on Meissl's results to find the quantity of maltose in any solution at $17\frac{1}{2}^\circ C$. [Table omitted.]

The rotation of 1 gramme of maltose in 100 c. c. of solution in a 200 mm. tube, according to Meissl, in Jellet-Cornu apparatus is calculated to be 8° . Soxhlet puts the reducing power of maltose in 1 per cent. solution at 113 copper for 100 of anhydrous maltose with 4 minutes' boiling; Salomon observed 116 of copper.

Characteristic properties of maltose.—It is soluble in water and strong alcohol; gives no reaction with iodine; the specific gravity of 10 grammes solution of anhydrous maltose in 100 c. c. at $17\frac{1}{2}^\circ C$. is 1.0390 ; 1 gramme of anhydrous maltose in 100 c. c. solution rotates the light 8° ; and 1 gramme reduces 1.13 of copper.

SOLUBLE STARCH.

This was first described in 1840 by Jaquelin. It is obtained as follows: 100 grammes of potato starch are stirred up with 5 grammes of sulphuric acid in 1 liter of water, and kept boiling for $2\frac{1}{2}$ hours on a salt-water bath. When cold it gives a reddish purple color with iodine. The solution is then saturated with barium carbonate, filtered, evaporated down a little, then precipitated with alcohol, and the precipitate dissolved in water, reprecipitated, and, after dissolving again, the solution is evaporated to a sirup. The white powder is repeatedly washed with water, alcohol, and ether, and dried at $105^\circ C$. This soluble starch is nearly insoluble in cold water, but dissolves with ease in hot water, forming a clear, transparent (not pasty) solution. In dilute solutions alcohol throws down a permanent precipitate; the following day nearly all is precipitated in form of powder. If the alcohol is not skillfully added, a slimy, stringy mess is precipitated. Upon adding a solution of iodine to a solution of the pure substance, a beautiful deep blue clear liquid is obtained; the presence of dextrose affects the color. It does not reduce the copper solution. One gramme of the substance caused a rotation of polarized light 11.01° in J. C. or S. V. S. apparatus.

Characteristics of soluble starch.—Soluble starch in aqueous solution is turned deep blue with iodine; does not reduce copper in Allihn's method; 1 gramme of soluble starch in 100 c. c. of solution has a specific gravity of 1.00401, and turns the ray of light 11.01° in the Jellet-Cornu apparatus.

DEXTRINE.

It is comparatively easy to prepare pure dextrine with dilute sulphuric acid if care be taken to check its action upon the starch in time. Salomon obtained a very pure dextrine which gave only a red color with iodine by simply pouring off the solution obtained in the preparation of soluble starch as above described, and which gave a deep red-brown color, from the precipitated starch. This liquid, which contained the dextrine, gave with iodine a pure brown color. The dextrine was precipitated with alcohol, and obtained as a tenacious mass by evaporating aqueous solution on a water-bath. After standing a long time over sulphuric acid in *vacuo* it became hard, vitreous, and brittle, so that it was easily rubbed to an impalpable powder; it dissolves easily both in hot and cold water. The one per cent. solution did not reduce any copper by Allihn's sugar method. The action of dextrine with iodine is very unreliable. A solution of dextrine in water gave at first a brownish-red color which disappeared immediately, and did not become permanent until the reagent had been repeatedly added, and is perhaps to be attributed to a slight residue of soluble starch. A solution containing 1 gramme of dextrine in 100 c. c. has a specific gravity of 1.0040. The specific rotatory power of this substance, according to the observations of Brown and Heron, corresponds to $\alpha_j = 216^\circ$, or according to Salomon $216\frac{1}{2}^\circ$, so that one gramme of dextrine in 100 c. c. solution in a 200 mm. tube rotates the light 11.3° J. C.

The important analytical elements of dextrine are the following: Fehling's solution is not reduced by dextrine with Allihn's method of testing; it is precipitated by alcoholic from aqueous solution; it gives no color with iodine solution; its specific rotatory power is $\alpha_j = 216\frac{1}{2}^\circ$. The rotatory power seems to be higher in acid solutions than in neutral.

The second portion of Salomon's paper relates to the action of sulphuric acid of different degrees of concentration upon rice starch. The third portion is more important, and relates to the saccharifying process. The final results of these investigations may be summarized as follows:

RESULTS.

We are in possession of all the data necessary for the detection and estimation of starch, dextrose, and maltose, and they rest upon a solid basis. Dextrine and "soluble starch" require further investigation, since the characters that are indispensable for recognizing them with certainty are dependent on so few experiments.

The conversion of starch into sugar by dilute sulphuric acid is not to be considered as a splitting up of the molecule into sugar and dextrine, as Musculus assumed in his day, but rests as Payen showed, upon a gradual change. The experience gained during the course of the investigation led him to think that the process goes on as follows: The first action of the sulphuric acid is the conversion of the starch molecule, which probably consists of several $C_6H_{10}O_5$ groups, into soluble starch, which has a more simply constituted molecule, and this into the still simpler dextrine. This change takes place with uncommon rapidity, so that the second phase of the process, the hydrating of the dextrine, which converts it into sugar, begins almost simultaneously with the other operations. As the saccharification is intimately related to the time and the strength of acid

used, so that twice as much acid will convert twice as much dextrine into sugar in the same time, we may look up the operation as very similar to that of making ether.

SACCHARIFICATION-ETHERIFICATION.

The sulphuric acid unites with a definite quantity of dextrene, hydrates the same, and then leaves it again, to unite at once with a new quantity of dextrene and convert that into sugar in the same way, and so on. By doubling the quantity of sulphuric acid the operation goes on twice as fast, *i. e.*, twice as much dextrene is converted into sugar in a unit of time. By doubling the quantity of starch the process is delayed to the same extent, because the amount of work that the acid has to do is twice as great. It is perhaps totally unnecessary to assume an intermediate stage corresponding to the ethyl-sulphuric acid, since the whole process consists to a certain extent of a slow combustion attended with loss of energy.

The substances formed by the action of dilute sulphuric acid upon starch are the following, and in the following order: soluble starch, dextrene, dextrose.

ORGANIC ACIDS.

In the conversion of starch into sugar by means of organic acids, it passes through the same stages as above described. The organic acids, such as oxalic, tartaric, and citric, act much more feebly, but yield no other products besides soluble starch, dextrene, and dextrose.

Finally, the author expresses the opinion that it would be of great practical value to extend the methods employed in this investigation to the study of the action of diastatic ferments upon starches, an idea that Brown and Heron's essay offers a valuable starting point.—*Jour. Pract. Chem.*

ON THE PREPARATION OF CERIUM OXIDE.

By M. H. DEBRAY.

FIVE hundred grammes of cerite, finely powdered, are stirred up in, at most, an equal weight of water, and 375 grammes of concentrated sulphuric acid are added while the mixture is being rapidly stirred. This operation is performed in a large platinum capsule with a flat bottom. The mixture becomes hot, swells up, and is rapidly converted into sulphate of the earths of cerite, and into gelatinous silica. The whole is evaporated until dense fumes of sulphuric acid begin to appear, stirring all the time to prevent the mass from adhering to the bottom of the capsule. The matter is then pulverulent, and the silica has become insoluble. When it is quite cold, it is thrown, little by little, into water kept at 0° by means of ice (5 or 6 liters at least); the sulphates, which are slightly acid, dissolve readily in the water if we prevent the rise of temperature which accompanies hydration. The liquid is filtered off and treated with a current of hydrogen sulphide; when saturated with this gas, it is left digest for twenty-four hours. A complex mixture of copper, bismuth, molybdenum, etc., sulphides is deposited. The mixture is heated to cause these sulphides to be perfectly precipitated, and filtered. The rose-colored filtrate is precipitated with concentrated oxalic acid. There is formed an abundant curdy deposit, which collects at first in a soft state at the bottom of the vessel, and is rapidly converted into a crystalline powder of the acids of the cerite earths. The acid liquid contains lime and iron. The oxalates are washed by decantation and converted into nitrates by attacking them with hot concentrated nitric acid.

So far the treatment indicated does not essentially differ from that commonly adopted for extracting from cerite the mixture of earths discovered by Mosander. It is chiefly in the treatment of the nitrates for obtaining cerium oxide that the process is distinguished from those hitherto adopted for separating creoso-ceric oxide from the didymium and lanthanum oxides.

The mixture of nitrates is melted with 8 or 10 parts potassium nitrate in a porcelain capsule, and the fused mass is kept between 300° and 350° by means of a gas furnace. Cerium nitrate is decomposed, forming a yellowish powder of cerium oxide, which retains a little nitric acid, but didymium and lanthanum nitrates, when melted with niter, are not appreciably decomposed even at 350° . A thermometer, plunged into the bath of nitrate, indicates its temperature. When the escape of nitrous fumes ceases, which requires several hours, the operation is stopped. When cold the melted mass is easily detached from the capsule, and the cerium oxide is found collected at the lower part. It is dissolved in water, and there remains a powder, yellowish if it contains mere traces of didymium, but reddish if it contains more. It is well to wash with a little weak nitric acid, which dissolves a little didymium subnitrate produced at the same time as the cerium oxide if the capsule is too strongly heated at certain points. This is of little consequence, as the cerium oxide obtained in the first operation always requires to be purified.

It may be entirely freed from didymium by transforming it into nitrate, which is melted a second time with 8 or 10 parts potassium nitrate. For this purpose the oxide is attacked with sulphuric acid diluted with an equal volume of water, taken up with water when everything dissolves if the liquid is sufficiently acid. The yellow creoso-ceric sulphate thus obtained is reduced with sulphurous acid, and the cerous sulphate is precipitated with oxalic acid. The cerous oxalate is then readily converted into nitrate by boiling with nitric acid. This second treatment gives a yellow powder, which contains neither didymium nor lanthanum, as the nitrate of the latter earth is still more stable than that of didymium. If it is transformed into colorless cerous sulphate, the spectroscopic does not detect the least trace of this body, which is always easy to recognize by its absorption-spectrum. The didymium and lanthanum nitrates which remain mixed with a large excess of potassium nitrate are evaporated and remelted, the temperature exceeding 350° . The remaining trace of cerium nitrate which has escaped decomposition in the former operation is completely destroyed, and there is even formed a small quantity of didymium subnitrate. But the bulk of the didymium remains with the lanthanum in the state of a soluble nitrate.

We have thus a certain and rapid method of obtaining the oxide or the salts of cerium free from didymium and lanthanum, or, on the other hand, a mixture of these two oxides absolutely free from cerium.—*Comptes Rendus*.

CYLINDERS FOR CALICO PRINTING.

By J. DEPIERRE and PAUL SPINAL.

THE metals best suited for printing are pure copper alloys containing from 25 to 30 of zinc to from 75 to 70 of copper. Lead, even if present to the extent of $\frac{1}{2}$ per cent., is injurious. The introduction of 1 per cent. of phosphorus in brass renders the grain more homogeneous.