necessary to dissolve and reprecipitate the calcium oxalate, for the first precipitate is sure to contain alkaline chlorides in very appreciable amount. The basic acetate precipitate cannot be used for the determination of alumina, since the manganese precipitate carries down a little iron with it, but apparently no determinable amount of zinc.

## ON THE DETERMINATION OF CANE-SUGAR IN THE PRESENCE OF COMMERCIAL GLUCOSE.[1]

BY H. A. WEBER AND WILLIAM MCPHERSON.

IN the analysis of a great many of the saccharine products found in the markets at the present time, the chemist is confronted with the problem of determining sucrose in the presence of commercial glucose. The official methods for such determinations, either by the use of Fehling's solution alone or supplemented by the polariscope, necessitate, as is well known, the inversion of the sucrose by the action of acids. The accuracy of these methods requires, as one condition, that the acid used in inversion exert no action upon any substance present, other than sucrose, that would in any way affect the reading of the polariscope or would change the power to reduce Fehling's solution. Since commercial glucose, however, contains a greater or less amount of dextrin, and since this undergoes hydrolysis when acted upon by acids, being changed thereby into dextrose, the question arose as to whether such a change might take place during the process of inversion of any sucrose present and thus vitiate the results. The specific rotatory power of dextrin being nearly four times as great as that of dextrose, it is evident that a very slight action would introduce serious errors.

The method of procedure was, first, to determine to what extent dextrin is present in commercial glucose; second, to ascertain whether any change is produced by heating with acids as in the common process of inversion, and finally to discover some method of eliminating this error, if present.

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[1] This paper and the one following were sent to Dr. H. W. Wiley to be read before the Association of Official Agricultural Chemists and then transmitted to the editor of this JOURNAL for publication. In consequence of a misunderstanding they were printed instead, in the Proceedings of the Eleventh Annual Convention of the above association. At the request of the authors, and with the consent of the Committee on Papers and Publications, they are now reprinted in full.—ED.

An examination of the literature accessible upon the subject of the composition of American glucose failed to give any information in regard to the amount of dextrin present.

The report on glucose, Washington, 1884, gives the analysis of some glucoses, but as suggested by Stone and Dickson,[1] improvement or variation in the manufacture since that time would probably cause a change in the chemical composition.

In order to obtain the desired information a number of samples were analyzed. Seven of the samples were kindly sent us by the American Sugar Refining Company, of Chicago, and represent the various grades placed on the market by them. Since this company controls the glucose manufacture in the United States, it is fair to presume that these samples represent, more or less fairly, an average glucose in the market. Two other samples were purchased in Columbus, but analysis showed a composition similar to those sent from Chicago, and inquiry revealed the fact that they had been purchased from the above-mentioned company.

## METHOD OF ANALYSIS.

A number of different methods have been proposed for the estimation of the constituents of glucose, all more or less objectionable. The shorter ones are only fairly approximate, making no attempt to estimate the amount of the so-called inert or unfermentable carbohydrates (gallisin). The longer methods are probably more exact, but, since the unfermentable carbohydrates are but imperfectly known, it follows that any attempt at finding the exact composition cannot be highly satisfactory.

The following method[2] was selected as giving approximately the relative amounts of dextrose, maltose, and dextrin present.

Twenty-five grams of the glucose were dissolved in water, and the solution made up to 250 cc. With this solution the following determinations were made:

*1. Specific gravity.*—This was determined by weighing with the pyknometer. The Westphal balance was first used, but the results were not so satisfactory as those obtained by direct weighing.

*2. Specific rotatory power.*—This was deduced from the direct

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[1] *J. Anal. Appl. Chem.*, 7, No. 6.

[2] See article Sugar, Thorpe's Dictionary of Applied Chemistry.

reading in a 200 mm. tube. The instrument used was the ordinary Schmidt and Haensch polariscope. Its accuracy was tested by a standard plate, kindly loaned by Dr. Wiley.

*3. Cupric reducing power.*—A gravimetric determination was made by adding ten cc. of the solution properly diluted to forty cc. of Fehling's solution previously heated in boiling water until it attained a like temperature and then heating for twelve minutes in water at 100°. The cuprous oxide was filtered through asbestos, well washed, and changed into the cupric form by igniting for fifteen minutes. The weight of the oxide multiplied by 0.4535 gives the amount of reducing sugar present. Experiment showed that good results could be obtained by exercising due care and adhering rigidly to the conditions.

*4. Ash.*—Fifty cc. of the solution were treated with sulphuric acid in a platinum dish until all the carbonaceous matter was burned away, the residue weighed, and the percentage of ash calculated.

The total organic solid matters per 100 cc. were determined by subtracting from the specific gravity of the solution (water = 1,000) the correction due to the ash, and dividing the difference between the result and 1,000 by 3.86. This is based on the assumption that ten grams of carbohydrates dissolved in 100 cc. of water give a solution of sp. gr. 1,038.6 (water = 1,000), also that one gram of ash per 100 cc. gives a specific gravity of 1,008. Now, if in a solution containing ten grams to 100 cc.,

S = total carbohydrates,
(A)d = specific rotatory power for ray D,
K = cupric reducing power in terms of dextrose,

then

$$\text{Maltose (M)} = \left(\frac{(A)d + 1.42K - 195}{27.2}\right)S$$

$$\text{Dextrose (D)} = \frac{SK}{100} - 0.61\ M.$$

$$\text{Dextrin} = S - (M + D).$$

It is evident that this method will give only approximate results, since it supposes that the only organic bodies present are maltose, dextrose, and dextrin. However, the results undoubtedly give a fair insight into the amounts of these present.

TABLE NO. I.—GLUCOSES ANALYZED.

| | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. | No. 6. | No. 7. | No. 8. | No. 9. | No. 10. |
|---|---|---|---|---|---|---|---|---|---|---|
| Specific gravity | 1030.60 | 1031.05 | 1031.40 | 1031.18 | 1033.16 | 1033.90 | 1031.17 | 1031.48 | 1033.50 | ...... |
| Total solids, grams | 7.8890 | 8.01 | 8.08 | 8.03 | 8.56 | 8.74 | 8.00 | 8.11 | 8.60 | ...... |
| Specific rotatory power | 133.33 | 132.90 | 120.60 | 135.40 | 132.10 | 127.80 | 149.30 | 130.31 | 134.91 | 40.20 |
| Ash, per cent | 0.18 | 0.19 | 0.24 | 0.21 | 0.17 | 0.22 | 0.37 | 0.29 | 0.37 | ...... |
| Cupric reducing power, per ct. | 56.56 | 57.00 | 60.60 | 54.90 | 56.70 | 55.90 | 43.60 | 50.65 | 48.75 | ...... |
| Maltose, per cent | 54.08 | 55.44 | 34.63 | 54.20 | 55.40 | 39.12 | 47.67 | 22.30 | 28.92 | ..... |
| Dextrose, per cent | 11.64 | 11.81 | 21.24 | 11.03 | 14.71 | 25.08 | 5.81 | 27.48 | 24.31 | ...... |
| Dextrin, per cent | 13.18 | 12.80 | 24.98 | 15.09 | 15.44 | 23.18 | 26.52 | 31.33 | 32.81 | ...... |

It is of interest to compare these results with the following, the first three of which are taken from the report on glucose above mentioned. The fourth is the analysis published recently of a product manufactured in England.

| | No. 1. Per cent. | No. 2. Per cent. | No. 3. Per cent. | No. 4. Per cent. |
|---|---|---|---|---|
| Maltose | 19.3 | 7.6 | .... | 36.10 |
| Dextrose | 36.5 | 36.5 | 39.0 | 18.75 |
| Dextrin | 29.8 | 40.9 | 41.4 | 25.41 |

The most noticeable feature of the above analyses is the high per cent. of maltose present and the comparatively low per cent. of dextrose. With a single exception the maltose present exceeds the dextrose, reaching a maximum difference in number 7, which contains 47.67 per cent. maltose and only 5.81 per cent. of dextrose. This particular sample was labeled "Brewers' Extract," the name suggesting a high per cent. of maltose, a characteristic property of the glucoses obtained from Chicago with a malt-like odor noticeable when dissolved in a slight amount of hot water. It will be noticed that the English sample contains almost twice as much maltose as dextrose.

The solid glucose or grape-sugar was not analyzed completely, since the specific rotatory power was so low as to exclude any possibility of the presence of dextrin.

It is of interest to compare the properties of the above glucoses with those examined by Stone and Dickson.[1] The determinations made by them were, in the main, different from those made by us, overlapping, however, in the determination of the specific rotatory power and ash. A marked difference exists in these. The average specific rotatory power of those examined by Stone and Dickson is given as 91.37, while those examined by us showed a variation from 120.6 to 149.3, calculated for ray D. It is possible that the former calculations may have been made for some other ray, and the apparent difference thus diminished. The percentage of ash in the samples examined by us was noticeably smaller, being about one-fourth as great.

The glucoses were next subjected to the same treatment as would be necessary to invert sucrose, if present, *viz.*, heating with acids. It is evident that in order to guard against any hydrolysis of the dextrin or to diminish it, if unavoidable, the temperature to which the acid solution is raised as well as the time during which this temperature is maintained should be no greater than necessary to insure complete inversion of the sucrose. Various methods of inversion have been proposed and various ones are in use by chemists at the present time. The official methods of the agricultural chemists for the years 1890 and 1891 require that the solution to be inverted, mixed with the proper amount of acid, be heated for ten minutes at 68°. This was changed in the report for 1892 and continued in the report for 1893, to heating gradually, reaching 68° at the expiration of ten minutes. This is also the method given by Allen,[2] as well as the one recommended by the "Association des Chimistes."[3]

Three different methods were tried: 1. The above-mentioned or official method; 2. The method recommended by the Association of Official Agricultural Chemists for the years 1890 and 1891, *viz.*, heating at 68° for ten minutes; 3. The German method, which amounts to heating at 67° to 70° for fifteen minutes.

Approximately 26.048 grams of glucose were dissolved in 200 cc. of water. Fifty cc. of this solution mixed with five cc. fuming

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[1] *J. Anal. Appl. Chem.*, 7, No. 6.

[2] Allen's Commercial Organic Analysis.

[3] Jour. des Fabr. de Sucre, 32, *1891*, No. 35.

hydrochloric acid were heated according to the above-mentioned methods.

TABLE NO. II.—READINGS OF AN APPROXIMATELY FIFTY PER CENT. SOLUTION OF THE VARIOUS GLUCOSES, BEFORE AND AFTER HEATING WITH ACIDS. TEMPERATURE, 20° C.

[Divisions on cane-sugar scale.]

| | No. 1. | No. 2. | No. 3. | No. 4. | No. 5. | No. 6. | No. 7. | No. 8. | No. 9. | No. 10. |
|---|---|---|---|---|---|---|---|---|---|---|
| Direct reading 200 mm. tube | 85.70 | 85.50 | 80.10 | 86.55 | 85.30 | 84.40 | 90.40 | 84.90 | 86.15 | 42.00 |
| Reading after inversion by first method | 85.20 | 84.85 | 79.58 | 86.00 | 84.90 | 83.90 | 89.85 | 84.20 | 85.55 | 42.05 |
| Difference | 0.50 | 0.65 | 0.52 | 0.55 | 0.40 | 0.50 | 0.55 | 0.70 | 0.60 | .... |
| Reading after inversion by second method | 84.25 | 83.90 | 78.75 | 85.15 | 84.00 | 82.90 | 88.95 | 83.00 | 84.45 | .... |
| Difference | 1.45 | 1.60 | 1.35 | 1.40 | 1.30 | 1.50 | 1.45 | 1.90 | 1.70 | .... |
| Reading after inversion by third method | 83.75 | 83.20 | 78.10 | 84.60 | 83.50 | 82.15 | 88.35 | 82.25 | 83.75 | .... |
| Difference | 1.95 | 2.30 | 2.00 | 1.95 | 1.80 | 2.25 | 2.05 | 2.65 | 2.40 | .... |
| Reading after boiling one hour with acetic acid (com.) | 85.30 | 84.90 | 79.75 | 86.15 | 84.85 | 84.05 | 89.90 | 84.30 | 85.65 | .... |
| Difference | 0.40 | 0.60 | 0.35 | 0.40 | 0.45 | 0.35 | 0.50 | 0.60 | 0.50 | .... |

The flasks were carefully calibrated and the duplicates agreed within the error of reading. The results are given in the above table. The solutions were of such a strength that the amount used was the same as would be used in the analysis of a substance containing approximately fifty per cent. glucose.

It will be noticed that in every case, with the exception of No. 10, which contains no dextrin, the reading is sensibly diminished, introducing thereby an error in the estimation of sucrose in the presence of commercial glucose, varying from one-tenth to over two per cent., according to the amounts of the two present and the method of inversion used. While this may not be large enough to cause one to draw unjust conclusions from the analysis of commercial saccharin products, it is nevertheless desirable to eliminate it if possible, or at least to reduce it to a minimum.

Experiments were made to find out the effects of other acids in the hope of finding one that would bring about the inversion without affecting the reading of the glucose. The result showed, however, that even an acid which would not bring about complete inversion would sensibly diminish the reading of the glucose. Thus acetic acid will cause a diminution of reading almost as large as that caused by hydrochloric acid, although it does not *seem* to cause complete inversion. In no case was a smaller error introduced than by the first method above used.

Since the error could not be eliminated by inversion with acids[1] an attempt was made to allow a correction for it. It is evident from the above results that the error is not a widely diverging one, if the samples can be regarded as average ones, and it could be largely diminished by allowing for the mean deviation.

It was necessary, however, before attempting this to find out what the effect would be when the amount of glucose present was varied. Solutions were made containing, approximately, 100, 50, 25, 10, and 5 per cent. of glucose, respectively, and subjected to the action of acids as before. The average results expressed as divisions on cane-sugar scale, were as follows:

| | 100 per cent. | 50 per cent. | 25 per cent. | 10 per cent. | 5 per cent. |
|---|---|---|---|---|---|
| Before........ | 170.7 | 85.00 | 42.35 | 16.8 | 8.6 |
| After.......... | 169.4 | 84.45 | 42.15 | 16.78 | 8.65 |
| | 1.3 | 0.55 | 0.2 | 0.02 | .... |

The results with the various glucoses are sufficiently uniform to warrant one to introduce corrections which, while not eliminating the error, would reduce it to a minimum.

This correction may be easily calculated as follows:

It can readily be seen that the reading due to glucose present may be approximately determined by subtracting from the direct reading three-fourths of the difference between (or sum of) the direct and invert readings (supposing that the temperature be about 20°).

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[1] This error would be eliminated by the inversion brought about by O'Sullivan and Thompson's invertase process (*Journal of the Chemical Society of London*, 59, 46). The method is not used to any extent, however, because of the time required as well as the increased labor of analysis.

Let $R$ equal the reading due to glucose, then the following formula deduced from a graphic representation of the above results will be found to give the correction ($x$) :

$$x = \frac{R-15}{130}$$

This correction must, of course, be subtracted from the numerator $(a \pm b)$ in Clerget's formulas. In order to test the accuracy of the above correction a number of mixtures of cane-sugar and glucose were analyzed. Good results were obtained in every instance. The following expressed as divisions on cane-sugar scale, will serve as examples :

| Glucose. Per cent. | Sucrose. Per cent. | Direct reading. | Invert reading. | Approximate glucose reading. | Correction. | Per cent. of sucrose found | |
|---|---|---|---|---|---|---|---|
| | | | | | | Without correction. | With correction. |
| 80 | 20 | 154.2 | 126.30 | 133 | 0.90 | 20.82 | 20.18 |
| 50 | 50 | 138.4 | 70.75 | 87 | 0.55 | 50.48 | 50.11 |
| 30 | 70 | 120.3 | 26.23 | 50 | 0.27 | 70.20 | 70.00 |
| 10 | 90 | 109.0 | 11.80 | 19 | 0.03 | 90.15 | 90.13 |

The results in Table No. 11 show the necessity of chemists using the same method of inversion. Even in the estimation of pure sucrose it has been shown by a number of chemists that the reading varies slightly according to the method used. In the presence of commercial glucose, however, the variation becomes much greater. When the inversion is accomplished by heating at 68° for ten minutes, the difference in reading due to the hydrolysis of the dextrin averages almost three times as great as when the first method is used, while the German method increases this to almost four times. It is barely possible that some of the widely varying results published by the reporter on sugar, in the report of the Association of Official Agricultural Chemists, may owe a part of their discrepancies to these facts.

## CONCLUSIONS.

Some of the conclusions reached may be summarized as follows :

(1) An error is introduced in the estimation of sucrose in the presence of commercial glucose, due to a slight hydrolysis of the dextrin present during the process of inversion of the sucrose by acids.

(2) This hydrolysis, and consequently the error, is reduced to a minimum when the inversion of the sucrose present is effected by heating for ten minutes, the temperature being gradually raised so as to reach 68° at the expiration of this time.

(3) The results with the different glucoses are sufficiently uniform to warrant the introduction of a correction for the mean error.

(4) In order that the results may be comparable, chemists ought to strictly adhere to one method of inversion.

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# ON THE ACTION OF ACETIC AND HYDROCHLORIC ACIDS ON SUCROSE.

BY H. A. WEBER AND WILLIAM MCPHERSON.

WHILE carrying out some experiments with glucose several facts were noted in reference to the action of acetic and hydrochloric acids on sucrose, which it is interesting to compare with the conclusions reached by Bornträger,[1] Jungfleisch and Grimbert,[2] and Ost.[3] Inasmuch as we were working with an entirely different object in view, the conclusions reached were in no way influenced by the conclusions reached by the above writers.

While making an examination of a large number of saccharine products, the writers were led to believe from certain results that complete inversion could be effected by means of acetic acid. This view was contrary to the general opinion of chemists, although as prominent ones as Jungfleisch and Grimbert[4] claim that acetic acid completely inverts sucrose at 100°, and that it is preferable to other acids, since its presence is without effect upon the levulose of invert sugar. This conclusion was reached from the fact that the specific rotatory power of pure levulose corresponded almost exactly with that of levulose calculated from invert sugar, the inversion being effected by acetic acid. Hydrochloric acid gives a higher invert reading, because, in some way, it acts upon the levulose and increases very percepti-

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[1] Boh. Zeit. Zucker. Ind., *1891*, 187. Bull. Assoc. Chim., *1892*, 559.

[2] *Compt. rend.*, 107, 390, and 108, 144.

[3] *Ber. d. chem. Ges.*, **24**, 1636.

[4] *Compt. rend.*, 107, 390.