

THE INVERSION OF CANE-SUGAR IN PRESENCE OF MILK CONSTITUENTS.

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It was observed by one of us, while making analyses of condensed milks containing cane-sugar, that the method of Stokes and Bodmer gave results which were appreciably too low.

This method was described in the ANALYST, vol. x. The following description of the principles involved is taken from Allen's "Commercial Organic Analysis," vol. i., p. 343, 1898 edition :

"Coagulation of the milk by citric acid, dilution to ten times its original volume, filtration and titration of a portion of the filtrate with Pavy's ammoniacal copper solution. To 100 c.c. of the same filtrate 2 grammes of citric acid are added, the liquid boiled for ten minutes, cooled, neutralized, made up to 200 c.c., and titrated as before. The difference between the reducing powers of the solution before and after inversion is due to the invert sugar derived from the cane-sugar present, the milk-sugar not being inverted by boiling with citric acid."

It was observed that by following the process above detailed the complete inversion of the cane-sugar was not effected in presence of the constituents of milk. That this incomplete inversion was not due to insufficiency of citric acid was shown by a series of experiments in which 5 per cent. solutions of sucrose were boiled with 2, 1, and $\frac{1}{2}$ per cent. of citric acid for ten minutes, and found to be fully inverted at the end of that time; it was therefore concluded that some constituent of milk exercised a retarding influence on the progress of the reaction.

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To investigate this point a series of experiments was instituted whereby the progress of the inverting action of citric acid could be followed on two similar solutions of cane-sugar, one containing milk constituents, the other not.

The two solutions were prepared as follows :

Two portions of 100 c.c. each of a solution containing approximately 25 per cent. of sucrose were measured out, and to each of these 12 grammes of citric acid were added ; to one solution 200 c.c. of whey, from which the curd had been precipitated by addition of a small quantity of citric acid, were added, and the two solutions then made up of 400 c.c. For further reference the solution containing milk constituents is termed A, and that not containing milk constituents B. The lactose in solution A was first determined by neutralizing the acidity of 25 c.c. by means of sodium hydrate, making up to 50 c.c., and determining by Fehling's solution.

The two solutions were then transferred to two flasks fitted with reflux condensers and with tubes whereby portions of liquid could be withdrawn without interfering with the progress of the reaction.

The two flasks were simultaneously heated up to the temperature of experiment, and from time to time portions of the contents withdrawn by means of the tubes provided. The portions withdrawn were rapidly cooled down to 30° C., 10 c.c. taken, neutralized with sodium hydrate, and made up to 100 c.c. with distilled water at 30° C.* The reducing sugars present were then determined by means of Fehling's solution.

Two series of experiments were performed. In the first series the two flasks were heated to 85° C. by immersing both in one large water-bath maintained at that temperature.

The following results were obtained :

SOLUTION A, CONTAINING CANE-SUGAR AND MILK CONSTITUENTS.			SOLUTION B, CONTAINING CANE-SUGAR ONLY.	
Time from commencement of experiment at which solution was withdrawn.	Invert Sugar Per Cent.	Lactose Per Cent.	Time of withdrawing solution in minutes.	Invert Sugar Per Cent.
10 minutes	3·74	2·43	10 minutes	5·87
20 "	5·36	—	20 "	6·68
30 "	6·32	—	30 "	6·96
40 "	6·59	—	40 "	7·26
50 "	6·74	—	50 "	7·26
60 "	6·90	—	60 "	7·26
80 "	6·98	—	80 "	7·26

It will be observed that in the case of solution A the inversion was not quite complete in the time of experiment.

A second series of experiments was performed at the boiling-points of the solutions, the liquid in the flasks being kept at a gentle ebullition over a small flame.

* 30° C. is the average laboratory temperature in the Leeward Islands, where these experiments were performed.

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The following results were obtained :

SOLUTION A, CONTAINING CANE-SUGAR AND MILK CONSTITUENTS.			SOLUTION B, CONTAINING CANE-SUGAR ONLY.	
Time from commencement of experiment at which solution was withdrawn.	Invert Sugar Per Cent.	Lactose Per Cent.	Time of withdrawing solution in minutes.	Invert Sugar Per Cent.
10 minutes	5.03	2.51	10 minutes	6.50
25 "	6.38	—	25 "	6.59
40 "	6.38	—	40 "	6.50
55 "	6.46	—	55 "	6.59
70 "	6.53	—	70 "	6.59
85 "	6.67	—	85 "	6.59
100 "	6.53	—	100 "	6.59
115 "	6.60	—	115 "	6.59

To ascertain definitely that citric acid is without action on lactose, as stated by Stokes and Bodmer, an experiment was performed in which 200 c.c. of whey were acidified with 12 grammes citric acid, made up to 400 c.c. with distilled water, and boiled as in the previous experiments, portions being withdrawn at equal intervals of time and the lactose estimated.

Time of withdrawal of solution in minutes.	Lactose Per Cent.
0 minutes	2.57
30 "	2.57
60 "	2.57
90 "	2.62
120 "	2.57

This experiment shows conclusively that, as stated by Stokes and Bodmer, citric acid is entirely without inverting action on lactose even after heating for a very considerable length of time.

From the results above detailed it is obvious that the presence of some constituent of milk exerts a marked retarding influence on the inversion of cane-sugar by citric acid, and that boiling for ten minutes, as advised by Stokes and Bodmer, is insufficient to insure complete inversion. To obtain satisfactory results the boiling should be continued for forty minutes.

On the electrolytic dissociation hypothesis the velocity of inversion of cane-sugar by acids depends on the active mass of the hydrogen ions present, reduction of the number of free hydrogen ions occasioning retardation of the reaction. This reduction, one would anticipate, would be occasioned by some dissociated substance in solution, which, interfering with the solubility product of citric acid, would cause reduction of the number of free hydrogen ions, and thus retardation of the reaction.

One would expect that the effect was not due to the presence of the lactose in

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solution, and that this is the case is shown by an experiment in which two similar solutions of cane-sugar, to one of which approximately 5 per cent. of lactose had been added, were boiled with 3 per cent. citric acid, portions being withdrawn and the reducing sugars determined from time to time as in the previous experiments.

SOLUTION A. CANE-SUGAR AND LACTOSE.			SOLUTION B. CANE-SUGAR.	
Time of withdrawal in minutes.	Invert Sugar Per Cent.	Lactose Per Cent.	Time of withdrawal in minutes.	Invert Sugar Per Cent.
10 minutes	6·55	5·20	10 minutes	6·25
20 ,,	6·55	—	20 ,,	6·65
35 ,,	—	—	35 ,,	6·55
60 ,,	6·55	—	60 ,,	6·60

These results show, as one would anticipate, that lactose is entirely without influence on the rate of inversion of cane-sugar.

The practical bearing of these experiments appears to be that, in following the method of Stokes and Bodmer, ten minutes' boiling is insufficient to effect the complete inversion of all the cane-sugar present, and a longer time should be allowed for its completion. Forty minutes' boiling would appear sufficient to effect the inversion of all the cane-sugar present, if the milk under examination has been diluted down till it contains between 5 and 10 per cent. of cane-sugar.

In the foregoing experiments the determinations were made by titrating the solutions against 10 c.c. of Violette's modification of Fehling's solution diluted with its own bulk of distilled water. This method gives results sufficiently accurate for the purposes of comparison required in this inquiry; for analytical purposes, where high accuracy is desired, it is preferable to use the gravimetric method as laid down by Brown and Morris.

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DISCUSSION.

The CHAIRMAN (Mr. Blount) said that, as far as he had been able to follow the paper without having read it beforehand, the authors seemed doubtful as to what effect would be produced on the activity of the citric acid by a substance like lactose. Clearly, however, on the dissociation hypothesis, lactose, which was not an electrolyte in aqueous solution, could have no influence at all. The rapidity of inversion must depend on the activity of the citric acid. That, in turn, must depend on the degree of dissociation, which, again, depends on the degree of dilution and the nature of the solvent. This small criticism, however, did not invalidate the authors' general argument.

Dr. THORNE said that he might perhaps add to the paper a few words of explanation. The authors had sent it to him with the request that it might be published as

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he deemed most suitable, and it seemed to him to be undoubtedly a paper which should be laid before that Society. He had taken an opportunity of first reading through the paper himself, and he thought that, when it came to be printed, it would be found not to justify the Chairman's criticism. The authors' experiments with lactose were merely for the purpose of obtaining definite proof of what, as the Chairman had indicated, was *a priori* to be expected. The main question was that of the determination, in preserved milk, of quantities of cane-sugar which were small relatively to those of milk products. The method of Stokes and Bodmer seemed under such circumstances to give too low results, and the authors had endeavoured to ascertain whether better results could be obtained by increasing the time of inversion. Their experiments indicated that in the milk constituents there was something, the nature of which they had not yet been able to determine, which had a retarding influence on the inversion of the cane-sugar by citric acid. When the cane-sugar was relatively small in quantity, the retardation was sufficient to impair the accuracy of the method, and it was necessary to increase the time of inversion to forty minutes in order to obtain satisfactory results.

Mr. BAKER expressed surprise that the authors had not tried the use of invertase as an inverting agent for the cane-sugar. It had no influence on the lactose, even at the inverting temperature of 50° to 55° C., and its use would, as it seemed to him, get over all the difficulties the authors had mentioned.

Dr. SCHIDROWITZ thought that anyone looking at the matter from a purely chemical point of view would at once dismiss the idea that lactose could, under the conditions of this process, have any influence on the inversion of cane-sugar. It afforded an excellent illustration of the disadvantages of the system, or, rather, fashion, which had sprung up of regarding all chemical phenomena from the purely ionic standpoint.

Mr. J. B. P. HARRISON said that in a recent paper before the Society (ANALYST, 1904, xxix, 248) he had described a polarimetric method for the determination of cane-sugar in sweetened condensed milk. The specific rotatory power was determined before and after inversion in an aqueous solution of the condensed milk from which the fat and proteids had been removed by precipitation with acid mercuric nitrate. An excess of this reagent was used, and the inversion was brought about by the action of the excess on boiling a portion of the filtrate for seven minutes.

