PREPARATION OF ACID-FAST CARAMEL. II. THE PREPARATION OF SUCROSE CARAMEL.*

BY G. D. BEAL AND GLADYS APPLEGATE.

INTRODUCTION.

One of the authors[1] presented to this Association last year a description of a method by which an acid-fast glucose caramel might be prepared. The preparation in a similar fashion of an acid-fast caramel from sucrose has been attempted, and the results are herein set forth.

There has been a tendency, for trade reasons, to base the production of caramel on a commercial scale upon glucose. On the other hand, there are certain advantages to the possibility of using sucrose, principally its ready accessibility to the pharmacist and the laboratory man, and the convenience of using such a substance as granulated sugar.

Acid fastness, in caramel, is the ability of the caramel to withstand the hydrolyzing and polymerizing action of dilute acids. While caramels which will not pass this test have been found to yield, in general, satisfactory results as a coloring agent for beverages and articles of food, the trade now largely demands such a preparation. Since the test serves as a method of standardizing caramel preparations, no objection can reasonably be offered.

Caramel is usually prepared by heating a commercial sugar until a certain degree of dehydration has taken place, known to the operator by the appearance of the mass. As a result a considerable proportion of char is formed, which is without value as a color. The color value of the product is indefinite and the yield is variable. Various so-called catalytic agents, as chemical salts and traces of acid have been introduced, oftentimes with beneficial results in the way of lessening the time required for conversion and deepening the color of the product.

Beal and Bowey (*loc. cit.*) have found that by the use of ammonium sulfate and hydrochloric acid in little more than traces, a glucose caramel of satisfactory tinctorial value and acid fastness can be prepared with time and temperature readily controlled. Their method is as follows: Place in a beaker or casserole one hundred grams of crystallized glucose and twenty-five cc of water. Heat the mixture upon a water- or steam-bath until the sugar is liquefied. Add to this heavy syrup five cc of ten per cent. ammonium sulphate solution and three cc of a dilute hydrochloric acid made by mixing one volume of 6-normal acid with sixteen volumes of water. Place a one-liter pyrex or Jena flask in an oil-bath and heat the bath to 200° C. While retaining this temperature add the glucose syrup and continue the heating for eighteen minutes. Remove the flask from the bath and add, as soon as sufficiently cool, enough water to dissolve the caramel. Allow to stand until solution is complete and remove the char by filtration.

The acid fastness of the color is determined in the following way. Dilute twenty-five cc of the filtered caramel solution with fifty cc of water and add five

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[1] Beal and Bowey, JOUR. A. PH. A., 12, 405, 1923.

cc of 6-normal hydrochloric acid. Boil the mixture gently in a small beaker. There should be no perceptible change in color on boiling for thirty minutes.

EXPERIMENTAL.

Sucrose was caramelized according to the method of Beal and Bowey, varying only the time of heating, and the caramel dissolved in five hundred cc of water. The quantity of char formed was determined by filtering the solution through a Gooch crucible. The char adhering to the flask was loosened by boiling with ten per cent. sodium carbonate solution and its weight added to that first obtained.

When the bath temperature was 200°, the mixture began to bubble at the end of fifteen minutes' heating, and in eighteen minutes the flask was almost filled with froth. The moment of frothing was found to vary with the temperature of the bath.

The relative color values of the different preparations were determined by means of a Dubosq colorimeter with a "daylight blue" lamp. For comparison a solution of glucose caramel, made by the method of Beal and Bowey, was used. The relation of color values is expressed arbitrarily in millimeters of solution having a color density equivalent to that of a definite column of the standard solution. The color values are, therefore, expressed in inverse ratio to each other. The order of the color of the sucrose caramel was sufficiently near that of glucose caramel to permit of ready comparison.

TABLE I.

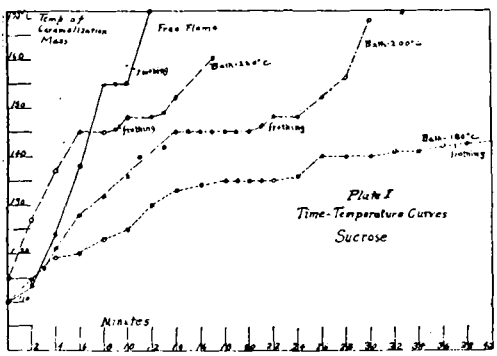
Effect of Caramelization of Sucrose with Time and Temperature of Bath Controlled.

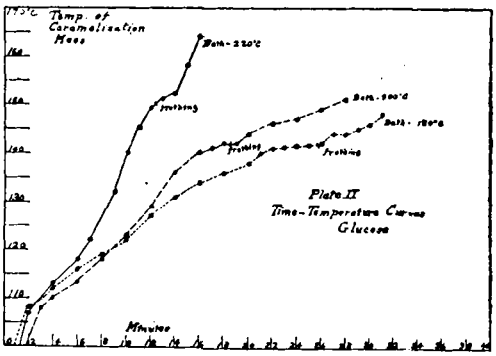
Series.	Temperature, deg.	Time.	Color value.	% Char.	Acid-fast.
A1	200	18	11	50.0	Yes
A2	200	16	13	0.875	Yes
A3	200	14	42	0.199	Yes
A4	200	12	51	0.165	Yes
A5	200	10	68	Insignificant	Yes
B1	195	18	13	30.0	Yes
B2	190	18	24	25.0	Yes
B3	185	18	35	0.50	Yes
C1	200	18	5	6.8	Yes
C2	195	18	17	0.1	Yes
C3	198	18	19	1.3	Yes
C4	200	17	18	1.0	Yes
C5	200	19.5	13	1.0	Yes
C6	200	30	25	1.0	Yes

Most of the char is apparently formed between the sixteenth and eighteenth minutes of heating. Samples which were not heated over sixteen minutes did not froth. Much of the material classed as char was really slowly soluble in water. In preparing Series C 100 cc of water was added to the caramel at the conclusion of the heating and the flask allowed to remain in the oil-bath three minutes longer. The remaining 400 cc of water was then added, bringing about more complete solution of the material.

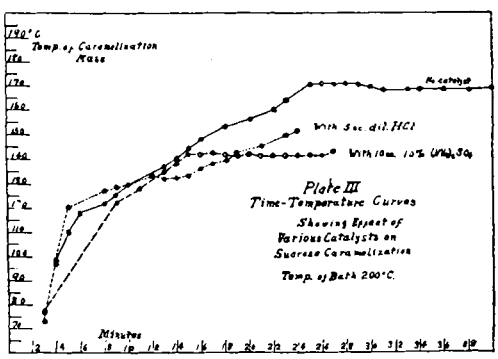
In order to more accurately determine the temperature at which caramelization takes place, a thermometer was placed in the flask during the heating. The oil-bath was used at 180° and 200°, and the flask also heated over a free flame.

The temperature was found to rise rapidly to 110° and somewhat more slowly to 140°, when the mass begins to take on color. At this point the color deepens rapidly with practically no temperature rise until the mixture is nearly black, when the temperature begins to rise a second time, the mass froths, and char begins to form. Plate I consists of time-temperature curves for sucrose, Plate II for glucose. Plate III shows a comparison of the temperature curves with and without a catalyst.





From an inspection of these curves it would seem that the best caramel would be obtained when the heating is stopped at the point where the temperature of the mass begins to rise after the flattening out. At this point we might expect to obtain maximum color with a minimum of char. By burning a sample of sucrose until this temperature rise was reached but before the mass had begun to froth, a caramel with a color value of 10 was obtained, with only 0.5% of char. By burning another portion until frothing had begun, a color value of 4.5 was reached, but 3% of char was obtained.



Apparently the process of caramelization of glucose and sucrose is in each case the resultant of a series of very definite chemical reactions, of an endothermic nature. If caramel is formed by a dehydration of the sugar molecule we might expect just such behavior. The various substances used catalytically would also tend to act as dehydrating agents, accounting for the fact that the flattening point in the curves in Plate III comes at a lower temperature with them than when they are omitted.

SUMMARY.

1. Sucrose will yield an acid-fast caramel when treated according to the method used by Beal and Bowey for glucose caramel. The color value of this caramel is practically the same as that of glucose caramel.

2. Taking the temperature of the sugar mass during caramelization shows a

definite endothermal reaction. Apparently the caramelization of any quantity of sugar can be readily controlled by temperature readings in the mass.

The senior author is continuing the investigation of this point, as well as the standardization of caramel preparations.

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ELECTROMETRIC ASSAY METHODS FOR CRUDE DRUGS. II.*

BY WILLIAM JAMES MCGILL AND LEONARD RANSOM WAGENER.

It has already been pointed out by one of the authors[1] as well as by others,[2] that the indicators at present recommended by the U. S. P. for alkaloidal titrations have been chosen with little regard for the conditions involved in such titrations. The inaccuracies resulting from their use are of relatively small magnitude, and yet if the Pharmacopœia is to be accepted as a compilation of scientific standards, the requirements contained therein should be as rational as is consistent with practicality. Adoption of the proper indicator for official acidimetric titrations can work hardship on no one; the replacement of the litmus paper test for the alkaloidal salts would give more uniform products than are now on the market. In some of our preliminary work on the p_H values of various alkaloidal salts, samples from different lots were found to vary greatly in this respect, although all of them conformed with the U. S. P. litmus paper test. More accurate determinations made possible by the substitution of a Leeds and Northrup type K potentiometer for our earlier portable set-up, have given practically the same results.

We have also previously emphasized the advantages to be gained by the substitution of electrometric methods in the assay of crude drugs, replacing the tedious percolation or shaking-out methods. Admittedly, electrometric crude drug assays give only "proximate" results, which is true of any method we may employ. Actually, the electrometric method of titration gives results closer to the truth than the indicator method.

Much of the literature found in the journals on the determination of hydrogen-ion concentration we believe to be of little value, because the work so reported seems to have been done without any very clear conception of the theoretical considerations underlying the behavior of aqueous solutions of electrolytes or of the apparent anomalies in the behavior of such solutions. For example, the "neutral salt" effect on the end-point of an electro-titration has not been precisely determined, and it is conceivable that there are factors which influence the true end-point in titrating an alkaloidal residue and whose influence cannot be easily formulated so that our results can be accordingly corrected. The very short method of preparation and purification which we employ admittedly retains some of the inert extractive of the crude drug in the residue to be dissolved and titrated. The only criteria

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* Scientific Section, A. Ph. A., Asheville meeting, 1923.

[1] McGill and Faulkner, JOUR. A. PH. A., 11, 1003, 1922; McGill, *J. A. C. S.*, 44, 2156, 1922.

[2] Evers, *Pharm. J.*, 470, 1921; Masucci and Moffet, JOUR. A. PH. A., 12, 609, 1923.