Papers Presented to Local Branches

PURIFIED CARAMEL AND THE STANDARDIZING OF CARAMEL SOLUTIONS.*

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The desire of the Committee engaged in the revision of the National Formulary to provide for preparations of uniform color wherever prepared if made in accordance with the Formulary recipes, has occasioned considerable study. This problem has been especially referred to a sub-committee on color standards whose reports have aroused considerable interest among those outside of the Committee as well as the members thereof.

The colorings most commonly used by pharmacists in elixirs, syrups, etc., at the present time, are caramel and cudbear. The attempt to standardize such indefinite substances has not proven an easy task and while a number of methods have been proposed, opinion has not yet crystallized into a conclusion that any of those proposed has entirely and satisfactorily solved the problems.

In the present communication the writer will confine himself to the consideration and review of the various propositions relating to caramel and leave the consideration of the problems relating to cudbear for another occasion.

Caramel is a complex mixture of a number of organic compounds produced by heating sugars to a temperature high enough to produce dark brown colorings without charring and, after the tumefaction has ceased, adding water. It is believed that it is now produced on the commercial scale entirely from starch sugar or glucose.[1] For the purpose of this communication it is unnecessary to enter into a detailed discussion of the chemistry of caramel. It is sufficient to state that it contains several coloring substances, an odorous principle separable by distillation, usually some undecomposed sugar, and a trace of caramelan a highly hygroscopic substance having a bitter taste and colorless when pure and varying proportions of water. The gravity usually ranges between 1.300 and 1.390; according to Wagner the manufacturer usually aims at 35° Baume = 1.312 at 15° C. The ash is usually quite small, rarely over 10 mg. per gram, and this commonly consists of sodium salts, chloride, sulphate and carbonate.

On heating sugars to the temperature necessary to produce caramel several dark colored bodies are produced some of which are soluble and others insoluble in either water or alcohol and at least one of these colored substances so produced requires for solution the presence of alkali or alkali carbonate and for this reason the manufacturer adds sodium carbonate or ammonium carbonate or ammonia in

*Read before the Philadelphia Branch of the American Pharmaceutical Association Tuesday evening, February 6, 1912.

[1]For details of the commercial methods of manufacturing Caramel, see Frankel's translation of Wagner's work on Starch, Glucose, Starch, Sugar, etc.

the process of manufacture. There is also usually produced a small amount of a brown colored lustrous substance not soluble in any of these solvents.

The writer has recently attempted to review and test out the various suggestions that have been offered as a means of standardizing Caramel and its solutions. This work has led him into experiments along certain lines not covered by the other investigators.

One of the first propositions made was, that in order to obtain uniformity, the pharmacist should prepare his own caramel and formulas for this purpose were proposed. The initial proposition presented in the Bulletin of the American Pharmaceutical Association, December, 1909, page 479, "is to heat 1 pound of sugar on the sand bath at 180° C. for 2 hours and dilute it to 1 pint." All of the authorities are agreed that on heating sugar to this temperature and cooling there is formed the allotropic modification of cane sugar known as "barley sugar." However, I tried the suggestion and, as was to be expected, obtained a mass with scarcely any darkening and which could in no way be considered as Caramel.

A later suggestion offered (Bulletin of N. F. Committee No. 31, page 364) was "sugar 1000 Gm., water a sufficient quantity. Heat the sugar in an appropriate vessel on a sand bath at 200° C. for 2 hours. Then add to the caramelized fluid enough boiling water to make the finished product measure 1000 cc." This product was to be standardized by requiring that "1 cc. of this diluted with 399 cc. of distilled water should have the same intensity of color as the Standard Caramel Testing Solution." The standard test solution was Stevens Standard, which will be referred to later. The adjustment of the Caramel to the standard was obtained by either dilution or concentration whichever was required.

A test of this method showed that it did produce more or less Caramel, but that for the complete caramelization of the sugar a somewhat higher temperature, 210° to 215° C., was necessary. The resulting product was treated with several portions of boiling distilled water, the solution filtered and concentrated to the volume directed in the formula and this compared with a good commercial sample of Caramel was deficient in tinctorial power and had to be further concentrated to obtain a liquid comparing with the standard proposed. The residue on the filter and in the dish was then washed with a warm weak solution of sodium carbonate and this yielded a dark brown solution of the coloring insoluble in the water alone.

A practical difficulty arises in carrying out this formula for Caramel. On heating sugar to the temperature necessary there is given off odorous vapors and fumes that fill the entire building and unless made under a hood connected with a good draught the manufacture of Caramel would be impracticable and the average pharmacist could certainly not make it satisfactorily nor economically. The resulting product as made on the small scale by different individuals will also vary considerably in composition.

There is still another phase of the subject that must be considered. If the National Formulary introduces a formula for Caramel, then that formula even though it is not in keeping with the commercial process becomes the legal formula and the product, even though inferior, becomes the legal standard for all Caramel. This might prove a very serious source of annoyance and trouble to other industries in which the consumption of Caramel is vastly greater than in pharmacy. For this reason I am constrained to believe that the proposition that the N. F.

should introduce a formula for Caramel and that the pharmacist should prepare his own is untenable.

For Tincture of Caramel a formula has been proposed in the Bulletin of the N. F. Committee No. 31, page 365, to be made as follows:

"Caramel..... 100 Gm.
Alcohol and water, each a sufficient quantity.

"Dissolve the Caramel in such quantity of alcohol 1 volume and water 3 volumes as may be necessary so that 1 cc. of the tincture when diluted with water to 100 cc. shall have the same depth of color as a standard solution prepared in accordance with the Stevens Standard Caramel Testing Solution."

The standard test solution proposed by Professor Stevens is as follows:

"Place 0.5 gm. sugar in dry test tube 20 mm. diameter. Immerse the tube to a depth of 5 cm. in a sulphuric acid bath, previously heated to 210° C. and keep at that temperature for 20 minutes. Remove the tube and when cold dissolve in sufficient water to make 200 cc. Add 50 cc. alcohol and sufficient water to make exactly 250 cc."

Several of the members who experimented with this formula claim that concordant results were not always obtained and that the width of the test tube and the degree of immersion in the bath as well as the quality of sugar used materially altered the results. The objection to sulphuric acid as a bath was met by a suggestion from Mr. Otto Raubenheimer that a bath of petrolatum be substituted therefor. As a result of my experimenting with this formula following out carefully the directions as to the amount of sugar, size of test tube, etc., I was enabled to obtain fairly uniform results. I prefer, however, to use a cottonseed oil bath to either sulphuric acid or petrolatum. On carrying out this test strictly in accordance with the instructions and attempting to dissolve Caramel in water it was found that the mass clung tenaciously to the test tube and was removed with difficulty. Further, that it was not entirely soluble in water. The insoluble portion was collected on a tared filter dried and weighed 145 mg. of residue insoluble in water. On heating this residue with a mixture of 10 cc. Sodium Carbonate test solution and 90 cc. of distilled water there dissolved out 75 mg. and I obtained a brown solution much darker in color than the original standard test solution. On making this up to the same bulk and then standardizing against the standard in Nessler tubes this was found to be 1.5 times as strong as the original standard. There still remained on the filter a portion of dark brown scales of colored material that was not soluble in either water, alkali solutions, alcohol or ether. These experiments were repeated with but very slight difference amounting to only 5 mg. of residue insoluble in water and the resulting fluids were practically identical.

Stevens Standard Caramel Testing Solution is subject to the criticism that it not only involves considerable time and routine on the part of the pharmacist, but still more, that it does not represent the entire Caramel as the stronger portion of the Caramel coloring, that requiring alkali for solution, is not taken up and his solution consequently represents only a part of the Caramel.

Dr. George A. Menge (American Journal of Pharmacy, March, 1911, 113) has criticized the Stevens process for standard caramel test solution and has recommended in place thereof a test solution made as follows:

"Make a sulphuric acid solution by adding 2 cc. of pure concentrated sulphuric

acid (specific gravity 1.84) to 12 cc. of water. Take 0.5 gm. of sugar in a test tube, add 5 cc. of the acid solution described above, and heat the mixture in a boiling water bath, with mixture continually submerged and with constant agitation, for exactly 5 minutes. Immediately add a littl cold water and then 35 cc. of the U. S. P. test-solution of potassium hydroxide; finally dilute to 100 cc."

I have found this method to yield fairly uniform brown colored solutions but not entirely of the same tint as that obtained by the Stevens method. The Menge process is the color reaction of glucose with potassium hydroxide which is well known under the name of Heller's or Mohr's Test when applied as a qualitative test in the examination of urine. The color is produced by glucose and not by Caramel and it is entirely an arbitrary standard as applied to standardizing of Caramel solutions.

F. A. Upsher Smith (American Journal of Pharmacy, September, 1911, 411) recommends a process for standardizing Caramel by comparison with an arbitrary standard consisting of a Nesslerized solution of ammonia using a standard solution of ammonium oxalate to which 2 cc. Nessler's solution is added as the arbitrary standard fixed for comparison. Here again we are comparing Caramel with another coloring which is dissimilar.

From the writer's experiments he has become convinced that the preparations of Caramel should be standardized against the Caramel color itself and not against substitutes therefor as has been done in these proposed standard test solutions. This has led to the attempt to purify commercial Caramel so as to isolate the coloring material and use this as a basis for a standard color solution to be used either as a coloring itself or to standardize commercial Caramels. It was argued that if a purified Caramel of fairly definite composition could be produced that standard solutions could then be made with but very slight variation that could be used for such purpose. Commercial Caramels contain an uncertain quantity of unconverted sugar and probably traces of caramelan and experiments to produce a desiccated Caramel by evaporation of a number of commercial samples yielded a hygroscopic material which could not be gotten into a sufficiently definite form to yield uniform results.

Experiments were then tried upon the precipitation of the Caramel colorings by strong alcohol and as a result of a number of trials the following formula was evolved for a Purified Caramel:

PURIFIED CARAMEL.

Caramel	1000 Gm.
Alcohol	3500 Cc.
Monohydrated Sodium Carbonate	4 Gm.
Water, a sufficient quantity.	

Weigh the Caramel in a capacious bottle or flask and add 250 cc. of boiling water and thoroughly mix. Then gradually add 3000 cc. of alcohol, shaking after each addition. Then set aside for six hours; decant the alcohol on to a filter and wash the precipitated Caramel color with two portions of 250 cc. each of alcohol, decanting each time the alcohol on to the filter. Drain the alcohol thoroughly from the precipitate and dissolve it in 1500 cc. of warm water. Add the Monohydrated Sodium Carbonate, filter the solution and evaporate it to the consistence of a thick syrup. Spread this upon sheets of glass or tin plates and when dry scrape off in scales the Purified Caramel and dry further in a desiccator over Sulphuric Acid for a day or until it ceases to lose weight.

In this process the alcohol dissolves out of the Caramel, the unconverted sugar and the bitter and most of the odorous principles and only a small amount of the coloring. By distillation the alcohol can be recovered with but very little loss and used over again. The Purified Caramel so made is in dark brown, shining, translucent scales, free from bitterness and without any perceptible sweet taste and practically odorless. It is non-hygroscopic and dissolves readily and clearly in water diluted with alcohol. The yield averaged 27 per cent., and the Purified Caramel when compared in solution with the Caramel from which it was made showed a tinctorial value of three times that of the latter. A sample of the Purified Caramel so made was exposed in an open vessel to the atmosphere during a rainy spell of two days when the air was charged with moisture, yet it remained in dry non-adhering scales which had absorbed but very little water and was readily dried by being placed for a short time in the desiccator. The addition of the small amount of Sodium Carbonate was found to be necessary as without it the Purified Caramel when once made and dried was not again entirely soluble in water. This is readily understood from the preliminary explanation regarding the composition of commercial Caramels.

Tincture of Caramel.—I submit the following formula for Tincture of Caramel:

TINCTURE OF CARAMEL.

Purified Caramel	50 Gm.
Ammonia Water	10 Cc.
Water	740 Cc.
Alcohol	250 Cc.

Mix the liquids and dissolve the Purified Caramel in the mixture; filter if necessary.

Tincture of Caramel so made appears to be permanent and can be used either as a coloring or to standardize Caramel solutions. 1 cc. tincture diluted with 99 cc. distilled water or better still 199 cc. distilled water will form comparative solutions against which commercial Caramels can be readily standardized.

It is to be noted that the formula proposed by the Committee for Tincture of Caramel was 10 per cent. of the Caramel prepared in accordance with the formula given. The formula now submitted contains but 5 per cent. of the Purified Caramel, but as this is three times the strength of the commercial Caramel the tincture resulting from this formula is very materially stronger than the formula first submitted to the Committee. If 5 per cent. be considered too strong then it can be reduced to 2.5 per cent. or to such strength as may be agreed upon.

A COMPARISON OF TEN SAMPLES OF CUDBEAR.*

HUGH CRAIG.

Ever since I was first attracted by the red and green show globes in the apothecary's windows, the color of pharmaceutical preparations has been of interest to me, and this interest has led me to much experimentation. This paper is the result of one series of experiments. But I had a particular reason for undertaking the experiments with cudbear: I was desirous of reconciling the frequent state-

*Read at the February meeting of the N. Y. Branch.