comes more difficult in that the desirable plant is not one which shows great medicinal qualities alone, but one which at the same time produces an abundance of leaves and roots. In the several years during which this work has been progressing, nothing has been found to indicate that any relationship exists between the physical appearance of the plant and its alkaloidal content. While no such general relationship may exist, there is always the possibility, however, of some of those unusually rich plants possessing at the same time the desired physical excellence which would make them the most valuable type from both the medicinal and the agricultural standpoint.

Much has been said and written concerning the production of alkaloids in belladonna. The influence of various soil constituents, excessive rainfall and drought, sunlight and shade have all been the subject of repeated investigations and the conclusions reached do not lack in variation. Of what value are all such investigations when the range of variation in individual plants is frequently greater than the difference in alkaloidal content attributed to different fertilizers or different climatic conditions? Until a type of plant is found which is at least fairly constant in the quality of alkaloids it produces, vital conclusions cannot be drawn from experiments such as those mentioned. The factor of individual variation must first be eliminated before the influence of environment can be definitely determined.

THE PREPARATION OF PURE SUCROSE AND DEXTROSE CARAMELS.

GEORGE D. BEAL AND HARPER F. ZOLLER, URBANA, ILL.

The attention of the authors was first directed to the preparation of caramels by the failure of the qualitative tests for caramel in a number of liquids to which it had been added as a coloring agent. In order to study these reactions we set out to prepare pure caramel and observe its behavior. A review of the literature on the subject interested us in the composition of caramels, and it is on this account that we have studied carefully the preparation of the caramels in the purest condition.

The recent communications of Beringer and others have induced us to report our findings to this section in the hope that they may be of some assistance. In nearly all papers caramel has been considered as a mixture of the products of the action of heat on sugars. Prof. Beringer has recently given us a method for the preparation of a purified caramel based on the use of alcohol and sodium carbonate, the latter to dissolve any water insoluble products. In our method we have avoided the formation of this insoluble product by a shorter time of heating, rendering unnecessary the use of the alkali.

Caramel may be defined as an intermediate product in the decomposition of a carbohydrate by heat, and its composition varies according to the source. This will be taken up in a later paper, now in preparation. In addition to the caramel a large amount of vapor is formed, consisting in part of water, formalde-

hyde, acetaldehyde, benzalhyde, acetic acid, and carbon dioxide. This is in the particular case of sucrose caramel.

Caramel may be prepared in the laboratory by heating the desired sugar in a flask suspended in a heating bath at a temperature of 210° C. Personally, we prefer a bath of cottonseed oil, although we have used rape-seed oil, paraffin, sulphuric acid and Wood's metal.

Preparation. In our experiments we proceeded as follows: 100 gms. of granulated cane sugar or crystalized dextrose were placed in a 500 cc. Florence flask, suspended in an oil bath together with a thermometer and heat applied. When the temperature of the bath reached 210° C. it was maintained at that point for 30 minutes.

Sucrose begins to melt at 160° and between 180° and 190° it has a clear yellow color, being then in the form of barley sugar. As the temperature rises to 210° the mass begins to foam, rapidly darkening in color, giving off vapors rich in acetic acid and benzaldehyde.

Dextrose begins to melt at 140°. As the temperature reaches 180° it begins to froth and with the rise in temperature to 210° the color changes from grayish white through yellow to orange, then a golden brown and finally brownish black.

When caramelization was completed the flask was removed from the heating bath, partially cooled, then about 250 cc. of water added and the mixture allowed to stand until solution was complete. We found that by caramelizing in this manner no insoluble substance was formed. If a caramel flavor is desired this solution may be used.

Purification. The caramel solution thus obtained contained unchanged sugar and all the decomposition products not yet volatilized. If the solution be evaporated at this point, a sticky mass will be obtained.

There are three methods of purification, only one of which we have found to be satisfactory. Caramel is not as soluble in alcohol as in water, therefore a concentrated aqueous solution of caramel may be precipitated by pouring it into alcohol. This requires a comparatively large amount of alcohol, and to obtain a pure product requires several precipitations, since part of the sugar and probably some of the other decomposition products are precipitated with the caramel. For this reason the method is expensive and unwieldy.

Caramel is unfermentable, although some varieties of mould will grow upon it. If the caramel solution is kept at a temperature of 35° and some yeast added, the sugar may be fermented out in about three days time. To remove the yeast cells, it is necessary to filter the fermented solution through a Pasteur-Chamberlain filter or through a layer of infusorial earth on a filter paper in a Büchner funnel. The caramel prepared in this manner is extremely bitter and acid to the taste. The reason for this is that the fermentation removes only the sugar. Also, the caramel cannot be obtained in a dry condition free from stickiness.

We sought for a cheap and rapid method for freeing the caramel from all other decomposition products as well as from the sugar. Sabaneef and Zsigmondy both state that caramel passes very slowly through dialysis membranes. We found that membranes of either parchment paper or collodion might be used, diffusion through the collodion being more rapid. The preparation of collodion membranes for dialysis is described by one of us in another paper.

A membrane, prepared in a cylindrical beaker or an Erlenmeyer flask is about half filled with the caramel solution, a small glass tube tied into the neck, and the bag suspended in water, with the water and solution at the same level. The diffusion is allowed to continue for thirty-six hours, either in running water, or water which is changed frequently. A small amount of caramel passes through the membrane and is lost. The solution at the end of the dialysis is odorless, and has only a faint bitter taste. It has only a very slight reducing power which we believe to be due to the caramel itself.

The dialysed solution is then evaporated to a thick syrup and poured onto clean glass plates. When the film of caramel becomes dry, it may be scaled off. Working in this way, we obtain a yield of 15 percent of the original weight of sugar.

The caramel forms shiny, reddish- or brownish-black scales, perfectly dry and readily soluble in water or alcohol. Sucrose caramel is more intensely colored than dextrose caramel. The ratio of the color of solutions of the two caramels of the same concentrations is about ten to one. For this reason we recommend cane sugar as the source of caramel, although it is stated on good authority that by far the greater part of that on the market is made from glucose.

As stated above, the composition of caramel varies according to its source. We have found that the composition of each variety of caramel is constant in a number of preparations, by a determination of carbon and hydrogen in the caramels themselves and their benzoyl derivatives, and determinations of their molecular weights.

SUMMARY.

Caramel is best prepared by heating cane sugar or glucose at 210° for thirty minutes. A somewhat higher yield is obtained by longer heating, but some insoluble matter is formed at the same time.

The best method of purification is found to be dialysis in a collodion membrane.

Sucrose caramel solutions are more densely colored than solutions of dextrose caramel of the same concentration.

All of this work is being continued and we hope to report progress from time to time.

CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS, June, 1913.