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The Nature of Sucrose Caramel

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In view of the observations on this subject recorded in the literature,[1] a study of caramel was undertaken in this Laboratory with the thought that the results of previous studies would lend themselves to an investigation of some of the early stages of coalification of a carbohydrate material. It soon developed, however, that the products "caramelan," "caramelen" and "caramelin" described previously as the true caramel constituents are mixtures, and that caramel in reality consists of a mixture of colorless compounds, closely related to the original sucrose, and a dark-brown, "humic" substance which shows the properties of a lyophobic colloid. The latter is kept in dispersion ("protected") by the former, and, on separation, coagulates irreversibly. While the study does not show promise of accomplishing the original purpose, and is being discontinued in this Laboratory, the work already done is being put on record here in the hope that the investigation will be completed elsewhere.

Experimental

Caramel was prepared by heating sucrose to a weight loss of 12% or more. No fixed temperature for the melting and decomposition of sucrose was observed, the process beginning (after several hours) at a temperature as low as 140°. At higher temperatures, it proceeds at a more rapid rate, but the caramel is of the same composition. Heating *in vacuo* or in the open air also leads to the same products.

The non-volatile products consist of the colloidal "humic" substance, I, and, as far as has been ascertained, of two colorless, amorphous substances, II and III. The presence of I in the colloidal state markedly affects the physical and chemical properties of II and III, increasing their thermal stability and diminishing their solubility. To illustrate, in the free state II and III decompose easily, being transformed to I and volatile products, and are soluble in a number of solvents. On the other hand, as the concentration of I increases during the caramelization process, they become very stable toward heat and increasingly difficult to dissolve, particularly in organic solvents. One may even prolong the heating of caramel to a point where it is transformed from a viscous fluid to a hard brittle mass and no longer evolves gas: even though this product is kept for hours at a temperature as high as 230° it still contains only about 25% of I, the rest being about 43% of II and 32% of III. This "hardened" caramel—designated by Gélis[1] as a "caramelin" modification—is insoluble in organic solvents and in cold water. It is slowly broken up by boiling water, and, on Soxhlet extraction, yields a water-soluble dispersion of I in II and III and a solid, non-dispersable residue of I. The hardening stage is reached roughly at about 20% weight loss. Before reaching this limit, the caramel preparations remain rather completely water soluble.

In order to separate I from II and III, the dried extract from "hardened" caramel, or a caramel of less than 20% weight loss, is digested with about four times its volume of methyl alcohol. Two phases are formed: the upper phase contains the bulk of the solvent, most of II and III and a comparatively small part of I; the lower phase, which is highly viscous, contains the larger part of I, the remainder of II and III and some solvent. The lower phase is separated from the upper one and vigorously stirred with fresh methyl alcohol. Again two phases are formed, and the operation is repeated until finally, due to partial coagulation of I, the lower phase becomes semi-solid. It is now transferred to a Soxhlet and further extracted with methyl alcohol. Of the protective substances, II is more soluble than III, and its extraction is complete long before all of III is dissolved. As coagulation progresses further in the Soxhlet, the residue, which in the earlier stages readily formed colloidal solutions in water, becomes for the most part non-dispersable. In order to accelerate the extraction rate of the residual III, water is now substituted for methyl alcohol. The water rapidly dissolves III and disperses some of I; but by far the greater part of the latter remains as a solid residue which shows no tendency to disperse even though the extraction is continued for weeks. The water extract is dried and treated with methyl alcohol, as before. Except for the absence of II, its behavior is the same as that of the original "softer" caramels, or extracts from "hardened" caramel.

The separation of II from III is based on the fact that the latter is practically insoluble in propyl alcohol (Table II). On adding this solvent to a methyl alcohol solution of a mixture of these substances, a flocculent precipitate is obtained which consists largely of III, and, incidentally, contains the larger part of the contaminating traces of I still present. There remains a small amount of III in solution, practically all of which precipitates, together with some II, on removal of the methyl alcohol by fractional distillation. The substance II which remains dissolved shows a specific rotation $[\alpha]^{25}\mathrm{D}$ of +24.5°.[2] A remaining trace of I may be removed by charcoal.

The precipitate from the methyl alcohol solution contains a rather large amount of II, from which it is freed by repeated solution in methyl alcohol and reprecipitation with propyl alcohol. The progress of purification of III can be followed by observing the specific rotations of successive precipitates, which approach a constant value, as shown in Table I. Starting with 3.3 g. of precipitate,

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[1] Gélis, *Ann. chim. phys.*, **52**, 352 (1858); **65**, 496 (1862); Cunningham and Dorée, *J. Chem. Soc.*, **111**, 589 (1917).

[2] Since II does not easily withstand heating, and is very hygroscopic, its drying to constant weight is difficult.

the weight of each subsequent precipitate is shown together with its specific rotation, $[\alpha]^{25}_D$.

TABLE I

Precipitate, g.	3.3	0.9	0.52	0.25
$[\alpha]^{25}_D$	+40°	+54°	+60°	+63°

The contamination of the precipitates by small amounts of I occasionally makes complete solution in methyl alcohol impossible, due to the formation of two phases. By charcoal filtration, I can be removed, but appreciable amounts of III are also retained.

The coagulated "humic" substance I is infusible and is thermally stable in the temperature range of these experiments, namely, up to 230°. Although it formed originally a colloidal dispersion, it cannot be dispersed again by any ordinary solvent, even in the presence of the substances II and III. It seems to be impossible to free it completely of the last traces of II and particularly III, even by prolonged extraction. This may be understood in the light of its large absorbing surface, particularly since charcoal retains III strongly. It appears difficult to find criteria for the chemical homogeneity of such a highly polymerized substance, and none can be offered at present. An "exhaustively" extracted sample (C, 62.0; H, 4.9) gave only a diffuse x-ray diffraction pattern, with intensity peaks indicating atomic spacings of 2.3 and 3.9 Å. (calculated by Bragg's law).

The substance II is colorless, amorphous and has a bitter and slightly burning taste; it is extremely hygroscopic, soluble in pyridine, glacial acetic acid and the lower alcohols (*cf.* Table II); slightly soluble in acetone; insoluble in ethyl acetate, ether, hydrocarbons and chlorinated hydrocarbons; it has no sharp melting point, but softens, melts and decomposes above 95°. With phenylhydrazine it forms an oily product and glucosazone. It reduces Fehling's solution. *Anal.* C, 43.9; H, 6.54. On refluxing with acetic anhydride and sodium acetate, an acetyl derivative is formed, which can be precipitated by water from alcoholic solution. *Anal.* C, 50.1; H, 5.60.

The substance III is colorless, amorphous and of sweetish taste; it is less hygroscopic than II; less soluble in the above organic solvents, and insoluble in all solvents which do not dissolve II. Its solubility decreases sharply in the lower alcohol series from methyl to *n*-propyl alcohol (Table II). It softens, melts and decomposes above 140°, and begins to decompose at lower temperatures without softening. It reduces Fehling's solution and gives instantaneous color reactions with resorcinol and diphenylamine in hydrochloric acid, and with β-naphthol in sulfuric acid, as does fructose. While III itself forms no water-insoluble compound with phenylhydrazine, the product of hydrolysis of III with dilute sulfuric acid reacts forming an oil and glucosazone. *Anal.* C, 44.9; H, 6.34. An acetyl derivative is obtained, as above: *Anal.* C, 50.0; H, 5.80.

TABLE II

SOLUBILITY OF II AND III IN ALCOHOLS AT 25°, IN WEIGHT PER CENT.

	Methyl alcohol, abs.	Ethyl alcohol, abs.	*n*-Propyl alcohol, abs.
II	Very soluble	3.0	2.4
III	4.7	0.026	0.005

Molecular weights of II and III and their acetyl derivatives, and also of sucrose and sucrose acetate, obtained by freezing point lowering of catechol,[3] are arranged in Table III. It is seen that sucrose, but not its acetyl compound, undergoes cleavage in catechol; the same evidently applies to III, while the value for II may be too low on account of moisture.[2]

TABLE III

MOLECULAR WEIGHTS IN CATECHOL

	Found	Calcd.
II	210–270	
II Acetate	*ca.* 650	
III	160–164	
III Acetate	525–675	
Sucrose	174	342
Sucrose octa-acetate	600–700	678

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Summary

1. Caramel, prepared by heating sucrose to a weight loss of 12% or more, *in vacuo* or in the open air, is a colloidal dispersion of a lyophobic "humic" substance I in a mixture of two protective substances, II and III.

2. I, on separation from II and III, coagulates irreversibly to a dark brown, infusible, insoluble (in all solvents tested) mass and shows a diffuse x-ray pattern. II and III are colorless, thermally unstable, amorphous substances, hygroscopic and soluble in a number of organic solvents. The specific rotation of II is +24.5°; of III slightly higher than +63°. Other properties are described.

3. In the presence of the colloidal substance I, the protective substances II and III show a marked thermal stability and resistance to solution.

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[3] Smith and Howard, THIS JOURNAL, 57, 512 (1935).