[CONTRIBUTION FROM THE NEW YORK SUGAR TRADE LABORATORY, INC.]

THE COMPOSITION AND CALORIFIC VALUE OF SIRUPS AND MOLASSES DERIVED FROM SUGAR CANE.

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Very accurate data are available as to the calorific value of the sucrose and invert sugar in sirups, but very little information is obtainable regarding the actual combustion units of the organic non-sugars which make up usually from 4 to 18% of the dry substance in the sirups and molasses derived from the sugar cane. It was to gain more knowledge upon the latter subject that the present investigation was begun.

Changes in Constituents of Juice during Sirup Manufacture.

The organic non-sugars in the sirups and molasses derived from the sugar cane consist partly of products derived from the juice of the sugar cane and partly of decomposition products formed during manufacture. In order to arrive at some understanding of the nature of these substances a brief reference must be made to the changes produced in the constituents of cane juice by the processes of clarification, filtration and evaporation.

In Table I a comparison is given of the approximate composition[1] of sugar cane juice and of low grade cane molasses.

TABLE I.—COMPOSITION OF SUGAR CANE JUICE AND MOLASSES.

	Juice. %	Molasses. %
Water	83.00	20.00
Sucrose	15.00	30.00
Invert sugar	0.80	30.00
Ash	0.45	8.00
Proteins	0.05	..
Nucleins	0.03	..
Proteoses	0.01	0.10
Nitrogenous bases (guanine, etc.)	Trace	0.40
Amids (asparagine, glutamine, etc.)	0.05	0.50
Amino acids (aspartic, etc.)	0.12	1.50
Other organic acids (aconitic, etc.)	0.10	1.50
Gums and pectins	0.10	2.00
Fiber particles	0.12	..
Fat and wax	0.10	..
Earthy matter	0.06	..
Chlorophyll, etc.	0.01	..
Decomposition products { lactic acid, saccharinic acid, glycinic acid,[2] caramel, etc.	..	6.00
	100.00	100.00

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[1] According to results given in *Bull.* 91 (1907) of the Louisiana Sugar Experiment Station.

[2] The term "glycinic" or "glucinic acid" was first introduced by Peligot to describe one of the unstable acid decomposition products formed by heating glucose with alkalies. See Lippmann's *Chemie der Zuckerarten*, 1, 330–1.

In the clarifying operations of liming, heating and filtering a considerable change is effected in the composition and distribution of the juice ingredients. The suspended impurities, removed from the cane in milling, such as fiber particles, fat and wax, dirt, chlorophyll, etc., are precipitated, the proteins and nucleins are coagulated, and a part of the gums and ash constituents are removed. But with the elimination of these ingredients a new class of degradation and decomposition products enters into solution. By the action of lime and heat a part of the nucleins are decomposed into nitrogenous bases, or purins, and variable amounts of the reducing sugars are destroyed with the formation of soluble salts of lactic, saccharinic, glycinic and other acids. A certain amount of sucrose also undergoes dehydration with the formation of caramel. The extent of these changes will vary with conditions. When an excess of lime is used the formation of new substances by the decomposition of nitrogenous ingredients and reducing sugars may proceed to such an extent that their presence affects the flavor of the product, the sirup, or molasses, being then, as is said, lime-burnt.

The effect of the above-mentioned changes is shown most strikingly by comparing the compositions of the ash of cane juice and cane molasses. Table II gives the average distribution of some of the constituents in the ash of cane juice and cane molasses, according to analyses made in Louisiana.[1]

TABLE II.—COMPOSITIONS OF ASH OF SUGAR CANE JUICE AND MOLASSES.

Ingredient, as oxide.	Juice. %.	Molasses. %.
Potassium (K_2O)	45.54	50.83
Sodium (Na_2O)	0.44	0.78
Calcium (CaO)	4.01	7.09
Iron (Fe_2O_3)	0.95	0.32
Aluminum (Al_2O_3)	0.54	0.24
Silica (SiO_2)	6.55	3.91
Phosphates (P_2O_5)	5.72	2.64
Sulfates (SO_3)	21.78	9.91
Carbonates (CO_2)	3.55	11.88
Alkalinity of ash (cc. 0.1 *N* acid to neutralize 1 g. of ash)	28	94

While the above results do not represent juice and molasses of the same origin, the analyses are an average of the product from different kinds of cane and from different factories. They may be considered therefore as fairly typical.

A comparison of the analyses shows about 17% less silica, phosphoric acid and sulfuric acid and about 17% more potash, soda, lime and carbonic acid in the ash of the molasses. These results, when considered in connection with the increase in alkalinity of the ash, show that a part

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[1] Louisiana Sugar Expt. Sta., *Bull.* 91 (1907).

of the basic elements of the mineral salts in cane juice enter as a result of clarification into new organic combinations with acid decomposition products, such as lactic, saccharinic and glycinic acids. In the process of evaporating and boiling the glycinic acid undergoes a partial dehydration with formation of humic acid substances of higher carbon content.

In the manufacture of what is termed "Refiner's Sirup" a part of the non-sugars in cane molasses are removed in the blow-ups and char filters. There is a further decrease in the mineral sulfates and phosphates and also in the calcium salts of organic acids. The decrease in glycinic acid and its decomposition products is made most apparent by the removal of color.

Changes in Calorific Value of Juice during Sirup Manufacture.

The calorific values of some of the constituents which may occur in the sirups and molasses derived from the sugar cane are given by various authorities as follows:

Formula.	Calories[1] per g.
Aconitic acid, $C_6H_6O_6$	2.750
Aspartic acid, $C_4H_7NO_4$	2.900
Asparagine, $C_4H_8N_2O_3$	3.444
Lactic acid, $C_3H_6O_3$	3.666
Invert sugar, $C_6H_{12}O_6$	3.750
Sucrose, $C_{12}H_{22}O_{11}$	3.955
Saccharin, $C_6H_{10}O_5$	4.055
Gums, estimated for $(C_6H_{10}O_5)n$	4.100
Humic acid, $C_{18}H_{14}O_6$	5.880

As regards the calorific values of the decomposition products formed during sirup manufacture, we may make a triple classification. (1) Little or no change in calorific value, as in the formation of lactic acid ($C_3H_6O_3$) and saccharinic acid ($C_6H_{12}O_6$) from invert sugar. (2) A decrease in calorific value, as in the formation of invert sugar from sucrose. (3) An increase in calorific value, as in the formation of dehydration products such as caramel, saccharin, glycinic acid and its humoid derivatives.

In the manufacture of sirup, the inversion of sucrose produced by concentrating sugar cane juice in acid solution, would tend, therefore, to diminish the heat units of the organic solids, while the formation of dehydration products by concentrating this juice in alkaline solution would tend to increase the heat units of these solids. As regards the organic non-sugars alone the operations of the sirup house and sugar factory would tend on theoretical grounds to cause an increase in their calorific value. On the other hand, the filtration of cane molasses over bone black

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[1] The calorie used in this paper is the greater or kilogram calorie, *i. e.*, the amount of heat required to raise the temperature of one kilogram of water one degree centigrade.

might produce a variable result according to the selective action of the char upon the non-sugars of lower calorific value, such as aconitic and aspartic acids, and upon those of higher calorific value such as glycinic acid and its dehydration products. The latter being in excess in ordinary cane molasses, filtration over animal charcoal would tend to eliminate more salts of glycinic acid than of aspartic or aconitic acid. These general deductions have been in large part confirmed by the following practical tests.

Experimental Part.

The following 8 samples were selected for comparison as to composition and calorific value:

1. A sample of the clear mother liquor from pure concentrated sugar cane juice. The cane juice was concentrated by simple evaporation, without the addition of lime or other chemicals, by Dr. F. W. Zerban at the Louisiana Sugar Experiment Station. After as much of the sucrose as possible had been crystallized from the sirup, the mother liquor was removed by decanting and filtering.

2. A sample of open-kettle molasses manufactured by Aurelien Simoneaux at Church Plantation, Plattenville, La. The expressed cane juice was treated with sulfur dioxide, limed, heated, allowed to settle and the clear juice concentrated in an open kettle heated by steam coils. The massecuite, after crystallizing in a cooler, was drained in hogsheads; the drippings constituted the molasses, from which the sample was taken.

3. A sample of first Cuban molasses, supplied by Dr. G. L. Spencer from Central Tinguaro, Cuba. The juice, from which the molasses came, was clarified with lime by the ordinary defecation process.

4. A sample of Refiners Sirup made by the Franklin Sugar Refining Company in Philadelphia, Pa.

5. A sample of Refiners Sirup made by the American Sugar Refining Company in Boston, Mass.

6. A sample of Refiners Sirup made by the American Sugar Refining Company in Jersey City, N. J.

7. A sample of Refiners Sirup made by the National Sugar Refining Company in Yonkers, N. Y.

8. A sample of Refiners low grade Molasses (black strap) made by the National Sugar Refining Company in Yonkers, N. Y.

TABLE III.

Analyses of the 8 Samples of Sirups and Molasses.

Sample.	1.	2.	3.	4.	5.	6.	7.	8.
Water	29.64	28.16	24.91	17.85	16.77	17.30	18.51	19.60
Invert sugar	13.93	14.28	12.84	29.72	33.18	31.19	26.76	22.53
Sucrose	49.86	51.92	48.13	36.12	38.00	37.57	41.58	37.87
Ash	3.60	2.50	4.82	5.30	4.46	5.97	4.04	6.53
Undetermined organic matter	2.97	3.14	9.30	11.01	7.59	7.97	9.11	13.47
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Alkalinity of ash, cc. 0.1 *N* acid to neutralize 1 g. of ash	51.2	92.9	64.2	81.5	77.0	102.2	123.4	126.2

In the above analyses water was determined by evaporating about 2 g. of the carefully weighed product in a glass-stoppered weighing bottle in a vacuum oven at a temperature not exceeding 70°. The drying was continued until constancy in weight was secured. The vacuum caused the substance to foam up in drying and the residue consisted of a porous, friable, hygroscopic mass. It was sealed and set aside for determination of the Calories.

Invert sugar was determined by the customary gravimetric method of copper reduction.

Sucrose was determined by the Clerget method of double polarization and also from the increase in copper reducing power after inversion. The average of the results by the two methods was the value taken.

Ash was determined by first carbonizing the product in a platinum dish at low heat. The residue was then ground and extracted with distilled water on an ashless filter. The carbonaceous residue was then incinerated in the platinum dish until a white ash was obtained; the aqueous extract of soluble ash was then added, the whole evaporated to dryness, heated to dull redness, cooled and weighed. The alkalinity of the ash was determined in the usual way by titrating with 0.1 N sulfuric acid.

Since the determinations of Calories were made upon the dry solids, the results of Table III were recalculated to a moisture-free basis.

TABLE IV.

Percentages Calculated to a Moisture-free Basis.

Sample.	1.	2.	3.	4.	5.	6.	7.	8.
Invert sugar	19.80	19.88	17.10	36.18	39.86	37.71	32.84	28.02
Sucrose	70.86	72.27	64.10	43.97	45.66	45.43	51.02	47.10
Ash	5.12	3.48	6.42	6.45	5.36	7.22	4.96	8.12
Undetermined organic matter	4.22	4.37	12.38	13.40	9.12	9.64	11.18	16.76
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Determinations of the Calories per gram of the moisture-free solids in the above 8 samples were performed by J. A. Fries of the Pennsylvania State College, with the following results:

Sample.	1.	2.	3.	4.	5.	6.	7.	8.
Calories per g. of solids	3.661	3.765	3.726	3.640	3.675	3.600	3.715	3.685

The results show that the dry matter of sirups and molasses derived from the sugar cane has a heat value ranging from 3.6 to 3.8 Calories per g.

The calorific equivalents of the invert sugar and sucrose in the moisture-free solids of the 8 samples, as calculated from the results of Table IV are as follows:

Sample.	1.	2.	3.	4.	5.	6.	7.	8.
Invert sugar	0.743	0.746	0.641	1.357	1.495	1.414	1.232	1.051
Sucrose	2.803	2.858	2.535	1.739	1.805	1.797	2.018	1.863
Cals. of sugars per g. of solids	3.546	3.604	3.176	3.096	3.300	3.211	3.250	2.914

The Calories due to the undetermined organic matter, found by subtracting the Calories of the sugars from the total Calories per g. of solids, are as follows:

Sample.	1.	2.	3.	4.	5.	6.	7.	8.
Cals. of undetermined organic matter per g. of solids.......	0.115	0.161	0.550	0.544	0.375	0.389	0.465	0.771

From the above figures and the percentages of undetermined organic matter in Table IV, the Calories per g. of undetermined organic matter were computed to be as follows:

Sample.	1.	2.	3.	4.	5.	6.	7.	8.
Cals. per g. of undetermined organic matter..............	2.725	3.684	4.443	4.060	4.112	4.035	4.159	4.600

The calorific value of the undetermined organic matter in the various products is lowest in sugar cane juice (Sample 1) and highest in the residual molasses (Samples 3 and 8). In the open kettle molasses (Sample 2), made by acid clarification with sulfur dioxide, the destructive action of lime is less apparent than in those products where lime had been used in greater excess. Comparing the sirups which had passed over bone black (Samples 4, 5, 6 and 7), with the two residual molasses the removal of dehydration products is indicated not only by the lighter color but by the lower calorific value of the organic non-sugars.

The calorific values of the undetermined organic matter, as above calculated, are no doubt a little too low in all cases, owing to the retention of water of crystallization by some of the organic and inorganic constituents in drying at 70°. Such a retention would not only lower the Calories of the solids but would make the percentages of undetermined organic matter too high. Unfortunately, no means could be found for estimating the water of crystallization retained by the vacuum-dried solids of sirups and molasses, as elevating the temperature much above 70° caused some of the organic matter to decompose. As an additional check, therefore, upon the accuracy of the work a comparison of 6 of the samples was made upon the basis of carbon content.

The carbon content of the organic constituents of the sirups derived from the sugar cane varies from about 36% in the case of aspartic acid to 60% or more in the case of humoid decomposition products. The following is a classification of some of these constituents:

Formula.	Carbon. %
Aspartic acid, $C_4H_7NO_4$..........................	36.10
Asparagine, $C_4H_8N_2O_3$..........................	36.36
Invert sugar, $C_6H_{12}O_6$..........................	40.00
Aconitic acid, $C_6H_6O_6$..........................	41.38
Sucrose, $C_{12}H_{22}O_{11}$..........................	42.10
Gums, $(C_6H_{10}O_5)n$..........................	44.44
Glycinic acid, $C_{12}H_{18}O_9$..........................	47.06
Caramelan, $C_{12}H_{18}O_9$..........................	47.06
Humic acid, $C_{18}H_{14}O_6$..........................	66.26

If the conclusions arrived at from comparing the calorific units are correct, then the accumulation of gums, caramel, glycinic acid and its humoid decomposition products in low grade molasses should cause the carbon content of the non-sugars in such molasses to be higher than it is in sirups made by sulfitation or by filtration over bone black. This was confirmed by the following determinations of carbon which were made by J. A. Fries upon the dried residues used for the determination of Calories:

Sample.	1.	2.	3.	6.	7.	8.
Total carbon in solids, %	38.945	40.138	39.790	38.159	39.394	39.249

The percentages of carbon due to the invert sugar and sucrose in the moisture-free solids of the above 6 samples, as calculated from the results of Table IV, are as follows:

Sample.	1.	2.	3.	6.	7.	8.
Carbon in invert sugar, %	7.920	7.950	6.840	15.084	13.136	11.208
Carbon in sucrose, %	29.832	30.426	26.986	19.126	21.479	19.829
Carbon in sugars, %	37.752	38.376	33.826	34.210	34.615	31.037

The percentages of carbon in the undetermined organic matter, found by subtracting the carbon in the sugars from the total carbon in the solids, are as follows:

Sample.	1.	2.	3.	6.	7.	8.
Carbon in organic non-sugars, %	1.193	1.762	5.964	3.949	4.779	8.212

From the above figures and the percentages of organic non-sugars in Table IV, the percentages of carbon in the organic non-sugars are computed to be:

Sample.	1.	2.	3.	6.	7.	8.
Carbon in organic non-sugars, %	28.27	40.32	48.17	40.97	42.74	49.00

The percentages of carbon in the organic non-sugars are thus seen to present the same relative order as that of the calories, being lowest in the cane juice and highest in the refinery molasses. The effect of bone black filtration in removing dehydration products of high carbon content is shown by comparing the low carbon percentages of Samples 6 and 7 with the high percentages of 3 and 8.

The percentages of carbon in the organic non-sugars as above estimated are probably in all cases too low owing to the retention of water of crystallization in the dried solids, as previously explained.

Conclusions.

In the manufacture of sirups and molasses from the juice of the sugar cane by the ordinary process of defecation with lime there is a progressive increase in the calorific value and carbon content of the organic non-sugars, owing to the formation of dehydration products such as caramel, glycinic acid and its humoid derivatives.

In the filtration of sirups and molasses over bone black there is a considerable removal of the lime salts of glycinic acid, the result being a lightening in color and a decrease in the calorific value and carbon content of the organic non-sugars.

In the manufacture of open kettle molasses by the sulfitation process, the formation of dehydration products is less pronounced than is the case by the defecation process, the result being a molasses of lighter color and with a lower calorific value and carbon content of the organic non-sugars.

The calorific value of the total solids in the sirups and molasses derived from the sugar cane was found to vary between 3.6 and 3.8 cals. per g. of dry substance, the average value being about 3.7 cals.

The calorific value of the organic matter in high-grade open-kettle sulfitation molasses and of high-grade refinery sirups was found to be about 3.9 Cals. per g. of dry organic substance.

The calorific value of the organic matter in sugar house defecation molasses and in refinery molasses was found to be about 4.0 Cals. per g. of dry organic substance.

The calorific value of the organic non-sugars in refinery sirups was found to vary between 4.04 and 4.16 Cals. per g. of dry substance.

The calorific value of the organic non-sugars in sugar house and refinery molasses was found to be 4.44 and 4.60 Cals., respectively, per g. of dry substance.

The carbon content of the total solids in the sirups and molasses derived from the sugar cane was found to vary between 38 and 40%, the average being about 39.5%.

The carbon content of the organic non-sugars in open-kettle and refinery sirups was found to vary between 40.32 and 42.74%.

The carbon content of the organic non-sugars in a sugar-house and refinery molasses was found to be 48.17 and 49.00%, respectively.

Finally, it may be noted that the results of this work have a certain bearing upon questions of nomenclature. It has been held by some that refinery sirups being a by-product of sugar manufacture should be termed molasses. But refinery sirups which have been filtered over bone black differ from defecation molasses so distinctly in the composition and calorific value of their organic non-sugars that in a chemical sense they cannot be grouped with such molasses.

In conclusion, the author desires to express his indebtedness to Mr. G. R. Bunker, of the National Sugar Refining Company, to Mr. H. E. Niese, of the American Sugar Refining Company, to Dr. G. L. Spencer, of the Cuban American Sugar Company, and to Dr. F. W. Zerban, of the Louisiana Experiment Station for furnishing him with samples of products. He is also under obligation to Mr. J. A. Fries, of the Pennsylvania

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THE ISOMERIC HYDROXYPHENYLARSONIC ACIDS AND THE DIRECT ARSENATION OF PHENOL.

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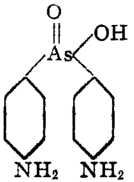
The present study of the action of arsenic acid upon phenol has demonstrated that this reaction is more complicated than has been heretofore assumed. As we shall set forth below, not only is *p*-hydroxyphenylarsonic acid formed in the reaction, but several other related substances as well.

Ehrlich and Bertheim,[1] in establishing the nature of the substance now known as arsanilic acid or *p*-amino-phenylarsonic acid (I), obtained by heating aniline with arsenic acid, drew the analogy between this substance and sulfanilic acid, obtained by a parallel method. As far as has been determined in these reactions, the substituent enters only the position *para* to the amino group. It was then found that the method of direct arsenation was capable of extension to other simple aromatic amines with a free *para* position. Only in the case of a few *para*-substituted arylamines was it possible to force the arsonic acid into the *ortho* position and then only with great difficulty as evidenced by the very poor yields.

Benda,[2] and independently, Pyman and Reynolds[3] later found that this reaction did not stop at the formation of the primary arsonic acid but that this condensed further to an appreciable extent with a second molecule of the amine to form the secondary arsonic acid (II) in which the arsonic acid residue again entered the *para* position in the second arylamine nucleus.

(I).



(II).

The method of direct arsenation has also been extended to include the simpler phenols. According to the method outlined in *D. R. P.* 205616,

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[1] *Ber.*, 40, 3292 (1907).

[2] *Ibid.*, 41, 2367 (1908).

[3] *J. Chem. Soc.*, 93, 1184 (1908).