potassium cyanide solution. Pour one of these two portions into each of the tubes of hydrogen peroxide. After a vigorous effervescence has started in the solution which contains no cyanide, add about 5 drops of the iodine solution to it.

Observations.—After the hydrogen peroxide has stood about a minute with the colloidal platinum solution, a vigorous effervescence occurs in the solution which contains no potassium cyanide, while in the solution in which the cyanide is present no appreciable evolution of gas occurs. Immediately after adding the iodine to the effervescing tube, the reaction slackens, and in the course of a few seconds the evolution of oxygen almost entirely ceases.

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THE POLARIZATION OF FRUITS, JELLIES, JAMS, AND HONIES.

BY L. M. TOLMAN.

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LARGE amounts of sucrose are added in the preparation of jellies and jams, some of which is inverted in the process by the action of the organic acids, such as citric, malic, or tartaric. As a rule the jams which are cooked the longest[1] show the largest amount of inversion as would be expected. In working with a large number of these products, however, the rather curious fact was noted that apparently complete inversion rarely if ever took place, or, at least, in polarizing before and after inversion there was always an increase in the minus reading on the sugar scale, often not more than from 1° to 2°, which calculated as sugar by the Clerget formula showed from 1 to 1.5 per cent. of cane sugar. The usual explanation of the phenomenon is that it is due to cane sugar, but it is probable that this change is due to an entirely different cause.

It must be remembered that the cane sugar in these products has been inverted by the action of the fruit acids and it is possible

[1] Tolman, Munson, and Bigelow: This Journal, **22**, 351 (1901).

to show by some investigations made by myself recently that this change in polarization is due to the action of hydrochloric acid on the invert sugar present. What this action is has never been explained, but it is a well-known fact that the simple presence[1] of hydrochloric acid increases the rotatory power of invert sugar. This is shown in the following table from Lippmann[2] in which is noted the effect on the polarization of an invert sugar solution at 20°, of different amounts of hydrochloric acid.

TABLE I.

Weight of sugar Grams.	Polarization Ventzke degrees.			
	5 cc. HCl.	10 cc. HCl.	15 cc. HCl.	20 cc. HCl.
26.048	−34.00	−35.04	−35.95	−36.80
13.024	−33.00	−34.12	−35.15	−36.03

Lippmann's polarizations were all made at 20° C., and in the case of the half-normal weight the reading was multiplied by 2 for comparison. This table shows that hydrochloric acid, by its simple presence, affects the polarization. It is but logical to suppose that, if each succeeding 5 cc. of the hydrochloric acid affected the polarization, the first 5 cc. must also, and that if an inversion were made without any acid present the reading would be still less.

In order to demonstrate this fact, *i. e.*, that an addition of hydrochloric acid increases the rotation of invert sugar, especially with regard to such invert sugar as has been prepared with organic fruit acids, and honey in which the sugar has perhaps been inverted in the digestive tract of the bee, and to justify the expectation that in making a polarization, before and after inversion, with these substances a change in reading of 1° or 2° would take place even when no sucrose was present, the following experiment was undertaken.

(It might be well to say in the beginning that all the polarizations were made in a water-jacketed tube and in that way the temperature was very exactly controlled. In most of the polarizations the greatest change in temperature was not more than 0.2° C., and correction was made for that difference.)

A strong solution of cane sugar was taken and inverted with citric acid (2 grams to 100 cc.) by boiling for one-half hour.

[1] H. A. Weber: This Journal, 17, 321, et seq.
[2] Lippmann: "Chemie die Zuckerarten," p. 800.

Fifty cc. portions were measured into 100 cc. flasks and each test was run in a duplicate, the average of a number of readings being taken.

One set of 2 flasks was made up to volume with distilled water. To another set 5 cc. of hydrochloric acid (sp. gr. 1.20) was added, the volume made up to 75 cc. and heated to 67° C., in fifteen minutes, according to the directions for the inversion of cane sugar used by the Association of Official Agricultural Chemists. To a third set 10 cc. of hydrochloric acid were added and treated as in the previous case. To a fourth and fifth set 5 and 10 cc. of hydrochloric acid were added and they were at once made up to volume in the cold and polarized, giving the acid practically no chance to exert any inverting action.

The second and third sets were cooled, made up to volume, and polarized. The results obtained are shown in Table II.

TABLE II.

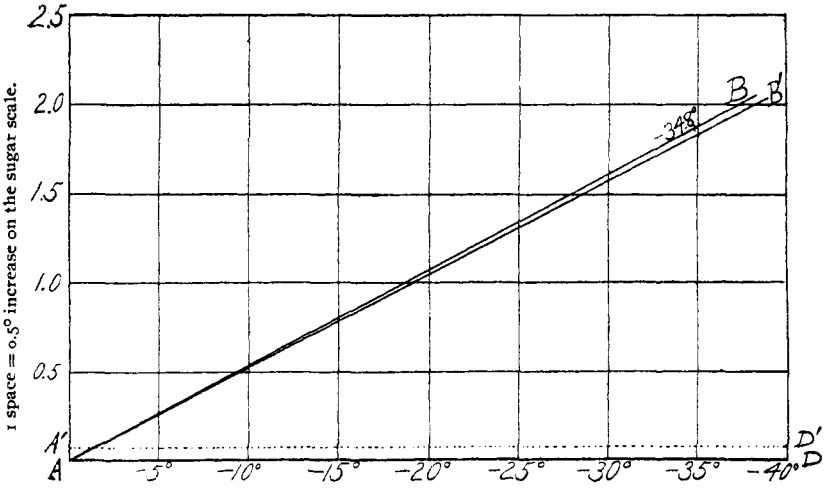
	Description of sample.	Ventzke 0°. Polarization	Temperature. °C.	Change in rotation.
No. 1.	Containing no HCl.....	— 23.0	18.0	..
No. 2.	Containing 5 cc. HCl, 67° C.....	— 24.2	18.4	1.2
No. 3.	Containing 10 cc. HCl, 67° C.....	— 25.0	17.8	2.0
No. 4.	Containing 5 cc. HCl (cold)	— 24.2	18.4.	1.2
No. 5.	Containing 10 cc. HCl (cold)	— 25.0	18.0	2.0
No. 6.	Containing 10 cc. HCl (N/4) (cold)	— 23.4	18.0	0.4

From this table it will be seen that it makes practically no difference whether the solutions are heated in order to invert any sucrose present or whether the acid is simply added and polarized before there could be practically any inversion. It is hardly possible to say that there had been immediate inversion in the cold by the acid of a small amount of sucrose present to account for the change in rotation caused by the acid in the cold, as it is well known that hydrochloric acid inverts very slowly in the cold.

It seems evident enough that the presence of hydrochloric acid increases the levo-rotatory power of invert sugar as shown in Table II, from the comparative effects of the 5 cc. and the 10 cc. of strong hydrochloric acid and of the weak N/4 hydrochloric acid.

This experiment is made under practically the same conditions as are present in jam in which the sucrose had been inverted with some fruit acid. The direct polarization is made, the hydrochloric

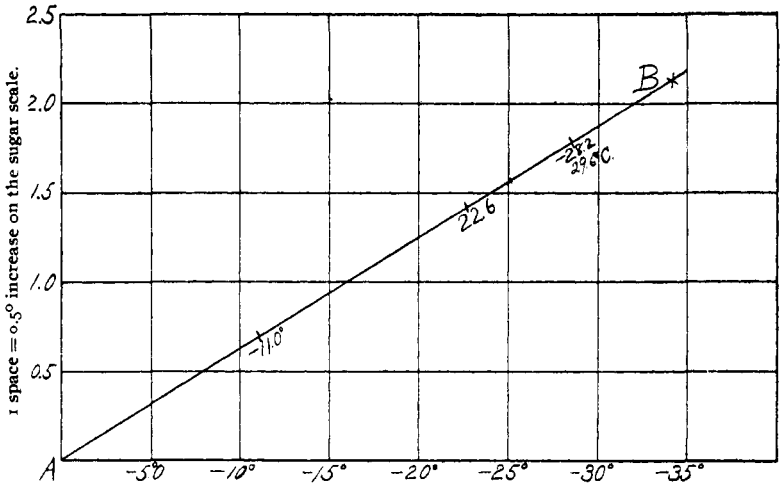
acid added to cause the inversion, and there is an increase of rotation to the left of from 1° to 2°, depending on the amount of invert sugar present and the amount of hydrochloric acid added. Calculated as cane sugar, this change amounts to from 1 to 1.5 per cent., whereas in reality there is no sucrose present and the change in rotation has been due to the causes explained above. The same conditions are present in honey in which there is a large amount of invert sugar. But even in case the inversion has been effected by hydrochloric acid and this acid is still present, the simple addition of more hydrochloric acid, as is shown in Tables I and II, causes an increased rotation. For these reasons it is not possible



Each space equals 5° on sugar scale, Schmidt and Haensch polariscope. B′ is calculated from Herzfeld's formula. 5 cc. HCl used in 100 cc. German official method.

Fig. 1.

to make any accurate determination, by polarization, before and after inversion, and the calculation by the Clerget formula, of a small amount of cane sugar in the presence of a large amount of invert sugar, unless a correction can be introduced to compensate for this action. The writer has endeavored to construct a formula which would correct this error. In order to show clearly the basis of the proposed correction, it is necessary to consider first Figs. 1 and 2 and the Herzfeld formula.



Each space = 5° on sugar scale of Schmidt and Haensch polariscope. 10 cc. HCl in 110 cc. Method of Association of Official Agricultural Chemists.

Fig. 2.

Fig. 1 shows graphically the effect of the hydrochloric acid used in inversion in the German method, in which 5 cc. is added to the solution to be inverted, the volume made up to 75 cc. and inverted by heating to 67° C. in fifteen minutes and cooled rapidly, after which the volume is increased to 100 cc. and the solution is polarized. The abscissas give the polariscopic readings of the solution of invert sugar in number of degrees to the left, and the ordinates give the increase in tenths of degrees that the addition of 5 cc. of hydrochloric acid causes.

Since the reading of the invert sugar before and after adding the hydrochloric acid was all that was needed in order to plot the diagram, two solutions of invert sugar were prepared: One by inversion with citric acid (2 grams to 100 cc.) and the other by use of N/5 sulphuric acid and the acid removed by the use of barium carbonate, which gives a solution of invert sugar free from any substances which might affect its optical action. Neither of these solutions was of a definite strength. Parallel experiments were carried on, using the two solutions; but the results as plotted in Fig. 1 were identical. The procedure in all of the following experiments was the same except for the varying amounts of hydro-

chloric acid added. Of the solution of invert sugar, 10, 15, and 50 cc. portions were measured into 100 cc. flasks, 5 cc. of hydrochloric acid (sp. gr. 1.20) were added to each in the cold and the solution was then made up to volume and polarized. For example, two 10 cc. portions were measured into 100 cc. flasks. To one, 5 cc. of hydrochloric acid were added, and the other was made up to volume and polarized at the same temperature. The one to which no acid had been added polarized —5.6°, and that to which the acid had been added polarized —5.9°, a difference of 0.3° which gives a point on the diagram. Another portion which polarized without acid —23°, polarized —24.2° with 5 cc. of hydrochloric acid, and a third portion which polarized —34.8° without the addition of acid, polarized —36.7° after its addition, an increase of 1.9° caused by the addition of the acid in the cold. These experiments show that with the same amount of acid the larger the invert reading the greater is the increase in the reading caused by the acid. Fig. 1 illustrates this point and from it one can easily determine in any particular case, as for instance, in polarizing a jam which reads —19.5° before inversion and —20.5° after inversion, that the change is not due to any sucrose present but is the change to be expected from the action of the acid. By examining the diagram it will be seen that 5 cc. of hydrochloric acid causes an increase of —1.05° in reading in a solution that polarizes —19.5° thus making the reading —20.55°. Any one who has polarized honey to any extent has noticed this slight change. In Table III, I have noted a number of polarizations of honies taken from U. S. Dept. of Agr., Div. of Chem., Bull. 13, and have corrected them from Fig. 2, which shows the effect of the amount of acid used in the method of the Association of Official Agricultural Chemists in which the larger amount of acid used (10 cc. in 110 cc., or nearly twice that used in the German method) causes a greater increase in the minus reading. The calculated minus readings are obtained by adding to the direct reading the correction for the effect of the acid as calculated from Fig. 2.

TABLE III.—POLARIZATION OF HONIES.

Direct.	Invert.	Degrees Ventzke. Cane sugar.[1]	Degrees Ventzke. Calculated invert reading.
— 20.00	— 20.90	0.72	— 21.25
— 17.60	— 18.32	0.93	— 18.59
— 16.8	— 18.40	1.23	— 18.20
— 15.8	— 17.5	1.31	— 16.78
— 11.0	— 12.0	...	— 11.68
— 13.2	— 15.6	...	— 14.00
— 16.50	— 18.00	...	— 17.52
— 14.80	— 15.60	...	— 15.70
— 9.40	— 10.67	0.96	— 9.98
— 12.90	— 13.86	0.73	— 13.70
— 14.40	— 15.40	0.76	— 15.39
— 11.30	— 12.65	0.99	— 12.00
— 11.50	— 12.65	0.85	— 12.21
— 13.50	— 14.00	0.30	— 14.33
— 9.5	— 10.00	0.30	— 10.05
— 11.0	— 12.00	0.70	— 11.68
— 10.0	— 11.00	0.70	— 10.62
— 11.0	— 12.00	0.70	— 11.68

Using the Herzfeld formula,[2]

$$S = \frac{a - b}{141.85 + 0.05\,b - \frac{T}{2}},$$

S = Sucrose.
a = Direct reading.
b = Invert reading.
T = Temperature,

in which 141.85, the factor for 1 gram of sucrose in 100 cc., is increased by 0.05 of the invert reading, and plotting a line in the same way as has been previously explained in plotting the results, it will be found that the two lines almost exactly coincide (see Fig. 1). For instance, suppose a minus polarization of — 35° is multiplied by 0.05, giving 1.75°. As Herzfeld begins with a polarization of —1.3°, corresponding to 1 gram of sugar at 20°, we mark off on the line AB the point at which —1.3° would intersect it and draw $A'D'$ and use that as a base line. At 35° on this base line measure 1.75° and it will be found to be almost exactly on

[1] As calculated from direct and invert reading.
[2] Herzfeld: *Ztschr. Rübenzucker-Ind.*, **40**, 194.

the line AB, which bears out the results previously obtained and shows that the method by which they were obtained is correct. In order to determine the effect caused by 10 cc. of hydrochloric acid in 110 cc. of sugar solution (the amount of acid used in the A. O. A. C. method), it is necessary to fix one point in Fig. 2 very carefully and from that to draw a straight line to the origin and there is obtained at once the correction to be made in the Herzfeld formula in order to obtain a new formula which will be correct for this method. In Fig. 2 is shown the determination of this correction. From Fig. 2 it is seen that the increase due to 10 cc. of hydrochloric acid (sp. gr. 1.20) in 110 cc. is 0.062 times the invert reading, while in the Herzfeld formula it was 0.050 times the invert reading. Therefore in order to make a formula for the official method, we substitute 0.062 for 0.050, also changing the factor 141.85, for 1 gram of sugar, to 141.79, which is apparently the limiting case if one plots the line. Thus we obtain the formula

$$S = \frac{a - b}{141.79 + 0.062\,b - \frac{T}{2}}.$$

While this formula may be used for calculating the amount of sucrose present, for any concentration, from polarization before and after inversion, it does not, stated in this form, give a means for calculating small amounts of cane sugar in the presence of large amounts of invert sugar. In order to make this determination, a slightly different method of calculation must be pursued. As $(0.062 \times b)$ is equal to the effect of the acid, if this is subtracted from b, it will give the true polarization, thus,

$$S = \frac{a - (b - (0.062 \times b))}{141.79 - \frac{T}{2}}$$

Now if a and $(b - (0.062 \times b))$ are equal, it is evident that all the change in polarization has been due to the effect of the acid used in inversion on the invert sugar, while if there is still a difference the cane sugar can be calculated by the use of $141.79 - \frac{T}{2}$. This formula will not apply to fruit products containing glucose, but is of special value in estimating small amounts of cane sugar

in fruits, pure fruit jellies, jams, and honies in which large amounts of invert sugar are present.

The action of acid on invert sugar mixed with glucose is the same as it is on the same amount of invert sugar alone, as the following results show:

TABLE IV.

	Polarized. °Ventzke.	Temperature. °C.
13.028 grams invert sugar + 25 cc. glucose solution	+9.8	21.0
The same + 10 cc. hydrochloric acid.....	+8.9	21.0
The same + 5 cc. hydrochloric acid.....	+9.4	21.0

This shows that when glucose which contains invert sugar is polarized before and after inversion, there will be a change of polarization even if there is no sucrose present. This condition would be almost always found in honey adulterated with glucose. This obviously can not be corrected by the formula given, and the writer is working on the use of inverting agents, such as citric acid, which have practically no effect on the opticity of invert sugar.

These results show that if you eliminate the effect of the acid used in inversion, *the Clerget formula will become a constant for any given temperature regardless of the concentration of the sugar solution.* This can be seen by noting from Fig. 1 that the increase of invert reading caused by the hydrochloric acid is 0.05 of the invert reading, so that Herzfeld's formula would be

$$S = \frac{a - b}{141.85 - \frac{T}{2}},$$

if the effect of the acid was removed, or a constant at any temperature.

If an inverting agent could be obtained which had no effect on the invert sugar, the question of concentration would practically be eliminated. But the elimination of this error would necessitate the determination of a new factor which would in all probability be 141.79 or perhaps a little less.

From this work it will be seen that the smaller the amount of hydrochloric acid used, the less is the effect on the negative reading, and therefore the smaller the error due to concentration. It

will be seen from Table II that the effect of N/4 hydrochloric acid is comparatively small, and the factor for any given temperature approaches a constant for all concentrations. All will agree that this is a most desirable condition for attaining accuracy.

The German method of using ½ normal weight (13.024 grams) and 5 cc. of hydrochloric acid reduces the error, as compared with the A. O. A. C. method, due to concentration, to a considerable extent, for two reasons. The smaller amount of acid has less effect on the negative reading and it has been shown from Table II that the smaller the amount of sugar used the less is the variation. As, for instance, the factor varies from 141.85 to 142.66, for 1 gram to 13 grams of sugar, a variation of 0.81°, and with the A. O. A. C. method it varies from 141.85 to 144.00, 2.1°.

The use of less acid for the inversion is desirable and it is in this direction that investigation should tend. The smaller the amount of the acid the less is the danger of destruction of the sugar and the smaller the error due to concentration, but it must be remembered that every change in the strength or amount of acid used requires the most careful determination of a new factor.

The work can be summed up in this way:

1. Hydrochloric acid increases levo-rotation of an invert sugar solution.

2. This increase, other things being equal, is proportional to the quantity of hydrochloric acid used.

3. Other things being equal and temperature varying, hydrochloric acid increases levo-rotation by a definite per cent. of the polarization.

4. In order to correctly calculate the percentage of cane sugar in invert sugar by Clerget's formula a correction depending on the amount of hydrochloric acid used must be made, which can be calculated from Fig. 1 or 2. All readings of the polariscope should be made at or about 20°.